SYMPOSIUM Ra/Rb

Assembly at the Nanoscale–Toward Functional Nanostructured Materials

November 27 - December 2, 2005

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TUTORIAL

FTRa/Rb: Nanoscale Sensors – From Molecules to Devices
Sunday, November 27, 2005
1:30 PM - 4:30 PM
Room 208 (Hynes)

Materials for Nanoscale Sensors
Nanotubes; Nanowires; Nanospheres; Dendrimers (organic nanoparticles); Inorganic-organic hybrid nanoparticles.

Fabrication Methodologies
Self-assembly techniques; Advanced manufacturing based on molecular nanotechnology; Environmentally clean, inexpensive, and efficient manufacturing of structures, devices, and "smart" products; Flexible control of architectures and processes at an atomic or molecular scale of precision.

Detection Capabilities
Chemical; Biological; Radiological; Explosive threats.

Detection Methodologies
Electrical; Optical; Resistive; Infrared-based identification.

Development of Nanoscale-Sensing Devices
Produce material parts at the nanoscale; Process material parts into components at the nanoscale; Order molecular components into structure and interconnect; Interface system components with the macroenvironment; Control a massive collection of miniature parts and systems; Provide a power system.

Instructors:
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SESSION Ra1/Rb1: Plenary Session I
Chair: Cengiz S. Ozkan
Monday Morning, November 28, 2005
Ballroom A (Hynes)

8:15 AM INTRODUCTORY REMARKS

8:30 AM *Ra1.1/Rb1.1
Some New Developments in Colloidal Self-Assembly. Younan Xia, Chemistry, University of Washington, Seattle, Washington.

This talk will be organized into two parts. In the first part, I will briefly discuss a number of synthetic approaches that my group recently developed for generating monodispersed colloidal particles with controllable shapes and structures. I will use selenium as an example to illustrate how this semiconductor can be synthesized as spherical colloids and then transformed into Ag2Se and CdSe without changiing the shape. These colloidal particles can serve as building blocks for self-assembly to fabricate photonic crystals. In the second part of this talk, I will discuss how template-assisted self-assembly (TASA) can be used to organize mesoscale building blocks into various structures with controllable sizes, shapes, and functions. I will use spherical colloids as a typical example of the building blocks. In principle, this approach can also be extended to cover building blocks with many other shapes and/or dimensions. I will concentrate on the fundamental mechanism of each method, as well as its potential extension to different systems

9:00 AM *Ra1.2/Rb1.2
Building-up Supramolecular Self-Assemblies on Surfaces: Towards Molecular Nanoelectronics. Denis Fichou, Alexandr Marchenko, Luc Piot, Etienne Menard, Aymeric Nion and Alexandre Popoff; DSM/DRECAM/SPCSI, CEA-Saclay, Gif-sur-Yvette, France.

Plastic electronics appears today as an alternative to conventional semiconductors technologies.1 Self-assembly of functional organic molecules on atomically flat surfaces opens new perspectives towards molecular nanoelectronics, a realistic strategy in the miniaturization of electronic devices. One simple way to investigate 2D supramolecular self-assemblies at the nanoscale is to generate them at a liquid-solid interface and observe them in situ by means of scanning tunneling microscopy (STM). A variety of 2D architectures have been recently obtained with functional molecules (liquid crystals, molecular wires, graphite-like molecules, etc) by controlling the subtle interplay between molecule-molecule and molecule-substrate interactions. We will illustrate this approach with various families of conjugated organic compounds such as trimethylsilyl-acetylenes2, alkoxy-triphenylenes3,4, fullerenes5, star-shaped oligothiophenes, the newly synthetized triazatrinaphthylenes, etc6 One step further, we recently demonstrated the possibility to work in the vertical dimension and pile-up two or three self-assembled monolayers (SAMs) of similar or different molecules on top of each other at a liquid-solid interface. A spectacular example is the controlled growth and manipulation of magic clusters, i.e. self-organized close-shell islands of exceptional stability, of long n-alkanes in ambient conditions. Even further, we now use SAMs of n-alkanes physisorbed on a solid substrate (graphite, gold, etc) as tailored templates for the growth of self-assembled bi- and trilayers of large conjugated discal molecules possessing electrical and/or optical properties.7 Finally, we will show that our low-current STM technique allows for the first time to image the surface of a bulk single crystal of an organic semiconductor (thickness ~1 mm) down to molecular resolution and also to record its intrinsic I/V transport properties at the nanoscale.8 In conclusion, the growth and handling of novel homo- or heteromolecular 2D and 3D functional self-assemblies can be easily controlled at the molecular level on atomically flat surfaces and then integrated as active materials into nanosize electronic devices. References [1] Schoonveld, W.A.; Wildeman, J.; Fichou, D.; P.A. Bobbert, B.J. van Wees, T.M. Klapwijk, Nature, 2000, 977. [2] Marchenko, A.; Katsonis, N.; Fichou, D.; C. Aubert, M. Malacria, J. Am. Chem. Soc. 2002, 124, 9998. [3] Katsonis, N.; Marchenko, A.; Fichou, D.; J. Am. Chem. Soc. 2003, 125, 13682. [4] Katsonis, N.; Marchenko, A.; Fichou, D.; Synth. Met. 2004, 147, 73. [5] Katsonis, N.; Marchenko, A.; Fichou, D.; Adv. Mater. 2004, 16, 309. [6] Saettel, N.; Katsonis, N.; Marchenko, A.; Teulade-Fichou, M-P.; Fichou, D. J. Mater. Chem., 2005, in press. [7] Piot, L.; Marchenko, A.; Wu, J.; Fichou, D.; Mullen, K. submitted. [8] Menard, E.; Marchenko, A.; Podzorov, V.; Gershenson, M.E.; Rogers, J.A.; Fichou, D. submitted.

9:30 AM *Ra1.3/Rb1.3
One-Dimensional Nanostructures as Subwavelength Optical Elements for Photonics Integration. Peidong Yang, Univ. Calif. Berkeley, Berkeley, California.

The manipulation of optical energy in structures smaller than the wavelength of light is key to the development of integrated photonic devices for computing, communications and sensing. Wide band gap semiconductor nanostructures with near-cylindrical geometry and large dielectric constants exhibit two-dimensional ultraviolet and visible photonic confinement (i.e. waveguiding). Combined with optical gain, the waveguiding behavior facilitates highly directional lasing at room temperature in controlled-growth nanowires with suitable resonant feedback. The nanowire optical emission has been studied in detail using high-resolution optical microscopy. This concept of using well-cleaved nanowires as natural optical cavities may be extendable to many other different semiconductor systems. We have further explored the properties and functions of individual ultralong crystalline oxide nanoribbons that act as subwavelength optical waveguides and assess their applicability as nanoscale photonic elements. The length, flexibility and strength of these structures enable their manipulation on surfaces, including the optical linking of nanoribbon waveguides and other nanowire elements to form networks and device components. We have demonstrated the assembly of ribbon waveguides with nanowire light sources and detectors as a first step toward building nanowire photonic circuitry.

SESSION Ra2/Rb2: Plenary Session II
Chair: Zhong Wang
Monday Morning, November 28, 2005
Ballroom A (Hynes)

10:30 AM *Ra2.1/Rb2.1
Modeling the size effect of nanoparticles entering cells via receptor-mediated endocytosis. Huajian Gao[1], Wendong Shi[1] and L. B. Freund[2]; [1]Max Planck Institute for Metals Research, Stuttgart, Germany; [2]Engineering, Brown University, Providence, Rhode Island.

Most bioparticles and viruses endocytosed by cells have characteristic sizes in the range of tens to hundreds of nanometers. The process of virus-like particles entering and leaving animal cells is mediated by the binding interaction between ligand molecules on the viral capsid and their receptor molecules on the cell membrane. How does the size of a bioparticle affect receptor mediated endocytosis? Here we study how a cell membrane containing diffusive mobile receptors wraps around a ligand coated cylindrical or spherical particle. It is shown that particles in the size range of tens to hundreds of nanometers can enter or exit cells via wrapping even in the absence of clathrin or caveolin coats and there exists an optimal particles size for the smallest wrapping time. This model can also be extended to including the effect of clathrin coating. The results seem to show broad agreement with experimental observations.

11:00 AM *Ra2.2/Rb2.2
Anisotropic Nanostructures: Synthesis, Assembly, and Function. Chad A. Mirkin, Chemistry Department, Northwestern University, Evanston, Illinois.

A novel approach that uses ambient fluorescent light to convert small silver nanospheres (6-8 nm) into large, triangular silver nanoprisms will be discussed. By varying the excitation wavelengths of light, one can tune the average edge length of the final nanostructures and their resultant optical properties. Current studies are focused on understanding the mechanism by which these novel nanostructures form, as well as incorporating them into a variety of biodetection and sensing applications. In addition, recent results including novel hybrid inorganic/organic nano rod structures will be addressed. These structures spontaneously assemble into sheets, tubes, and mushroom-shaped aggregates, depending upon rod composition and length. Structure, properties, and potential applications will be discussed.

11:30 AM *Ra2.3/Rb2.3
Fabricating and Printing Inorganic Semiconductor Nano/microelements for Macroelectronic Systems. John Rogers, University of Illinois, Urbana, Illinois.

Solution processable conductors, dielectrics and semiconductors represent enabling materials for electronic circuits that can be fabricated on plastic sheets by continuous, high speed printing techniques. It is generally believed that these types of systems, which can cover large areas, will be important for new applications in consumer electronics. This talk describes the operational aspects of flexible transistors and circuits that use printable semiconductors based on nano/microelements - wires, ribbons, disks, platelets, etc - of single crystal silicon, gallium arsenide, indium phosphide and gallium nitride. Excellent dc and high frequency performance in individual devices and simple circuits and the behavior of these systems under bending conditions will be presented.

SESSION Ra3: Biomimetics I
Chair: Federico Rosei
Monday Afternoon, November 28, 2005
Room 207 (Hynes)

1:30 PM *Ra3.1
Abstract Not Available Angela Belcher

2:00 PM Ra3.2
Assembly of Nanoparticle Ring Structures based on Protein Templates. Silke Behrens[1], Wilhelm Habicht[1], Kerstin Wagner[2] and Eberhard Unger[2]; [1]Forschungszentrum Karlsruhe, Karlsruhe, Germany; [2]Institut fuer Molekulare Biotechnologie, Jena, Germany.

The bottom-up wet-chemical synthesis of inorganic materials provides tools for generating nanostructures from particles to one-dimensional structures, but these chemical techniques usually offer little control over the deposition of metals or metal particles as nanosized ring structures although interesting properties are expected. Our results provide a straightforward and rapid synthesis to ring-like nanoparticle arrays not accessible via any of the known conventional synthetic methods. Applying appropriate conditions, tubulin dimers, proteins of 4-5 nm diameter and a length of 8 nm, self-assemble by specific recognitions capabilities into defined superstructures. Ca2+ ions, e.g., direct the assembly of tubulin into 50 nm sized, ring-like structures. In our approach, these ring-like protein assemblies serve as a functionalised scaffold where the metal is generated in situ and deposited into spiral-shaped particle arrays, reflecting the arrangement of the protein subunits within the assembly. The mean distance between the Ag particles was 7.3 nm and indicated the specific deposition of one Ag particle per tubulin subunit. The resulting size and crystalline structure of the materials were examined using Transmission Electron Microscopy and Scanning Force Microscopy. This synthetic capability will allow a potential wet-chemical synthesis of Aharonov-Bohm rings.

2:15 PM Ra3.3
Biomimetic Self-Assembly Of Charged Block Copolymers into Toroids or Disks. Darrin Pochan, [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

By considering charged synthetic polymer molecules in the materials self-assembly design process, one can take advantage of electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicty, to define hierarchical material structure and consequent properties. Synthetic, amphiphilic triblock copolymers, polystyrene-b-polymethacrylate-b-polyacrylic acid (PS-PMA-PAA) with one charged/ion-containing block (PAA) can be assembled in dilute water/tetrahydrofuran mixtures containing multivalent organic counterions to produce biomimetic assembly structures. By altering the water content of the solvent mixture, the hydrophobic polystyrene chain length, the chemical structure of the diamine counterions, and diamine counterion concentrations, one can controllably access different micelle structure. Different multivalent organic counterions at different concentrations allow one to controllably access different micelle structures with the same block copolymer. Two structures to be specifically discussed are toroidal, or ring-like, micelles and disk, or stomatocyte-like, micelles. The ring-like, toroidal micelles with an average outer diameter on the order of several hundred nanometers are formed via a mechanism similar to the toroidal bundling of charged semiflexible biopolymers like DNA in the presence of multivalent counterions. Disk-like micelles, with an average diameter of several hundred nanometers, and stacks of discs are readily formed. In addition, a disc-to-rod transition (rods growing out from discs) can also be readily observed via direct electron microscopy imaging. The system has been investigated by means of transmission electron microscopy (TEM), cryo-TEM, dynamic light scattering (DLS), and small angle neutron scattering (SANS). Different pathways en route to disc or toroid formation, the thermodynamic stability of the morphologies, the mechanism of disk stacking, the kinetics of the disk-to-cylinder transition, and the importance of organic counterion multivalency will be discussed.

SESSION Rb3: Nanowires, One Dimensional Nanostructures I
Chair: Gregory Lopinski
Monday Afternoon, November 28, 2005
Room 208 (Hynes)

1:30 PM Rb3.1
Phase Diagram and Road Map for Large-Scale Growth of Aligned ZnO Nanwires and CdSe Nanostructures. Jinhui Song, Christopher Ma, Xudong Wang and Zhong L. Wang; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

In vapor-liquid-solid (VLS) growth, it is generally believed that nanowires would grow as long as the right catalysts and substrate are supplied as well as the growth temperature is adequate. We show here, however, that oxygen partial pressure plays a key role in determining the quality of the aligned ZnO nanowires. We present a phase diagram between the oxygen partial pressure and the growth chamber pressure for synthesizing high quality aligned ZnO nanowires on GaN substrate [1, 2]. This result provides a road map for large-scale, controlled synthesis of ZnO nanowires on nitride semiconductor substrates with the potential to meet the needs of practical applications. The chemical process involved in the growth process is also systematically elaborated based on experimental data received under different conditions. We also show a systematic investigation on the synthesis parameters affecting the morphology of VLS-grown one-dimensional CdSe nanostructures using gold as catalyst [3]. The relationship between morphology and pressure/temperature has been discussed, and a roadmap for guiding the synthesis has been defined. The main conclusions can be summarized as follows: 1. The temperature at the source is to stimulate the vaporization of the source materials, and the subsequent growth is controlled dominantly by the local temperature and pressure at the substrate. 2. There is an increase in the growth temperature range where deposition occurs with a decrease in the system pressure. 3. Lower temperature at the source material (630 oC), higher chamber pressure (600 mbar) and 575 +- 5 oC substrate temperature produces the highest percentage of nanosaws/nanocombs. 4. Lower temperature at the source material (700 oC), lower chamber pressure (4 mbar) and 575 +- 8 oC substrate temperature produces the highest percentage of nanobelts. 5. Growth of nanowires is less restrictive and it can be carried out at a wide range of temperature and pressure. 6. High source temperature favors the growth of nanowires rather than nanosaws and nanobelts. [1] Jinhui Song, Xudong Wang, Elisa Riedo and Zhong L. Wang, Systematic Study on Experimental Conditions for Large-Scale Growth of Aligned ZnO Nanwires on Nitrides, J. Phys. Chem. B, published online (2005). [2] Xudong Wang , Jinhui Song , Peng Li , Jae Hyun Ryou , Russell D. Dupuis , Christopher J. Summers and Zhong L. Wang, Growth of Uniformly Aligned ZnO Nanowire Heterojunction Arrays on GaN, AlN, and Al0.5Ga 0.5N Substrates, J. Am. Chem. Soc., 127 (2005) 7920-7923. [3] Chris Ma, Yong Ding, Daniel Moore, Xudong Wang and Z.L. Wang, J. Am. Chem. Soc., 126 (2004) 708. [4] For details: www.nanoscience.gatech.edu/zlwang

1:45 PM Rb3.2
Functional Semiconductor/Metal Oxide Core/Shell Nanowire.

Hao Yan[1], Yue Wu[1], Guihua Yu[1] and Charles M. Lieber[1,2]; [1]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; [2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

One-dimensional nanostructured materials such as nanowires and nanotubes represent a promising class of building blocks for nanoelectronic devices. Critical to continued development of these devices, as well as circuits and systems, will be the introduction of controlled structural complexity and function in the nanoscale building blocks since the added function can provide unique opportunities distinct from conventional planar devices. To this end we demonstrate a general approach towards semiconductor/metal oxide core/shell nanowires via combination of vapor-liquid-solid growth and atomic layer deposition (ALD), where ALD is used to grow uniform oxide shells on semiconductor nanowire cores. As an example of this approach, we demonstrate the synthesis of $Si/ZrO_2/BaTiO_3$ core/shell/shell nanowire heterostructures. High-resolution transmission electron microscopy imaging and analysis were used to characterize the structure and composition of these new heterostructures. Notably, electrical transport measurements demonstrate that these heterostructures function as ferroelectric field effect transistors, with the $BaTiO_3$ exhibiting well-defined and stable ferroelectric behavior. Fundamental device characteristics of these nanowire heterostructures will be reported, as well as studies of nonvolatile memory and programmable logic arrays.

2:00 PM Rb3.3

Electrochemical Deposition of Metal-Semiconductor-Metal Nanowires. Xu Wang[2], Sathyajith Ravindran[2] and Cengiz Sinan Ozkan[1]; [1]Mechanical Engineering, University of California at Riverside, Riverside, California; [2]Chemical and Environmental Engineering, University of California art Riverside, Riverside, California.

Nanowires of many compositions have been prepared using porous templates as molds. Anodic alumina oxide (AAO) and nuclear track etch polymer membranes are two commonly used templates. They have been used to make nanowires composed of metals, semiconductors, and polymers. We report the synthesis of Metal-Semiconductor-Metal nanowires by electrochemical replication of AAO. The semiconductor could be CdTe or BiSb, which is sandwiched between metal segments. Cadmium telluride (CdTe) is one of the most important II-VI group compound semiconductors due to its interesting photoelectric properties. It has a direct energy band gap (1.4-1.5 eV), a relatively high optical absorption coefficient, and advanced photovoltaic properties, which make it suitable for fabricating photoelectron devices and solar cells. Bulk Bi1-xSbx alloys are among the best n-type low temperature thermoelectric (TE) materials. And recent studies show the TE efficiency will be improved by making nanowires of bulk TEs. Dissolving the template yields a colloidal suspension of free-standing nanowires. The structures of the composite nanowires are identified by SEM and TEM. The composition of the semiconductor segments is characterized by XRD. By changing the solution concentrations and the growth rate, the composition, crystallinity, and morphology of the nanowires can be tuned. The end-on junction between the semiconductor and the metal makes it possible to align these nanowires between metal contact pads and to make contact exclusively to the metal segments.

2:15 PM Rb3.4

Functional Assembly of One-Dimensional Nanostructures from Nanothermometers to Nanowire Heterostructures. Jinhua Zhan[1], Yoshio Bando[1], Junqing Hu[2] and Dmitri Golberg[1]; [1]Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]International Center for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

One dimensional (1D) nanomaterials have attracted considerable attention due to their potential applications as building blocks in nanoscale circuits and optoelectronic devices[1]. Nanotube filling with foreign elements, compounds and/or substances is a relatively new and exciting field of the nanomaterial research. 1D nanomagnets, nanocables and other functional nanomaterials may be synthesized through taking advantages of tiny nanotube channel dimensions and related confinement effects, and functional properties of guest species encapsulated within, e. g. ferromagnetism, piezoelectricity, electro- and thermoconductivity etc. Moreover, focusing on new properties and a wide selection of nano-building blocks for nanosized electrical and optical lines, it is important to obtain a potential barrier between adjacent constituting components showing the rectifying current-voltage characteristics. This can be realized through the creation of various heterostructures including p-n junctions, metal-oxide-semiconductor junctions or metal-semiconductor contacts, which allow signal processing to be reliably performed. Metallic gallium melts at nearly room temperature and has one of the widest liquid ranges among all metals. It was shown that Ga encapsulated in carbon nanotubes has a potential application as a nanothermometer due to its temperature-dependent expansion and contraction within a wide range [2, 3, 4]. We demonstrate an effective approach for bulk synthesis of gallium metal nanowires sheathed with carbon. We also demonstrate that gallium nanowires sheathed with carbon can be welded, cut and encapsulated using convergent electron beam. Furthermore, we demonstrate the fabrication of In-Si end-to-end nanowire contacts[5] and ZnS/Si side-by-side composite nanowires[6]. Their morphological and structural characteristics were also thoroughly analyzed. Within a In-Si junction, the In and Si subnanowires are crystallographically oriented with respect to each other and sheathed with a silica nanotube. Linear thermal expansion of an In branch (after its melting under heating) makes possible the design of a temperature-driven switch and/or sensor within an electronic device. Side-by-side ZnS/Si nanowires were prepared through tin-catalyst-confined-growth. Simultaneous thermal evaporation of ZnS and Si provide precursor vapors which are condensed on Sn droplets resulting in the nucleation and anisotropic growth of composite nanowires made of adjacent ZnS and Si domains. References: [1] Y. Xia, P. Yang, Y. Sun and et. al., Adv. Mater. 2003, 15, 353. [2] Y. Gao and Y. Bando, Nature 2002, 415, 599. [3] Z. Liu, Y. Bando, M. Mitome and J. Zhan, Phys. Rev. Lett. 2004, 93, 095504-1. [4] J. Zhan, Y. Bando, J. Hu, D. Golberg, H. Nakanishi, J. Phys. Chem. B., in press [5] J. Zhan, Y. Bando, J. Hu, Z. Liu, L. Yin, D. Golberg, Angew. Chem. Int. Ed. 2005, 44, 2140. [6] J. Zhan, Y. Bando, J. Hu, T. Sekiguchi, D. Golberg, Adv. Mater. 2005, 17, 225.

SESSION Ra4: Electrically Directed Assembly
Chair: Denis Fichou
Monday Afternoon, November 28, 2005
Room 207 (Hynes)

3:30 PM Ra4.1

Directed Assembly of Nanoelements Using Electrostatically Addressable Templates. Xugang Xiong[1], Prashanth Makaram[1], Kaveh Bakhatri[1], Ahmed Busnaina[1], Jason Small[1], Sivasubramanian Somu[1], Glen Miller[2] and Jingoo Park[3]; [1]The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, Northeastern University, Boston, Massachusetts; [2]The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, University of New Hampshire, Durham, New Hampshire; [3]Hanyang University, Ansan, South Korea.

The directed assembly of nanoparticles in nonuniform patterns using templates (Au nanowires on SiO2 substrates) has been demonstrated. Electrostatically addressable templates using DC voltage are used to assemble fluorescent polystyrene latex (PSL) nanoparticles. The negatively charged nanoparticles are attracted to the surface of the positively charged nanowires. Nanoparticles down to 50 nm have been successfully self-assembled to form uniform monolayer patterns along the conductive nanowires of the templates. The field assisted directed assembly approach can also be used to assemble single wall carbon nanotubes in aqueous solution into micro or nanoscale patterns using the templates. The assembled patterned particles are then transferred to another patterned substrate to function as part of a sensor or a device. The technique provides a simple, fast, scalable approach for directed assembly of nanoelements.

3:45 PM Ra4.2

Transport, assembly and rotation of nanowires in suspension by AC electric fields. Donglei Fan[1,2], Frank Q. Zhu[2], Robert C. Cammarata[1] and C. L. Chien[2]; [1]Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; [2]Department of Physics and Astronomy, Johns Hopkins UNiveristy, Baltimore, Maryland.

Nanowires are potential building blocks for nanoscale devices. Manipulation of nanowires in suspension to produce functional nanostructured materials has been a formidable problem. Using AC electric fields applied to strategically designed microelectrodes [1], nanowires in suspension can be driven to align, to chain, to accelerate in directions parallel and perpendicular to its orientation, to concentrate onto designated places, and to disperse in a controlled manner with high efficiency despite an extremely low Reynolds number at the level of 10^{-5}. Randomly oriented nanowires in suspension can be rapidly assembled into extended nonlinear structures within seconds. We show that both the electric field and its gradient play the essential roles of aligning and transporting the nanowires into scaffolds according to the electric field distributions inherent to the geometry of the microelectrodes. Furthermore, nanowires have been rotated by AC electric fields applied to strategically designed electrodes [2]. The rotation of the nanowires can be instantly switched on or off with precisely controlled rotation speed (to at least 1800 rpm), definite chirality, and total angle of rotation. This new method has been used to controllably rotate magnetic and non-magnetic nanowires as well as carbon nanotubes. We have also produced a micromotor using a rotating nanowire that can drive particles into circular motion. This has application to microfluidic devices, microstirrers, and micro electromechanical systems (MEMS). All of the features discussed offer great promise and flexibility with regard to producing a variety of nanoscale assemblies involving metallic, semiconductor, and biological materials. 1. D.L. Fan, F.Q. Zhu, R.C. Cammarata, and C.L. Chien, Appl. Phys. Lett. 85, 4175 (2004). 2. D.L. Fan, F.Q. Zhu, R.C. Cammarata, and C.L. Chien, Phys. Rev. Lett. in press.

4:00 PM Ra4.3
Non-impact electrostatic manipulation of a conductive micro-object by rapid control of applied voltage. Shigeki Saito[1], Kenji Kurihara[2] and Kunio Takahashi[3]; [1]Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, Tokyo, Tokyo, Japan; [2]Department of Mechanical and Control Engineering, Tokyo Institute of Technology, Tokyo, Tokyo, Japan; [3]Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Tokyo, Japan.

The size of an object to be manipulated has decreased in the electrical and mechanical engineering field for fabricating highly functional micro-electro-mechanical systems and photonic crystals. In micromanipulation, even if we can pickup micro-objects, it is difficult to detach the micro-objects because adhesional force is dominant. To date, some research groups have tried to manipulate conductive micro-objects by applying voltage because electrostatic force has been considered effective in micromanipulation. Excessive impact by constant voltage at landing of a detached object, however, is still a difficult problem to develop the reliable method of micromanipulation. Thus, in this study, an optimal voltage as a time-dependent function is theoretically derived; the effectiveness is demonstrated through the experiment by electrostatic micromanipulation system. The voltage function is determined so that the kinetic energy of a micro-object could be controlled during the flight after detachment from a probe-tip and become zero at landing on a substrate. Additionally, since the energy absorbed due to the adhesional hysteresis exists at the contact of the micro-object to the substrate, an allowable error of voltage for the energy absorption is evaluated. In order to realize the derived voltage function, a power source with high voltage and high-speed response is developed. With this power source, a solder ball with the diameter of 30 um is successfully deposited on the substrate after detachment from the probe-tip in the experiment of electrostatic micromanipulation. These results theoretically and experimentally show that this method could be applied to IC packaging or micro-device assembly.

4:15 PM Ra4.4
Nanopatterning, electropatterning, and nanocharging of organic and polymer semiconductors using the precursor polymer approach. Rigoberto Advincula[1], Valiyaveettil Suresh[2], Jegadessan Subiah[2] and Akira Baba[1]; [1]Department of Chemistry, University of Houston, Houston, Texas; [2]Department of Chemistry, National University of Singapore, Singapore, Singapore.

Nanopatterning of precursor polymers electrochemically using soft-lithographic and nanolithographic methods will be reported. Several strategies for the synthesis, fabrication, and characterization of these unique conjugated polymer ultrathin films will be presented. The application of these cross-linked materials is towards electro-optical devices, e.g. patterned polymer light emitting diode (PLED) devices will also be described. By controlling the deposition site using micro-contact printing, patterns on the electrode surface can be formed prior to electropolymerization. Electrochemical Nanolithography (ECN) is a technique in which a pattern is created by applying a potential between the AFM tip and the substrate (conducting AFM set-up) during "writing". By utilizing an electrochemical cross-linking strategy while patterning, robust and conducting patterns are established which are selectively addressable by SPM methods. Nanocharging is demonstrated in terms of a reversible (read-write) change in charge transport property localized in patterns addressed by the SPM tip at various biased voltages. Thickness, film homogeneity, wetting, etc. are important parameters that affect the patterning and charging experiments.

4:30 PM Ra4.5
Dielectrophoretic Assembly and Reconfiguration of Nanowire Interconnects. Alexander David Wissner-Gross[1] and Charles M. Lieber[2]; [1]Physics, Harvard University, Cambridge, Massachusetts; [2]Chemistry, Harvard University, Cambridge, Massachusetts.

Localized electric fields are powerful tools for programmable assembly and reconfiguration of nanostructure circuits. In this work, dielectrophoretic trapping of silicon nanowires as electrical interconnects is demonstrated. A suspension of heavily doped silicon nanowires is hermetically sealed above fabricated Au electrodes. Radio frequency biases applied between electrode pairs trap and make ohmic contacts with the nanowires. The voltage and frequency dependence of positive dielectrophoresis is measured and compared with theory. Low-k dielectric protective layers are used to inhibit trapping except at electrode tips. This technique is shown to scale from 2-electrode circuit completions to the assembly of 4- and 8-electrode networks. Applications of dielectrophoretically assembled nanowire circuits to physical implementations of graph algorithms are discussed.

4:45 PM Ra4.6
An Electrical AFM Approach to the Definition of Anchor Sites for Layered Biomolecular Structures. Nicola Naujoks and Andreas Stemmer; Nanotechnology Group, Swiss Federal Institute of Technology, Zurich, Switzerland.

Atomic force microscopy (AFM) based lithography has proven useful for local modification of surfaces at the nanoscale. Achieving control over localized positioning of particles and molecules is a key factor for nanosensor fabrication or for creating scaffolds for building up nanostructures. We previously reported on a method that uses electrostatic forces to guide particle deposition in liquid environments [1,2]. The electrostatic field is created by nanoscale charge patterns written into the sample with a conductive AFM tip. In this contribution, we will present how this general method defines anchor points with specific binding sites that allow for the docking of functionalized biomolecules and particles. By this means, larger structures, potentially serving as biosensors, are built up locally in a layer-by-layer procedure. The guided assembly process consists of two parts: After defining the patterns via AFM-based charge writing, the sample is developed in a water-in-oil emulsion. Driven by electrostatic forces, the water droplets carry particles or molecules to the patterns. The basic characteristics of this deposition have been studied for a water-particle-oil model-system for different substrates [1]. Using the same process, biotin-labelled immunoglobulinG (IgG-biotin) was deposited with sub-?m resolution onto charge patterns on poly (methyl methacrylate) (PMMA) samples [2]. The IgG molecules at the same time help in stabilizing the emulsion [3]. As the samples are dried after developing them in the emulsion, re-wetting the structures is a necessary step prior to any further modifications made. To this end, the dry samples are immersed into a buffered blocking solution, which also prevents unspecific binding during the following reactions. As the emulsification and the drying steps might have caused conformational changes of the IgG, the activity and accessibility of the biotin groups on the IgG have to be proven. We verified the biotin activity by incubating the sample in a solution containing fluorescently labelled anti-biotin molecules, which are known to bind specifically to biotin. For the layered structures, a streptavidin linker is used to attach 40 nm sized biotin-labelled polymer beads (biotin-beads) from aqueous solution. Fluorescently labelled biotin-beads bind to the free binding sites of previously attached streptavidin facing inside the solution. Fluorescence images reveal the high specificity of both reactions. The IgG-biotin still has enough functionality to detect the biotin-beads via a streptavidin linker. [1] N. Naujoks, A. Stemmer, Microel. Eng. 78-79 (2005) 331. [2] N. Naujoks, A. Stemmer, Coll. Surf. A 249 (1-3) (2004) 69. [3] S. Magdassi, A. Kamyshny, A. Baszkin, J. Disp. Sci. Technol. 22(4) (2001) 313.

SESSION Rb4: Alternative Nanofabrication Techniques I

Chair: Juriaan Huskens
Monday Afternoon, November 28, 2005
Room 208 (Hynes)

3:30 PM *Rb4.1
Abstract Not Available Stephen Chou

4:00 PM Rb4.2
Nanostenciling: A Versatile Approach for Parallel Patterning of Ferroelectric Complex Oxides. Cristian Victor Cojocaru, Catalin Harnagea, Olivier Gautreau, Alain Pignolet and Federico Rosei; Materials Science, INRS - EMT, Varennes, Quebec, Canada.

Fabricating functional structures from a variety of materials with controlled size and shape as well as precise positioning on a substrate of choice is essential to the development of several technologies. For instance the progress of micro/nano-electronics and memory technologies as well as the nanoscale design of MEMS/NEMS and sensors and actuators is prompting the development of novel surface patterning techniques. Advances in these technologies are relying mostly on ongoing improvements of lithography based techniques (DUV, EUV, and EBL), focused-ion-beam (FIB) or more recently nanoimprint lithography (NIL) to achieve complex features with dimensions in the nanometer range. However, these techniques require expensive ultra-specialized equipment and are usually performed in a cleanroom environment. We have investigated in details an alternative approach, nanostenciling [1] and along with its suitability for direct patterning of complex materials we demonstrated its unique flexibility in the combination functional material / substrate [2]. Among the latter, members of the complex oxides family display a range of interesting and useful properties in response to combinations of electric, magnetic, and stress fields. These properties include piezoelectricity, ferroelectricity, colossal magneto-resistance, high-temperature superconductivity, etc. and these have been shown to be related to their fabrication process and the quality of ultra-thin films. Using microfabricated miniature shadow-masks, selective deposition of ferroelectric perovskites (e.g. BaTiO3, BiFeO3, and PZT) was swiftly achieved by interposing a nanosieve between the substrate surface (Si, Pt-coated-Si, SrTiO3 and SrRuO3) and the rotating target from a PLD deposition chamber. The patterns designed in the nanomask are accurately transferred to the substrate, and 3D-nanostructures of functional materials are directly deposited with the desired geometry. We are also presenting the application of a nanoscale multi-level-stenciling approach that gives the opportunity for rapid prototyping of functional stacks of materials such as metal-oxide-metal and magneto-electric heterostructures grown by sequential depositions. The morphology and composition of theses nanostructures were characterized by SEM, AFM, XRD and XPS techniques and their local ferroelectric properties were detected using piezoresponse force microscopy (PFM). The application of this process is meant for research (e.g. studying the size effects on the functional properties of the structures) but also represents a promising universal tool for parallel deposition of high-resolution and high-purity nanostructures of functional materials under high and ultra-high vacuum. [1] J. Brugger, J.W. Berenschot, S. Kuiper, W. Nijdam, B. Otter and M. Elwenspoek, Microelectron. Eng. 53, 403, (2000) [2] C. Cojocaru, C. Harnagea, F. Rosei and A. Pignolet, M.A.F. van den Boogaart, J. Brugger, Appl. Phys. Lett. 86, 183107, (2005)

4:15 PM Rb4.3

Supramolecular Nano-Stamping. A. Amy Yu[1], Tim Savas[2], Enzo Di Fabrizio[3], Henry I. Smith[2] and Francesco Stellacci[1]; [1]Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]Department of Electrical Engineering, MIT, Cambridge, Massachusetts; [3]Lilit, TASC-INFM, Basovizza, TS, Italy.

As the size of devices drastically shrinks, the need of a method that can fabricate a small size pattern and reproduce it in a mass scale in a short time has increased. Supramolecular Nano-Stamping (SuNS) is a novel printing method that can replicate a patterned DNA monolayer on another substrate with just three steps. It is composed of a hybridization-contact-dehybridization cycle: on a surface containing features each made of single stranded DNA (ssDNA) of known sequence, the complementary DNA molecules are hybridized, spontaneously assembling onto the original pattern due to sequence-specific interactions. These complementary DNA strands, on the end that is assembled far from the original surface, are modified with chemical groups ("sticky ends") that can form bonds with a target surface brought into contact. Heating induces dehybridization between DNA strands. The resulting transferred pattern is the mirror image of the original one, and can be used as a new master to stamp another copy. Additionally, SuNS, based on specific interaction between complementary DNA sequences, is capable of printing multiple DNA sequences simultaneously. This implies that it can transfer not only spatial information, i.e. size and pattern's shape, but also chemical information (i.e DNA sequence). Here we will show pattern successfully printed with high resolution (<30nm) and high complexity using gold-thiol chemistry. We will also present SuNS on modified poly methyl methacrylate (PMMA) substrates. A comparison between the advantages of these two approaches will be presented.

4:30 PM Rb4.4

Phase Transition in Nanoscale Direct Deposition Processes. Narae Cho[1], Byeongju Kim[1], Juwan Kang[1], Sungyoung Park[1], Byung Yang Lee[1], Kyung-Eun Byun[1], Seol Ryu[2], George C. Schatz[2] and Seunghun Hong[1]; [1]Physics and Nano Systems Institute, Seoul National University, Seoul, South Korea; [2]Department of Chemistry, Northwestern University, Evanston, Illinois.

We report the first observation of phase transition in nanoscale direct deposition processes. Even though nanoscale direct deposition processes such as dip-pen lithography (DPN) have been extensively utilized to pattern a broad range of molecular species on solid surfaces, its mechanism and even the phase of deposited molecular inks have not been fully understood. We propose the "surface mobile layer" model, where the DPN process is explained by the transport of mobile surface molecules driven by multiple mechanisms (e.g. thermal energy, adsorbed solvent layer, etc). We also propose that the bulk molecular ink under the surface molecules remains solid, and it works as an ink reservoir to regulate the DPN deposition rate. We performed DPN experiments to measure the deposition rate and its scaling behavior under various temperature and humidity conditions. Significantly, the scaling analysis of the deposition rate confirms our model and shows clear indication of the phase transition of the molecular ink in the DPN process.

4:45 PM Rb4.5

Integrating Self-Assembled Nanopore Arrays. Xiaoyuan Qi[1], Jia Zou[1], Liwen Tan[2] and Bethanie J. H. Stadler[1]; [1]Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota; [2]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Anodic aluminum oxide nanopores with long range order (mm) were integrated onto a variety of surfaces (Si, SiO2, and yttrium iron garnet) for use as nanoscale etch masks. Typical self-assembly of nanopores within anodic alumina occurs using a two-step anodization of bulk Al foil. Domains of order are produced in the first step and continuous, ordered, parallel pores are grown in the second step. The ordering step occurs over a long period of time (tens of hours), which makes it difficult to integrate the pores using thin films of Al because the films may be fully anodized before ordering can occur. In this work, thin films of Al were grown via sputtering and evaporation. These films were then anodized using both a two-step process and a directed assembly technique called nanoimprinting which allows long-range ordering over very short anodization times. A variety of pore sizes were fabricated by varying the anodization conditions, such as voltage, temperature and electrolyte. In the case of nanoimprinting, master nanoimprint stamps of Si3N4 were fabricated using LPCVD, ebeam lithography, and reactive ion etching. The resulting array of nitride posts was then imprinted onto numerous aluminum films. Atomic force microscopy (AFM) was used to observe that the patterns of the master stamps were transferred onto the aluminum sheet after the imprinting. Next, anodization was carried out using parameters that matched the different lattice constants to those of the stamps. Scanning electron micrographs (SEM) showed that perfectly ordered porous arrays were obtained with center-center spacings of 100-500nm over as large an array as a few millimeters squared. . The nanopores were then etched into the underlying surfaces of Si, SiO2 and YIG, respectively, using reactive ion etching. Several stamps were made with microscopic arrangements of the nanoscopic nitride posts, and these microscopic features were used to align subsequent layers to the nanoscopic pores via an optical microscope. For example, strips of metallization were aligned with the nanopores using photolithography. These results are important for both the ability to nanostructure a variety of materials, and also for the ability to connect the nanoscopic and microscopic regimes.

SESSION Ra5/Rb5: Poster Session I
Chair: Gregory Lopinski
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra5.1/Rb5.1

Assembly Design Concepts and Methods of Tailoring of CNT Orientation and Dispertion for Damping/Dynamic Properties of Nanoparticle-Reinforced Multifunctional Materials. Maksim Kireitseu, NAS of Belarus, Minsk, Belarus.

Assembly design concept of carbon nanotube (CNT)-based multifunctional materials can offer possibility to control molecule-level mechanism that can have on the dynamic/damping properties of CNT-reinforced materials thus providing more multifunctionality. The nanoparticle assembly technology for novel nanocomposites and thier dynamic mechanisms involved in such materials need to be understood. Manufacturing design concept could be combined with modeling techniques so as to enable efficient synthesis and design of the next generation of CNT-based mechanical systems. The focus in this paper is directed toward to the investigation into technological issues of assembly techniques of novel CNT-based materials and their dynamic/damping characterization. Particular aim of the work is a control over nanocomposite assembly methodology (CVD, PVD). Simultaneous optimization of a class of CNT-reinforced materials can be achieved by using numerical simulations and virtual reality environment. Thus effective solutions can be found to have wide-ranging technical benefits with direct relevance to industry in areas of transportation and civil infrastructure development.

Ra5.2/Rb5.2

Growth Mechanism of Phase Separated Al-Si Thin Films. Kazuhiko Fukutani, Koichi Tanji, Tatsuya Saito and Tohru Den; Inorganic Material Reseach Dpt., Canon Inc., Atsugi, Japan.

Due to their unique structures and exceptional properties, one-dimensional structures such as nanowires and nanotubes have received considerable interest in recent years for their potential applications in many fields. In particular, nanowire arrays are considered to be promising materials for high-density magnetic recording media, sensors and thermoelectric devices. Phase separated Al-Si films, composed of Al nano-cylinders (one-dimensional structures) embedded in an amorphous Si matrix, are interesting materials because the fabrication method, sputtering deposition, is simple and widely used to fabricate commercial electronic devices. In addition, the materials are very useful to fabricate ultrahigh density nanowires by template-assisted growth.* In this presentation, the phase separated Al-Si films prepared by various fabrication conditions were investigated. By controlling the deposition rate, substrate temperature and film composition, the average diameter of the Al cylinders can be varied systematically from less than 5 nm to 13 nm with a cylinder density ranging from 10^{15} to in excess of 10^{16} m^{-2}. In addition, a three-dimensional simulation of phase separation in binary thin films was performed using a modified Chan-Hilliard equation to understand the growth mechanism. The simulation studies indicate that the surface diffusion length and film composition are important factors which determine film morphology. Experimental and simulation studies are compared and discussed. *K. Fukutani, K. Tanji, T. Motoi, T. Den, Adv. Mater. 16, 1456 (2004).

Ra5.3/Rb5.3

Abstract Withdrawn

Ra5.4/Rb5.4

Discontinuous Monolayer can Control Metal/Molecule/Semiconductor Junctions. Hossam Haick[5], Marianna Ambrico[1], Teresa Ligonzo[3], Raymond Tung[4] and David Cahen[2]; [1]CNR-IMIP Sez. di Bari, Bari, Italy; [2]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel; [3]Dipartimento di Fisica and Instituto Nazionale di Fisica della Materia, Universita' degli Studi di Bari, I-70126 Bari, Italy; [4]Department of Physics, Brooklyn College, City Univ. of New York, Brooklyn, New York; [5]Division of Chemistry and Chemical Engineering, California Inst. of Technology, Pasadena, California.

Molecules can control charge transport across a metal/semiconductor interface, also if they form only a partial monolayer at the interface. This is because of the long-range electrostatic effect of (molecular) dipole domains, which affects also semiconductor regions under the film pinholes. This finding extends significantly the variety of molecules that can be used, by including all those that yield, as a partial monolayer, a net dipole perpendicular to the interface. We reach our conclusion by complementary electrical characterizations of junctions, formed by indirect evaporation of Au and Pd, and, in specific cases, by ready-made contacts, on a set of molecular monolayers that are chemisorbed on n-GaAs. The set is formed by using a well-studied series of molecules with systematically varying dipole moments. The electrical characterizations that we used are current-voltage-temperature, capacitance-voltage, and internal photoemission. The resulting data were analyzed taking into account the limitations of each of the techniques and using theoretical models that were modified to account for the presence of a partial, discontinuous molecular monolayer at the interface. In this way we find that the simplest description for the experimentally observed behavior is in terms of a parallel conductance model.

Ra5.5/Rb5.5

Self-assembling nanodot arrays arranged in parallelogram and rectangular guides. Kaori Kimura and Masatoshi Sakurai; R&D Center, Toshiba Corp., Saiwai-ku, Kawasaki, Kanagawa, Japan.

Magnetic nanodot arrays have gatherd attentions for applications in high-density patterned magnetic media. We have demonstrated fabrication of magnetic nanodot arrays in linear groove guides using block copolymer templates. In this method, block copolymer nanodots formed lines in a linear groove, but the position of the nanodot was not controlled in its line. For practical magnetic media, it is necessary to control the position of nanodots with a high accuracy. In this research, parallelogram and rectangle groove guides were fabricated on photoresist film by a nanoimprint lithography method. The parallelogram guide with a corner of 60° is suitable for a hexagonal lattice of block copolymers. And rectangle guide with a corner of 90° matches the angle between the main axis and the second axis that has *sqrt*3 times wider spacing than the main axis. These guide groove patterns were imprinted by a Ni stamper on a photoresist film which was spincoated on substrate. Block copolymer of polystyrene-polymethylmethacrylate (PS-PMMA) was dissolved into propylene glycol monomethyl ether acetate (PGMEA), and spincoated onto the guided substrate. The PS-PMMA has a molecular weight of 89,300 and periodicity of 45nm. After annealing at 180°C, phase segregation occurred. The condition of arrangement was observed by AFM phase mode measurement. PMMA dots arranged parallel to the wall of the guide. In the parallelogram guide, PMMA dots arranged with few defects, for example, a dot surrounded by five or seven dots. On the other hand, in a rectangular guide, PMMA dots formed some domains caused by the surface tension from wall of the guide. Mostly, the longer side of rectangle had a stronger surface energy, so the domain of the longer side tends to be larger than that of the shorter one. In the square guide, the domain area and direction was not controlled because it has the same length as the sides. Especially, in some of the smallest square guide, there was no domain wall. This work was supported by the IT-program (RR-2002) of the Ministry of Education, Culture, Sports, Science and Technology (NEXT), Japan.

Ra5.6/Rb5.6

Microwave Plasma-Enhanced Chemical Vapour Deposition Growth of Non-Surface Bound Carbon Nanowalls. Alfred Tung-hua Chuang[1], Bojan Boskovic[2] and John Robertson[1]; [1]Department of Engineering, University of Cambridge, Cambridge, United Kingdom; [2]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Carbon nanowalls are well-aligned and self-assembled carbon sheets with a thickness in the range of several nanometers. Wu et al. [1] reported fabrication of two-dimensional carbon nanostructures (carbon nanowalls) using microwave plasma-enhanced chemical vapour deposition (PECVD) process on insulated substrates. Subsequently, Hiramatsu et al. [2] reported fabrication of carbon nanowalls using rf-PECVD, assisted by hydrogen radical injection without catalysts. Carbon nanowalls have enormous surface area that is important for electrochemical and many other applications [3]. They can also serve as growth templates for other types of nanostructures [4]. Here we report non-surface bound (freestanding) carbon nanowall growth without catalyst using microwave PECVD. The clear advantages of this new synthesis method are the scale of production, and ease of harvesting. While these graphite sheets have thickness and length in nanometer scale, carbon nanowall clusters can compound and grow into a freestanding structure measured up to 5 centimeters in length for a 10-minute growth. Considering the non-surface bound nature of this growth phenomenon and the absence of catalyst, a moderate amount of carbon nanowalls can be easily obtained and deployed for further development and applications. Correlation between variable growth rate, growth quality and synthesis parameters were drawn for this synthesis method. Field emission properties and surface area of carbon nanowalls were also measured. As a proof of concept, specimens of carbon nanowalls were used as catalyst carriers for synthesis of carbon nanofibers to demonstrate the feasibility of growth template applications. References: [1] Wu YH, et al., ADV MATER 14 (1): 64-67 JAN 4 2002 [2] Hiramatsu M, et al., APPL PHYS LETT 84 (23): 4708-4710 JUN 7 2004 [3] Wu YH, et al., J MATER CHEM 14 (4): 469-477 FEB 21 2004 [4] Yang BJ, et al., NANO LETTERS 2 (7): 751-754 JUL 2002

Ra5.7/Rb5.7

Manipulation of microporous aluminophosphate lamellae for the formation of polymer/molecular sieve nanocomposite membranes. Joshua A. Sheffel and Michael Tsapatsis; Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

The manipulation of layered inorganic materials in order to achieve functional nanostructures is important in areas such as heterogeneous catalysis, specific adsorption, nonlinear optics, self-consistent films, and nanocomposites. The swelling and intercalation chemistry of clays, for example have generated much interest relating to the formation of thermally stable pillared materials. Likewise, much study has been conducted on the intercalation of the layered zirconium phosphates, vanadium phosphates, and transition metal oxides. The family of crystalline aluminophosphates, however, is so far little understood in regards to swelling and intercalation chemistry. The layered aluminophosphates under consideration consist of crystalline inorganic layers formed by alternating AlO4-6 and PO4 polyhedra [Yu, J.; Xu, R. Acc. Chem. Res. 2003, 36, 481-490]. These anionic layers are characterized by a molecular sieve-type structure where 4- to 12-member rings are present, giving the possibility of microporosity. The layer charge is balanced by protonated organic amines located in the gallery space between the layers. These structure-directing amines also form extensive hydrogen bonds with the inorganic layers. The swelling and intercalation chemistry of these materials is of interest for potential use in microporous-mesoporous materials and high-performance composites for separations. More specifically, our group has recently reported the use of these molecular-sieving aluminophosphate layers for the formation of polymer nanocomposite membranes that show enhanced selectivities for the separation of oxygen from nitrogen and carbon dioxide from methane [Jeong, et. al., Chem. Mater. 2004, 16, 3838-3845]. Procedures for swelling, exfoliating, and, in some cases, reassembling these layered aluminophosphates have recently appeared in the literature. However, complete characterization of the material at each stage of the swelling process has yet to be reported. In most cases, it is not even clear that the final, swollen material possesses the same Al-O-P connectivity and crystal structure as the original inorganic layers. A more complete understanding of this nanoscale assembly process will pave the way for rational design of advanced materials from these layered microporous materials. We will present results on the swelling, exfoliation, and re-assembly of layered aluminophosphates, and the structure of the material will be characterized at each step with x-ray diffraction, small-angle x-ray scattering, solid state NMR, and transmission electron microscopy. We will also present results on the application of these materials to nanocomposite polymer/molecular sieve membranes for gas separations.

Ra5.8/Rb5.8

Amphiphilic Photoresponsive Azobenzene-Containing Polymers. Smeet P. Deshmukh, Lev Bromberg and Alan Hatton; Chemical Engineering, MIT, Cambridge, Massachusetts.

Light represents an attractive trigger to change properties of a polymer solution because it would enable structural control without requiring changes in solution conditions, and it is externally reversible; thus, it is amenable to device design and automation. Amphiphilic copolymers with azobenzene moieties are of interest due to the ability of the azobenzene to undergo reversible trans-cis photoisomerization leading to the conformational isomers with significantly dissimilar dipole moment and hydrophobicity, and thus ability to aggregate into nanoscale structures in aqueous media. Herein, we describe novel poly(4-methacryloyloxyazobenzene-co-N,N-dimethyl acrylamide) (MOAB-DMA) copolymers that undergo trans-to-cis photoisomerization under UV irradiation at ?max of around 325 nm. The MOAB-DMA copolymers with at least 0.18 molar fraction of the methacryloyloxyazobenzene groups are water-soluble and exhibit a pronounced photoviscosity effect, expressed in over 10-fold enhancement of the zero-shear viscosity of the irradiated aqueous solutions. A critical concentration of the copolymer (cac) was observed that lead to the appearance of compact aggregates (∼30 nm according to the DLS tests) capable of solubilizing a water-insoluble dye, Nile Red. This cac corresponded to the critical micellar concentration observed in dynamic surface tension studies. Photoisomerization kinetics studies of the MOAB-DMA copolymers in aqueous solutions were based upon the time-dependent decay of the intensity of the electronic absorbance peak at 325 nm after irradiation. The rate constants of the photoisomerization decreased with the polymer concentration, concomitantly with the hydrodynamic radius and in tandem with the surface tension of the solution. Dynamic changes in the aggregation behavior of photoresponsive polymers enable novel opportunities for the control of viscosity and other properties of importance for the development of the applications of these novel nanostructured materials.

Ra5.9/Rb5.9

Electrochemical Dip-Pen Nanolithography of Conductive Wires on the SiO2 Surfaces. Fapei Zhang[1,2], Ryo Yamada[2,3] and Hirokazu Tada[2,3]; [1]JSPS Fellow, Toyko, Japan; [2]Department of Materials Physics, Osaka University, Osaka; [3]JST-CREST, Tokyo, Japan.

Fabrication of conductive nanowires on insulator is a key technology in molecular electronics. Recently AFM-based dip-pen nanolithography (DPN) has been invented by which various nanostructures can be written directly on suitable surfaces with high degree of control over location and geometry. In this study, we have systematically explored the fabrication of conducting nanowires on insulating SiO2 substrates by electrochemistry-assisted DPN (E-DPN). Nanowires are grown on the photolithographically-defined Au pad initially and then the growth is expanded over SiO2 surface using the produced wire as working electrode. We have systematically examined various parameters of E-DPN including the effects of coating methods and the types of the tips on electrodeposition behavior. It was found that the chemically-modified Si AFM tips by hydrogen termination and moderately oxidation in UV ozone showed a favorable conductivity and high hydrophilicity suitable for DPN. Pt nanowires with a line width of 100 nm were prepared on the Au pad. The parameters optimized for E-DPN of metal and polymer nanowires on SiO2 surface will be presented.

Ra5.10/Rb5.10

Surface-enhanced Raman Scattering of Rhodamine 6G Using Physically Self-assembled Ag Nanorod Arrays. Takao Fukuoka[1], Motofumi Suzuki[2], Yoshinori Wada[2], Kaoru Nakajima[2], Kenji Kimura[2] and Yasushige Mori[3]; [1]JST Kyoto CREATE, Seika chou, Kyoto, Japan; [2]Department of Micro Engineering, Kyoto University, Kyoto, Japan; [3]Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Japan.

Design of the nano-ordered structure and development of the manufacturing method at the level of the mesoscopic size become essential in order to utilize localized plasmon resonance of the noble metal nanoparticles efficiently as new optical devices and sensors. The dynamic oblique deposition (DOD) is one of the most suitable methods for the formation of the novel nano-ordered structures. Recently, we have succeeded to directly create the Ag nanorods arrays in which the major axes are aligned almost parallel to each other. [1] These nanorod arrays seem to be advantageous to the surface-enhanced Raman scattering (SERS) substrates since the Ag nanorods can be regularly lined up at various surface densities. Here, we demonstrated first application of the Ag nanorods arrays fabricated by DOD to SERS measurement. The Ag nanorod arrays were directly formed on the template layer of SiO2 prepared by serial-bideposition. During the serial-bideposition, the deposition angle measured from the surface normal, was set to a fixed value (from 72 to 86), while the azimuthal angle was changed rapidly by 180 with each deposition of a 10 nm-thick layer. After repeating (from 15 to 30 cycles) of the serial bideposition, Ag was evaporated at a deposition angle (from 70 to 79) onto the fabricated template layer. The amount of deposited Ag was 4-14 nm in average thickness. Owing to the self-shadowing, the major axes of the Ag nanorods are aligned perpendicular to the deposition plane of SiO2. The morphology of Ag nanorod arrays was confirmed by SEM micrograms. We selected most appropriate substrate in which Ag layers remained discontinuous on the template and had enough surface density as SERS substrate. Using Raman microspectroscopy with 785nm semiconductor laser, the Raman scattering spectra of rhodamine 6G (R6G) ethanol solution on the Ag nanorod array were measured. Apparent peaks corresponding to the SERS of R6G have been observed, while no significant peak was observed for the glass plate without Ag nanorod. The SERS intensity was dependent on polarization of incident laser and alignment of Ag nanorod. Although it has been known that the chain-like aggregation of noble metal nanoparticles is effective for the near infrared SERS, conventional techniques are insufficient to control the morphology and configuration of nanorods. This DOD method is promising candidate for manufacturing the SERS active nano-ordered structure. [1] M. Suzuki, W. Maekita, K. Kishimoto, S. Teramura, K. Nakajima, K. Kimura and Yasunori Taga, Jpn. J. Appl. Phys., 44 (2005) L193.

Ra5.11/Rb5.11

Si Nano-Assemblies made by Arc Plasma Method in Water. Shu-man Liu, Seiichi Sato and Keisaku Kimura; Graduate School of Material Science, University of Hyogo, Hyogo, Japan.

Si nano-materials are currently the focus of intense research interest since nano-sized Si exhibits new properties such as visible and UV luminescence at room temperature, which is expected to guide new functionality in the field of optoelectronic devices. Fabrication of Si nanocrystal usually requires sophisticated vacuum system for the pyrolysis of silane or Si ion implantation into SiO2 film except the method of electrochemical etching of Si wafer, which is conducted in water and produce porous Si nanostructure in the surface layer of Si wafer. In this case, nano-architectures formed on the Si substrate are difficult to conduct further manipulation and prevent extended application. Hence it is strongly desirable that assemblies must be produced in well isolated form such as carbon onions and nanotubes. Here we describe a simple method for producing high-quality Si nano-assemblies in large quantities in water. The Si nanoparticles are generated by an arc-discharge between two Si electrodes submerged in water. This technique is low-cost and environmentally cleans, and produces non-contaminated nano-architectures, which may be used in many applications, such as opto-electronic devices. Recently, arc discharge technique in water has been used for preparation of carbon nanostructure by Sano et al by using layer structured graphite electrodes. However syntheses of Si nanoparticles, nano-horns and nano-belts by arc in water have not been reported so far. The apparatus consisted of two Si electrodes, and the arc discharge was initiated by an instant contact of a Si anode (diameter of 5mm) with the Si cathode (diameter 20mm). The discharge current 10A was sustained by adjusting the cathode-anode gap to be about 1mm. Ar was continuously supplied to purge O2 out from water. The Si nanoparticles were floated on the air water interface and other architectures suspended in water, with some large particles falling to the bottom of the beaker. We investigated the as-prepared Si particles suspended in water by scooping a Cu grid using a Hitachi 8100-transmission electron microscope (TEM) operated at 200kV. Histogram of size distribution was obtained form conventional TEM image. High resolution TEM (HRTEM) image and transmission electron diffraction pattern showed the structure of Si nano-belt, nano-horn and nanoparticles. The average diameter of Si nanoparticles is ∼6nm, with good crystallinity consistent with the diamond cubic structure of bulk Si. Increasing the arc current can optimize production rate of Si nano-particles. Continuous arc plasma for 1 hour gave a mass production.

Ra5.12/Rb5.12

Thermo Control on Assembly and Dispersion of Gold Nanoparticles. Shin-ya Onoue[1,2] and Toyoki Kunitake[2]; [1]R&D Department, Kyoritsu Chemical & Co., Ltd./PRESTO, JST, Kisarazu, Chiba, Japan; [2]FRS, Riken, Wako, Saitama, Japan.

We report on the experimental study of thermo-responsive aggregation of highly stable gold nanoparticles covered by simple alkyl chains in various solvents. It is known that they provide a wide range of possibilities for display devices and optical materials. In this study, gold nanoparticles stabilized by various types of organic molecules were prepared in the liquid phase. Behavior of dispersion and aggregation of gold nanoparticles into solvents and liquid resins were investigated by UV-Vis spectra and TEM observation.

Ra5.13/Rb5.13

Sub-micron Fibers from Electrospinning of Polymer Melts and Heated Solutions. Huajun Zhou and Yong Lak Joo; Cornell University, Ithaca, New York.

Electrospinning which utilizes an electric force to elongate a charged jet has now regained its popularity to produce nano-sized fibers. Over one hundred polymer and ceramic fibers have been successfully obtained by electrospinning. These fibers can have a very high surface area to volume ratio and can easily be functionalized, and thus are finding uses in many fields such as filtration, tissue scaffolding, drug delivery and gas sensors. Despite their great potential uses, nanoscale fibers of some polymers such as Polypropylene and Ultra High Molecular Weighted Polyethylene (UHMWPE) have not been obtained from conventional solution electrospinning, since they have no proper solvents at room temperature. In the present study, we investigate the possibility of processing these polymers into sub-micron fibers either directly from melts or from solutions at elevated temperatures. Three systems are chosen: Poly Lactic Acid (PLA) for melt electrospinning, Polypropylene and UHMWPE for heated solution electrospinning. Using an electrospinning setup with inventive heating capacity, we were able to obtain sub-micron fibers in all three systems. Our studies indicate that nozzle temperature and nozzle size are two most dominant factors in controlling the fiber size. To improve the fiber mechanical strength, organically modified nanoclays were intercalated into our polymer systems and the effect of nanoclay inclusion on the fiber structures and mechanical properties was investigated. Our results reveal that nanoclay inclusion increases both yield strength and elastic modulus of fibers due to their significant alignment throughout the fiber. Finally, a possible mechanical and thermal degradation of polymers during the process is discussed.

Ra5.14/Rb5.14

Investigation of Structural Properties of Silicon-Germanium Composites in Diatom Frustules. Timothy Gutu[1], Jun Jiao[1], Clayton Jeffryes[2], Shuhong Liu[2], Gregory L. Rorrer[2] and Chih-hung Chang[2]; [1]Department of Physics, Portland State University, Portland, Oregon; [2]Department of Chemical Engineering, Oregon State University, Corvallis, Oregon.

Diatoms are single-celled microalgae. They have the unique ability to make complex nanoscaled three-dimensional silica structures that offer attractive possibilities for their application in nano-biotechnology. This ability was exploited in incorporating germanium into the diatom cell in a two-stage photoreactor cultivation process (biosynthesis), leading to the formation of nanostructured silicon-germanium (Si-Ge) oxide. In the development of this perfusion-based bioreactor processing strategy for the biosynthesis of Si-Ge oxides, the TEM and SEM are extensively used to monitor progress at each stage. Si-Ge oxides possess attractive optoelectronic properties such as photoluminescence. A state-of-the-art FEI Tecnai F-20 field emission high resolution TEM (200kV) equipped with an embedded digital scanning transmission electron microscopy (STEM) capability and an energy dispersive x-ray spectrometer (EDS) were used to study the structural properties and chemical composition of Si-Ge nanocomposites in diatom frustules. The integrity of the diatom cell mass was validated by characterization with an FEI Sirion field emission scanning electron microscope (FESE), also equipped with an Oxford EDS. Structural properties of the Si-Ge oxides composites and distribution of Ge and Si within the frustules were determined. The intensity variation of Ge signal in the diatom frustules similar to that of Si though it is lower by two orders of magnitude. The results also suggest that Ge exists in smaller pockets or nanoparticles than Si. Having located the Ge sites in the diatom frustules, the further challenge lies in relating these sites to anatomical structures of the diatoms. [1] Acknowledgements 1. This report was supported by the National Science Foundation (NSF) Nanoscale Science and Engineering Initiative, Nanoscale Interdisciplinary Research Team Award, BES-0400648 and DMR-0353738 (REU Site).

Ra5.15/Rb5.15

Invertible Assemblies of Novel Amphiphilic Homopolymers. Hossein Baghdadi[1], Dharma Rao[2], Surita R. Bhatia[1] and S. Thayumanavan[2]; [1]Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts; [2]Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts.

We report small-angle neutron scattering (SANS) studies of the assembly of a novel class of amphiphilic homopolymers. The amphiphilic nature is achieved by incorporating both hydrophobic (benzyl) and hydrophilic (carboxylic acid) moieties into each repeat unit. In water, these polymers form micelle-like structures with a hydrophilic corona and hydrophobic core. However, in apolar solvents (toluene with a small amount of water), the structure inverts to an assembly with a lipophilic corona. Thus, these materials are extremely sensitive to their solvent environment and have the potential to be used as stimuli-responsive "smart" materials for controlled release or catalysis. Like conventional small-molecule micelles, these assemblies may be used to solubilize hydrophobic pharmaceuticals. However, unlike classical small-molecule micelles, the critical micelle concentration is quite low, in the range 10^{-7} to 10^{-9} M. In addition, there is evidence that the micelle rigidity is dependent on the polymer concentration. This can be used to tune the release rate of solubilized pharmaceuticals. Finally, we see that the characteristic sizes of these assemblies are in the range 30-90 nm, somewhat larger than typically encountered for block copolymer micelles. This may be desirable for certain delivery applications. SANS spectra can also be used to qunatify the amount of solvent in the interior of the micellar assemblies. These studies yield insight into new materials and routes for nanoscale assembly, as well as impact applications such as controlled drug release, smart adhesives and catalysis.

Ra5.16/Rb5.16

Millimeter-scale surface nano-structuring using focused ion beam milling. Katharine Dovidenko, Radislav A. Potyrailo, Laurie A. Le Tarte, Hong Piao and James Grande; GE Global Research, Niskayuna, New York.

New patterning schemes for variety of applications including sensors and photonics are explored. We present here a comprehensive study of using focused ion beam (FIB) milling to modify surfaces over millimeter-scale areas with nano-patterns of dimensions down to 30 nm. A typical example of a pattern is 40 nm diameter x 40 nm depth wells with a 200 nm pitch. Pyramids and other shapes can be produced as well. Typical sample materials are metals, but polymer patterning is available as well. We are also evaluating the surface of the patterned materials to ensure there are no negative effects of these patterning schemes on the future device performance. FIB milling is known to produce substantial, and not always desired, alterations on the surface. Utilizing the dual-beam FIB-SEM (scanning electron microscope) system, we are able to exclude sample surface exposure to the ion beam when setting up the patterns. Hence, no structural damage is typically observed (SEM) on the surface of patterned materials. However, there are secondary ion scattering effects taking place during pattering, as well as subtle effects of rustering the electron beam over the sample surface in conjunction with milling. These effects can potentially create a monolayer-scale surface modification. We are using Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy to evaluate the surface quality after pattering and prove methods applicability for various applications. The effects of plasma cleaning on the patterned surface are also discussed.

Ra5.17/Rb5.17

Controlled direct growth of vertical and highly-ordered 'carbon nanotube - silicon' heterojunction array. Teng-Fang Kuo, Aijun Yin, Chih-hsun Hsu, Daniel Straus, Marian Tzolov and Jimmy Xu; Brown University, Providence, Rhode Island.

Carbon nanotubes (CNT) has been studied intensively for explorations of its unique electrical and mechanic properties in many applications. However, direct integration carbon nanotube with silicon to form an electronically functional structure or device, though highly desirable, has remained a great challenge. Whereas vertical aligned bundles of nanotubes have been grown previously on silicon, the integration is mechanical, rather than electronical, in nature. In the present work, we report on controlled direct growth of vertical and highly-ordered array of 'carbon nanotube - silicon' (CNS) heterojunctions of uniform diameter, length, and alignment. The as-grown CNS heterojunction structure is not only electronically functional but also strongly rectifying with an on-off ratio as high as five orders of magnitude in current-voltage characteristics measured at room temperature. The controlled direct growth of the CNS heterojunction array of such high uniformity is enabled by the formation of a highly ordered nanopore array alumina matrix directly on the silicon, following a precisely controlled anodization of aluminium thin film evaporated on silicon. Iterations of anodization process development and condition optimization and real-time monitoring and control of the anodization process were required for the formation and adhesion of the alumina growth matrix directly on silicon. Under the carefully controlled and optimized conditions developed in this work, we are able to obtain an abrupt heterointerface between the carbon nanotube and the silicon, without an intermediate barrier layer, as required for an electronically functional CNS heterojunction.

Ra5.18/Rb5.18

Crystalline TiO_2 Macrocellular Foams with Highly Nano-Mesoporous Framework. Florent Carn, Stephane Reculusa and Renal Backov; Centre de Recherche Paul Pascal (UPR-CNRS 8641), Pessac, France.

Titanium dioxide photoactivity is becoming very attractive today regarding an extensive range of photocatalytic applications: air or water purification, photovoltaic cells, photochemical cancer treatment, and so forth. This increasing interest has motivated the design of highly crystalline micro- and/or mesoporous TiO_2 monoliths. In addition to this nanoscale design, an optimal structure necessitate a rational macroscopic shaping in order to reach an optimal diffusion of reagents and products. In this last issue, we aim to present the synthesis and characterization of highly cristalline nano-mesoporous macrocellular scaffolds of titanium dioxide with emphasis toward rational design over the macroscopic void space sizes and shapes. This novel route[1] allows a strong control over the macropore morphologies, namely: cell wall width, length and curvature in a large range of size (cell wall length from 50 μm up to 600 μm) while maintaining mesoporosity. The control over the macroscopic shape is obtained by a dynamic approach based on a continuous control over foam's liquid fraction and bubble's size during the mineralisation process while mesostructuration is obtained using either P123 copolymer mesophases or latex nanoparticles as patterning entities. The specific surface associated to those materials is appreciably enhanced ($S_{BET} \approx 400\ m^2.g^{-1}$) regarding materials obtained through previous study.[2] The TiO_2 scaffold cristallinity (Anatase and/or Rutile allotropic phase) is monitored by the thermal treatment employed for the organic template removal. This strategy provides low cost and well define monolithic materials as highly mesoporous crystalline titanium dioxide macrocellular foams. 1- F. Carn, M-F. Achard, O. Babot, H. Deleuze, S. Reculusa and R. Backov, J. Mater. Chem., (submitted). 2- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, C. Sanchez, R. Backov, Adv. Mater., 2005, 17, 62.

Ra5.19/Rb5.19

Engineered Planar Defect in 3D Colloidal Photonic Crystals. Pascal Masse and Serge Ravaine; Centre de Recherche Paul Pascal (CRPP), Pessac, France.

In recent years there has been a growing interest in modulating the band gap properties of photonic crystals by incorporating defects within them in a controlled manner in order to obtain new photonic properties. We present here the controlled insertion of a defect layer of submicrometer silica particles into 3D colloidal crystals made by the successive transfers onto a solid substrate of pre-organized two-dimensional arrays of smaller silica particles using the Langmuir-Blodgett technique. Scanning Electron Microscopy investigations reveal that the position of the defect layer inside the colloidal crystal is perfectly controlled while the overall thickness of the materials is constant and uniform. NIR experimental transmission spectra show that the defect layer acts as a photonic microcavity and induces a pass band into the forbidden band gap. Both the wavelength and the magnitude of the pass band are found to continuously vary with the position of the planar defect layer inside the material. These experimental results were also successfully simulated using a model based on a 2D rigorous theory of diffraction. Results of these simulations are presented and discussed in terms of a degradation of the crystalline ordering of the top stack close to the defect layer.

Ra5.20/Rb5.20

Morphologically Controlled Hybrid Assemblies Starting from Spherical Colloidal Particles. Adeline Perro[1,2], Etienne Duguet Duguet[2] and Serge Ravaine[1]; [1]CRPP, Bordeaux, France; [2]ICMCB, Bordeaux, France.

One area of particular effort recently is the use of colloidal particles as precursors in engineering new materials. Nevertheless, these particles are nearly always spheres. This places limitations on the structures that can be built, especially in making photonic-bandgap materials. Therefore, it is a great challenge to create new colloids with an original shape, i.e. different from the sphere, in a controllable manner. We present here an original approach to create hybrid organic-inorganic colloidal particles with a perfect controlled shape. The synthetic route of these structures, which are composed of spherical silica spheres surrounded by a varying number of polystyrene beads, consists in the emulsion polymerization of styrene in presence of silica particles, which had been surface-modified by a coupling agent containing polymerizable groups. The influence of the size of the silica particle and of the nature of the coupling agent on the resulting colloidal particles morphologies was carefully analyzed. We show in particular that the number of growing polystyrene beads varies homogeneously with the diameter of the mineral spheres. A main advantage of this technique is also that we can precisely control the reaction time, allowing us to tune the final morphology of the hybrid structures. These colloidal assemblies are original building blocks for the elaboration of new functional materials.

Ra5.21/Rb5.21

Field-theoretic Simulations of Block Copolymer/Nanoparticle Composites: Preliminary Results of Hybrid MC/SCFT Algorithm. Scott Wilson Sides[1] and Glenn Fredrickson[2]; [1]Tech-X Corp., Boulder, Colorado; [2]University of California - Santa Barbara, Santa Barbara, California.

Using block copolymers as mesoscale templates for organic/inorganic nanoparticles has the potential to create patterned particle aggregates that could be used as magnetic storage media and semiconductor materials. More generally, polymer nanocomposites such as these are being investigated for the potential to develop materials with specifically tailored optical, electrochemical, thermal and mechanical properties. Whether polymer/particle mixtures are used in a nanoscale templating strategy or in a “nano-alloying” strategy that combines the various materials properties of the constituent polymers and/or particles, the overall behavior of the nanocomposite system depends on the morphology of the polymer chains as well as the arrangement of the particles in the polymer matrix. However, predicting the chain configurations in a system of block copolymers alone can be extremely difficult. Self-consistent field theory (SCFT) for dense polymer melts has been highly successful in describing complex morphologies in block copolymers. Field-theoretic simulations such as these are able to access large length and time scales that are difficult or impossible for particle-based simulations such as molecular dynamics, while still incorporating more realistic polymer models than many macroscopic, continuum simulations. In this talk I will outline the SCFT method, discuss some efficient methods of numerically solving the SCFT equations and present preliminary results for spherical nanoparticles embedded in an AB diblock copolymer melt. These results have been obtained using a hybrid MC/SCFT approach that treats the polymer in a field theory framework while explicitly retaining the individual nanoparticle coordinates as degrees of freedom.

Ra5.22/Rb5.22

Controlled Synthesis of Inorganic Nanostructures with Modulated Architectures in Micellar Systems. Limin Qi, Hongtao Shi, Yurong Ma, Nana Zhao and Jiming Ma; College of Chemistry, Peking University, Beijing, China.

Both reverse and normal micelles have been used as nanostructured media for the facile, low-temperature synthesis of inorganic nanostructures with various morphologies such as one-dimensional (1D) nanostructures (nanowires, nanobelts, and nanotubes) and nanostars. Unique catanionic reverse micelles formed by mixed cationic-anionic surfactants are employed for the controlled synthesis and hierarchical assembly of 1D BaXO4 (X = Cr, Mo, W) nanostructures. The effects of various factors, such as the mixing ratio between the anionic and cationic surfactants, the temperature, and the polymeric additives, on the formation of 1D BaXO4 nanostructures and the architectural control of their complex superstructures are examined. A plausible two-stage growth mechanism has been proposed for the formation of the penniform BaXO4 nanowire/nanobelt superstructures. On the other hand, normal micelles of nonionic surfactants are employed for the controlled synthesis of single-crystalline nanotubes, nanowires, and nanobelts of trigonal selenium (t-Se). In particular, well-defined t-Se nanotubes are fabricated in micellar solutions of poly(oxyethylene(23)) dodecyl ether (C12EO23) whereas single-crystalline t-Se nanobelts are obtained in micellar solutions of poly(oxyethylene(20)) octadecyl ether (C18EO20). It is revealed that the nonionic micelles play an important role in controlling the distribution and diffusion of amorphous Se in the solution and hence exert delicate control over the morphology of the 1D t-Se nanostructures. Moreover, uniform star-shaped PbS nanocrystals are readily produced in micellar solutions of mixed cationic-anionic surfactants. These results demonstrate the great potential of micellar systems in facile, low-temperature, solution synthesis of inorganic nanostructures with controlled architectures. References: [1] H. Shi, L. Qi, J. Ma, H. Cheng, J. Am. Chem. Soc. 2003, 125, 3450. [2] H. Shi, L. Qi, J. Ma, H. Cheng, B. Zhu, Adv. Mater. 2003, 15, 1647. [3] H. Shi, L. Qi, J. Ma, N. Wu, Adv. Funct. Mater. 2005, 15, 442. [4] Y. Ma, L. Qi, J. Ma, H. Cheng, Adv. Mater. 2004, 16, 1023. [5] Y. Ma, L. Qi, W. Shen, J. Ma, Langmuir 2005, dx.doi.org/10.1021/la050801l.

Ra5.23/Rb5.23

Fabrication of Hollow Silica Aerogel Spheres for Direct Drive Inertial Confinement Fusion (ICF) Experiments. Reny R. Paguio[1], A. Nikroo[1], M. Takagi[2] and M. Thi[3]; [1]General Atomics, San Diego, California; [2]Lawrence Livermore National

Laboratory, Livermore, California; [3]University of California, San Diego, La Jolla, California.

Hollow foam spheres are needed for laser fusion experiments on the OMEGA laser facility at the University of Rochester as part of the national campaign for demonstrating the feasibility of fusion energy. Previously polymer based foam and aerogel shells have been produced using resorcinol-formaldehyde (R/F) and divinylbenzene (DVB). In this paper we discuss the development of silica aerogel (SAG) shells as an addition to the polymer based system. SAG may have the advantage of increased robustness, which is important in processing these laser targets. SAG shells were fabricated by the microencapsulation method using a triple orifice droplet generator. This technique allows for precise control of the shell diameter and wall thickness. Changes to aerogel gelation time have significant effects on the ability to fabricate the shells. Reduction of the gelation time is crucial in fabrication of intact shells with high yield. In addition, the proper choice of the components of the different phases of the microencapsulation process is essential for fabrication of intact SAG shells with proper sphericity and wall uniformity. The density of shells fabricated is approximately 100 mg/cc and the diameter ranges from 700μm-1200μm, with a wall thickness of 50-100μm. Development of a full density permeation barrier for retention of the fusion fuel will also be discussed. Work supported by U.S. Department of Energy under Cooperative Agreement DE-FC03-92SF19460 and W-7405-ENG-48.

Ra5.24/Rb5.24

Study of In2O3 Micro- and Nanostructures Grown During Sintering Treatments. Alina Magdas, Ana Cremades and Javier Piqueras; Dpt. Fisica de Materiales, Universidad Complutense de Madrid, Madrid, Spain.

Indium oxide is an important wide band gap semiconductor with different applications in optoelectronics, optical transparency or gas sensing. Nanostructured indium oxide is considered of interest for gas detection because of the enhanced sensitivity related to high surface to volume ratio. In particular, elongated indium oxide nanostructures in form of wires, and belts have been grown by chemical routes and by thermal evaporation methods. In this work, elongated micro- and nanostructures of In2O3 have been grown during high temperature sintering of compacted powder under argon flow. With this method, which has been used to grow elongated nanostructures of different semiconductors with high specific surface (1-4), the structures grow on the sample surface, which acts as source and as substrate. The growth of the In2O3 elongated structures has been performed during thermal treatments of compressed In2O3 and InN powders and the samples have been characterized by SEM and by cathodoluminescence (CL) in SEM. The low dimensional structures have been found to grow on InN by vapor- solid process at temperatures as low as 650 C. The structures obtained during the different treatments are micro- and nanowires with lengths of up to hundreds of microns. Other structures, which appear to correspond to different growth stages, are nanonecklaces and well formed rods terminated in pyramids. The morphology and size of the structures depend on the growth parameters. Spatial resolved CL shows a reduced luminescence emission from the pyramids as compared with the rods and wires. Spectral CL emission from the different micro- and nano-structures is investigated. 1) A.Urbieta, P.Fernandez and J.Piqueras, Appl. Phys. Lett. 85, 5968 (2004) 2) D. Maestre, A.Cremades and J.Piqueras, J.Appl. Phys. 97, 044316 (2005) 3) E.Nogales, B.Mendez and J.Piqueras, Appl. Phys. Lett. 86, 113112 (2005) 4) J.Grym, P.Fernandez and J.Piqueras, Nanotechnology 16, 931 (2005)

Ra5.25/Rb5.25

Sintering Atmosphere as a Control Parameter for Grain Growth in Nanocrystalline Barium Titanate Ceramics. Anton Polotai[1], Kristen Breece[1], Elizabeth Dickey[1], Andrey Ragulya[2] and Clive Randall[1]; [1]Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; [2]Institute For Materials Science Problems NAS of Ukraine, Kiev, Ukraine.

Barium titanate is the most widely used dielectric material in surface mount components and is presently under development for the mass production of submicron grain size ceramics. Over the next ten years, these dimensions will become nanoscale if present trends continue. The production of fully dense nanocrystalline barium titanate ceramics is a difficult task due to enhanced grain growth during the final stage of sintering. To win the competition between densification and grain growth, the right green sample microstructure, dopant type and sintering conditions should be selected. In this work, the effect of oxygen partial pressure on sintering nanocrystalline barium titanate powder is discussed. A sintering atmosphere with a low oxygen partial pressure has a positive effect on densification by facilitating the improvement of grain microstructure and the suppression of grain growth. Sintering in a heavy reduction atmosphere (pO2 = 10-18 ÷ 10-19 atm) is more useful in respect to decreasing the final grain size. This suppression of grain growth corresponds with the appearance of Ti3+ ions. The combination of colloid sample preparation, sintering schedule and heavy reduction atmosphere used in this research enables the production of fully dense pure BaTiO3 ceramics with ∼100 nm average grain size without using pressure assisted sintering or electro consolidation methods.

Ra5.26/Rb5.26

Abstract Withdrawn

Ra5.27/Rb5.27

Immobilization of TAT Peptides on the GaAs Surface. Youngnam Cho[1] and Albena Ivanisevic[1,2]; [1]Chemistry, Purdue University, W. Lafayette, Indiana; [2]Biomedical Engineering, Purdue University, W. Lafayette, Indiana.

A series of TAT peptide fragments were used to functionalize GaAs surface by adsorption from solution and microcontact printing. Different sequences of TAT peptides were employed in recognition experiments. A synthetic RNA sequence was tested to verify the specific interaction with TAT peptide. We have examined the adhesion between TAT peptide patterns and a tip modified with RNA using chemical force microscopy. GaAs surface functionalzed with different sequences of TAT peptides were employed to measure adhesion forces with AFM tip coated with RNA in solution. We characterized the modified GaAs surfaces by contact angle, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), and Fourier Transform-Infrared Reflection Absorption Spectroscopy (FT-IRRAS). AFM studies were used to compare the surface roughness before and after functionalization. XPS allowed us to characterize the chemical composition of the GaAs surface and conclude the monolayers composed of different sequences of peptides have similar surface chemistry. Finally, FT-IRRAS experiments enabled us to deduce that the TAT peptide monolayers have fairly ordered and densely packed alkyl chain structure.

Ra5.28/Rb5.28

Colloidal Lithography with Crosslinkable Particles: Fabrication of Hierarchical Nanopore Arrays. Jun Hyuk Moon[1,2], Se Gyu Jang[2], Jong-Min Lim[2] and Seung-Man Yang[2]; [1]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Engineering, Daejeon, South Korea.

Two-dimensional (2D) porous substrate has been attracted in various applications ranging from photonic crystals to catalytic supports. Recently, self-assembled colloidal particle arrays have been intensively studied because they provide a simple and cost-effective lithography mask to produce patterned pores. Meanwhile, in addition to allowing bulk nanopore arrays, the structural hierarchies are an essential step toward the practical application of these substrates. In this paper, we demonstrated a photolithographic process to produce hierarchical nanopore arrays with colloidal lithography. To do this, we synthesized polymer particles containing glycidyl methacrylate, which can be crosslinked by photo-induced ring-opening. The particle array was exposed to UV through a mask and heat treated above the glass transition temperature (Tg) of the particles, the exposed particles were not substantially deformed because Tg was increased by crosslinking of the epoxide, while the particles in the unexposed region were deformed and the interstices between particles disappeared. Therefore, the RIE etching or deposition through the interstices between the particles was only achieved in the exposed region. Finally, we produced hierarchically patterned nanopore arrays. The present method of hierarchical patterning can be used as a practical design tool of nanopatterned substrates.

Ra5.29/Rb5.29

DNA Nanopatterns Produced by Electron Beam Lithography of Self-Assembled Monolayer Resist. Guo-Jun Zhang[1], Takashi Tanii[2], Yuzo Kanari[2] and Iwao Ohdomari[1,2]; [1]Institute of Biomedical Engineering, Waseda University, Tokyo, Japan; [2]Department of Electronical Engineering and Bioscience, Waseda University, Tokyo, Japan.

DNA nanopatterns have attracted much attention on biological applications including disease diagnosis, DNA sequencing, drug discovery and so on. Nanopatterned DNA arrays allow one to precisely deposit DNA on the substrate on the nanoscale with low nonspecific binding, and such high-density DNA arrays are anticipated to obtain controlled homogeneous spots, thereby resulting in high detection sensitivity and massive parallelization with smaller amounts of reaction reagents and more biochip components. Herein, we present amino-modified oligonucleotides are immobilized on nanopatterns on a silicon surface fabricated by EB lithography of self-assembled monolayer resist (octadecyltrimethoxysilane), surface hybridization process is conducted using biotinylated complementary target oligonucleotides, finally the binding event is illustrated by AFM measurement of Au nanoparticles labeling (adsorption of streptavidin-gold nanoparticles conjugate) instead of fluorescence dyes. This novel approach allows the precise control over pattern size, shape, pitch, and DNA attachment and hybridization on the nanopatterned arrays, which will provide the potential for development of ultrasmall DNA biosensors and biochips.

Ra5.30/Rb5.30

Design, Synthesis and Characterization of Artificial Proteins for Biomolecular Materials. Ting Xu, Joseph W. Strzalka, Shixin Ye, Sophia P. Wu, Michael J. Therien and J. Kent Blasie; Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania.

Artificial protein models, based on both alpha-helical bundle and beta-sheet structural motifs, can be designed to incorporate biological cofactors and retain a range of specific functional elements of their natural counterparts, but within much more simple structures. Amphiphilic 4-helix bundle peptides have been previously designed to selectively incorporate heme and other natural cofactors within both the hydrophilic and hydrophobic domains and have proven to possess characteristic electronic and optical properties of natural electron-transfer proteins. However, it is non-trivia to incorporate both the electron donor and acceptor inside the 4-helix bundles in a controlled manner. Extended pi-electron systems have been designed and tailored, with appropriate donors, acceptors and constituents, to exhibit selected light-induced electron transport and/or proton translocation over large distances. These non-biological cofactors have the advantage of including the electron donor and the acceptor within the same prosthetic group and offer an independent means to modulate the properties of electronically excited states, intrinsic cofactor midpoint potentials, cofactor-cofactor electronic coupling, and the nature of the charge distribution. We studied the binding between a series of non-biological metalloporphyrin cofactors and the designed amphiphilic 4-helix bundles peptides at selected locations. The interior of the artificial protein can be used to control the solubility, position, orientation of the cofactors, while the exterior can be used to control the macroscopic orientation. Incorporation of the non-biological cofactors into the 4-helix bundle via bis-histidyl ligation did not change the protein secondary structure or the 4-helix bundle formation. The amphiphilic protein/cofactor complexes have good thermal stability and maintain more than 85 percent of the original helicity up to 80 degree. This development may potentially lead to functional biomaterials with novel electron transfer properties and it is crucial to control the macroscopic ordering of the artificial proteins in one, two or three dimensions. The artificial protein Langmuir monolayers, both the apo- and holo-form, can be oriented vectorially at the air/water interface upon compression as shown by the x-ray reflectivity data. However, Grazing Incidence X-ray Diffraction (GIXD) data from Langmuir monlayers at higher surface pressure show a broad maximum for momentum transfer parallel to the monolayer plane. This diffraction arises from the interference between parallel helices and demonstrates that the di-helices aggregate to form 4-helix bundles with glass-like inter-bundle positional ordering in the monolayer plane. Nanoporous thin films made from diblock copolymers are ideal templates to assemble the artificial proteins with laterally hexagonal order. We will discuss the efforts on re-designing the artificial proteins to incorporate them into these nanoporous templates.

Ra5.31/Rb5.31

Hydrogen-bonded Multilayer Coatings on Microparticles and Potential Applications. Daeyeon Lee[1], Zhifeng Li[1], Robert E. Cohen[1] and Michael F. Rubner[2]; [1]Department of Chemical Engineering, MIT, Cambridge, Massachusetts; [2]Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Layer-by-layer (LbL) assembly of polymers presents opportunities for creating conformal and robust coatings with molecular scale precision and a wide range of physical properties. This method has been extended to the coating of 3-D structures including colloidal particles. We demonstrate that hydrogen-bonded multilayers composed of poly(acrylic acid) (PAA) and polyacrylamide (PAAm) can be assembled onto micron-sized spherical particles. Hydrogen-bonded multilayers were deposited on microparticles at low pH conditions by LbL assembly and were subsequently crosslinked by a water-soluble carbodiimide chemistry. The multilayer-coated surfaces, both on planar and colloidal supports, exhibited excellent resistance toward mammalian cell adhesion. These hydrogen-bonded multilayers offer potential applications in the biomedical arena where the surfaces of particles need to be rendered bio-inert. We also show that hydrogen-bonded multilayer thin film coatings assembled on colloidal particles can be used as templates for the in situ synthesis of nanoparticles. The concentration and size of nanoparticles grown within the coatings can be varied by the number of loading and reduction cycles. The core particles can be extracted by treating the nanocomposite coated particles with tetrahydrofuran leaving the nanoparticles embedded within the resultant multilayer hollow microcapsule walls. Our method provides a general approach to create nanocomposite microcapsules that contain various types of nanoparticles including magnetic, catalytic and semiconductor nanoparticles. We demonstrate that micron-sized superparamagnetic microspheres coated with silver nanoparticle-loaded hydrogen-bonded multilayer thin film coatings can be used as antibacterial agents that can be delivered to specific locations using magnetic fields. The effect of film thickness and Ag nanoparticle concentration on the antibacterial properties of Ag nanoparticle-loaded multilayer films was investigated by using a disc-diffusion test. Finally, we show that hydrogen-bonded multilayer coated microparticles can be utilized to create asymmetrically functionalized microparticles, also known as Janus particles. Hollow Janus microcapsules can be created by dissolving and extracting the core particles. These asymmetric structures will enable the assembly of complex suprastructures that may find applications in fields such as photonics and biomedical engineering.

Ra5.32/Rb5.32

Single-Step Synthesis of Gold/Porous Silica Nanocomposite Materials. Arijit Bose[1], Jayashri Sarkar[1], Vijay John[2] and Ganapathiraman Ramanath[3]; [1]University of Rhode Island, Kingston, Rhode Island; [2]Chemical Engineering, Tulane University, New Orleans, Louisiana; [3]Materials Science and Engineering, Rensselaer Polytechnic, Troy, New York.

Gold-porous silica nanocomposite materials have been formed in microemulsions by simultaneous hydrolysis/condensation of a silica precursor along with reduction of the gold precursor. Striking the right balance between these simultaneous reactions is the key to succeed in synthesis of well-dispersed gold nanoparticles within the porous silica matrix. The microemulsion is formed using Iso-octane/AOT (Sodium bis (2-ethylhexyl) sulfosuccinate)/Lecithin/TEOS (Tetraethyl orthosilicate) /HAuCl4 (Auric Chloride)/NaBH4 (Sodium borohydride). This system is chosen because of its ability to manipulate the underlying viscosity of the precursor phase, helping to immobilize the particles once they are produced. Changing the aqueous content as well as the auric chloride concentration has a distinct effect on the morphology and size of the resulting gold particles, as well as their dispersion in the porous silica matrix. Additional experiments where hydrophobically modified gold nanoparticles are formed in a single step in situ experiment are described. These experiments provide an interesting pathway for the formation of catalyst-support composite materials.

Ra5.33/Rb5.33

Novel Silicon-Carbon Nanostructures: An Ab Initio Study on the Stability of Si60C20 Clusters. Aravind Srinivasan, Muhammad Nurul Huda and Asok Kumar Ray; Physics, University of Texas at Arlington, Arlington, Texas.

Discovery of the magically stable C60 fullerene cage and the subsequent discovery of the carbon nanotubes have prompted scientists to study fullerene-like silicon structures. Cage-like compact clusters are particularly important for two reasons: they can be used as building blocks of more stable materials and the hollow space inside the cage can be used to dope different atoms yielding a wide variety of atomically engineered materials. Obviously, this has strong implications for nano-scale semi-conducting devices. We have recently shown that carbon dimers trapped into medium size silicon clusters Sin (n=8-14) produces highly stable structures and in particular, we have predicted, based on ab initio Hartree-Fock based Moller Plesset perturbation theory calculations, that Si14C2, with a close fullerene-like structure, is a magic cluster. The formalism of generalized gradient approximation to density functional theory was then used to produce a class of highly stable nanostructures by putting multiple carbon atoms inside a Si20 cage [1]. In the present study, we will report our results on investigating the possibility of stabilizing Si60 fullerene cages by placing C20 clusters, believed to be the smallest fullerene structure [3], inside them. Full geometry optimizations have been performed using the Hay-Wadt pseudopotential basis set without any symmetry constraints using the Gaussian 03 suite of programs [2]. Our studies indicate that the additions of C20 clusters to Si60 fullerene cage do produce structures with higher stability. We have investigated the addition of various possible C20 structures in different orientations with the Si60 cage and we will report detailed results on binding energies, ionization potentials, electron affinities, band gaps, dipole moments, and the bonding nature of the stable Si60C20 nanostructures. As an example, the addition of C20 bowl shape structure, which is also the ground state structure for C20, in Si60 cage has the binding energy per atom of 4.480eV and a band gap of 0.128eV compared to binding energy per atom of 3.61eV and band gap of 0.775eV for the bare Si60 cage. Adding C20 pentagonal cage inside the Si60 cage did not produce as high a binding energy, mainly due the fact that the carbon atoms were concentrated near the center of the cage and Si-C interactions were minimal. In general, we find that Si-C interaction is one of the most important factors for the higher stability of these cages. Possibilities of developing functional nanostructured materials from these studies, such as SiC nanotubes, will be discussed. *Work supported, in part, by the Welch Foundation, Houston, Texas (Grant No. Y-1525). [1] M. N. Huda and A. K. Ray, Phys. Rev. A (Rapid Comm.) 69, 011201 (2004); Eur. Phys. J. D 31, 63 (2004). [2] Gaussian 03, M. J. Frisch et al. Gaussian Inc., Pittsburgh, PA. [3] J. C. Grossman, L. Mitas, K. Raghavachari, Phys. Rev. Lett. 75, 3870 (1995); M. F. Jarrold, Nature 407, 26 (2000).

Ra5.34/Rb5.34

Study of Faraday Rotation in Three-Dimensional Opal Photonic Crystals. Alexander Baryshev[1,3], Rintaro Fujikawa[1], Kazuhiro Nishimura[1], Hironaga Uchida[1] and Mitsuteru Inoue[1,3]; [1]Toyohashi University of Technology, Toyohashi, Japan; [2]Ioffe Physico-Technical Institute, Saint-Petersburg, Russian Federation; [3]CREST, Japan Science and Technology Corporation, Tokyo, Japan.

Lately, there has been much interest in a new class of artificial materials known as photonic crystals owing to many different new electromagnetic effects that were predicted in them. Magnetophotonic crystals (MPCs) [1], photonic crystals fabricated from magnetic materials, and also composite materials in which magnetic materials are implanted into a photonic crystal, have attracted major interest, since the control of the electromagnetic wave by MPC is expected to be a key technology for future applications in optoelectronics. We reported that 1D MPCs exhibit remarkable magneto-optical properties accompanied by a huge augmentation in their Kerr and Faraday rotations [1], and a giant enhancement of the nonlinear magneto-optical response was observed [2]. As for the study of 2D and 3D MPCs, the available theoretical and experimental data are incomplete, and the results remain ambiguous. The goal of this work is to study magneto-optical properties of 3D MPCs. We examined an opal-magnetoactive liquid system and investigated the correlation between transmissivity of opals and the Faraday rotation in the chosen system. High quality samples had the (111) growth surface of 10x10mm2 in size and about 1 mm in thickness. The sample under study was immersed in a transparent paramagnetic liquid: the saturated isopropanol solution of terbium nitrate, turpentine oil, propylene glycol. We studied angle-resolved Faraday rotation and transmission spectra of the sample along X-U-L-K path in the high-symmetry plane LΓX of the Brillouin zone of fcc lattice. The Faraday rotation spectrum of the opal-magnetoactive liquid system, $\theta(\lambda)$, shows characteristic bands corresponding to the bands in transmission spectrum taken along the same crystallographic direction. The dependence $\theta(\lambda)$ follows the behavior of the Faraday rotation of magnetoactive immersion liquid outside photonic bandgaps. However, the strong change of Faraday angle of rotation θ can be observed as the transmissivity of light thought the opal sample decreases. For a specific direction in the opal sample, the angle θ unexpectedly tends to be positive (or negative) in spite of the characteristic properties of the immersion liquid. Namely, if the rotation of polarization plane in the immersion liquid is negative (positive), the angle θ is positive (negative). Such a behavior of value of θ can be caused by the simple (or multiple) Bragg diffraction inside opal photonic crystal, but the complete interpretation of the observed phenomena still remains unclear. [1] M. Inoue and T. Fujii, J. Appl. Phys. 81, 8 (1997). M. Inoue, K. I. Arai, T. Fujii, and M. Abe, J. Appl. Phys. 85, 8 (1999). [2] A. A. Fedyanin, T. Yoshida, K. Nishimura, G. Marowsky, M. Inoue, O. A. Aktsipetrov, JETP Lett. 76, 527 (2002).

Ra5.35/Rb5.35

Fabrication of Densely-Packed, Well-Ordered, High-Aspect-Ratio Silicon Nanopillars Over Large Areas Using Block Copolymer Lithography. Vignesh Gowrishankar[1], Nathaniel Miller[1], Michael McGehee[1], Matthew Misner[2], Du Yeol Ryu[2], Thomas Russell[2], Eric Drockenmuller[3] and Craig Hawker[3]; [1]Materials Science and Engg., Stanford University, Stanford, California; [2]Polymer Science and Engg., Univ. Massachusetts, Amherst, Massachusetts; [3]IBM Almaden Research Center, San Jose, California.

Vertically oriented nanopillars and nanowires have sparked considerable interest in a variety of fields. Sub-100 nm nanopillar periodicities are desirable for many applications, which include bulk-heterojunction organic-inorganic photovoltaic devices, two-dimensional photonic crystals and waveguides, vertically-oriented field-effect transistors (FETs) and stamps for nano-imprint lithography. Using self-assembled block copolymer (BCP) lithography and reactive ion etching (RIE), we fabricated well-ordered silicon nanopillars over centimeter-sized areas, which are taller than 100 nm, have aspect ratios as high as 10 and occur with a periodicity of less than 35 nm. Various unique aspects of the materials and processing techniques enabled key features of the nanostructures: BCP lithography facilitated the small periodicity and the well-ordered arrangement of the pillars, a unique lift-off technique facilitated large-area patterning and a highly selective and anisotropic NF3 based RIE chemistry achieved the final nanopillar structure. We study the effect of different processing conditions on the physical characteristics, such as periodicity, aspect-ratio and height, of the pillars and the chemical composition of the pillar surface. We discuss the potential applications of these nanostructures and also suggest suitable processing modifications to obtain nanopillars that meet the different requirements for such applications.

Ra5.36/Rb5.36

Chiral organization of colloidal particles by porous silicon templating methods. Michal Tymczenko[1], Lluis F. Marsal[2], Isabelle Rodriguez[1], Trifon Trifonov[2], Josep Pallares[2], Angel Rodriguez[3], Ramon Alcubilla[3] and Francisco Meseguer[1]; [1]Centro Tecnologico de Ondas-UA CSIC/UPV, Universidad Politecnica de Valencia/CSIC, Valencia, Spain; [2]Dep. Electronic Engineering, Universitat Rovira i Virgili, Tarragona, Spain; [3]Dept. Electronic Engineering, Universitat Politecnica de Catalunya, Barcelona, Spain.

Ordered assemblies of nano-micro sized particles with chiral structure provide potential applications in many areas of science as photonic crystals, biomaterials, and chemical sensors, among others. Colloidal assemblies produced within confined cylindrical channels are especially interesting because they can offer a variety of chiral and achiral packing geometries [1]. Recently, F. Li et al. have produced silica colloidal crystals with tubular-like packing using silicon and alumina membranes [2-3]. Here, we report the preparation of colloidal crystals by direct assembly of Polystyrene (PS) microspheres into a porous Silicon membrane. The macroporous silicon membrane with well-ordered pores is prepared by electrochemical etching [4]. PS spheres of several diameters between 0.5 micron and 2 microns are infiltrated into membrane by vacuum filtration. To provide a stable colloidal crystal, the pores are infiltrated with Polydimethylsiloxane (PDMS). Finally, PS-spheres/PDMS composite is released by immersing the sample in Tetramethylammonium hydroxide (TMAH) to remove the silicon membrane. As pores in the Silicon membranes have conical profile, different sphere packing schemes are found. Usually, the spheres pack to produce columns with helical strands. The structural arrangement is determined by the ratio between the diameter of the cylindrical pores and the diameter of the spherical colloids. Thus, it is possible to get a wide range of column close package chiral and achiral structures. Such structures with chiral arrangements are expected to offer interesting applications in photonic crystal and liquid crystals. The strategy to control the growth, arrangement, and homogeneity of these structures will be presented and discussed. [1] G.T. Pickett, M. Gross and H. Okuyama, Phys. Rew. Lett.,85, 3652 (2000) [2] F.Li, X. Badel, J. Linnros and J.B. Wiley, J. Am. Chem. Soc, 127, 3268 (2005) [3] F.Li, J. He, W.L. Weilie and J.B. Wiley, J. Am. Chem. Soc, 125, 16166 (2003) [4] T. Trifonov, L. F. Marsal, A. Rodriguez, J. Pallares and R. Alcubilla, Phys. Stat. Sol. (c) 2, 3104 (2005).

Ra5.37/Rb5.37

Self Assembly Studies of Ring Opening Metathesis Polymerisation (ROMP) derived well defined Amphiphilic Block Copolymers. Kurt Stubenrauch[1], Alexandra Lex[1], Christian Moitzi[2], Gerhard Fritz[2] and Gregor Trimmel[1]; [1]Institut for Chemistry and Technology of Organic Materials, Graz University of Technology, Graz, Austria; [2]Institute of Chemistry, Karl Franzens University, Graz, Austria.

The design of highly ordered and nanostructured materials is one of the most challenging tasks in material chemistry. In this context the self-organizational behavior of well defined amphiphilic block-copolymers (BCPs) has gained attention for the synthesis of highly functional and hierarchical polymeric materials. Combining different polarities and functionalities into BCPs requires versatile polymerization methods with a high group tolerance. This can be realized by ROMP with either Grubbs type initiator of the first generation or the recently introduced third generation initiator. The latter in particular has enhanced reactivity and a higher group tolerance than most other initiators. Amphiphilic block copolymers of different conformations and lengths were synthesized. As hydrophobic blocks we used norbornene-dicarboxyclic-acid-dimetylester and dibutylester; as the hydrophilic moiety we investigated norbornene carboxylic acid and alcohol derivatives. For example to guarantee a reproducible synthesis and characterisation the carboxylic acid functionalities were protected as tert-butylesters. After full characterization of the polymers by NMR, IR, GPC and DSC trifluoro acetic acid was used to remove the protecting group. The micro phase separation of the block copolymers was examined with small angle X-ray scattering (SAXS). The micelle formation in solution was explored by dynamic light scattering (DLS). Compared to commodity material block copolymers the self assembly of the ROMP block copolymers is also influenced by the stereochemistry of the norbornenes and the by the catalyst governed cis/trans ratio of the double bonds in the polymer backbone. The self assembly of these polymers is of high interest for example for organic/inorganic hybrid materials.

Ra5.38/Rb5.38

Self-stabilized etching of complex 3D silicon networks with complete photonic bandgap. Sven Matthias, Frank Mueller, Reinald Hillebrand and Ulrich Goesele; Max Planck Institute of Microstructure Physics, Halle, Germany.

Three-dimensional structures for photonic crystal applications have been fabricated up to now either by pure bottom-up approaches like colloidal self-assembly, by pure top-down approaches using VLSI technology or by interference lithography. Here we demonstrate the fabrication of three-dimensional silicon networks by a self-stabilized electrochemical etching technique on lithographically prestructured single crystaline substrates [1,2]. Using a square two-dimensional lattice and a modulated current-voltage-profile, a columnar porous structure with strong diameter modulations is obtained. Subsequent homogenous and isotropic (i) or even anisotropic (ii) etching converts the columnar structure to a cubic geometry of high porosity and an air filling fraction of 80%. In the case of an isotropic etching the porous material is build up of intersecting air spheres in silicon [3]. The optical characterizations along various high symmetry directions of the crystal confirm the achieved periodicity and shape and suggest this material for photonic crystal applications. According to theory this arrangement of air spheres in silicon opens a complete three-dimensional photonic bandgap of about 4.9% centered at 3 μm. Moreover, the subsequent anisotropic etching of the initial porous structure, which exploits the crystallographic nature of the substrate used, converts the former circular cross-section of the pores into an almost squared one [4]. We theoretically study the dispersion behavior of PCs being fabricated by this developed technique. In addition, we present experimentally realized structures and characterize the photonic crystal optically. The reflectance measurements are in good agreement with corresponding bandstructure calculations. This process allows the introduction of defect layers laterally during the etching process as well as vertically - by lithography - achieving a three-dimensional nanopositioning control. Moreover, the introduced process extends the variety of designing and sculpturing three-dimensional microstructures to meet the requirements of a multitude of micro- and nano-technological applications [5]. [1] V. Lehmann, J. Electrochem. Soc. 140, 2836 (1993). [2] S. Matthias, F. Müller, J. Schilling, and U. Gösele, Appl. Phys. A 80, 1391 (2005). [3] S. Matthias, F. Müller, C. Jamois, R.B. Wehrspohn, and U. Gösele, Adv. Mater. 16, 2166 (2004). [4] S. Matthias, F. Müller, and U. Gösele, J. Appl. Phys. in press (2005). [5] S. Matthias and F. Müller, Nature 424, 53 (2003).

Ra5.39/Rb5.39

Determination of Nanotube Density by Gradient Sedimentation. Qi Lu, Gayatri Keskar, Razvan Ciocan, Rahul Rao, Lyndon L. Larcom and Apparao Rao; Physics and Astronomy, Clemson University, Clemson, South Carolina.

Density gradient centrifugation is a high resolution technique for the separation and characterization of large molecules and stable complexes. Densities can be resolved to better that 0.001 g/cm^3. We have analyzed various carbon nanotube (CNT) structures by preparative centrifugation in sodium metatungstate-water solutions. Bundled single-wall nanotubes (SWNTs), isolated single-walled nanotubes, acid solubilized single-wall nanotubes, AND multi-wall nanotubes formed sharp bands at well defined densities. The structure of the material in each band was confirmed by transmission electron microscopy. The experimental densities obtained will be presented compared with the corresponding calculated densities.

Ra5.40/Rb5.40

Production and Properties of Glass Fibre-Reinforced Polymer Composites with Nanoparticle Modified Epoxy Matrix. Malte H. G. Wichmann, Florian H. Gojny, Jan Sumfleth, Bodo Fiedler and Karl Schulte; Polymer Composites, Technische Universitaet Hamburg-Harburg, Hamburg, Germany.

Fibre-reinforced polymer composites are gaining more and more importance in lightweight constructions, especially in the aerospace/aircraft industry. Increasing the mechanical performance, e.g. strength, toughness and fatigue properties, of composites is the objective of many ongoing research projects. The general weaknesses of polymer composites are the limited matrix dominated properties such as interlaminar strength and creep behaviour. Nanoparticles, e.g. carbon nanotubes (CNTs) and fumed silica, provide a high potential for the reinforcement of polymers. Their size in the nanometre regime makes them suitable candidates for the reinforcement of fibre reinforced polymers, as they may penetrate the reinforcing fibre-network without disturbing the fibre-arrangement. The reinforcing effect of nanoparticles in polymers has been intensively studied in recent years. Mechanical properties of polymers were found to be significantly enhanced at relatively low filler contents. The fracture toughness of epoxy resins, for example, could be increased by 55% with the addition of only 0.5 wt.% of fumed silica nanoparticles. In this work, glass fibre-reinforced epoxy composites with nanoparticle modified matrix systems were produced and investigated. Different types of particles, such as carbon black, CNTs and fumed silica, were dispersed in the matrix, using a high shear mixing process. GFRPs containing different volume fractions of the nanofillers were produced via resin transfer moulding. Matrix dominated mechanical properties of the GFRP laminates could be improved by the incorporation of nanoparticles. The addition of only 0.3 wt.% CNTs to the epoxy matrix, for example, increased the interlaminar shear strength from 31.8 to 37.8 MPa (+19%). Furthermore, the application of electrically conductive nanoparticles enables the production of conductive nanocomposites. This offers a high potential for antistatic applications and the implementation of functional properties in the composite structures. Stress-/strain sensing, as well as damage detection capabilities are of special interest for aircraft applications. The effect of different filler types and volume fractions on the electrical properties of the GFRPs were investigated. GFRPs containing 0.3 wt.% of CNTs, for example, exhibit an anisotropic electrical conductivity. The in-plane conductivity of the laminates was observed to be one order of magnitude higher than out-of-plane. Furthermore, an electrical field was applied to the composites during curing. The effects on the resulting electrical and mechanical properties are discussed.

Ra5.41/Rb5.41

Layer-by-Layer Deposition of Carbon Nanotubes. Marco Palumbo[1], Kye Ung Lee[3], Anil Suri[2], Karl Coleman[2], Dagou Zeze[1], David Wood[1], Byung Tae Ahn[3] and Michael Charles Petty[1]; [1]School of Engineering and Centre for Molecular Engineering and Microsystems, University of Durham, Durham, United Kingdom; [2]Chemistry, University of Durham, Durham, United Kingdom; [3]Materials Science and Engineering, Photoelectronic Materials Laboratory, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

In this paper, we shall describe an improved method for making thin film architectures incorporating carbon nanotubes (CNTs) and present some data on the electrical properties of the layers. Single and multiwall nanotubes with an anionic or cationic coating have been prepared by exploiting the ability of certain surfactants to form a monolayer shell around the CNTs. This treatment promotes the dispersion of the nanotubes bundles, increasing their solubility. The presence of electrically charged functional groups on the surface of the CNTs then allows thin film deposition to proceed via the electrostatic layer-by-layer (LbL) method. The self-assembly process was monitored using both the quartz microbalance technique and Raman spectroscopy, while the morphology of the resulting thin layers was studied using atomic force microscopy. A variety of different CNT architectures has been built up. In one arrangement, a single species of a modified CNT (anionic or cationic) was assembled with a *passive* polymer to form a composite superlattice structure, while in another, a multilayer film composed of alternating anionic and cationic modified CNTs was fabricated. The in-plane and out-of-plane dc conductivities of the thin film films were measured at room temperature and contrasted with reference architectures (i.e. those containing no CNTs). All the tests showed clearly that the incorporation of CNTs into the multilayer assemblies resulted in electrically conductive thin films. A high anisotropy of the conductivity was noted, with the films being at least six orders of magnitude more conductive along the length of the carbon nanotubes (in-plane tests) than across them (out-of-plane experiments). At high electric fields, a super-ohmic current versus voltage dependence was observed; the value of the current was approximately proportional to the square of the applied voltage. For the in-plane tests, the dc conductivity was also measured as a function of the distance between the electrodes and, in particular, with an electrode separation equal to the length of the nanotubes. Full details of the electrical behaviour will be presented. Furthermore, some initial attempts to integrate the multilayer architectures into more complex systems, such as chemical sensors and photovoltaic structures, will be discussed.

Ra5.42/Rb5.42

Engineering DNA-Mediated Colloidal Self-Assembly: Preparing Sterically Stable Particles and Assembling Them Into Ordered Crystal Structures. Anthony Ji Kim[1], John C. Crocker[1] and Paul L. Biancaniello[2]; [1]Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Physics & Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania.

The goal of these experiments is the self-assembly of novel, 3-dimensional colloidal crystal structures. The specific binding of complementary DNA strands is used to create short-range attractive interactions between DNA-grafted micron-sized colloids. These colloidal interactions will create multi-component colloidal mixtures where the interactions between each component are independently "programmed". In theory, this technique should be able to produce well-ordered BCC, SC and diamond structures, as well as their alloy counterparts, the CsCl, NaCl and ZnS structures, all at densities near close-packing. We have synthesized the sterically stable DNA-grafted particles using the solvent swelling/deswelling technique. PEG chains provided this extra steric stabilization for these particles. The particles showed the temperature dependent phase behavior and they were also reversible with temperature. In addition, we have successfully assembled the first colloidal crystal structures using them. The crystal structures showed a faceted shape that resembles the RHCP stacked colloidal crystals. The crystals melted immediately when the temperature was raised above the melting temperature (Tm), confirming that they were formed and held together by DNA hybridization. We also find that the particle crystallization kinetics became faster as the grafted DNA density was increased. In addition, we have developed the simple thermodynamic model that predicts the phase behavior (Tm) of the system to within a few degrees. Finally, we also investigate the binary alloy and superlattice structures formed using DNA-mediated self-assembly.

Ra5.43/Rb5.43

Carbon Nanospheres with High-Activity Surfaces by Template-Free Liquid Crystal Assembly. Aihui Yan, Indrek Kulaots and Robert H. Hurt; Division of Engineering, Brown University, Providence, Rhode Island.

The surfaces of most carbon nanomaterials are rich in graphene basal planes and have a corresponding low chemical reactivity and low polarity. This creates challenges for covalent grafting, interfacial bonding in composites, and dispersion in biological fluids or other aqueous media. Here we synthesize a new form of carbon nanoparticle with inverted crystal structure that places high concentrations of graphene edge planes on the outer surfaces. A continuous ultrasonic spray pyrolysis process is to fabricate carbon nanoparticles from a water-soluble lyotropic liquid crystalline precursor, indanthrone disulfonate. This disk-like polyaromatic compound assembles in solution into rod-like aggregates, which in turn assembly parallel to the outer surfaces of the droplets driven be configurational entropy at the interface. This assembly mode leaves exposed polyaromatic edges upon drying that are converted to exposed graphene layers upon carbonization. This paper reports on the fabrication, crystal structure, annealing behavior and surface activities of this unique new carbon nanomaterial using SEM, HRTEM, XRD, TGA, contact angle measurement and N_2 vapor absorption. The spray pyrolysis process allows careful control over particle size, which to date has been systematically varied from 2 μm to 80 nm. As expected, high resolution TEM shows the presence of graphene layers assembled perpendicular to the outer surface in the 700 ^{o}C nanocarbon, but this high-energy surface reconstructs upon annealing above 2500 ^{o}C to form "closed" pyramidal surface domains easily seen in both FE-SEM and TEM. Work is underway to measure their surface properties relative to carbon black as conventional carbon nanomaterial with graphene basal-rich surfaces. Results to date show the liquid crystal derived nanospheres to have a higher reactivity toward molecular oxygen, higher hydrophilicity (lower contact angle with water), and better dispersion and stability in aqueous media. We anticipate a variety of applications for these unique carbon nanospheres, in which the active surfaces provide a flexible platform for chemical functionalization, and the bulk composition can be flexibly controlled by selecting the precursor solution, e.g. to include a magnetic material component.

Ra5.44/Rb5.44

Broadband Antireflective Coating Based on Bilayer Nanoporous Organosilicate Thin Films. Suhan Kim[1], Jinhan Cho[2] and Kookheon Char[1]; [1]School of Chemical and Biological Engineering & NANO Systems Institute - National Core Research Center (NCRC), Seoul National University, Seoul, South Korea; [2]LG Chemical Research Park, Daejeon, South Korea.

Nanoporous materials have recently attracted much interest owing to its potential application for low dielectric insulating materials, sensors, waveguides and antireflection coatings. In present study, nanoporous organosilicate thin films were realized by the microphase separation of a pore generating component mixed with an organosilicate matrix. A thermally labile tetrafunctional block copolymer, Tetronic (BASF), was used to generate nanopores and polysilsesquioxane (PMSSQ) copolymer was chosen for the matrix material. The refractive index of such nanoporous organosilicate films can be varied in the range of 1.40 $\sim$ 1.22. Optical properties of prepared nanoporous organosilicate films were also tested toward the application to antireflection coating. With a nanoporous single layer with n $\sim$ 1.22, 99% transmittance in the visible range was achieved. In order to overcome the limitation on the narrow wavelength for high transmittance imposed by single nanoporous thin films, bilayer thin films with different reflectance in each layer were prepared. For the facile fabrication of nanoporous bilayer films, the addition of photoacid generator (PAG) to the organosilicate thin film is followed by UV treatment. The PAG generates acid upon UV exposure and facilitates the vitrification of the organosilicate matrix. As a result, 85% of Si-OH groups was found to condense only after 10 minutes of curing at 150 °C. After the UV pretreatment followed by low temperature cure, a second layer with higher porogen loading was deposited on top of the first layer by spin-coating. The bilayer films were finally cured at 420 °C for 1 hour to realize nanoporous structures in both layers. By changing the porogen loading in each layer, nanoporous bilayers with different combinations of refractive indices were successfully fabricated and electron density profile and porosity in each layer were also quantitatively characterized by x-ray reflectivity experiments. Optical properties of nanoporous bilayer films thus prepared were compared with nanoporous single layer films and it is demonstrated that the novel broadband antireflection coating with improved transmittance can be easily achieved by the nanoporous bilayer thin films described in this study.

Ra5.45/Rb5.45

Radiopaque flame-made Ta_2O_5/SiO_2 nanoparticles with controlled refractive index and transparency. Heiko Schulz[1], Lutz Madler[1], Sotiris E. Pratsinis[1], Peter Burtscher[2] and Norbert Moszner[2]; [1]Department for Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland; [2]Ivoclar Vivadent AG, Schaan, Liechtenstein.

Dental fillings made of composite organic monomers and ceramic fillers (particles) are used for tooth shaded dental restoration of anterior lesions and small - medium sized defects in the posterior region. This is a result of the excellent esthetic properties of these fillings as well as health concerns with amalgam fillings regarding mercury release. Therefore, the relation of filler properties to composite characteristics such as radiopacity, tensile strength, hardness, shrinkage, wear and transparency have been intensively studied in the last few years. Mixed Ta_2O_5-containing SiO_2 powders with high specific surface area, controlled refractive index, transparency and crystallinity were prepared by flame spray pyrolysis as fillers for dental composites. The production rate ranged from 6.7 - 100 g/h in a lab scale reactor. The effect of the Ta-precursor, the solvent, the total metal concentration and the Ta-content were studied by nitrogen adsorption, x-ray diffraction, light microscopy, HRTEM, DIFTS analysis, as well as the composite transparency within a polymer matrix of dimethylacrylate for dental restoration applications. Filler properties such as transparency, crystallinity and Ta-dispersion in the SiO_2 matrix altered the composite performance. Ta_2O_5 crystallites and a low Ta-dispersion within the SiO_2 matrix decreased the filler and composite transparency. Powders with identical specific surface area, refractive index and Ta_2O_5-loading (24 wt.%) showed a wide range of composite transparencies from 33 - 78 % depending on filler properties. Fillers with an amorphous structure, a high Ta-dispersion and a matching refractive index with the polymer matrix showed the highest composite transparency of 86 % for a 16.5 wt.% filler loading including 35 wt.% Ta_2O_5 giving an optimal radiopacity.

Ra5.46/Rb5.46

Ionic Transport Through Nanoporous Ceramic Membranes Functionalized with Self-Assembled Monolayers. Anthony Ku and James Ruud; Ceramics and Metallury Technologies, General Electric, Niskayuna, New York.

Self-assembled monolayers (SAMs) are widely used to activate surfaces for a broad range of biological and electrochemical applications. However, the use of SAMs to tailor the transport and surface properties within porous materials is still relatively unexplored. We have studied the effect of SAM structure on the ionic transport in hydrophobized nanoporous ceramic membranes. The membranes were prepared by functionalizing the internal surfaces using alkylsilane SAMs with different alkyl chain lengths. The ionic transport through the membranes was characterized using impedance spectroscopy.

Ra5.47/Rb5.47

Synthesis of PbTe Nanoboxes Using a Solvothermal Technique. Wenzhong Wang, Bed Poudel, Dezhi Wang and Zhifeng Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

PbTe nanoboxes have been synthesized in high-yield via a solvothermal route for the first time. The effects of experimental conditions, such as capping agent (PEG) concentration and the volume ratio of ethanol to water, on the formation of nanoboxes have been studied in detail. The experimental results showed that both surfactant PEG and the volume ratio of ethanol to water played key roles to the formation of nanoboxes. The as-prepared nanoboxes were characterized by an X-ray diffractometer (XRD, Cu K?, Bruker AXS), a field emission scanning electron microscope (SEM, JEOL-6340F), and a transmission electron microscope (TEM/HRTEM, JEOL-2010F) equipped with an energy-dispersive X-ray spectrometer (EDS). SEM images clearly demonstrate that the majority of the nanocrystals have a regular cubic shape. TEM investigations indicate that the as-prepared nanocrystals show regular cubic shape with edge length of about 80-180 nm, and a strong contrast difference with dark edge and bright center, indicating hollow interior. The SAED and HRTEM studies indicate that the as-prepared PbTe nanoboxes via our present method are highly crystallized single crystals. Based on our experimental results, a possible formation mechanism of the nanoboxes has been proposed. The following figures show the TEM images of two typical PbTe nanoboxes.

Ra5.48/Rb5.48

Integrated Conducting Polymer Nanowire Devices for Biological Sensing Applications. Adelaja Arojuraye[1], Shaun Filocamo[3], Catherine M. Klapperich[1,2], Selim Unlu[4,1] and Mark W. Grinstaff[3,1]; [1]Department of Biomedical Engineering, Boston University, Boston, Massachusetts; [2]Department of Manufacturing Engineering, Boston University, Boston, Massachusetts; [3]Department of Chemistry, Boston University, Boston, Massachusetts; [4]Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts.

An integrated conducting polymer nanowire device is being fabricated. The device will enable us to demonstrate and investigate the conducting properties of polymer nanowires and the mechanisms for conducting polymer formation using AFM electrochemical dip pen nanolithography (e-DPN) process. Conducting polymers conjugated with biological ligands have the potential to detect specific biological binding events. Biomolecules or ligands can be incorporated into the conducting polymer in a single step during electrochemical polymerization using AFM e-DPN technique. Optimization of processing techniques will allow for more precise measurements and provide a foundation for future integration of nano and micro scale technologies involving conducting polymers.

Ra5.49/Rb5.49

Directed Patterning of Monolayer-Protected Inorganic Nanoparticles onto Surface Monolayer Templates. Kensuke Akamatsu, Shoji Samitsu, Takaaki Tsuruoka, Jun Hasegawa and Hidemi Nawafune; Konan University, Kobe, Japan.

Thin films of the organic/inorganic hybrid nanocomposites that are composed of metal and/or semiconductor nanoparticles embedded in dielectric matrix are the subject of recent intensive research for fabrication of next generation nanodevices. Although recent researches have made promising advances that provide methods for site-selectively depositing or growing the nanoparticles on the substrates of interest, the development of a facile process for fabrication of nanocomposite thin film patterns still remains a great challenge. In this study, we present a simple approach and unique procedure for fabricating patterns of nanogranular films composed of monolayer-protected metal and semiconductor nanoparticles onto surface monolayer templates pre-deposited on the substrates. The gold and CdSe nanoparticles protected by 11-mercaptoundecanoic acid (MUA) were used as model building blocks for nanocomposites. In the present approach the nanoparticle granular films, in which the each nanoparticles are assembled via hydrogen bonding network between carboxylic acid moiety of MUA, were deposited and integrated as two-dimensional microscopic circuit patterns through the process of simple coating of the solution containing the nanoparticles and drying followed by solvent-induced lift off. Selective integration of the nanoparticles onto either hydrophobic or hydrophilic region on the substrates could be achieved by selective lift-off of nanoporous granular films, which can be due to penetration of solvents into interface between the films and the monolayers on the substrates, depending on the polarity of solvents and monolayers. The process is described as one-pot, subtractive-based strategy and provides effective methodology for desirable integration of monolayer-protected inorganic nanoparticles through simple solution-based processing.

Ra5.50/Rb5.50

Nano-Structured Beta-Gallia-Rutile Surfaces as Substrates for DNA Self-Assembly. Nathan H. Empie and Doreen Edwards; NYS College of Ceramics, Alfred University, Alfred, New York.

A nano-structured beta-gallia-rutile (βgr) substrate capable of binding DNA was synthesized. Beta-gallia groups diffuse into [001] single crystal rutile along $\{210\}_r$ planes. This process generates hexagonally shaped tunnel sites between the beta-gallia subunits (repeating $\sim$1 nm). The tunnel sites, approximately 2.5 $\AA$ in diameter, are preferred regions for cation incorporation. Divalent cations have been used previously to adsorb DNA to mica surfaces. For the βgr system, the site selectivity of the cations for tunnel sites could lead to a controllable / tailor-able DNA adsorption. A variety of cation species and concentrations were applied to DNA buffers exposed to βgr substrates. The DNA adsorption was investigated with tapping mode atomic force microscopy to determine the suitability of using βgr substrates as a means to self assemble DNA constructs for nano-electronic applications.

Ra5.51/Rb5.51

Atomically-Controlled Assembly of Nanoscale Devices With Subnanometer Precision Using Bioengineered Polypeptides. Seiichiro Higashiya[1], Natalya I. Topilina[1], Vladimir V. Ermolenkov[1], Ludmila A. Popova[1], Christopher C. Wells[1], Narender Rana[2], Autumn Carlsen[2], Christopher Kossow[2], Eric T. Eisenbraun[2], Alain E. Kaloyeros[2], Robert E. Geer[2], Igor K. Lednev[1] and John T. Welch[1]; [1]Department of Chemistry, University at Albany, Albany, New York; [2]College of Nanoscale Science and Engineering, University at Albany, Albany, New York.

Control of the self-assembly of well-defined polymers with precisely designed intra- and intermolecular recognition is challenging, yet essential to the successful atomic scale integration of nanoscale devices with subnanometer precision. The present investigators have focused on the synthesis and characterization of β-sheet forming repetitive polypeptides as nanoscale building blocks and templates for assembly of functional devices. Accordingly, we have already reported the successful preparation of β-sheet forming Gly-Ala repeats with amphiphilic pendant residues X^1 and X^2, such as $[(GA)_3GX^1(GA)_3GX^2]$ with more than 1000 amino acid residues (corresponding to scaffolds of 180 nm^2). The polypeptides showed highly ordered structure on graphite and well-characterized fibrils in solution depending on the sequences, preparation, and post modification. The effects of changing the length of GA repeats, turn moieties, physico-chemical conditions, such as pH, and ionic strength, templated assembly, and selective modification will be discussed.

Ra5.52/Rb5.52

Nanofabrication of Ordered Interface of Organic Thin Films and Electrode through Chemical Bond Formation toward High-performance Photofunctional Devices. Hiroshi Moriyama, Noriaki Ikeda, Nobutama Mitomo, Hiroshi Higuchi and Chyongjin Pac; Department of Chemistry, Toho University, Funabashi, Japan.

Nanofablicated organic thin films with ordered orientation have been drawn much attention from the viewpoint of electronic and biological devices. Molecular-based nanomaterials have great potential to fabricate novel assembly with intriguing optical/electronic properties. Supramolecular arrays and related thin films comprised of redox-active molecules in these films have recently become of increasing interest. We have been developing a simple bottom-up method enables us to control density of redox-active molecules at the surface. The fabrication of chemically and mechanically tough nanofilms on solid substrates is a fundamental subject in applications of dyes to devices. We have developed an effective way for the fabrication of chemically linked dye-inorganic hybrid multilayers using tris-chelated ruthenium(II) complexes and phthalocyanines (MPc) as the dye molecules, because of their excellent photofunctional properties and high chemical stability. The fabrication of organic thin films involving gold nanoparticles coordinated by π-organic materials such as fullerene C60, origothiophene, and porphyrin has been also developed and investigation on photofunctional behavior of these films is now in progress. Nanofablication through chemical bond formation should be an important concept to achieve facile electron-transfer reactions in thin-film redox systems.

Ra5.53/Rb5.53

Force Spectroscopic Investigation of Electro-Oxidative Nanolithography. Daan Wouters[1,2], Jurriaan H. K. van Schaik[1], Stephanie Hoeppener[1,2] and Ulrich S. Schubert[1,2]; [1]Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; [2]Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

To make full use of novel material properties observed in nanodimensional materials it is essential to develop tools for a guided assembly of individual nano-objects on a surface. Surface patterning approaches play here an important role and are strongly in focus. We utilize an electro-oxidative lithography approach that allows the local functionalization of a robust, chemically inert self-assembled n-octadecyl trichlorosilane (OTS) monolayer on silicon. This oxidation process is mediated by negative bias voltages, which can be locally applied to the surface via e.g. a conductive Scanning Force Microscope

(SFM) tip, a conductive stamp (e.g. conductive TEM grid) or simply via a water droplet placed on the monolayer. Oxidation experiments are performed in order to investigate the kinetics of the chemical modification process in more detail. In particular Scanning Force Spectroscopy, performed during the oxidation allows the in-situ monitoring of surface properties by the analysis of characteristic events observed within the recorded force-distance curves. Additional information can be obtained by local oxidation experiments performed in a droplet of water. Simultaneous measurements of the water contact angle reveal characteristic stages of the monolayer oxidation, and the subsequent growth of silicon oxide after the monolayer is degraded.

SESSION Ra6: Nanostructures for Biology and Medicine I

Chair: Mehmet Sarikaya
Tuesday Morning, November 29, 2005
Room 207 (Hynes)

8:30 AM *Ra6.1
Getting to "Mind" – The Foundation Development of a Room Temperature Biological Supercomputer.
Carlo Montemagno, Bioengineering, University of California, Los Angeles, Los Angeles, California.

Recent advances in our ability to manipulate matter at the scale of individual molecules have created an incredible level of excitement in both the scientific community and the general population. The excitement over this new capability, commonly labeled nanotechnology, is vested in the expectation of the development of new materials and systems that offer unparalleled functionality. Materials that autonomously adapt their shape and physical properties in response to the their surroundings, computers that instead of operating by switching the flow of electrons, manipulate information through the management of the ethereal world of quantum states and, molecular sized machines that actively repair damage to our bodies and function as molecular scale prosthetics are all expectations of nanotechnology. While the question of whether or not this vision is truly achievable is still open, the truth is that much of the expectations for nanotechnology are already realized in living systems. Living systems however, are more than a product of matter manipulation at the molecular scale; the richness of functionality associated with living systems is a direct product of the information generated from both the interactions between molecules and the overall supra-molecular structure of the system. In essence living systems are "living" because of the fusion of nanotechnology and informatics. Living systems result from the precision assembly of matter with prescribed modalities for the transport and transduction of information among supra-molecular clusters. The concept of Integrative Technology, the intersection of the precision assembly of matter, nanotechnology, coupled with the functional building blocks of nature, biotechnology, and fused by the network flow of spatiotemporal information, informatics, is presented. The power of Integrative Technology is manifested through the engineering of synthetic biological systems. The ultimate example of which would be the fabrication of a synthetic biological processor. The design, modeling and experimental results associated with the fabrication and engineering of Excitable Vesicles, a nano-sized building block with the ability to intrinsically process information will be discussed. Excitable vesicles have the potential of controlling and manipulation of information that would ultimately lead to the manifestations of emergent higher-order behavior. These systems are designed, engineered and produced from nanoscale components to create complex systems and materials that self-organize on multiple length scales to manifest complex emergent functional behaviors.

9:00 AM Ra6.2
Poly(propyleneoxide)-Poly(amidoamine) Based Linear Dendritic Block Copolymers for Drug Delivery.
Phuong M. Nguyen and Paula T. Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A novel series of linear-dendritic block copolymers with amphiphilic characteristics have been developed that have the capability of self-assembling in solution and creating an interior hydrophobic core for drug encapsulation.
Poly(amidoamine)-poly(propyleneoxide)-poly(amidoamine) (PAMAM-PPO-PAMAM) has been synthesized from generations 1 through 6, and the solution-state behavior of this series of polymers have been characterized. The critical micelle concentration (CMC) of this set of polymers has been determined with tensiometry and pyrene as a hydrophobic fluorescent probe. With increasing PAMAM generations, the CMC increases from 1e-6 M to 1e-5 M. The formation of micelles has been confirmed through dynamic light scattering and TEM. A model hydrophobic drug, irgasan, has been utilized to ascertain the polymers' drug encapsulating ability. The linear-dendritic amphiphilic block copolymer micelles show promise as drug encapsulating nanoparticles with high loading capacity and the ability for specificity with the conjugation of targeting ligands to the multivalent dendrimer outer shell.

9:15 AM Ra6.3
Building and Characterizing Nano-complexes of Liposome Encapsulated Nanocrystals. Idan Mandelbaum[1], Cheryl H. S. Lau[1], Kunio Nagashima[2], Jeeseong Hwang[1] and Angela R. Hight Walker[1]; [1]Physics Laboratory/Laser Application Group, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Image Analysis Laboratory, National Cancer Institute-Frederick, Frederick, Maryland.

Novel approaches involving manufacturing of nanoscale complexes combining biotic and abiotic materials have been of increasing interest for a variety of biochemical and biomedical applications including single cell diagnostics, drug targeting and delivery, and tumor imaging and diagnostics. We will present our efforts on manufacturing nano-complexes of liposomes encapsulating fluorescent semiconductor nanocrystals (NCs) potentially useful for a wide range of biomedical applications. This technique will be of immediate use towards targeting, labeling, and analyzing biological cells. Upon being triggered, the liposomes fuse to the plasma membrane of a targeted cell and release their contents, in this case NCs, inside the targeted cell. Accordingly, the targeted cell can be analyzed with a wider range of fluorescence measurement techniques. Optical properties of the NCs are superior to conventional organic dyes: the NCs show higher fluorescence quantum yield, narrower emission spectra, better photo-stability against photo-bleaching, and relatively longer fluorescence lifetime. These advantages provide more sensitive and quantitative measurement in medical diagnostic and cellular imaging. In this presentation, we will present techniques to encapsulate NCs with different surface functional coatings within approximately 100nm unilamellar liposomes prepared by a variety of methods such as injection, extrusion, and electro-formation. Fluorescent lipid analogs were used to label liposomes to verify the encapsulation by assessing fluorescence resonance energy transfer between the donors (NCs) and the acceptors (lipid analogs) in total internal reflection fluorescence microscopy (TIRFM). The TIRFM allows us to excite only liposomes near the substrate surface therefore substantially enhances the signal to noise ratio in detection. We will also discuss the characteristics of each component, liposomes and functionlized NCs, and their complexes from results obtained by other methods including confocal fluorescence microscopy, polarization modulation optical microscopy, and electron microscopy.

9:30 AM Ra6.4
Bilateral, Difunctional Nanosphere Aggregates to Construct Biosensors and their Application to Ligand-Receptor Binding Interactions. Suzanne Barber[1], Tonya Kuhl[1], Timothy Patten[2], Philip Costanzo[2] and Nathan Moore[1]; [1]Chemical Engineering and Materials Science, University of California, Davis, Davis, California; [2]Chemistry, University of California, Davis, Davis, California.

We have developed an efficient method for producing difunctional, bilateral nanospheres/nanoparticles of various materials, including superparamagnetic and ferromagnetic materials. By variation of the base particle and metal deposited onto the surfaces of the nanoparticles, bilateral nanoparticles were formed. The different regions of the nanoparticles were selectively functionalized with polymer linkers containing specific terminal groups, thereby creating bilateral, difunctional nanoparticles. Subsequent covalent cross-linking of different nanoparticles enabled the formation of stable architectures with programmed hierarchy and controlled chemical composition. We propose that by modulating the length and chemical composition of the polymer linker and its binding energy to the particles, the interaction potential between particles can be specified. This ability to fine-tune the interaction energy of the system is a key aspect for creating novel hierarchical materials for specific applications, including development of a biosensor for the measurement of receptor-ligand binding interactions. We construct biosensors for the detection of ligand-receptor binding events utilizing magnetic particles. We show preliminary data indicating the efficiency of such a biosensor construction and propose its use for measurement of ligand-receptor binding strength and binding affinity.

9:45 AM Ra6.5
A correlational study of photoluminescence and vibrational spectroscopy - Protein adsorption on the surface functionalized Si. Li-Lin Tay[1], Nelson Rowell[1], David Lockwood[1] and Rabah Boukherroub[2]; [1]National Research Council, Ottawa, Ontario, Canada; [2]Interdisciplinary Research Institute, Villeneuve d'Ascq, France.

We have recently investigated the interaction of Bovine Serum Albumin protein and surface functionalized porous Si (pSi). Due to the presence of 1D and 2D nanocrystallite in the porous Si matrix, the imposed quantum confinement effect in pSi leads to a bright visible room temperature photoluminescence (PL). Surface functionalization not only stabilizes the PL but also introduces bio-specificity and chemical functionality to the sidewalls of the pSi. This allows the subsequent cross-linking reaction (e.g. binding of analyte and target molecules) to take place. An in-situ monitoring of the protein and pSi interaction revealed a red shift in pSi PL. Although it was suspected such shift is due to protein molecules being incorporated into the Si matrix, the heterogeneous nature of the pSi material make it difficult to prove this correlation. To understand the origin and nature of the shift and to fully correlate such events to protein adsorption, we carried out a further investigation of protein adsorption on surface functionalized planar Si. The planar Si (100) was first degreased in acetone and then cleaned in piranha bath at an elevated temperature. The cleaned wafer was then dipped into 5% of HF to remove its surface oxide and to passivate the surface with Si-H bonds. By exposing the hydrogen passivated wafer surface to UV radiation while immersed in a degassed undecylenic acid solution, a radical initiated hydrosilylation reaction cleaves Si-H bonds and replaces them with more stable Si-C bonds. This process produced a monolayer of undecylenic acid molecules self-assembled on the Si(100) surface. A single bounce attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic technique was developed to monitor the vibrational spectra of such monolayer films. The observed vibrational spectrum showed a clear carbonyl stretch at 1714 cm-1 from the undecylenic acid on the Si (100) surfaces. Furthermore, a small band at 2100 cm-1 indicated there were un-used Si-H bonds. The presence of the acid functional group on planar Si serves as a convenient cross-linker to the BSA protein. The planar Si also exhibited a weak PL signature, which was produced from carrier recombination. This PL was excited at room temperature with 457.9 nm Ar laser excitation and detected by a Ge detector. We monitored the PL evolution for the planar Si in-situ while the sample was incubated in a 0.02 mg/ml BSA solution. In this presentation, we will correlate the PL evolution to the ATR-FTIR results obtained on the Si: undecylenic acid: protein complex. We will show a correlation between the diminishing of Si-H stretch with the decrease of PL intensity. We will also confirm the observation of a red-shift in planar Si PL due to protein adsorption on the Si surfaces. This PL shift will be discussed in conjunction with the vibrational data obtained from ATR-FTIR study.

SESSION Rb6: Nanowires, One Dimensional
Nanostructures II

Chair: Geoff Strouse
Tuesday Morning, November 29, 2005
Room 208 (Hynes)

8:30 AM *Rb6.1

Functionalization of Nanotips: From Field Emission, Antireflection to Molecular Sensing Devices. Surojit Chattopadhyay[1], Yi-Fan Huang[1], Kuei-Hsien Chen[1,3], Hung-Chun Lo[2], Chia-Fu Chen[2], Chi-Hsun Hsu[3] and Li-Chyong Chen[3]; [1]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; [2]Department of Materials Science & Engineering, National Chiao Tung University, Hsinchu, Taiwan; [3]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

We have applied an on-chip approach for the development of the nanotip arrays as building blocks toward field emission, antireflection and molecular sensing devices. Nanoscale engineering and a strategy for self-assembly of metals on the nanotip arrays to enhance their functionality will be presented. Well-aligned nanotip arrays with a nanotip density as high as 10^{12} cm^{-2} were achieved by a single-step electron cyclotron resonance plasma process using gas mixtures of silane, methane, argon and hydrogen.[1] Formation of SiC cap was observed on each individual nanotip, implying a self-mask etching mechanism. This technique was applied to a variety of wafers such as Si, GaN, GaP, Al, sapphire and glass, indicating its general applicability.[1] The nanotip arrays so produced showed superior field emission as well as antireflection properties. The sharp tip geometry provides large field enhancement, therefore a low turn-on field (<1V/micrometer), while the sub-wavelength nanostructured surface exhibits an ultra low reflectivity (<0.1%) in visible and IR. Moreover, the high surface curvature of nanotips efficiently self-assembles metal nanoparticles on their surface upon simple sputtering of the metal. This is a clean-room compatible self-assembly strategy where wet chemistry is derelict. The silicon nanotip arrays dispersed with Ag nanoparticles showed excellent surface enhancement in Raman scattering (SERS).[2,3] Enhancement up to 8 orders has been achieved, suggesting potential application of nanoparticle-dispersed nanotip arrays in molecular sensing. The on-chip approach also helps accelerating the progress of nanodevice fabrication. [1] C. H. Hsu, C. F. Chen, H. C. Lo, D. Das, J. Tsai, J. S. Hwang, L. C. Chen and K. H. Chen, *NanoLett.4*, 471 (2004). [2] S. Chattopadhyay, H. C. Lo, C. H. Hsu, L. C. Chen and K. H. Chen, Chem. Mater. 17, 553 (2005). [3] S. Chattopadhyay, S. C. Shi, Z. H. Lan, C. F. Chen, K. H. Chen, L. C. Chen, J. Am. Chem. Soc. 127, 2820 (2005).

9:00 AM Rb6.2

Synthesis, Structural and Mechanical Characterization of Boron Nanowires. Hai Ni and Xiaodong Li; Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina.

Boron nanowires with a diameter ranging from 30 nm to 100 nm were successfully synthesized wiht a chemical vapor transport medthd. By controlling growth temperature, cooling rate, and vapor sources, long and well aligned boron nanowires were obtained. XRD and HRTEM were used to study the composition and structure of the wires. Mechanical properties of the wires were measured by nanoindentation and AFM bending tests. A nanomanipulator was used to perform tensile tests directly on the wires. The boron nanowires show very high elastic modulus. The chemical vapor transport method used in this study can produce boron nanowires at a high volume production rate. Finally, the growth mechanisms of boron nanowires are discussed in conjunction with possible reactions, temperature ranges, and structural characteristics.

9:15 AM Rb6.3

Self-assembled InAs nanowire networks. Kimberly Dick[1], Mikael T. Bjork[1], Knut Deppert[1], Lisa S. Karlsson[2], Magnus W. Larsson[2], Jan-Olle Malm[2], Thomas Martensson[1], Werner Seifert[1], L. Reine Wallenberg[2] and Lars Samuelson[1]; [1]Solid State Physics, Lund University, Lund, Sweden; [2]Materials Chemistry, Lund University, Lund, Sweden.

Research in semiconductor nanostructures has indicated great promise for applications of these structures in the electronics, materials science and life science fields. The step from production of building blocks, such as nanoparticles and nanowires, to more complex nanostructured systems is key to the realization of this potential. We demonstrate here a method for production of complex self-assembled three-dimensional networks of III-V semiconductor nanowires on a substrate. The nanostructures are formed by sequential seeding of hierarchical levels of nanowires by Au nanoparticles. These particles operate as collectors of vapor-phase source material, which then grows epitaxially on the material underneath the particles. The first level of nanoparticles is produced by electron beam lithography of a pattern of dots followed by evaporation/lift-off of Au. Nanowires are subsequently grown by low pressure metallorganic vapor phase epitaxy (LP-MOVPE), using metallorganic Group-III precursors and hydride Group-V precursors. All nanowires grow normal to the substrate, as determined by the substrate crystal orientation and experimental parameters. The pattern of dots produced is specifically designed to orient further generations of nanowires to form a network pattern. To produce the first and subsequent levels of branching, Au-In alloy nanoparticles produced by an evaporation/condensation method are deposited onto the nanowire array. Size and density of these particles are selected, and position on the first-generation wires can be influenced by surface masking during deposition. Nanowire growth directions outwards from the first level of vertically-growing wires are then determined by the selected material system and growth conditions. Thus, by correct alignment, nanowire branches will grow towards the neighbouring branched structure so that they become connected, and a self-assembled network of interconnected structures is formed. If functional elements are incorporated at appropriate places in this network, designed conditions for inter-node signalling can be created. The use of nanoimprint lithography to define the initial array of Au nanoparticles allows for the possibility of large-scale nanowire circuits. We will report the production of complex InAs nanowire networks, grown on InP substrates so as to electrically isolate the structure from the substrate. Evaluations of the electrical, morphological, and microstructural properties will be discussed.

9:30 AM Rb6.4

DC plasma CVD Synthesis of ZnS nanowires with heterocrystalline and bicrystal structures. Jiansheng Jie, Yang Jiang, Wenjun Zhang and Shout-tong Lee; Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, Hong Kong.

Nano-structured materials have attracted considerable attention because they are potential building blocks for nano-scale electronics and optoelectronics. The novel physical and chemical properties of nano-materials, which mainly origin from the nanometer size, are extensively researched in the past decade. On the other hand, the ability of flexibly control the crystal structures and components of the one-dimensional semiconductor nanostructures is especially critical for both exploring the new physical and chemical properties of the nanomaterials and the applications of the nanomaterials in practice.

As one of the most fascinating properties in compound semiconductors, polytypism is the common feature of some binary semiconductors such as SiC, CdS, Cdse, and ZnS. Wurtzite (WZ) and zince blende (ZB) represent the most ordinary polytypes, having a layer stacking of ABAB along the [0001] direction and of ABCABC along the [111] direction, respectively. Despite the structure similarities between WZ and ZB, their electronic structures can be very different and thus a new type of heterocrystalline superlattice which combines the WZ and ZB polytype is proposed. In contrast to conventional superlattices which consist of two chemically inequivalent materials, both the heterocrystalline and bicrystal superlattices are expected to be free of stress and dangling bonds, because the interface between two crystal structures or two crystal orientations is almost perfectly lattice matched. Hence the heterostructure of WZ and ZB and the bicrystal structure have a great potential in band-structure engineering. Herein we report on the synthesis of ZnS nanowires with ZB / WZ heterocrystalline and bicrystal structures by DC-plasma CVD. The nanowires are typically tens of micrometers in length, and 20-80 nm in diameter. In heterocrystalline ZnS nanowires, the ZB phase zones and WZ phase zones alternately align on the transverse (or longitudinal) direction of the nanowires. In particular, the (1-11) planes and [21-1] direction of ZB phase zone parallel to (00-1) planes and [-1-20] direction of WZ zone, respectively. As for the bicrystal ZnS nanowires, they usually compose of two ZnS fragments with ZB structure, which have common growth direction of [0-11] but different zone axis of [-111] and [0-1-1], respectively. The bombardment of Ar2+ ions involved in the DC-plasma process is believed playing an important role in the fabrication of ZnS nanowires with these unique structures. Furthermore, the plasma assistant growth method is hopeful used for the synthesis of other II-VI semiconductor nanowires with heterocrystalline or bicrystal structures.

9:45 AM Rb6.5
Novel Boron Nitride Nanotube-Polymer Composites. Chunyi Zhi[1], Yoshio Bando[1], Chengchun Tang[1], Kuwahara Hiroaki[2], Susumu Honda[2], Kazuhiko Sato[2] and Dmitri Golberg[1]; [1]Nanomaterials Laboratory, National Institute for Materials Science,, Tsukuba, Ibaraki, Japan; [2]Innovation Research Institute, Teijin Ltd., Iwakuni, Yamaguchi, Japan.

Compared with carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) possess notably better chemical stability and resistance to oxidation and exhibit nearly similar mechanical properties and thermal conductivity. In addition, BNNTs are transparent to visible light. Many of these advantageous properties can be exploited through the incorporation of BNNTs into some functional matrix materials. However, the studies on BNNT containing composites have been hindered because of significant difficulties in getting highly pure BNNTs at high yield. For CNTs, the composites based on various matrixes have been prepared and drastic improvement of matrix mechanical properties has been achieved. The specific optical and thermal properties of CNT containing composites have also been investigated. We report here with on highly pure BNNTs synthesized at high yield via a carbon-free chemical vapor deposition method. For the first time, BNNTs were perfectly dissolved in various organic solvents by wrapping them with a polymer. Then, BNNT-polystyrene composites were produced from BNNT solutions for detailed microscopic, optical and mechanical analyses. Tensile tests indicated that the elastic modulus of the newly prepared composites increased more than 20% by using 1wt.% BNNT fraction, that is compatible with CNT composites. Most importantly, opposed to conventional CNT-polymer composites, the novel BNNT-polymer films displayed excellent transparency. Detailed analysis of the BNNT composite thermal and other properties is underway and will be the subject of presentation.

SESSION Ra7: Nanostructures for Biology and Medicine II

Chair: Johannes V. Barth
Tuesday Morning, November 29, 2005
Room 207 (Hynes)

10:30 AM *Ra7.1
Optically Probing Bio-Structures via Nano Surface Energy Transfer. Geoffrey Strouse and Travis Jennings; Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida.

Ribonucleic acid structures (RNA, DNA, etc) are known to change conformation to initiate disease states or to trigger biological activity. Such structural changes, which include folding, cutting or twisiting, can form the basis of molecular beacons for disease state detection or bio-weapon detection. Many of the techniques used to probe structure rely on either classical methods or use of NMR and crystallography. While optical techniques such as Forster Resonance Energy Transfer (FRET) offer viable alternatives, the interactions are limited to short range encounters typically < 10 nm. Nano-surface energy transfer (NSET) is an alternative technology that allows distances on the order of 21 nm to be readily sampled and more importantly incorporated into molecular beacons. Using NSET, we show experimentally that rapid detection of ribozyme kinetics and activity is possible by monitoring energy transfer processes to small gold nanoparticles. NSET allows for real-time monitoring of nucleic acid folding and cleavage events, while maintaining bio-compatibility and without altering DNA or ribozymal (RNA) activity. A major advantage of NSET is the ability to observe simultaneous quenching events of a wide variety of organic dyes covering energies from the visible to the IR. This technique is effective for, but not limited to ribonucleic acid structures but can provide dynamics and kinetics information.

11:00 AM Ra7.2
Phage-QuantumDot Nanocomplexes for Quantitative Nanobiotechnology. Jeeseong Hwang[1], Rotem Edgar[2], Michael McKinstry[2], Kunio Nagashima[3], Gary Giulian[4], Sankar Adhya[2] and Carl Merril[4]; [1]Optical Technology Division, Physics Laboratory, NIST, Gaithersburg, Maryland; [2]Section of Developmental Genetics, National Cancer Institute, NIH, Bethesda, Maryland; [3]Image Analysis Laboratory, National Cancer Institute, NIH, Frederick, Maryland; [4]Section of Biochemical Genetics, National Institute of Mental Health, NIH, Bethesda, Maryland.

Since phage(pl.) were first discovered and isolated about 100 years ago, phage have been the main model systems in molecular biology for many decades, providing rigorous paradigms for many areas of biology. The phage are also of practical (industrial and economic) importance directly affecting the quality of human life. As the scope of applications involving phage display and detection widens, scientists began to realize phage can be an ideal self-replicating and robust tools such as nano-probe and nano-delivery vehicle for a variety of applications for nano-biotechnology. Among other interests, high-sensitivity single cell detection and analysis of pathogenic bacteria has been of great importance as early detection of pathogens and bio-terrorism agents became an urgent issue. Rapid mass production capability of phage also made the fast detection of pathogens possible at a very low cost while growth of bacteria in culture to increase cell number is time-consuming and costly. This work reports our achievement of a simple and inexpensive technique capable of specifically targeting a desired bacterial strain and quantitatively measuring phage-bacteria infection with the sensitivity to the single copy level. Using the basic building blocks of phage and fluorescent nanocrystals , quantum dots (QD), we manufactured phage-QD nano-complexes capable of targeting bacterial strains and providing quantitative fluorescence measurements of phage-bacteria infection. This technique has a potential of broad application involving targeting, detecting, isolating, and destroying pathogenic bacteria from environmental and clinical isolates.

11:15 AM Ra7.3
Theoretical Study of CdSe-based Nanomaterials for Nanomedicine Application. Rodion V. Belosludov[1], Vijay Kumar[2,3], Hiroshi Mizuseki[3], Atsuo Kasuya[4] and Yoshiyuki Kawazoe[3]; [1]ARCMG, Institute for Materials Research, Tohoku University, Sendai, Miyagi, Japan; [2]Dr. Vijay Kumar Foundation, Chennai, India; [3]Institute for Materials Research, Tohoku University, Sendai, Miyagi, Japan; [4]Center for Interdisciplinary Research, Tohoku University, Sendai, Miyagi, Japan.

Colloidal semiconductor quantum dots have recently received enormous attention for their potential application to fluorescence diagnostics. CdSe-core quantum dots (QDs) are an example of a nanomaterial that has been shown to be useful as an alternative to conventional organic fluorophores for use in biological imaging [1]. The currently used CdSe-core QDs have are crystalline in structure. In spite of the advantages of such crystalline nanoparticles, there are several limitations in the application of such nanoparticles to medicine. There is a potential cyclotoxicity that is correlated with the liberation of free Cd^{2+} ions due to deterioration of the CdSe lattice [2]. One solution that can be used to solve this problem is the design and synthesis of new nanocomposites which are more stable than crystalline QDs. We use *abinitio* ultrasoft pseudopotential plane wave method with generalized gradient approximation for the exchange and correlation energy. The lowest energy structures are obtained by optimizing selected structures of CdSe clusters using the conjugate gradient method. The adsorption spectra of selected CdSe clusters have been also performed. The structural optimization of (CdSe)$_n$ clusters with n up to 35 has been performed. It has been found, in good agreement with experimental data that clusters with n = 13, 19, 33 and 34 are magic and have a large value of HOMO-LUMO gap [3]. The calculation result shows that the CdSe cage-like structures are more energetically favorable than the nano-size bulk crystalline fragments of CdSe. These (CdSe)$_n$ clusters (n = 13, 19, 33, 34) have cage structures 12, 18, 28, and 28 with 1, 1, 5, and 6 CdSe molecules inside, respectively. Cage with n=12 can accommodate $(CdSe)_1$ inside as just the right sizes to form basically tetrahedral networks, making up stable $(CdSe)_{13}$. The optimal structure of $(CdSe)_{19}$ is a low symmetry $(CdSe)_{18}$-cage encapsulating $(CdSe)_1$ with local maximum in the binding energy leading to its magic nature in the mass spectrum [3]. For $(CdSe)_{33}/(CdSe)_{34}$, $(CdSe)_5/(CdSe)_6$, respectively, fit in well in $(CdSe)_{28}$-cage keeping a similar network. The largest calculated diameter of this polyhedron, 1.45 nm, agrees with AFM estimate of 1.5 nm. This structure lies 5.16 eV lower in energy than the most stable bulk fragment of $(CdSe)_{34}$. The calculated adsorption spectra for magic clusters are in agreement with experimental data. Similar tendencies have been found for CdS, CdTe, ZnS and ZnSe nanoparticles. These results indicate that the CdSe-core QDs can be also realized with the same structural features. These stable puckered cage-like CdSe-based particles with nanometer diameter may prove useful to cancer photodetection by reducing the toxicity and side effects of the diagnostic nanoagents. [1] W.C. Chan and S. Nie, Science 281, 2016-2018, 1998. [2] A.M. Derfus et al., Nano Lett. 4, 11-18, 2004. [3] A. Kasuya et al., Nature Materials 3, 99-102, 2004.

Ra7.4
Abstract Withdrawn

11:30 AM Ra7.5
Nucleation and growth of polymorphs of pharmaceuticals on chemically modified surfaces.

John C. MacDonald, Kasim Biyikli, Branko Zugic, Garrett Ebersole and Joshua Allor; Department of Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

We are investigating whether nucleation and growth of polymorphs of pharmaceuticals such as barbital can be controlled on surfaces modified with self-assembled monolayers (SAMs) of organic molecules on gold substrates. We have crystallized barbital from solutions placed on SAMs functionalized with a variety of polar and nonpolar organic groups. Growth of polymorphs has been achieved by slow evaporation of solvent at RT (thermodynamic conditions) and by rapid cooling of hot solutions to RT (kinetic conditions). Temperature was controlled using a heating/cooling stage built in our laboratory. We have carried out similar crystallization experiments in microfluidic devices to screen for polymorphs using simultaneous high throughput crystallization on a range of surfaces. These devices consist of PDMS (polydimethylsiloxane) that has been patterned with microchannels and then bonded to gold or glass substrates. The results of these experiments and the influence of chemically modified surfaces in controlling polymorphism are discussed.

SESSION Rb7: Nanowires, One Diminsional Nanostructures III

Chair: S. Picraux
Tuesday Morning, November 29, 2005
Room 208 (Hynes)

10:30 AM Rb7.1
Template-Directed and SAM-Mediated Synthesis of Au-TiO2-Au Heterojunction Nanowires.

Jing-Jong Shyue and Nitin P. Padture; Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

The concept of engineered metal-oxide-metal (MOM) heterojunction nanowires, where two metal nanowires (50 to 100 nm diameter; Au or Pt) are separated by a nanoscale segment (50-100 nm length) of a functional oxide, has been proposed. In other words, a MOM nanowire has a functional oxide of precise nanoscale dimensions with metal interconnects integrated within the nanoscale building block. The functional oxide can be a sensor, ferroelectric, piezoelectric, dielectric, semiconductor, or magnetic material. Thus, the MOM nanowires have the potential to take the field of "bottom up" nanoelectronics to the next level of sophistication and control. Moreover, the MOM nanowire architecture affords the rare opportunity for measuring directly the fundamental functional properties of nanoscale oxides. In the present study, we have synthesized Au-TiO2-Au nanowires using a novel combination of template-directed, self-assembled monolayer (SAM)-mediated methods. We have used electroplating to deposit the Au part of the nanowires inside anodic aluminum oxide (AAO) nano-hole templates. The exposed Au top surface is then functionalized with sulfonate-terminated self-assembled monolayer (SAM) to assist in the subsequent chemical-bath deposition of the TiO2 segment on the Au surface inside the confines of the AAO nanoholes. The chemical precursor used here is dilute titanium tetraisopropoxide (TTIP). The MOM nanowires synthesis mechanisms and the nanostructures of the resulting MOM nanowires will be presented and discussed. The MOM nanowires, in conjunction with focused ion beam (FIB), have been used to fabricate devices for electrical-properties measurements. Current-voltage and chemical-sensing properties of individual MOM nanowires will be presented, together with a discussion of structure-properties relations.

10:45 AM Rb7.2
Porous alumina templates for nanowire and carbon nanotube field-effect transistors.

Travis Lee Wade[1], Jean-Eric Wegrowe[1], Jean-Francois Dayen[1], Quang Anh[1], Mihaela Cristina Ciornei[1], Mohamed Barki[1], Anna Rumyantseva[1], Xavier Hoffer[1], Anna Fontcuberta i Morral[2], Costel-Sorin Cojocaru[2] and Pribat Didier[2]; [1]Laboratoire des Solides Irradies, ECOLE Polytechnique, Palaiseau Cedex, France; [2]Laboratoire de Physique des Interfaces et Couches Minces, ECOLE Polytechnique, Palaiseau Cedex, France.

Porous alumina is commonly used as a template for nanowire synthesis. It is made by anodization of aluminum in acidic solutions. The anodization process forms a self-assembled, triangular network of nanometer diameter pores. This is because the pore diameter, distribution, and pore length can be tailored to suit the needs of the user by varying the anodization conditions: electrolyte, voltage, time, and temperature. The chosen pore size determines the resulting nanowire dimensions. Another reason is that once the nanowires have been made in the alumina template, they can be electrically contacted at the top and bottom of the membrane for physical measurements without the need for lithography. With two contacts a scientist can study many interesting phenomena such as magnetoresitance and electron transport in the nanowires. Two contacts, however, are not enough if one wants to make a device such as a transistor or sensor for applications or research. A third contact or electrode is needed. We have developed new 3D alumina templates that allow placement of a third electrode close enough to the nanowires or carbon nanotubes for an electric-field effect. One structure starts with an aluminum wire, which is anodized perpendicular to its axis to form an isolation layer onto which a gate electrode is sputtered. Next, the wire is cut and anodized in the interior to form a network of pores parallel to the wire axis as a template for the synthesis of nanowires. The nanowires can be grown and contacted with the gate electrode already in place. Results have been obtained with tellurium nanowires and demonstrate a Coulomb blockade field effect. This new template is interesting because it can be made totally in a basic chemistry lab without the need for an expensive clean room or lithography. The next template is formed by depositing an aluminum layer on a silicon substrate which is anodized parallel to the substrate to form a lateral template for the growth of nanowires. A gate electrode is then deposited onto the lateral template. The lateral anodization has been demonstrated with pore diameters as small as 5 nm. The advantage of this approach is that it could be implemented into existing processor fabrication. This presentation will show the results for these approaches to field-effect transistors based on anodized aluminum templates.

11:00 AM Rb7.3
Synthesis and characterization of Au-ZnO core-shell composite nanowires.

Yu Zhang, Sathyajith Ravindran, Senthil Andavan and Cengiz Sinan Ozkan; Mechanical Engineering, University of California at Riverside, Riverside, California.

The focus of this work is to investigate the electrical and optical properties of semiconducting ZnO shell formed over gold nanowires. We use chemical vapor deposition technique to coat ZnO axially around gold nanowires. We studied the structural properties of these composite nanowires using SEM, TEM, electron diffraction and x-ray diffraction analysis and their composition with energy dispersive spectroscopy. We performed photoluminescence studies for their optical properties. Focused ion beam milling was used to make electrical contacts to these composite nanowires and studied their electrical properties. In addition, we report the morphology dependence with the operating temperature. The optimized experimental temperature for cylindrical coating was around 600C. Results show that these composite nanowires have a high potential in both electrical and optical nano devices.

11:15 AM Rb7.4
Engineered Metal-Oxide-Metal (MOM) Heterojunction Nanowires: Synthesis, Characterization, and Properties.

Jason Scott Tresback, Alexander L. Vasiliev and Nitin P. Padture; Materials Science & Engineering, Ohio State University, Columbus, Ohio.

There has been growing interest in the "bottom up" approach to building nanoelectronic devices, where nanoscale building blocks, such as nanowires (metals, semiconductors, oxides), are fabricated in isolation and assembled into nanocircuits. In the case of oxides, current nanoelectronics technology uses all-oxide nanowires that are assembled across photo-lithographically deposited metal contact-pad electrodes to create devices. In this case, the length of the nanowire spanning the electrodes defines the active region, which is difficult to control, limited by the resolution of lithography, and requires high operating voltages. In order to address these critical issues, we have proposed the concept of engineered metal-oxide-metal (MOM) heterojunction nanowires, where two metal nanowires (50 to 100 nm diameter; Au or Pt) are separated by a nanoscale segment (50-100 nm length) of a functional oxide. In other words, a MOM nanowire has a functional oxide of precise nanoscale dimensions with metal interconnects integrated within the building block. The functional oxide can be a sensor, ferroelectric, piezoelectric, dielectric, semiconductor, or magnetic material. Thus, the MOM nanowires have the potential to take the field of "bottom up" nanoelectronics to the next level of sophistication and control. Moreover, the MOM nanowire architecture affords a rare opportunity to measure directly the fundamental functional properties of nanoscale oxides. We have used a unique combination of template-directed electrochemical synthesis and selective oxidation to synthesize such MOM nanowires. This method is generic, and it can be used to synthesize a wide variety of MOM nanowires. Here we have synthesized two specific examples of MOM nanowires: Au-SnO2-Au (sensor) and Au-NiO-Au (ferromagnetic). The synthesis mechanisms and the nanostructures of the MOM nanowires will be discussed. Electron-beam lithography and focused ion beam (FIB) patterning have been used to fabricate devices providing the opportunity to measure functional-properties of the MOM nanowires. Current-voltage, chemical-sensing, and magnetic properties of individual MOM nanowires will be presented, together with a discussion of structure-properties relations.

11:30 AM Rb7.5

Off-axis Electron Holography and High-resolution Transmission Electron Microscopy of Internal p-n Junctions within Si Nanowires.

Dan Zhi[1], Paul A. Midgley[1], Chen Yang[2] and Charles M. Lieber[2]; [1]Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; [2]Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Off-axis electron holography is a promising technique for the examination of semiconductor devices, since it provides the ability to record not only the amplitude of a scattered wave but also its phase. The phase difference between regions of different doping concentration or composition results in modulations in the interference fringes in an off-axis hologram, from which two-dimensional maps of electrostatic potential can be obtained. As a result, electron holography can be very useful for distinguishing the dopant profile in a diode or MOS transistor, especially for devices using light dopants such as boron. Nanowires, with the dopant modulated along the axial direction during the synthesis, are novel nanostructures which can open up many opportunities in nanoelectronics and nanophotonics. In this paper, we apply off-axis electron holography, together with high-resolution transmission electron microscopy (HRTEM), to the internal p-n junctions within the Si nanowires grown by a chemical vapour deposition method. 20 and 40 nm diameter Si nanowires have been studied. Growth direction, morphology and crystal perfection of the nanowires are determined by HRTEM performed along two crystallographic zone axes. Junctions for holographic study are chosen carefully in order to avoid extraneous contrast arising from changes in the diffraction condition either side of the junction. Electrostatic potentials across the p-n junctions have then been successfully profiled using off-axis electron holography. Our results indicate that electron holography is a powerful technique for direct investigating the electrical properties of nanostructured semiconducting devices.

11:45 AM Rb7.6

New Ultraviolet Photodetector Using Bridging GaN Nanowires with Ultra-High Responsivity and Gain.

Reui-San Chen[1], Shiao-Wen Wang[2], Zon-Huang Lan[1], Jeff Tsung-Hui Tsai[3], Kuei-Hsien Chen[1], Li-Chyong Chen[4], Chia-Chun Chen[2], Yan-Tang Liu[5] and Ying-Sheng Huang[5]; [1]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; [2]Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan; [3]Graduate Institute of Electro-optical Engineering, Tatung University, Taipei, Taiwan; [4]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; [5]Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan.

We have developed a new ultraviolet (UV) photodetector (PD) using the free-standing gallium nitride (GaN) nanowires (NWs) as the photoconductor. This approach has allowed us to connect an ensemble of one-dimensional (1D) nanostructured system on-chip, which is a critical process of nanodevice. GaN NWs have been grown across to the active channel and are bridged between two side walls of highly doped GaN film electrodes. An interesting symmetric and tilted alignment of GaN NWs with $[1\underline{1}00]$ long-axis on the GaN{1000} side walls has been observed. In this investigation, three samples of detectors with different wire numbers of 8, 50±5, and 1500±150 were utilized to characterize their device performance. The photoconductivity (PC) spectra show a single and abrupt absorption at photon energy higher than 3.4 eV bandgap position, demonstrating excellent visible-blind character of the GaN NWs. It is worth noting here that the maximal PC responsivity R of GaN NWs PDs has exceeded the value of 10^6 A/W while absorption at 4.0 eV and bias at 4.0 V, which is near three to six orders of magnitude higher than the traditional thin film photoconductors (R = 1-2000 A/W). The mechanism behind the high responsivity has been discussed and attributed to the equivalently high current gain ($G \sim 5\times10^6$) in NWs PDs. The natures of small size (length) and 1D geometry of NW providing short and anisotropic electronic transport channel have been found to be the major factors contributing the extraordinary high gain. The probably high lifetime and mobility of excess carriers in GaN NW have been inferred and correlated to the geometric confinement effect of the 1D nanostructure.

SESSION Ra8: Magnetic Nanostructures I
Chair: Alain Pignolet
Tuesday Afternoon, November 29, 2005
Room 207 (Hynes)

1:30 PM *Ra8.1

Functional Magnetic Nanostructures Based on Polymer Nanocomposites and Self-Assembled Arrays.

Srikanth Hariharan, James Gass and Pankaj Poddar; Department of Physics, University of South Florida, Tampa, Florida.

Functional magnetic nanostructures for many applications require controlled dispersion of nanoparticles in a host matrix. Magnetic nanoparticles embedded in polymer matrices have excellent potential for EMI shielding and biomedical applications. However, uniform dispersion of particles in polymers without agglomeration is quite challenging. We have synthesized a variety of superparamagnetic and strongly interacting ferromagnetic nanoparticle clusters (Fe, Fe_3O_4, Fe_2O_3, Mn-Zn and Ni-Zn ferrites) in the form of blended polymer composites and self-assembled arrays deposited by Langmuir-Blodgett method. Processing conditions have been optimized to achieve high quality, uniform dispersion and tunable magnetic response. Static and dynamic magnetization studies have been done to monitor the systematic changes in superparamagnetic and ferromagnetic properties. In particular, a unique RF susceptibility technique developed by us has been used to precisely probe the magnetic anisotropy, switching and interactions in these systems. Our studies reveal insights into the collective behavior of strongly and weakly interacting clusters of magnetic nanoparticles and their promise in applications ranging from EMI shielding to refrigeration based on the magneto-caloric effect (MCE). Work supported by the US National Science Foundation through Grants ECS-0140047 and CTS-0408933.

2:00 PM Ra8.2

Approaches for Fabricating Bulk Magnets from Magnetic Nanoparticles.

Z.Q. Jin[1,2], N. N. Thadhani[2], Z. L. Wang[2], M Kozlov[3], T. Vedantam[1] and J. P. Liu[1]; [1]Department of Physics, University of Texas at Arlington, Arlington, Texas; [2]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; [3]NanoTech Institute, University of Texas at Dallas, Richardson, Texas.

FePt alloys are important for the development of high performance permanent magnets and magnetic recording media due to their high magnetocrystalline anisotropy and chemical stability. In this study, chemical synthesis of monodispersed 4 nm FePt and FePt/Fe_3Pt nanoparticles and their fabrication into nanocomposite bulk magnets were investigated. The nanoparticles of chemically disordered fcc structure were prepared first by reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl and then processed using a controlled thermal annealing treatment at low temperature. Thermal annealing removes the retained surfactant induced during chemical synthesis and results in a partially disorder-to-order phase transition at 400 °C. A coercivity up to 5.3 kOe has been obtained for the low-temperature annealed nanoparticles. The magnetic hardening due to the ordering transition was usually reported to be realized at higher annealing temperature (>500 °C) for FePt nanoparticles or by addition of some transition metals, such as Cu and Ag. The annealed nanoparticles were then packed into steel capsules at ∼45% theoretical mass density and consolidated by shock compaction at room temperature using a three-capsule plate-impact gas-gun loading system, and also by warm static compaction at 200 °C and 400 °C. The recovered bulk disk-shaped magnets were then characterized by x-ray diffraction, transmission electron microscopy and magnetic properties measurements. Shock densification to ∼90% higher than the initial packing density was observed, which is above the theoretically predicted density for packing (0.74) of equal size spheres. High resolution transmission electron microscopy (HRTEM) revealed intensive deformation of nanoparticles, contributing to the densification. Propagation of shock wave through the nanoparticles also resulted in transition from ordered fct to disordered fcc phases in certain local regions of the compacts. In the case of warm compaction, however, a disorder-to-order transition was observed. TEM analysis revealed the retention of the nanostructure in the bulk magnets. Upon annealing at a high temperature of 700 °C, a completely ordered structure was observed in the shock consolidated and warm compacted magnets. Magnetic properties measurements revealed maximum energy product (BH)max up to 14 MGOe and coercivity up to 14.6 kOe for the shock compacted samples and 16 MGOe and 12.6 kOe for warm compacted samples, respectively. Both FePt and FePt/Fe$_3$Pt magnets showed a remanence ratio of $\sim$0.65, revealing the existence of interaction between the nanoparticles. The study shows that the shock compaction and warm compaction are feasible approaches for producing bulk magnets from the magnetic nanoparticles.

2:15 PM Ra8.3
Controlled Anchoring of SMM Clusters on Si(100). Guglielmo Guido Condorelli[1], Andrea Cornia[2], Maria Favazza[1], Ignazio Luciano Fragala[1], Dante Gatteschi[3], Alessandro Motta[1], Paola Nativo[1] and Giovanna Pellegrino[1]; [1]Dipartimento di Scienze Chimiche, University of Catania and INSTM UdR of Catania, Catania, Italy; [2]Dipartimento di Chimica, University of Modena e Reggio Emilia and INSTM UdR of Modena, Modena, Italy; [3]Dipartimento di Chimica, University of Firenze and INSTM UdR of Firenze, Firenze, Italy.

The continuous scaling down of the size of integrated circuits (IC) has shown considerable limitations (lithographics, physics or economics) for top-down technologies, whilst, the bottom up approach, using molecules as single data-handling devices, represents an enormous challenge in terms of storage and data-handling density. Recently, it has been shown that some molecules can be used to store magnetic information. The most studied, prototypical molecule of this class of materials, referred to as a single molecular magnet (SMM), is a dodecamanganese (III/IV) cluster, [Mn12O12(OAc)16(H2O)4] 4H2O 2AcOH. An important goal for the development of the SMM cluster as a magnetic information storage building block integrated in the silicon technology relies upon an accurate control of the cluster anchoring process on the host surface. Recently, a reproducible way to drive the orientation of thiol-substituited Mn12 clusters anchored on a gold substrate and a possible approach to anchor oriented Mn12 on silicon have been proposed. On the other hand, Fe4 clusters (such as [Fe4(OMe)6(dpm)6]), which are among the simplest SMMs so far synthesized, are particularly suitable for the realization of chemically-stable, oriented arrays. In this paper, the possible control of the density of Mn12 and Fe4 clusters anchored on silicon (100) is examined. The anchoring strategy is based on the pre-functionalization of silicon surfaces through the hydrosilylation reaction with suited functional ligands (such as 10-undecenoic acid or the tripodal C9H17-C(CH2OH)3) possessing strong affinity toward Mn12 or Fe4 clusters. In order to control the anchoring of the SMM cluster, the proposed method tunes the density of bridging functional ligands on surfaces, using 1-alkenes as a spectator spacers. There is, in fact, evidence that overcrowding precludes ligand exchange with Mn12 clusters, whilst negligible cluster sticking occurs on Si-grafted 1-decene monolayers. Therefore, suited dilution of the exchangeable coordinating functional bridge with spectator spacers represents a viable route to control the clusters density on the silicon surfaces. Modified surfaces were analyzed with FTIR-ATR, XPS spectroscopy and AFM imaging. XPS and FTIR-ATR show that the surface mole ratio between grafted functional bridges and alkenes is strongly related to that of the source solution. The surface density of SMM clusters is, in turn, strictly proportional to the ester mole fraction. Well resolved and isolated Mn12 clusters were observed with AFM, adopting a diluted ester/decene 1:1 solution.

SESSION Rb8: Nanowires, One Dimensional Nanostructures IV

Chair: Cengiz S. Ozkan
Tuesday Afternoon, November 29, 2005
Room 208 (Hynes)

1:30 PM *Rb8.1
Tailored Inorganic/Organic Nanostructured Interfaces for Control of Surface Hydrophobicity. S. Tom Picraux[1,2], J. L. Taraci[2], D. Yang[2], P. Aella[2], M. McLauchlin[2], M. D. Gust[2], A. A. Garcia[2] and M. Hayes[2]; [1]Los Alamos National Laboratory, Los Alamos, New Mexico; [2]Arizona State University, Tempe, Arizona.

New approaches to sensing and biochemical analyses being enabled by nanoscale devices present novel challenges for systems integration. It is well known that the interaction of fluids with surfaces depends on a complex interplay of surface energy and morphology. These interactions can be become the major factor in controlling fluid behavior as dimensions are decreased to the nanoscale. We discuss here studies exploiting these interactions for control of surface wetting, hysteresis, and droplet motion through the combined design of nanoscale surface morphology and monolayer photoswitchable coatings. The vapor-liquid-solid technique is used to synthesize Si nanowires on surfaces with control over a wide variety of morphologies through the size of the metallic seeds and the growth parameters. These nanowire surfaces are then functionalized with organic monolayer coatings that include tethered photochromic molecules such as spiropyrans to tailor the surface properties. We show that the surface energies of these photo-responsive organic/inorganic interfaces can be reversibly switched in aqueous environments in situ by the opening and closing of the photoactive molecules. These morphologies and monolayer coatings are being used to locally form superhydrophobic surfaces and thereby control the interaction of water droplets with surfaces. Examples include amplifying the light-induced change in water contact angles, patterning of surfaces for droplet pinning, forming droplet arrays, and moving droplets solely with light (no electric field). We will discuss our surface nanoscale designs, selected results illustrating the control and measurement of the fluid interactions, and some potential applications.

2:00 PM Rb8.2
The Self-Assembling "Grow-in-Place" Process: An Environmentally Friendly Approach to Nanowire Device Fabrication. Yinghui Shan, Ali Kaan Kalkan and Stephen J. Fonash; Center for Nanotechnology Education and Utilization, The Pennsylvania State University, University Park, Pennsylvania.

Silicon nanowires and nanoribbons (SiNW/Rs) were fabricated directly from the Si source gas into pre-fabricated permanent nanochannel templates by our self-assembling "grow-in-place" approach[1]. The size, shape, position, orientation, and number of the SiNW/Rs can be precisely controlled by the pre-fabricated nanochannel templates. The templates can be fabricated with built-in contacts and integrated into the final devices, providing contacts, interconnects, and passivation/encapsulation. Our approach solves major manufacturing problems associated with nanowire devices since it results in a multiplicity of precisely positioned, oriented, and electrically contacted nanowires without the need for any SiNW/R post-synthesis processing, such as "pick-and-place". The "grow-in-place" architecture and methodology remove the need for template dissolution, post-synthesis nanowire manipulation, and post-synthesis electrical contacting. In addition, our approach is also environmentally benign and friendly[2] since only the exact number of SiNW/Rs needed was grown and the SiNW/Rs were always confined in the nanochannel templates. The nanowires, therefore, have little possibility of escaping into the environment. We have developed a variety of built-in ohmic and rectifying contact structures and approaches for the "grow-in-place" methodology. In this report, we focus on the introduction of our self-assembling "grow-in-place" approach, electrical characterization of SiNW/Rs, and nanowire device designs/structures. We will also discuss our initial work on the SiNW/R nanowire transistors. (1) Shan, Y.; Kalkan, A. K.; Peng, C. Y.; Fonash, S. J. Nano Lett. 2004, 4, 2085; (2) Roco, M., Environmental Science & Technology, March 1, 2005, 107A

2:15 PM Rb8.3
Metal-Semiconductor Nanowire Heterostructures. Yue Wu[1], Hao Yan[1] and Charles M. Lieber[1,2]; [1]Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; [2]Division Of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Proof-of-concept nanoelectronic devices based on semiconductor nanowire building blocks have exhibited performance that is comparable to or enhanced compared to conventional planar devices. Yet, an ultimate integrated nanosystem will not only require high-performance functional semiconductor units but also highly conductive metallic units, for example, for contacts, gates and interconnects. To this end, we have developed bottom-up approaches to the incorporation of metallic materials into semiconductor nanowires to yield several different classes of metal-semiconductor heterostructures. Electron microscopy structural analyses demonstrate the successful and controlled synthesis of these heterostructures, and electrical transport measurements demonstrate the potential of utilizing their unique properties for integrated device arrays with enhanced performance.

SESSION Ra9: Magnetic Nanostructures II

Chair: Srikanth Hariharan
Tuesday Afternoon, November 29, 2005
Room 207 (Hynes)

3:30 PM Ra9.1
Development of Tunable Self-assembled Magnetic Nanowire Arrays. Hao Jing[1], B. A. Evans[2], Onejae Sul[2], L. Carroll[2], M. Falvo[1,2], S. Washburn[1,2] and R. Superfine[1,2,3]; [1]Materials Science,

University of North Carolina Chapel Hill, Chapel Hill, North Carolina; [2]Department of Physics and Astronomy, University of North Carolina Chapel Hill, Chapel Hill, North Carolina; [3]Department of Computer Science, University of North Carolina Chapel Hill, Chapel Hill, North Carolina.

Free standing Magnetic nanowires have been assembled or directly grown by different methods such as template methods, lithography or assembly methods by surface tension or capillary force. We are exploring the magnetic assembly of previously produced nanorods. This offers the advantage of increased fabrication flexibility by separating the nanorod fabrication and patterning steps. Based on the Stoner and Wolfarth model, it is feasible to treat magnetic nanowires with high aspect ratio as magnetic dipoles along their easy axis. These magnetic dipoles experience a net force along the magnetic field gradient as well as a torque under an external magnetic field. Soft-magnetic nanowires with mean radius 200 nm were electrodeposited in anodically etched commercial aluminum oxide membranes. Based on finite element analysis modeling, parabolic magnetic potential wells were realized with a home-made solenoid electromagnet. We found the magnetic nanowires form self-assembled patterns in response to the potential well formed by the spatially varying magnetic field. The lattice distances were tunable from several microns to tens of microns depending on field strength, total number of the nanowires and nanowire dipole strength. A dimensionless Monte Carlo simulation was performed on an idealized model for better understanding the self-assembly patterns. Free standing magnetic nanowire devices were fabricated based on this strategy by planting the roots of nanowires into a curable thin soft polymer layer spin coated on a flat surface. After curing this thin layer of polymer, we demonstrated the fast response actuation by putting the standing nanowire devices in an oscillating external magnetic field. These free standing devices may find applications in surface morphology controls for optical devices or nano-fluidic controls.

3:45 PM Ra9.2
Self-Assembled Single Crystal Ferromagnetic α-Fe Nanowires: Perpendicular Recording Media and Carbon Nanotube Growth. Ladan Mohaddes-Ardabili[1,2], H. Zheng[2], S. B. Ogale[1,3], Q. Zhan[2], J. H. Han[4], S. Y. Yang[1,2], L. Salamanca-Riba[1], J. B. Yoo[4], D. G. Schlom[5], M. Wuttig[1] and R. Ramesh[2]; [1]Materials Science and Engineering, University of Maryland, College Park, Maryland; [2]Materials Science and Engineering, University of California, Berkeley, California; [3]Physics, University of Maryland, College Park, Maryland; [4]Department of Materials Engineering, Sungkyunkwan University, Suwon, South Korea; [5]Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

A novel approach to create self-assembled ferromagnetic nanostructures for new magnetic recording media with high storage capacity is reported, which involves spontaneous phase decomposition of a single-phase perovskite oxide during film growth. We are exploring the stability in a nominally single phase LaSrTMO3 (TM = Fe, Co, Mn) system as a function of oxygen pressure, using thin film heteroepitaxy as the processing route. We find that the film structure and microstructure depends systematically on the oxygen pressure during deposition. Deposition under reducing environments leads to the formation of self-assembled arrays of nanowires. Specifically, in the case of a system containing Fe the deposition under reducing conditions leads to spontaneous formation of an array of single crystalline ferromagnetic α-Fe nanowires embedded in an antiferromagnetic matrix with nominal composition of LaSrFeO4. The diameter of α-Fe nanowires is controlled by growth temperature and the height is controlled by film thickness. At high growth temperatures of 840 C, square shaped α-Fe pillars with a lateral width of d = 50-60 nm are formed. As the deposition temperature is reduced the diameter of the nanowires is progressively reduced to 4-6 nm for the growth at 560 C and the shape is circular. In the case of Co the growth temperature window is smaller and the nanowires with d = 60-70 nm are formed at around 700 C. The magnetic properties of these nanowires are dependent on both their average diameter and height. The maximum coercivity of Hc = 3000 (Oe) is achieved for 200 nm thick nanowires with average diameter of 15-20 nm grown at 760 C (M = 0.95 Msat). The large remanence and sizable coercivity of the nanowires make them desirable for high-density data storage and other magnetic device applications. Additionally, these thin films were used as a template to grow vertically aligned carbon nanotubes using Plasma Enhanced Chemical Vapor Deposition (PECVD). Acetylene (C2H2) and ammonia (NH3) were used as a carbon source and diluting gas, respectively. The growth temperature was lower than 600 C. Self-assembled α-Fe nanowires serve as nucleation sites for the growth of vertically well-aligned multiwall carbon nanotubes (MWCNTs). The size of carbon nanotubes can be controlled by changing the diameter and thickness of the α-Fe nanowires. The field emission from these MWCNTs was measured and the results will be presented.

4:00 PM Ra9.3
Laser-assisted chemical vapor deposition of carbon coated cobalt nanoparticles. Oscar Alm and Mats Boman; Materials chemistry, Materials chemistry Angstrom laboratory, Uppsala, Sweden.

Carbon coated nanoparticles were synthesised by laser-assisted (ArF excimer laser, $\lambda = 193$ nm) chemical vapor deposition (LCVD). The particles were formed in the gas-phase by photolytic dissociation of cobaltocene in argon and the particles were deposited onto a silicon substrate. Typical laser fluencies were 70 - 90 mJ/cm^2. The deposited particles were mostly amorphous as analysed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Some crystalline particles were observed in the TEM for the highest fluence, 90 mJ/cm^2. They were identified as α-Co, β-Co and Co_3C. This indicates that more crystalline particles can be deposited if higher fluencies than 90 mJ/cm^2 are used. When a magnet was added below the substrate more particles were deposited indicating ferromagnetic properties of particles. X-ray photoelectron spectroscopy (XPS) measurements showed that the particles have large carbon content. After 10 s of sputtering cobalt oxide appeared and at longer sputtering times only metallic cobalt was observed. Thus from the XPS and TEM examinations it is probable that the particles have a carbon shell-like structure and a nucleus of metallic cobalt together with a narrow shell of cobalt oxide between the nucleus and the carbon. From TEM micrographs the size distributions for particles deposited at different laser fluencies were obtained and typical mean sizes were 20 - 50 nm. Also from the TEM micrographs different morphologies of the particles were observed. The majority of the particles had a spherical shape but also rod shaped nanostructures were observed. The intention is also to use a Differential Mobility Analyser (DMA) in order to separate certain particle sizes and analyse these particles by TEM to determine if different cobalt phases can be deposited as a function of particle size.

4:15 PM Ra9.4
Hybrid Colloidal Nanostructures with Paired Plasmonic, Semiconducting and Magnetic Functionalities. Weili Shi[1,4], Hao Zeng[2], Yudhisthira Sahoo[3,4], Mark T. Swihart[1,4] and Paras N. Prasad[3,4]; [1]Department of Chemical and Biological Engineering, The University at Buffalo (SUNY), Buffalo, New York; [2]Department of Physics, The University at Buffalo (SUNY), Buffalo, New York; [3]Department of Chemistry, The University at Buffalo (SUNY), Buffalo, New York; [4]The Institute for Lasers, Photonics, and Biophotonics, The University at Buffalo (SUNY), Buffalo, New York.

Hybrid particles with paired combinations of plasmonic, semiconducting and magnetic functionalities have been chemically fabricated. Three kinds of such hybrid nanoparticles: Au-Fe3O4, Au-PbS and PbS-Fe3O4 are reported here. These particles were synthesized by decomposition of organically soluble precursors, iron acetylacetonate (Fe(acac)3) or Pb-oleate complex, onto the surface of separately synthesized gold or PbS nanoparticles that serve as nucleation centers in high boiling point solvents. The growth of Fe3O4 on gold or PbS cores and the growth of PbS on gold cores appear to be quasi-epitaxial, as observed by high resolution transmission electron microscopy (HRTEM). By rationally tuning the synthetic parameters, such as heating rate, solvent, and ratio of precursors to seeds, the growth of nanoparticles could be controlled to give different morphologies. The optical properties of gold or PbS nanoparticles, and the magnetic properties of Fe3O4 are appreciably affected by the presence of the conjugate material. These kinds of hybrid nanostructures have a broad range of potential applications in heterogeneous catalysis, for magnetophoretic delivery of drugs or genes, for biological sensing, in magneto-optical switching, and as building blocks for spintronic devices.

4:30 PM Ra9.5
Preferred Orientation and Epitaxial Morphological Transition of Block Copolymer Directed by Lattice-like Magnetic Nanoparticle Aggregates. Moon Jeong Park[1], Jongnam Park[2], Taeghwan Hyeon[2] and Kookheon Char[1]; [1]School of Chemical and Biological Engineering & NANO Systems Institute - National Core Research Center (NCRC), Seoul National University, Seoul, South Korea; [2]National Creative Research Center for Oxide Nanocrystalline Materials and School of Chemical and Biological Engineering, Seoul National University, Seoul, South Korea.

We investigate the effect of hard additives, i.e., magnetic nanoparticles (NPs) and metal NPs, on the ordered morphology of a block copolymer by varying concentration of NPs. In order to characterize the structural changes of the block copolymer associated with different NP concentrations small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) were performed. Monodisperse maghemite (γ-Fe2O3) NPs and silver NPs with surfaces modified by oleic acid have been synthesized and two PS-b-PI diblock copolymers showing lamellar and cylindrical morphologies are used as structure-directing matrices for the NP arrangement. Poly(styrene-block-isoprene) (PS-b-PI) can serve as a model system to investigate the subtle change in morphology upon the addition of NPs since the PS-b-PI has a narrow interface between the two blocks. Moreover, we can refer to existing theoretical models on the NP/block copolymer mixtures, based on the strong segregation limit approximation. As the NP concentration is increased, domains of NP aggregates are observed for both magnetic and metal NPs. In the case of PS-b-PI / silver NPs mixtures, with absence of particle-particle interaction, the ordered morphology is getting disordered with increase in NP concentration. It is, however, surprising to note that the regular lattice-like aggregate structure of γ-Fe2O3 NPs induces an intriguing morphological transition from hexagonal cylinders (hex) to the body-centered cubic spheres (bcc) via undulated cylinder for cylinder-forming PS-b-PI not showing such order-order transition without NPs. The interplay between magnetic NPs and block copolymers was also tested with different size of magnetic NPs and also with different block copolymer microdomains. When larger magnetic NPs (14 nm γ-Fe2O3 instead of 7 nm γ-Fe2O3) were used, the same morphological transition from hex to bcc was obtained even at a lower NP concentration probably due to the enhanced magnetic interactions. Also, when a lamellae-forming PS-b-PI (16K-18K) was mixed with 7 nm magnetic NPs, the same undulation of lamellar domains in the vicinity of lattice-like NP aggregates was observed. We have also demonstrated the preferred orientation of anisotropic microdomains of block copolymers and the epitaxial morphological transition in the presence of magnetic NP aggregates. The fact that PS-b-PI diblock copolymers with a small difference in polarities of the two blocks, which is known to be difficult to orient by applying external fields such as electric or magnetic field, is oriented and even go through the epitaxial morphological transition by lattice-like magnetic NP aggregates, can add more flexibility in nanostructure control and orientation opening up more potentials for applications such as high-density storage and photonic materials.

4:45 PM Ra9.6
Self-Organization of FePt Nanoparticles on Photochemically Modified Diblock Copolymer Templates. Nataliya Yufa[1], Amadou Cisse[1], Seth Darling[2], Sam Bader[2] and Steven Sibener[1]; [1]James Franck Institute, University of Chicago, Chicago, Illinois; [2]Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Combining inorganic and organic components to create functional materials has been an active area of research in recent years. The inorganic components possess useful electric, photonic or magnetic properties while the organic components self-assemble into a variety of morphologies on the nanoscale. We have created a hierarchically self-assembled magnetic nanostructure. Thin (30 nm) films of poly(styrene-block-methacrylate) (PS-b-PMMA) copolymer were used as a scaffold. Upon annealing PS-b-PMMA forms lying-down cylinders of PMMA in a matrix of PS. These thin films were modified by exposure to ultraviolet light in vacuum which etched away the PMMA leaving behind a corrugated surface. We find that superparamagnetic FePt nanodots capped with oleic acid deposited on this surface show a very high degree of preference for the etched phase.* In the future this hierarchical self-assembly method may prove useful for producing bit-patterned magnetic memory. Funding is acknowledged from the University of Chicago-Argonne National Laboratory Consortium for Nanoscience Research, MURI, the NSF-MRSEC at the University of Chicago, and the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences. * S.B. Darling, N.A. Yufa, A.L. Cisse, S.D. Bader, and S.J. Sibener, Avanced Materials (in print)

SESSION Rb9: Alternative Nanofabrication II
Chair: Hedi Mattoussi
Tuesday Afternoon, November 29, 2005
Room 208 (Hynes)

3:30 PM *Rb9.1
Unconventional Approaches for Advanced Nanotechnology: Functional Patterning and Microfluidic Synthesis. Kyung M. Choi, Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

Since industry has sought new advances in nanotechnology, developments of new materials and novel nanofabrication techniques have been pursued to meet our growing demands in miniaturization. In this talk, we will present fundamental challenges in nanotechnology for diverse applications such as *'New materials for advanced soft lithography'*, *'Functional patterning'*, *'Microfluidic synthesis'*, and *'Novel applications of organic/inorganic hybrid glasses for nanotechnology'*. In the first section, we will introduce a new version of functional stamp materials with molecularly tailored functionalities. We also demonstrate here its elastic photopatternability and nano-resolution soft lithography, which have proven to be difficult using commercial stamps. In the second part, microfabrication of functional polymers that have specific molecular recognition for biological or chemical detection devices will be presented. As an example of functional patterning, we used a molecularly imprinted polymer (MIP) system, which is produced by "molecular imprinting" to create "synthetic receptor sites" with specific molecular recognition for organic molecules in cross-linked network polymers. Microfluidic synthesis has received considerable attention for the synthesis of novel materials at the micro-scale since it can produce specific advantages, that can not be achieved via conventional bulk-scale synthetic routes. We are thus interested here in the operation of microfluidic reactors for microsynthetic purposes, taking advantage of micro-scale mixing of multiple reagents and of the use of quenching sequences for greater reaction selectivity. Novel applications of organic/inorganic hybrid glasses containing nanoparticles will also be presented.

4:00 PM Rb9.2
Generation of Dense, Well-controlled Nanopatterns of Self-assembled Monolayer over Large Areas on Gold Surfaces Using a Simple Template-confined Approach. Han Gao, Jie Deng and Nitya Nand Gosvami; Micro- & Nano Systems Cluster, Institute of Materials Research and Engineering, Singapore, Singapore.

The ability to fabricate chemically patterned surfaces at nanoscale is of great importance in nanoscience and nanotechnology. A variety of methods such as photolithography, particle beam lithography, microcontact printing, and scanning probe lithography have been developed to generate nanopatterns of self-assembled monolayers (SAMs) on gold surfaces with more or less success. Significant efforts are still needed to explore other simple unconventional methods for fabricating SAM nanopatterns over large areas, at low cost, and with high throughputs. We demonstrate a simple template-confined method for generating dense ($> 10^{10}/\mathrm{cm}^2$), well-controlled SAMs nanopatterns (< 30 nm diameter) over a large area ($> 5\ \mathrm{cm}^2$) on gold surfaces. In this approach, hexagonally ordered patterns of anodic aluminum oxide (AAO) template, prepared by two-step anodization of aluminum, were transferred onto a silica/Au/Si wafer to form a porous silica template on Au/Si wafer via a RIE technique, which spatially confined the self-assembly of thiol molecules on the exposed Au surfaces. After removal of the silica template, the prepared SAMs patterns can be used as resists for generating three-dimensional arrays of gold nanoparticle on silicon wafers via wet chemical etching. This approach is a simple and inexpensive process that results in SAM patterns as small as 30 nm with convention laboratory setups. In this approach, the patterns directing the self-assembly of thiols are naturally formed in AAO preparation and no expensive and complicated facilities are required. AAO is a well-known template with easily tunable structure by simply varying preparation conditions, the pattern size and spacing are only determined by the structure of AAO template and not by any other factors such as lateral diffusion and template distortion which are inherent in microcontact printing and dip-pen lithography. In addition, large-area SAM patterns can be achieved ($5\ \mathrm{cm}^2$ in our setup) by a composite protective layer that prevents AAO from cracking in the process. This approach can also create second functional groups on the bare spaces, after removal of silica templates, to form binary chemically patterned surfaces. Finally, monolayers assembled from thiol solution can be used as resists for generating three-dimensional Au particle arrays.

4:15 PM Rb9.3
A Chemical Approach to 3-D Lithographic Patterning of Ge Nanocrystals. I. D. Sharp[1,2], Q. Xu[1,2], D. O. Yi[1,3], C. Y. Liao[1,2], J. W. Ager[1], J. W. Beeman[1], K. M. Yu[1], D. C. Chrzan[1,2] and E. E. Haller[1,2]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Materials Science and Engineering Department, University of California, Berkeley, Berkeley, California; [3]Applied Science and Technology Group, University of California, Berkeley, Berkeley, California.

Ge nanocrystals are frequently synthesized by implantation of Ge into silica followed by thermal annealing. We demonstrate that nucleation and growth of Ge nanocrystals can be suppressed by co-implantation of oxygen prior to annealing. At Ge/O dose ratios exceeding one, fully miscible silica germania alloys are formed rather than Ge nanocrystals. This chemical deactivation of Ge is utilized to achieve patterned growth of Ge nanocrystals. Ge is implanted into a thin SiO_2 film on a Si substrate and a lithographically defined mask is created through which oxygen is subsequently implanted. Rapid thermal annealing (RTA) of the co-implanted structure yields two-dimensionally patterned growth of Ge nanocrystals under the masked regions. We further demonstrate that this process, when applied to implanted silicon-on-insulator (SOI) structures, allows for three-dimensional patterning of Ge nanocrystals; the buried oxide thickness and depth providing the third dimension of control. We apply a previously developed process to obtain exposed Ge nanocrystals by selective HF etching of the silica matrix to these patterned structures. [I.D. Sharp, *etal.*, JAP (in press)] Atomic force microscopy (AFM) of etched structures reveals that exposed nanocrystals are not laterally displaced from their original positions during the etching process. Therefore, this process provides a means of achieving patterned structures of exposed nanocrystals which, if functionalized, could controllably interact with the surrounding environment. The possibilities for scaling this chemical-based lithography process to nanoscale features using electron beam lithography and for applying it to other nanoscale materials systems will be discussed. This work was supported in part by US NSF Grant Nos. DMR-0405472 and EEC-0085569, and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

4:30 PM Rb9.4
Directed Assembly of Complex, Heterostructured, Multi-Material Nanoarchitectures. Erik D. Spoerke, James A. Voigt, Thomas L. Sounart and Jun Liu; Electronic and Nanostructured Materials, Sandia National Laboratories, Albuquerque, New Mexico.

Semiconducting nanostructures hold great promise as technological materials, owing to their diverse electronic, optical, even piezoelectric capabilities. Naturally, integrating these materials to form complex heterostructures promises to access new properties and architectures, unique to these multi-materials. We have developed methods for the growth of heterostructured and multi-material nanostructures based on wide band-gap semiconductors such as cadmium sulfide and zinc oxide. Taking inspiration from biology, we exploit biomimetic materials, such a peptides, and the bio-inspired application of similar organic modifiers to control the growth and assembly of these nanomaterials into functional structures such as extended thin films. This talk will explore the use of multi-stage, hydrothermal synthetic approaches to assemble complex nanomaterial structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

4:45 PM Rb9.5
Directed Self-Assembly of Dual-Functionalized Microspheres and Microrods by Nucleic Acid Interactions. Paul Laibinis[1,2] and Manish Bajaj[2]; [1]Chemical and Biomolecular Engineering, Rice University, Houston, Texas; [2]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Self-assembly provides a convenient strategy for building higher-level structures from smaller components. Examples include the formation of densely packed films by the self-assembly of molecules onto surfaces and the generation of multilayered structures by the layer-by-layer assembly of polymers. Chemical interactions are responsible for the self-assembly of these supramolecular and hierarchical structures. A goal for self-assembly has long been the generation of controllably complex nano- and microstructures from individual constituents by the simple mixing of species together and their self-formation into specific aggregates and coupled structures. Such directed bottom-up self-assembly would build from the developed (and constantly improving) technology base of microfabrication and the developing technologies for producing nanoparticles, nanorods, and related systems. To address this problem, we have targeted the creation of species containing multiple individually tailorable regions that can each express a specific recognition behavior. In this regard, we have prepared and studied the assemblying characteristics of various anisotropic building blocks that express oligonucleotides on their surfaces. Specifically, we have created microspheres and microrods by shadow deposition techniques that expose individual surface regions of gold and silica. By combining methods of solid-phase synthesis and self-assembly, we have functionalized the regions on these objects individually and selectively with different oligonucleotide sequences to produce so-called 'Janus' particles and rods that serve as anisotropic building blocks of selectable size, shape, and nucleic acid sequence for directed self-assembly. The resulting dual-functionalized surface regions are each active towards specifically recognizing oligonucleotides of complementary sequence. We have used this ability to generate purposeful aggregates and self-assembled multi-component structures by combining these 'Janus' objects with nanoparticles or other object that express complementary oligonucleotide sequences on their surfaces. The approach is general and modular as the surface chemistry, dimensions, and compositions of each assemblying object can be selected as is the set of species placed together for the directed self-assembly event. The advantages of specific shapes and the abilities to generate objects expressing beyond dual functionality will be highlighted.

SESSION Ra10: Biomimetics II
Chair: S. Picraux
Tuesday Evening, November 29, 2005
Room 207 (Hynes)

6:00 PM *Ra10.1
Molecular Biomimetics: Genome-based Materials Science and Engineering. Candan Tamerler[1], Francois Baneyx[2], Alex Jen[1,3], David Ginger[3], Ram Samudrala[4], Beth Traxler[4], Daniel T. Schwartz[1,2], Y. Xia[3] and Mehmet Sarikaya[1,2]; [1]Materials Science and Engineering, University of Washington, Seattle, Washington; [2]Chemical Engineering, University of Washington, Seattle, Washington; [3]Chemistry, University of Washington, Seattle, Washington; [4]Microbiology, University of Washington, Seattle, Washington.

Physical and chemical functions of organisms are carried out by a very large number (billions) of proteins and peptides through predictable and self-sustaining interactions. In Nature, biomolecule-material interaction is accomplished via molecular specificity and high efficiency leading to the formation and self-assembly of controlled functional constructs, structures, tissues, and systems at all scales of dimensional hierarchy. Through evolution, Mother Nature developed molecular recognition via successive cycles of mutation and selection. Molecular specificities of probe-target interactions are all based on specific peptide-molecular recognition. Structural and compositional control of inorganic materials at the molecular-scale is a key in the synthesis of novel, functional, practical material systems. With the recent developments of nanoscale engineering in physical sciences, and the advances in molecular biology, we are now able to combine genetic tools with synthetic nanoscale constructs, and create a hybrid methodology, molecular biomimetics. Using biology as a guide we have adapted bioschemes including combinatorial biology, post-selection engineering, bioinformatics, and modeling to select and tailor short peptides (7-60 amino acids) with specific binding to and assembly on functional materials, e.g., metals, ceramics, and semiconductors. Based on the fundamental principles of genome-based design, molecular recognition, and self-assembly, we can now engineer polypeptides for inorganic surfaces and synthetic functional molecules and use them as nucleators, catalyzers, growth modifiers, molecular linkers and erector sets, fundamental utilities for nano- and nanobio-technology. We will review the latest developments from our collaborative research group,s as well as from other international groups active in this rapidly developing polydisciplinary field, focusing on i. Genetic engineering of inorganic-binding polypeptides; ii. Nature of binding, specificity and assembly of peptides on selective materials using experimental (e.g., surface plasmon resonance spectroscopy, quartz crystal microbalance and atomic force microscopy) and theoretical tools (protein structure prediction); iii. Biosynthesis and functional organization of hybrids using inorganic-binding peptides for photonic and medical applications. The research is supported by an ARO-DURINT and a NSF-MRSEC Programs.

6:30 PM Ra10.2
Using1D and 2D Chemical Templates Formed by Scanned Probe Lithography to Create Organized Virus Arrays for Hierarchical Assembly of Nanomaterials. Sung-Wook Chung[1], Chin-Li Cheung[3,1], James DeYoreo[1], Anju Chatterji[2], Tianwei Lin[2] and John E. Johnson[2]; [1]Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Molecular Biology, The Scripps Research Institute, La Jolla, California; [3]Department of Chemistry, University of Nebraska, Lincoln, Nebraska.

Organizing nanostructures and functional molecules into deterministic patterns at surfaces is a fundamental challenge of nanoscience. Self-assembly methods are generally limited to creation of uniform 2D films. Printing methods, which have the potential for organizing nanostructures through creation of templates, can rarely achieve patterning below 50nm, and then controlling orientation of individual nanostructures is difficult. One approach to achieving higher density of functionality and shorter range of order is to use viruses as programmable templates for nanoparticle formation as well as for placement of molecular moieties with optical or electronic functions. These building blocks are typically many tens of nanometers in size and can perhaps be organized using templating methods operating at 50-100 nm. Here we report results using scanned probe nanolithography to create chemical templates for organization of viruses and in situ AFM imaging to investigate the dynamics of organization at these templates. As a model system, we chose Cowpea Mosaic Virus (CPMV) genetically engineered to present histidine (His) tags at specific sites on the capsid surface. Atomically-flat gold substrates coated with self assembled monolayers (SAMs) of polyethylene glycol (PEG) terminated alkyl thiols were patterned with nickel-chelating nitrilotriacetic acid (Ni-NTA) terminated alkyl thiols using scanned probe nanolithography. The Ni-NTA patterns had feature sizes ranging from 10-100nm and attached to the His-tags on the viruses through a metal coordination complex linkage with the Ni-NTA. Force microscopy was then used to investigate the degree of ordering, packing geometry, assembly kinetics, and cluster-size distribution both on the regions patterned to bind chemoselectively with the virus, as well as the surrounding PEG-terminated region. We show that the degree of ordering depends on all parameters chosen: the surface chemistry, the virus concentration, the PEG concentration, and the feature size of the patterns. For example, as the solution PEG concentration is increased, which increases the virus-virus interaction through hydrophobic effects, 2D arrays of viruses evolve from poorly-ordered, to well-ordered rhombehedral, and then hexagonally close packed assemblies and 1D patterns increase in width one virus to multiple rows of viruses. Disordered clusters form on the PEG functionalized regions, but the dynamics of cluster growth is altered. Taking cues from previous work in both epitaxial and colloidal systems, we present a physical picture of assembly at templates where the dominant factors are the ratio of virus flux to surface mobility and the strength of the virus-virus interact, the latter being modulated by hydrophobic interactions and or/covalent bonds. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

6:45 PM Ra10.3
An engineered virus as a scaffold for 3-D assembly on the nanoscale. Amy Szuchmacher Blum[1], Carissa M. Soto[1], Charmaine D. Wilson[1], Terence L. Schull[1], Steven K. Pollack[3], Anju Chatterji[2], Tianwei Lin[2], John E. Johnson[2] and Banahalli R. Ratna[1]; [1]Code 6930, Naval Research Lab, Washington, District of Columbia; [2]Department of Biochemistry and Molecular Biology, The Scripps Research Institute, La Jolla, California; [3]Division of Chemistry and Materials Sciences, Office of Science and Engineering Laboratories, Center for Devices and Radiological Health, Food and Drug Administration, Rockville, Maryland.

Significant challenges exist in assembling and interconnecting the building blocks of a nanoscale device and being able to electronically address or measure responses at the molecular level. Self-assembly is one of the few practical strategies for making ensembles of nanostructures and will therefore be an essential part of nanotechnology. However, in order to generate complex structures through self-assembly, it is crucial to develop methods by which different components in solution can come together in an ordered fashion. Using viruses as nanoscale scaffolds for devices offers the promise of well-defined positioning on the nanoscale, using a particle that can either interface with currently available lithographically defined structures, or undergo further self-assembly into extended structures by itself. Here we show that exquisite control over positioning nanoscale components on a protein scaffold allows bottom-up self assembly of nanoscale devices. Using Cowpea Mosaic Virus, modified to express cysteine residues on the capsid exterior, gold nanoparticles were attached to the viral scaffold in a pattern to produce specific interparticle distances. The nanoparticles were then interconnected using thiol-terminated conjugated organic molecules that can act as "molecular wires", resulting in a three-dimensional spherical conductive network which is only 30 nm in diameter.

7:00 PM Ra10.4
Peptide-Mediated Formation of a Titania/Single Wall Carbon Nanotube Composite Material. Mark Pender[1], Jeffrey Hartgerink[2], Morley Stone[1] and Rajesh Naik[1]; [1]Air Force Research Laboratory, Wright-Patterson AFB, Ohio; [2]Department of Chemistry, Rice University, Houston, Texas.

Carbon nanotubes (CNTs), both multiwall and single wall, are proving to be critical components for emerging electronic, sensor, and structural systems. In many instances, the key to success is the development of methods for the manipulation and functionalization of CNTs that do not compromise their structural or electronic properties. Coating single wall carbon nanotubes with oxide based ceramics to form either hetero- nanomaterials with targeted properties or nanocomposite materials has been previously demonstrated. Titanium dioxide is of particular interests for photovoltaics where the single wall carbon nanotubes could aid electron transport through dye-sensitized solar cells or function as supports for photocatalysts where high surface areas, electronic addressability, and chemical inertness are all important factors. While there are several examples of TiO_2 coatings or particles on the surface of multiwall carbon nanotubes (MWNTs) there are fewer examples for single wall carbon nanotubes (SWNTs). This is due, in large part, to the poor solubility of individual SWNTs in solutions required for processing and a lack of specificity for titania formation exclusively at the surface of the SWNTs. Here, we demonstrate a bifunctional peptide which can suspend SWNTs as individuals and nucleate the growth of titania from solution precursors at the surface of the nanotubes without covalent functionalization of the carbon nanotube. A peptide (P1) with a strong affinity for the surface of SWNTs produced by the HiPco (high pressure carbon monoxide) method was isolated via phage display techniques. Starting with this amino acid sequence, a larger peptide (P1R5) was synthesized consisting of the P1 fragment, a 4-glycine linker and the R5 peptide, which has been shown to mineralize silica and titania from precursor solutions. This peptide suspended SWNTs as individuals and small bundles in aqueous solution and was found to initiate the formation of anatase titania at the surface of the nanotubes when a precursor solution was added. This method and characterization of the products are presented.

7:15 PM Ra10.5
Templated Beta-Sheet Supramolecular Assemblies and Beta-strand Orientation of de novo Polypeptides for Biomolecular/bioelectronic Structure Formation.
Narender Rana[1], Seiichiro Higashiya[2], Christopher Kossow[1], Natalya Topilina[2], Autumn Carlsen[1], Christopher Wells[2], John Welch[2], Eric Eisenbraun[1], Robert Geer[1] and Alain Kaloyeros[1]; [1]College of Nanoscale Science and Engineering, University at Albany - SUNY, Albany, New York; [2]Department of Chemistry, University at Albany - SUNY, Albany, New York.

Templated assembly of a 524 residue de novo polypeptide sequence on a highly oriented pyrolytic graphite (HOPG) substrate is presented. Beta-sheet-forming polypeptides prepared from de novo designed artificial genes were extensively studied by atomic force microscopy and UHV-scanning tunneling microscopy. The formation of highly rectilinear parallel supramolecular fibril arrays which display a three-fold symmetry consistent with HOPG templated assembly is observed via both AFM . A six-fold symmetric 2D fourier transform ofStrand separation of approximately 0.8 nm matches well with predictions from molecular modeling. Atomic-scale imaging via scanning tunneling microscopy also reveals individual beta-sheet strands oriented approximately 50 degrees relative to the fibril axis. Molecular modeling of beta-sheet folding for this de novo polypeptide confirms that this orientation is energetically favorable for strands containing even numbers of amino acids and unidirectional turns. The experimental observation of individual molecular beta-sheet strands and the demonstration of fibril assembly from such high-molecular weight de novo beta-sheets have not been previously reported and have important implications regarding biomolecular/bioelectronic structure formation.

7:30 PM Ra10.6
Protein-Directed Self-Assembly of Gold and Latex Nanoparticles. Alexey Vertegel[1], Wen Shang[1], Jonathan Dordick[1,3] and Richard Siegel[1,2]; [1]Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; [2]Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; [3]Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Many proteins and peptides are known to form self-assembled structures. Use of protein-directed self-assembly provides exciting opportunities for creating nanostructures due to the diversity of possible forms (wires, rings, catenans) and the possibility to control the assembly/disassembly process in situ since proteins are extremely sensitive to minor changes in such parameters as pH, Ca^{2+} concentration, presence of ATP, etc. In addition, protein-protein interactions are characterized by very high specificity. Here we have employed highly specific protein-protein interactions for controlled assembly of 5 nm colloidal gold and 20 nm polystyrene latex nanoparticles. The proteins were attached to the corresponding nanoparticles by either physical adsorption on Au nanoparticles or by covalent binding to the latex nanoparticles. Since protein size is in the same range as the size of nanoparticles, the conditions could be optimized to have stoichiometric protein/nanoparticle conjugates with one, two, or more protein molecules per nanoparticle. Such stoichiometric conjugates of proteins, which strongly interact with each other, can be used to build nanoparticle "molecules". Here we employed antibody-antigen and lectin-glycoprotein interactions to perform nanoassembly. A high yield of dimers has been observed in both cases when equivalent amounts of 1:1 conjugates of interacting proteins have been mixed. In the case of lectin-glycoprotein interactions, the nanostructures can also be destroyed in a controllable way by adding an excess of mannose, which competitively binds to the lectin and breaks the protein-protein interactions within the nanoassembly. Varying the stoichiometry of protein/nanoparticle conjugates enables one to control the process of self-assembly and obtain variety of nanostructures, including dimers, trimers, and 1-D structures. The trimers can also be constructed by mixing 1:1 conjugates of antigene, antibody, and anti-antibody (here we used horseradish peroxidase (HRP), anti-HRP rabbit IgG, and Fab' fragment of goat anti-rabbit IgG, respectively). We believe this approach may prove useful not only for the formation of the assemblies of nanoparticles with bio-inspired structures, but also for probing/visualizing the structure of various protein-protein complexes. The materials synthesized by protein-directed self-assembly may find applications in drug delivery or as biosensors. This work was supported by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number DMR-0117792.

7:45 PM Ra10.7
M13 Virus Scaffold for Self Assembly of Nanostructured Lithium Battery Electrode. Ki Tae Nam[1], Dong-Wan Kim[1], Pil J. Yoo[2], Chung-Yi Chiang[1], Soo Kwan Lee[3], Paula T. Hammond[2], Yet-Ming Chiang[1] and Angela M. Belcher[1,3]; [1]Department of Material Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Biological Engieering Division, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Biological self assembly and biomolecular interactions continue to inspire novel approaches for the development of functional nanostructured materials with diverse applications. Here, we demonstrate the use of genetically engineered M13 filamentous viruses as a biological scaffold for self assembly of nanostructured lithium battery electrodes. The M13 virus was engineered to express metal ion binding peptides in the major coat protein, to nucleate cobalt ions from solution. The sequence of this peptide was derived based on the fundamental interaction mechanisms involved in peptide-mediated biomineralization of metal ions. The spontaneous oxidation following the incubation and the reduction of cobalt ion with the engineered phage resulted in the assembly of monodisperse, crystalline cobalt oxide nanowire at room temperature. These nanowires were characterized by high resolution transmission electron microscopy (HRTEM) and electron diffraction pattern. This biologically inspired, room-temperature, aqueous synthesis technique is both environmentally benign and has the potential for high throughput synthesis, and avoids the use of high temperature and organic solvents commonly used for making oxides. Furthermore, manipulation of the nanostructure and the morphology of the cobalt oxide nanowire were demonstrated by controlling the interaction between the nucleating peptides and metal ions. The virus templated cobalt oxide nanowires were assembled as Li battery anodes and the electrochemical properties was characterized. The result of cyclic voltammograms and cycle curve will be presented. Virus based assembly of Li battery anodes could improve the characteristics such as charging rate performance or energy density. Next, the virus-based lithium anodes were incorporated with solid polyelectrolyte thin film which has high ionic conductivity of lithium ions. It was found that these engineered viruses assembled into highly ordered nanostructures on solid polymer electrolytes, composed of alternating multilayers of anionic and cationic polymer, which may be attributed to the entropically driven ordering process and electrostatic charge interaction. Further biomineralization of the two-dimensional ordered virus scaffold on ion conducting solid electrolyte enabled assembly of dense, highly ordered, nanostructured battery electrodes. Therefore, we have demonstrated the assembly of enhanced, nanostructured lithium electrode using principles of biological self assembly and biomineralization.

SESSION Rb10: Alternative Nanofabrication III
Chair: Gregory Lopinski
Tuesday Evening, November 29, 2005
Room 208 (Hynes)

6:00 PM Rb10.1
The Microtome: A Tool for Nanofabrication. Qiaobing Xu and George M. Whitesides; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

We will present a new, convenient technique to fabricate metal nanowires, and to manipulate them into arrays. This technique combines thin-film deposition by electron-beam with thin-film sectioning using a microtome. The procedure begins by embedding a thin metal film in an epoxy matrix. The resulting structure is sectioned in a plane perpendicular to the metal film using the diamond knife of a microtome. The cross-section of the metal wires encapsulated in these thin epoxy sections is tuned by controlling the thickness of the metal film (to values as small as 10 nm), and the thickness of microtome sections (as small as 50 nm). The embedded nanowires can be transferred and positioned onto a solid substrate by manipulating the thin polymer film. Etching removes the polymer film, and releases the wires. Sectioning generates multiple copies of the polymer slabs with similar thickness. We demonstrate the fabrication of crossed gold nanowires by transferring two epoxy thin film containing multiple nanowires successively on top of one another, and then removed the epoxy.

6:15 PM Rb10.2
Automated Large-Scale Scanning Probe Nanolithography: Macro and Mesoscopic Surface Patterning with Nanometer Resolution. Daan Wouters[1,2] and Ulrich S. Schubert[1,2]; [1]Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; [2]Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

Scanning probe patterning techniques such as dip-pen nanolithography (DPN) and oxidative probe lithography have been demonstrated to be very promising methods for the preparation of functional nanodevices. Using self-assembly techniques the created patterns can be locally modified, introducing chemical functionality on spatially defined spots on a substrate. Recently, a number of publications have been presented in which, for example, progress is reported towards the preparation of nanoscale electrical circuits , multi-component nanoparticle and protein arrays. However, for an industrially viable application of these techniques the fabrication speed has to be still further improved. in this contribution we present the application of an automated atomic force microscope for a large-scale surface patterning. We choose to demonstrate the principle by performing the automatic local probe oxidation of octadecyl trichlorosilane (OTS) monolayers on silicon substrates because this particular technique offers a very versatile platform for a broad range of subsequent surface modification reactions. When local probe oxidation is performed on a SAM of OTS, the terminal methyl groups in the OTS monolayer are converted into carboxylic acid (-COOH) functionalities. Subsequently the formed patterns of carboxylic acid groups can be used as a template in additional surface decoration steps. Using a tailor-made automated AFM with dedicated software and a programmable sample stage we have demonstrated the automated patterning of large areas on a surface with very high resolution. Although the final results of the surface patterning still depend on tip quality and applied contact force, we have demonstrated the writing and subsequent surface functionalization of a large number (>1000) of patterns on a milimeter-sized substrated using a single AFM-tip covering the gap from nanometer patterning to millimeter-sized applications. The surface oxidation may be performed in two distinct modes. In the first mode the tip is continuously rastered over the sample surface. In the second mode the tip follows a pre-defined vector trajectory over the surface without the need for pre-imaging the surface. The last method greatly enhances the tip-life and reproducibility of the results. The application of large scale, high-resolution surface patterning could be of great importance for applications such as sensors. Additional advantages of patterning large areas emerge from additional surface characterization techniques such as XPS that can be applied.

6:30 PM Rb10.3
Directed Diblock Copolymer Self Assembly For Nanometer-Scale Semiconductor Microfabrication. Ricardo Ruiz, Charles T. Black and Robert L. Sandstrom; IBM T.J. Watson Research Center, Yorktown Heights, New York.

Thin films of diblock copolymers have demonstrated strong potential as high-resolution lithographic templates in semiconductor microfabrication, as they are capable of defining smaller dimensions than conventional optical lithography. We have employed lithography and self assembly in a combined "top-down/bottom-up" fabrication technique to direct the self assembly of diblock copolymer thin films comprised of cylindrical and lamellar phases of poly(styrene-b-methylmethacrylate) (PS-b-PMMA). The resulting self-assembled nanowire arrays have 20nm widths and run micrometers in length. Moreover, these structures self-align to lithographically pre-patterned silicon and silicon nitride features. We have separately used this technique with three different PS-b-PMMA phase morphologies: cylinders, inverse-cylinders, and lamellae. We will discuss the differences between these three geometries and the relative advantages of each in semiconductor microfabrication.

6:45 PM Rb10.4
Investigating the Limits of Surface-Directed Self-Assembly of Pure Block Copolymers. Gregg M. Wilmes[1,2], Nitash P. Balsara[1,2,3] and J. Alexander Liddle[2]; [1]Department of Chemical Engineering, University of California, Berkeley, California; [2]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Block copolymers of appropriate molecular weights will self-assemble into regular, ordered patterns with periodicities on the order of 5-100 nm. If the components of the block copolymer have sufficiently different properties, thin films of these copolymers on surfaces can be used as templates for nanolithography or as scaffolds for higher molecular ordering. Such patterning has great utility for a variety of applications such as fuel cells, batteries, optoelectronic devices, and flash memory. Although block copolymers do form regular structures, the grain sizes of these structures are relatively small and are often randomly oriented throughout the sample. A combination of top-down/bottom-up techniques is used to overcome these limitations. Advanced lithography is used to chemically modify a surface. The interaction of the block copolymer with the surface then results in the formation of long-range order. Current technologies such as electron-beam lithography allow the patterning of arbitrary nanometer-scale features. Block copolymers of a given composition have an equilibrium morphology and domain-spacing. Conforming to a surface pattern with features not corresponding to that equilibrium morphology will result in some energetic penalty due to polymer chain bending, stretching, compression, or curvature; if that penalty is too large the surface patterns will not be transferred to the polymer. Knowledge of the degree to which guided self-assembly of block copolymers is possible would be of great value for determining what sorts of patterns and devices can be constructed. We here report investigations of the directed self-assembly of the pure block-copolymer poly(styrene-block-methyl methacrylate) on a silicon-supported polystyrene brush patterned with electron-beam lithography and chemically modified with an oxygen/argon reactive ion etch. We find arbitrary amounts of curvature can be induced down to the domain spacing size of the block copolymer with perfect alignment to the patterned surface.

7:00 PM Rb10.5

Generation and formation mechanism of functional mesoporous thin films of metal oxides with crystalline pore walls using novel block copolymer templates.

Torsten Brezesinski[2] and Markus Antonietti[2]; [1]Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany; [2]Colloid Chemistry, MPI of Colloids and Interfaces, Potsdam, Germany.

Mesoporous metal oxide thin films have attracted significant attention due to their potential use in photocatalysis, redox reactions, electrochromic devices, sensing etc. The most straightforward preparation method involves sol-gel chemistry in combination with a suitable structure-directing block copolymer. Typically, a substrate is dip-coated by a solution containing a metal salt (chlorides, etc.) as precurosor in the presence of a template, leading to the formation of the corresponding mesoporous oxide after temperature treatment. However, the fabrication of such films with entirely crystalline walls (e.g. TiO2, CeO2) was reported to show severe difficulties due to mesostructural collapse, and several metal oxides (e.g. SnO2, Fe2O3, HfO2, WO3, MoO3) have not been reported at all as well-ordered mesostructured films. In the present study, a general new methodology is introduced for the generation of such films, taking advantage of a novel type of block copolymers (KLE) in combination with suitable temperature treatment conditions. KLE was synthesized in our institute and has a hydrophilic PEO block and a poly(ethylene-co-butylene) hydrophobic block, thereby possessing advanced templating properties in terms of the thermal stability and hydrophilic-hydrophobic contrast [1,2]. The block lengths were designed to be long enough to allow for sufficiently thick walls, i.e. nanocrystals in the pore walls of at least 5 nm, being compatible with the nucleation of nanoparticles in the walls without disrupting the mesostructure. bcc or fcc cubic mesostructures were obtained by the KLE polymers used in this study. The crystallisation mechanism and mesostructural changes (lattice contraction) upon temperature treatment were studied by the combination of Small-and Wide-Angle x-ray scattering (SAXS/WAXS). These studies revealed that the main benefit of this type of polymers is the higher temperature stability compared to recently used polymers such as Pluronics F127: the polymer (or its fragments) is able to mechanically stabilize the still highly ordered mesopore structure of an amorphous and almost dried metal oxide at ca. 400 deg C, which is then converted into its crystalline counterpart in a solid-solid transition, contrary to previous assumptions. Based on these insights, well-ordered mesostructured films SnO2, HfO2, CeO2, MoO3 and WO3 were achieved, and this concept even allowed for the facile preparation of mesoporous metal oxides undergoing crystalline-crystalline transformations: For the first time, the KLE polymers enabled the fabrication of mesoporous goethite, even tolerating the conversion into mesoporous hematite. The mesostructure and crystallinity were studied by a new evaluation SAXS approach, in combination with Electron Microscopy, Atomic Force Microscopy, nitrogen and krypton sorption, providing the aspect ratio of the deformed spherical pores. [1] Thomas et al. Langmuir 2003, 19, 4455. [2] Smarsly et al. Chem. Mater. 2004, 16, 2948.

7:15 PM Rb10.6

Placement Accuracy of Directed Self-assembled Block Copolymers. Joy Y. Cheng[1], Feng Zhang[2], Filip Ilievski[1], Edwin L. Thomas[1], Henry I. Smith[2], G. Julius Vancso[3] and Caroline A. Ross[1]; [1]Material Science & Engineering, MIT, Cambridge, Massachusetts; [2]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [3]Materials Science and Technology of Polymers, University of Twente, AE Enschede, Netherlands.

The self-assembly process is a simple and low cost method to produce large-area nanostructures. However, self-assembled block copolymer thin films typically contain a population of uncontrolled defects and therefore lack long-range order and placement accuracy, which are required for applications such as high-density magnetic recording and plasmonic waveguides. Topographical templates such as shallow grooves have been used to induce long-range order in block copolymer thin films. However, there has been little study on the achievable placement accuracy of these templated self-assembled nanostructures. We investigated the placement accuracy and pattern registration of arrays of polystyrene (PS) -b-polyferrocenyldimethylsilane (PFS) spherical block copolymer microdomains formed within one-dimensional and two-dimensional topographically patterned substrates. Our experiments showed that placement errors originate from both template edge roughness and fluctuations in the size and spacing of polymer domains. Placement errors of the polymer domains near the edge of the template are proportional to the template roughness. On the other hand, positions of the center polymer domains are almost unperturbed by the template roughness, because polymer domain-domain interactions tend to maintain domain order at the center of the groove. Fluctuations in the size and spacing of the polymer domains provide another source of placement error. The size and spacing distribution of block copolymers can be narrowed, but not eliminated by the use of a template. Therefore, intrinsic fluctuations in the polymer determine the ultimate placement accuracy in directed self-assembled block copolymers. We have quantified the order in templated polymer arrays, and showed that placement error of about 3 nm was achieved using a two-dimensional template.

7:30 PM Rb10.7

Directed Self-Assembly of Block Copolymer Blends for Patterning at the Nanoscale. Mark P. Stoykovich[1], Marcus Mueller[2], Sang Ouk Kim[1,3], Harun H. Solak[4], Erik W. Edwards[1], Juan J. de Pablo[1] and Paul F. Nealey[1]; [1]Department of Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin; [2]Department of Physics, University of Wisconsin, Madison, Wisconsin; [3]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; [4]Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, Villigen, Switzerland.

The fabrication of microelectronic and photonic devices with nanometer scale features has traditionally utilized the photolithographic process. The essential attributes of the lithographic technique include the ability to 1) produce high resolution patterns over large areas, 2) place and register features within exacting tolerances and margins, and 3) pattern features of nonregular geometries. Current lithographic processes and materials breakdown, however, and cannot be extended to the fabrication of devices with features having 30 to 50 nm critical dimensions. Consequently, our group is pursuing novel approaches for integrating self-assembling materials into traditional nanomanufacturing processes and overcoming the limitations encountered by photolithography at sub-50 nm dimensions. We have recently demonstrated a patterning technique involving the directed self-assembly of block copolymers on chemically nanopatterned surfaces with tailored interfacial interactions. The defect-free ordering of block copolymer domains has been achieved over arbitrarily large areas and in registry with the lithographically-defined underlying surface pattern. This hybrid approach, known as directed assembly, couples the advantages of top-down advanced exposure tools (pattern perfection and registration via the surface pattern) to the principles of bottom-up molecular self-assembly (thermodynamic control over the structure organization and dimensions). Symmetric ternary blends consisting of a block copolymer and its corresponding homopolymers are also suitable materials for directed self-assembly. Block copolymer-homopolymer blends, although similar in most respects to pure block copolymers, hold two distinct advantages for patterning applications. First, the characteristic length scale of the self-assembled structures can be finely tuned by adjusting the blend composition. We have therefore characterized the polymer physics and fundamental phase behavior of ternary blends in thin films and on chemical surface patterns for a wide range of blend compositions. Second, the ternary blend domains can be directed to self-assemble into nonregular device-oriented geometries such as nested arrays of sharp bends, arcs, and T-junctions. We demonstrate, via mean field simulations, that the localized redistribution of homopolymer within the blend domains greatly facilitates the defect-free self-assembly of these nonregular structures. The ability to pattern a variety of geometries suggests that fabrication methodologies based on self-assembling materials such as ternary blends will become increasingly important for the manufacturing of complex devices at the nanoscale.

7:45 PM Rb10.8

Control of Colloidal Crystal Growth by External Fields.

Siegmund Greulich-Weber, Elisabeth von Rhein and Paul Miclea; Physics, University of Paderborn, Paderborn, Germany.

Since the introduction of the concept of a photonic crystal much effort has been targeted at producing 3D photonic crystals working in the visible wavelength range. The most promising way is by self-assembly of monodisperse sub-micron spheres made of silica or organic materials resulting in fcc and hcp colloidal crystals. However, the large scale fabrication and thus their application in photonics suffer from the reproducible growth of defect-free extended bulk crystals. Commonly used 'natural' sedimentation is unacceptably slow and often results in low crystal quality showing cracks and stacking faults or reveals a disordered bulk below an apparently ordered surface. On the other hand dip-coating procedures are much faster, however, provide only thin layers. In literature there are several examples, where additional external fields such as electric or acoustic fields were applied, which to a certain extent enhanced the crystal quality. However, the reproducibility of such experiments depends on many parameters like the chemical composition of the spheres, the solvent, the density ratio of spheres and solvent, and many more. To have control of all this parameters during crystal growth is essential for reproducible preparation of extended bulk colloidal crystals. We will present details of our computer controlled crystal growth experiments using specific external fields. In classical crystal growth methods (e.g. Czochralski-growth), one avails of temperature gradients. In analogy, we use acoustic noise gradients instead of temperature gradients for optimizing crystal growth. We systematically investigated various bandwidths, frequencies and amplitudes of acoustic noise fields. The crystal growth and evaporation of the suspension is monitored by CCD-cameras and thus computer-controlled. Such colloidal crystals made of PMMA, PS or silica nano-spheres are practically free of dislocations. The crystal quality only depends on the monodispersity of the nano-spheres used.

SESSION Ra11/Rb11: Poster Session II
Chair: Federico Rosei
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra11.1/Rb11.1

Capillarity-Driven Colloid Self-Assembly in Shallow Nanoscale Surface Corrugations. Anant Mathur and Jonah Erlebacher; Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

Ordering of submicron spheres after evaporative deposition from colloidal suspension on shallow corrugated substrates with optical wavelengths and nanoscale amplitude was examined. The spheres were found to deposit overwhelmingly in the valleys of the surface corrugations rather than their peaks, even when the amplitude of the substrate features was a few nanometers, nearly 100 times smaller than the sphere diameter. The behavior is found to arise from capillary forces on the spheres when the colloid film thickness is of order the sphere diameter. The observation that substrate features significantly smaller than the sphere diameter can influence deposition morphology may lead to simple methods to create large domains of order in colloidal crystals.

Ra11.2/Rb11.2

Environmental Effects on Single-Walled Carbon Nanotube Raman Spectroscopy. Lars Ericson and Pehr Pehrsson; Chemistry, Naval Research Laboratory, Washington, District of Columbia.

Raman spectroscopy is a common tool used to characterize the composition of nanotube devices and probe the effectiveness of electronic separation schemes. Raman spectroscopy of single-walled carbon nanotubes (SWNTs) suspended using common aqueous surfactants and DNA has been performed for both liquid suspensions and samples prepared via dielectrophoretic deposition. Changes in the radial breathing modes, disorder mode, and tangential mode have been explored as a function of aggregate state, surfactant presence, and pH. Analysis of both Stokes and Anti-Stokes spectra under these various environmental conditions has been performed in the context of resonance shifts, charge transfer effects, and SWNT electronic separation.

Ra11.3/Rb11.3

Abstract Withdrawn

Ra11.4/Rb11.4

Conjugate of Cytochrome-c and Monolayer Protected Gold Nano-clusters. Chinmay P. Soman[1], Brian Huffman[2], Madalina Ciobanu[2], Aren Gerdon[2], M. Danielle Garrett[2], Mark Groseclose[2] and David Cliffel[2]; [1]Interdisciplinary Materials Science, Vanderbilt University, Nashville, Tennessee; [2]Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

We present evidence for the synthesis of a nanoparticle-protein conjugate. This novel nanostructured material can potentially offer new opportunities in molecular electronics, molecular recognition, and biomaterials synthesis. Cytochrome-c was modified using Traut's reagent (2-iminothiolane hydrochloride) - resulting in a sulfhydryl-terminated linker arm, and place exchanged with the tiopronin (n-(2-mercaptopropionyl)glycine) molecules on tiopronin monolayer protected gold nano-clusters. The reaction mixture was separated on a carbomethoxycellulose column. Cyclic voltammetry and square wave voltammetry experiments on the purified conjugate clearly indicate that the conjugated cytochrome-c is electrochemically active. The conjugate is also quite stable and does not show any loss of activity for over a week. Results from chronoamperometry, dynamic light scattering particle size measurement, nuclear magnetic resonance, and circular dichroism provide additional evidence for conjugate formation.

Ra11.5/Rb11.5

Novel Electrical Switching and Logic in Y-Junction Carbon Nanotubes. Prab Bandaru[1], Chiara Daraio[1], Sungho Jin[1] and Apparao Rao[2]; [1]Materials Science & Engineering, University of California at San Diego, La Jolla, California; [2]Department of Physics, Clemson University, Clemson, South Carolina.

To realize a truly integrated nanoelectronic architecture, it is desirable to have nanoelectronic elements to harness new functionalities peculiar to nanomaterials such as a novel Y-junction carbon nanotube (CNT) configuration, which contains a built-in, three-way-operable gate structure. The presentation focuses on the measurements of unique electrical properties of a multi-walled nanotube (MWNT) Y-junction which is grown by modified chemical vapor deposition (CVD) processes(1). Through this work, we are enabling and adding a new functionality, i.e., switching, to nanotube electronics making an overall CNT based nanoelectronic architecture more complete and feasible. We show evidence for a dramatic electrical switching behavior in a nano-particle-containing Y-junction carbon nanotube morphology(2). We observe, for the first time, an abrupt modulation of the current from ON to OFF state, presumably mediated by defects and the topology of the junction. The mutual interaction of the electron currents in the three branches of the Y-junction is shown to be the basis for a potentially new, three-way logic device. This is the first time ever that such switching and logic functionalities have been experimentally demonstrated in Y-junction nanotubes, without the need for fabrication of an external gate. Previously, only a diode like behavior was observed in Y-junctions. An entirely new class of nanoelectronic architecture and functionality, which extends well beyond conventional field effect transistor technologies, is now possible. (1) N. Gothard, C. Daraio, J. Gaillard, R. Zidan, S. Jin, A.M. Rao, Controlled growthof Y-junction nanotubes using Ti-doped vapor catalyst, Nano Letters vol.4, 213-217 (2004). (2) P. R. Bandaru, C. Daraio, S. Jin, and A.M. Rao, Novel Electrical Switching Behavior and Logic in Carbon Nanotube Y-junctions, Nature Materials vol.4, 2005 (in press).

Ra11.6/Rb11.6

Characterization of transparent and conductive single-walled carbon nanotube thin films. Husnu Emrah Unalan, Aurelien Du Pasquier, Giovanni Fanchini and Manish Chhowalla; Materials Science and Engineering, Rutgers University, Piscataway, New Jersey.

Single-walled carbon nanotube (SWNT) thin film devices provide an alternative to individual SWNT devices. Uniform and reproducible SWNT thin films can be deposited over several centimeters, allowing fabrication of devices over large areas. Several methods are being employed for the fabrication of SWNT films, including the recently reported vacuum filtration method [1]. Although the device characteristics of the SWNT thin films have been characterized[2], no detailed investigation of the film properties has been reported. In this work, we will present a detailed analysis of the SWNT thin film properties using the vacuum filtration method. We will present the variation of the SWNT thin film properties as a function of the film thickness and the nanotube concentration in the filtrated solution. The SWNT thin films were found to be highly transparent and conducting with values comparable to indium tin oxide (ITO) [3]. Specifically, at the lowest nanotube concentration, the transmission of the SWNT thin films exceeded the values of ITO. The SWNT thin films were always found to be more transparent in the UV in comparison to ITO. The transmission and sheet resistance of the SWNT thin films were found to decrease with the film thickness and SWNT concentration in the filtrated solution. The SWNT thin films have a highly porous structure which can be used to explain the optical and electrical properties. We will also present our thin film transistor characteristics which show an on-to-off ratio of $10^2$and mobility of $\sim 1 \mathrm{cm}^2$/V-s. [1] Z.Wu, Z.Chen, X.Du, J.M.Logan, J.Sippel, M.Nikolou, K.Kamaras, J.R.Reynolds, D.B.Tanner, A.F.Hebard, A.G.Rinzler, Science 305 (2004) 1273. [2] E.Artukovic, M.Kaempgen, D.S.Hecht, S.Roth, G.Gruner, Nanoletters, 5(4) (2005) 757. [3] A.Du. Pasquier, H.E.Unalan, A.Kanwal, M.Chhowalla, Advanced Materials, accepted.

Ra11.7/Rb11.7

Large scale honeycomb and hexagonal arrangement of ZnO nanowires via modified nanosphere lithography. Hongjin Fan[1], Bodo Fuhrmann[2], Roland Scholz[1], Frank Fleischer[1], Armin Dadgar[3], Alois Krost[3] and Margit Zacharias[1]; [1]Max Planck Institute of Microstructure Physics, Halle, Germany; [2]Interdisciplinary Center of Materials Science, Martin-Luther-University Halle, Halle, Germany; [3]Institute of Experimental Physics, Otto-von-Guericke University, Magdeburg, Germany.

Nanosphere lithography (NSL) has become widely used for preparation of large-scale ordered nanostructures, including semiconductor nanowires (NW). There are several reports on the growth of ZnO NW arrays on sapphire using the self-assembled polystyrene spheres as template. However, the ZnO NW in these reports are either not patterned in a nanoscale because of the large size and interconnection of the deposited Au, or not truly vertically-aligned due to unoptimized growth conditions and/or imperfect lattice matching between the sapphire substrates and ZnO NW. These drawbacks might hinder the consideration of such NW arrays for device applications. In our work, we have applied a modified NSL process to fabricate large-scale ordered, truly vertical-aligned, and spatially well-separated ZnO NW. The process involves nanosphere self-assembly and mask transfer, deposition of Au nanodots, and vapor-liquid-solid (VLS) growth of ZnO NW. Self-assembled polystyrene nanospheres are transferred from hydrophilic glass substrate onto hydrophobic nitride layers using a novel mask transfer technique. As the nanospheres can be assembled into both mono- and bilayers, the resulting ZnO NW are forced correspondingly into honeycomb and hexagonal pattern. Cross-sectional transmission electron microscopy studies confirm the VLS mechanism and the single crystallinity of the NW. In contrast, the NW prepared without applying the mask transfer technique have no large-scale ordering, although they are also vertically aligned to the substrate. The well-ordered NW arrays could be assembled into devices like sensor arrays and vertical field-effect-transistor arrays because all the wires are spatially well separated. The second part of our talk is the mechanical manipulation and electrical measurement of the NW using a SEM-based manipulator system. A movie clip will show how individual NW are in-situ bend, cleaved, and positioned. The I-V curves of the NW are measured using two sharp metal tips as electrodes. A model is proposed to explain the I-V behavior.

Ra11.8/Rb11.8

Synthesis of Millimeter Long Vertically Aligned Single-Walled Carbon Nanotubes by Point-arc Microwave Plasma CVD. Takayuki Iwasaki, Tsuyoshi Yoshida, Takumi Aikawa, Goufang Zhong, Iwao Ohdomari and Hiroshi Kawarada; Department of Science and Engineering, Waseda university, Tokyo, Japan.

A decade has passed since the discovery of single-walled carbon nanotubes (SWNTs), but the main methods for synthesizing SWNTs such as laser ablation, arc discharge and thermal (or catalytic) chemical vapor deposition (CVD) are still subject to the following disadvantages; high (800-1200°C) growth temperature requirement, low production yield (the mass ratio of SWNTs to catalyst) or high catalyst contamination, and out of control of the as grown SWNTs (usually randomly oriented, entangled bundles or ropes). All these make the purification and application of SWNTs very difficult. Plasma assistant CVD is good at controlled growth of multi-walled carbon nanotubes (MWNTs) at low temperatures. However it rarely succeeded in the growth of SWNTs. In this study, we demonstrate the low temperature (600°C) synthesis of very dense (1E16/m2) and vertically aligned SWNTs by point-arc microwave plasma CVD [1], which overcomes all the above mentioned disadvantages. Vertically aligned SWNTs were synthesized at a low temperature of 600°C on Si substrates coated with a sandwich-like structure Al2O3 /Fe /Al2O3 (/Si). Al2O3 between Si and Fe is a buffer layer to prevent them from reacting. On the other hand, Al2O3 above the Fe film works as a barrier of the surface diffusion of catalytic atoms so that the aggregation of Fe atoms can be suppressed during the pre-heating time. As a result, high dense catalytic particles can be formed and extremely dense and vertically aligned SWNTs can be synthesized. To identify the SWNT samples, TEM and Raman spectroscopy were used. TEM observations show that almost all tubes are single-walled. Raman spectra of as-grown SWNTs have fingerprint features of SWNTs: the sharp tangential mode G peak, the shoulder of G peak and the radial breathing mode (RBM) peaks. From the RBM peaks, their diameters range from 1.0 to 3.0 nm. The thickness of SWNTs can increase as the growth time increases, and the lifetime of the catalyst is more than 10 hours, so millimeter long vertically aligned SWNTs can be synthesized. A production yield (mass ratio of SWNTs to catalyst) and a volume density are 2,500,000% and 66 kg/m3, respectively. The production yield is 50 times as high as that reported by Hata[2]. Up to now, the growth temperature about 600°C is the lowest, while both the volume density and the production yield are the highest for the synthesis of SWNTs. [1] G. Zhong et al., Chem. Vap. Deposition 11, 127 (2005) [2] K. Hata et al., Science 306, 1362 (2004)

Ra11.9/Rb11.9

The Assembly of Nanoscale and Microscale Particles in Thermal Grease. Huang-Chin Hung, Chih-Chun Kao, Ching-Chang Hsieh and Jin-Der Hwang; Materials Research Laboratories, Industrial Technology Research Institute, Tainan, Taiwan.

The transfer of heat is a very important issue nowadays. As electronic components become smaller, lighter and muti-functional, the heat generated by these tiny components increase. The undesired heat is very likely to be trapped within the small electronic devices, causing stability and reliability problems of the devices. Effective transfer of heat by conducting requires materials of high thermal conductivity to transfer heat. When the heat must be transferred between different interfaces, the thermal material must be flexible enough to provide good thermal contact between interfaces, such as thermal grease. SiC is a material of very high thermal conductivity. By choosing SiC of nano scale as filler for the thermal grease, these nano particles can fit themselves into tiny voids between interfaces and enhance thermal contact. With higher BET surface area, smaller filler also holds polymer matrix better than bigger filler and prevent phase separation. However, nano particles also increase the thermal interfaces due to their high BET surface area. Our experiments show that particle size distribution of filler is of great importance to the thermal impedance and the stability of the thermal grease. With appropriate assembly of nanoscale and microsacale particles as filler, the performance of thermal grease can be optimized. The relationship between particle size to viscosity and thermal conductivity is also discussed.

Ra11.10/Rb11.10

New method of colloidal crystal synthesis from 3D-ordered nano-composite. Vladimir Novikov, Institute of Solid State and Semiconductor Physics, Minsk, Belarus.

Nano-arranged materials such as colloidal crystals, nanocrystal superlattices or mesoporous structures have been synthesized by a number of methods based on a surfactant template self-assembly [1-3]. We describe a new way for colloidal crystals (CCs) synthesis by decomposition of a 3D-ordered composite of nanoparticles embedded in an inorganic salt matrix. The method includes first formation of a nano-composite by a co-crystallization of an inorganic salt solution and colloidal particles during evaporation of a solvent from the colloid. The composite appears as quasicrystals of highly ordered nano-particles embedded into a salt matrix. Nanoparticles form various types of a sublattice depending on their functional shell and the salt. Ordering process in the nano-composite leading to quasicrystals occurs if the nanoparticles have a functional cover with a strong affinity to the matrix salt components. A driving force of this process is not only an interaction between the functionalized particles like in the surfactant method, but also a minimization of an elastic energy in the salt/particle system. Therefore, one expects that an anisotropic character of the elastic interaction may provide a wide variety of structural types of nano-particle arrangements beside surfactant templated nanostructures ordered in the cubic or hexagonal structures only. At the second stage CCs are formed from the composite by sublimation of an inorganic component, while preserving the nano-particles structure integrity. CCs of both carbon and silver halogenides nano-particles were synthesized by this method. Nanoparticles have been functionalized by nickel chloride. This step followed an oxidation of nano-particles in aqueous solution of hydrogen peroxide added with ammonium chloride. After that the colloid solution was dried up to obtain the nano-composite NH4Cl/nanoparticles quasicrystals of a few microns in size. Ammonium chloride was then sublimated from the composite at 200oC to produce the CCs. Size and morphology of these CCs were nearly the same as that of the precursor quasicrystals implying unchanged nanoparticles arrangement. Microstructure of the CCs was studied by means of X-ray diffraction and a scanning electron microscopy. 1. Peidong Yang et al. Nature 396 (1998) 152. 2. C.J. Brinker et al. Advanced Materials 11 (1999) 579. 3. C.B. Murray et al. IBM J. Res. & Dev. 45 (2001) 47.

Ra11.11/Rb11.11

Developing Superhydrophobic Fabrics via Electrospinning. Minglin Ma[1], Randal Hill[2], Yu Mao[1], Malancha Gupta[1], Karen Gleason[1] and Gregory Rutledge[1]; [1]Cheme, MIT, Cambridge, Massachusetts; [2]MIT, Cambridge, Massachusetts.

Superhydrophobicity has attracted tremendous attention from both academia and industry due to its applications involving water-proofing, self-cleaning and anti-fouling capabilities. Superhydrophobicity requires a low surface energy as well as a high surface roughness. We recently found that an electrospun fiber mat had the appropriate surface roughness for superhydrophobicity. We have developed several strategies to produce superhydrophobic fabrics via electrospinning. The first strategy is to electrospin a hydrophobic material poly(styrene-b-dimethylsiloxane) block copolymer. Contact angle measurements indicate that the resultant nonwoven fibrous mats are superhydrophobic, with a contact angle of 163° and contact angle hysteresis of 15°. The superhydrophobicity is attributed to the combined effects of surface enrichment in siloxane as revealed by X-ray photoelectron spectroscopy and surface roughness of the electrospun mat itself. The second strategy is to combine electrospinning and initiated chemical vapor deposition (iCVD). A selected polymer was first electrospun into beaded or bead-free fibers with different diameters and then coated with a thin layer of hydrophobic polymerized fluoroacrylate by using iCVD. The hierarchical surface roughness inherent in the electrospun mats and the low surface free energy of the coating layer yielded a stable superhydrophobicity with a contact angle as high as 175°. Some other strategies have also been developed. The effect of fiber morphology on superhydrophobicity will be discussed.

Ra11.12/Rb11.12

Aqueous Phase Laser Ablation Chemistry (APLAC) for Synthesis of Co-Pt Nanoparticles. R. K. Rakshit and R. C. Budhani; Department of Physics, Indian Institute of Technology - Kanpur, Kanpur, UP, India.

Magnetic nanocomposites have attracted considerable attention in recent years because of their technological applications in areas such as high density data storage, mechanics, biomedical/drug delivery systems and catalysis. These applications are driven by the unique magnetic behavior of the individual nanoparticles. The random anisotropy and competing interparticle interactions in an assembly of magnetic nanoparticles make them a fundamentally exciting and technologically relevant system for research. Several chemical methods have been developed in recent years to synthesize mono-dispersed colloids of ferromagnetic nanoparticles. While these techniques work well for elemental ferromagnets such as Fe, Co and Ni, there are difficulties in producing alloy nanoparticles through the chemical route. Here we describe the use of pulsed laser ablation in aqueous medium to synthesize nanoparticles of technologically important ferromagnetic alloys such as Co-Pt. In addition to offering the key advantage of multielemental nanoparticle synthesis, the technique is simple and does not involve use of hazardous chemicals. A plate of Co-Pt synthesized by arc melting of high purity (4N) cobalt and platinum chunks, and suspended horizontally in milliq water, was irradiated with pulses of Nd-YAG laser from the top. The laser was operated at 20 Hz with a combined energy density of 14 J/cm^2 at 1064 nm and 532 nm wavelengths. A light brown but clear solution, with no evidence of any sedimentation, was obtained after 25 minutes of ablation. In order to avoid agglomeration of particles, sodium dodecylsulfate was added to the solution at the end of ablation. The magnetic behavior of the Co-Pt nanoparticles has been measured with SQUID magnetometry. In order to minimize interparticle magnetic interactions, solid samples were prepared by adding a low melting point ($\sim$ 330 K) water soluble polymer to the colloid. The low melting point of the matrix facilitated rotation of the particles and subsequent alignment of their magnetic easy axis at $\sim$ 310 K and 2 Tesla field. The zero-field-cooled and field-cooled magnetization measurements reveal a low ($\sim$ 4 K) blocking temperature (T_B). As expected, for temperatures below T_B the magnetization curves are hysteretic. We have investigated the dynamics of the superparamagnetic phase of these aligned nanoparticles and have analyzed the results in the framework of the Néel-Brown theory. This analysis, as well as measurements of magnetic viscosity, suggests a particle size of $\sim$ 2 nm. The coercive field of these essentially single domain particles at 2 K is $\sim$ 400 Oersted. Acknowledgement: This research has been supported by a grant from the Indo-French Centre for Promotion of Advanced Research.

Ra11.13/Rb11.13

CNT formation process from 6H-SiC (000-1). Takahiro Maruyama[1,2], Yasuyuki Kawamura[1], Hyungjin Bang[2], Naomi Fujita[1], Tomoyuki Shiraiwa[1], Kenji Tanioku[1], Yoko Hozumi[1], Shigeya Naritsuka[1,2] and Michiko Kusunoki[3]; [1]Dept. of Materials Science and Engineering, Meijo University, Nagoya, Japan; [2]Meijo University, 21th COE program, Nagoya, Japan; [3]Japan Fine Ceramics Center, Nagoya, Japan.

It has been reported that carbon nanotubes (CNTs) were formed through the decomposition of SiC(000-1) surfaces by heating in a vacuum. By this growth technique, well oriented zigzag-type CNTs can be selectively grown without any catalysts and the diameters of these CNTs are fairly uniform. Although some studies have been reported on the formation mechanism of CNT from SiC surfaces, a detailed mechanism of the initial stage of CNTs growth has not yet been clarified. In this study, we investigated the decomposition of 6H-SiC(000-1) surfaces and the formation process of CNT by using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). After being etched with hydrofluoric acid (10%), 6H-SiC(000-1) samples were annealed at various temperatures between 1000 and 1700 °C in a vacuum electric furnace ($\sim 1\times10^{-4}$ torr). Then, STM observation and XPS measurements were carried out to investigate their surface structures and chemical species. In order to investigate the initial stage of the formation of CNT clearly, we also carried out STM observation for SiC annealed under ultrahigh vacuum (UHV) ($\leq 1\times10^{-7}$ torr). STM images were obtained with a tip bias in the range of -3.0$\sim$3.0 eV and a tunneling current in the range of 0.05$\sim$0.3 nA. XPS measurements were performed at 90° and 20° take-off angles to change the depth of photoelectron detection. From the results of XPS measurements for the samples annealed in a vacuum electric furnace, the increase of O 1s peak intensity was seen at 1000 and 1100°C. The peak deconvolution analysis showed the oxidization of the SiC surface. The SiO^2 layer was desorbed and graphite-like carbon appeared on the surface at 1150°C. After annealing at 1200°C, CNT nano-cap structures were observed by STM. On the other hand, the samples annealed under UHV showed an appearance of nano-size amorphous carbons even below 1000°C, where no oxidation was occurred, and the formation of CNTs was also confirmed above 1200°C. So, we consider that these nano-size amorphous carbons transformed into nano-cap structures around at 1200°C. It is also confirmed that the diameter of nano-size amorphous carbon determined the size of nano-caps formed at the initial stage and eventually the size of CNTs.

Ra11.14/Rb11.14

SAXS of Self-Assembled Mesostructured Films With Oriented Lamellae, 2D Cylinder Arrays or Spheres: an Advanced Method of Evaluation. Bernd Smarsly, Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

The present work is dedicated to a further developed general analysis of the small-angle x-ray scattering (SAXS) of oriented metal oxide mesostructured films of lamellae, 2D hexagonal arrays of cylinders and cubic lattices of spheres (micelles or mesopores), measured in symmetrical reflection (SRSAXS). The main goal is to establish a general approach for a quantitative structural characterization of such materials, complementing microscopic techniques and physisorption. It is demonstrated that SRSAXS data can be effectively fitted using well chosen scattering functions with physically reasonable parameters, which can be easily implemented on standard software. As the only precondition, the method requires a high accuracy of intensity measurements of films in reflection mode over several decades, which are accessible from standard laboratory x-ray reflectivity setups. Various relevant structural parameters describing the mesostructure (mesopore or micellar diameter, its polydispersity, lattice parameter, lattice distortions, average stack height, etc.) can be extracted from SRSAXS curves by the fitting with models based on lamellae, arrays of cylinders or spheres. In particular, our method allows for a quantification of the polydispersity of the nanodomains (lamellae, cylinders or spheres), which was neglected previously. As a further improvement, our approach provides the degree of preferred orientation with respect to the substrate. Such analyses were applied to various types of mesostructured coatings, prepared by Evaporation-Induced Self-Assembly using CTAB (lamellar mesostructures), non-ionic Brij surfactants (cylinders being oriented parallel to the substrate) and block copolymers (KLE, bcc spherical mesostructures) as structure-directing agents. The KLE block copolymers enabled the preparation of mesoporous, crystalline films of various metal oxides such as titania, WO3, SnO2 and MoO3 [1]. The data were acquired from both synchrotron (APS) and laboratory reflectivity setups. In combination with SAXS in grazing incidence geometry, the method results in a comprehensive characterization of the mesostructures providing accurate values for the radius, the lattice parameter, their variances and the average stack height, while most of the previous analyses only determined the d-spacing [2]. As a main benefit, this SAXS methodology allowed for the first time the differentiation between the thermally induced distortions of the mesopores and those of the pore walls, which gave further insights into the crystallization mechanism of metal oxides within the confinement of the mesostructure. Also, the pore sizes obtained from the SRSAXS analysis were in good agreement with independent physisorption measurements and microscopic analyses (AFM, TEM), proving the general suitability of the approach [3]. [1] Smarsly et al. Chem. Mater. 2004, 16, 2948. [2] Smarsly et al. Langmuir 2005, 21, 3858-3866. [3] Smarsly et al. Chem. Mater. 2005, 17, 1683-1690.

Ra11.15/Rb11.15

The Formation of Polyelectrolyte Multilayer Films at Interfaces between Thermotropic Liquid Crystals and Aqueous Phases. Nathan A. Lockwood[1], Katie D. Cadwell[1], Frank

Caruso[2] and Nicholas L. Abbott[1]; [1]Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin; [2]Chemical and Biomolecular Engineering, University of Melbourne, Melbourne, Victoria, Australia.

We report the formation of polyelectrolyte multilayer (PEM) films at interfaces between aqueous phases and thermotropic liquid crystals. These experiments employ a planar interface between the nematic liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB) and an aqueous solution, and sequential contact of the interface with the polyelectrolytes poly(sodium-4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH). The results of our study demonstrate that 1) despite the mobility of the polyelectrolytes at the fluid aqueous-5CB interface, PEM films grow in a linear fashion with sequential contact with the polyelectrolytes; 2) the PEM film is coupled to the orientations of the liquid crystal and preserves the orientation even when the aqueous phase is removed and the interface is dried in air; and 3) the presence of the PEM film at the aqueous-liquid crystal interface can alter the interactions of a solute present in the aqueous phase (sodium dodecyl sulfate) with the interface of the liquid crystal. These results identify new methods for preparing PEM films and studying their organization at fluid interfaces. The results also provide new approaches to controlling the interfacial chemical functionality of liquid crystals.

Ra11.16/Rb11.16

Ignition in Al-Fe_2O_3 Nanocomposites.

Bhargava Ram Kanchibotla[1], Sridhar Patibandla[2] and Latika Menon[1]; [1]Physics, Northeastern University, Boston, Massachusetts; [2]Electrical Engineering, Virginia Commonwealth University, Richmond, Virginia.

Novel energetic nanocomposites have been fabricated which undergo an exothermic reaction when ignited at moderate temperature. The nanocomposites are a mixture of Al (fuel) and Fe_2O_3 (oxidizer) where Fe_2O_3 is in the form of arrays of nanowires embedded in the thin Al film. We have achieved very high packing density of the nanocomposites, precise control of oxidizer-fuel sizes at the nano scale level and direct contact between oxidizer and fuel. Ignition in these nanocomposites has been demonstrated using several different methods. Ignition properties such as flame temperature, energy release have been studied and results will be reported.

Ra11.17/Rb11.17

Determining the mechanism for polymer-controlledinorganic nanoparticle synthesis. Nily Dan[1] and Rina Tannenbaum[2]; [1]Chemical and Biological Eng., Drexel University, Philadelphia, Pennsylvania; [2]Materials Science and Eng., Georgia Inst of Technology, Atlanta, Georgia.

One of the challenges in the synthesis of inorganic nanoparticles is the need for a methodology that can produce monodisperse particle populations that resist flocculation. Studies have shown that the synthesis of inorganic nanoparticles in polymeric media (suspensions of bulk) yields narrow particle size and morphology distributions under ambient conditions. Moreover, the particles thus formed are sterically stabilized by an adsorbed polymer layer. Despite numerous studies, the mechanism by which polymers control the aggregation and formation of nanoparticles is not understood. Here we present a combined experimental and theoretical study of the kinetics of nanoparticle formation in polymeric media. We show that, contrary to expectation, the particle properties are set by the kinetics of nucleation and growth, rather than through an equilibrium capping mechanism.

Ra11.18/Rb11.18

Close-packed Nanoparticle Arrays as Surface Enhanced Raman Spectroscopy (SERS) Substrates. Hui Wang[1,3] and Naomi J. Halas[2,1,3]; [1]Department of Chemistry, Rice University, Houston, Texas; [2]Department of Electrical and Computer Engineering, Rice University, Houston, Texas; [3]The Laboratory for Nanophotonics (LANP), Rice University, Houston, Texas.

Using plasmonic nanostructures to control and optimize the surface enhanced spectrocopies has been the focus of increasing attention over the past few years as the spectroscopy-based molecular identification methods have widespread applications in chemical and biological sensing. Efforts to develop, control and optimize surface enhanced Raman spectroscopy (SERS) as an analytical tool depend on the methods for fabricating substrates with high sensitivity, stability, and reproducibility of the SERS signals. Using periodic nanostructured substrates for SERS measurements can provide quantitative correlations between surface structures and SERS enhancements. We exploit a convenient and cost-effective approach to the self-assembly of cetyltrimethyl ammonium bromide (CTAB)-capped Au nanoparticles into highly ordered close-packed Au nanoparticle arrays on solid substrates using a solvent evaporation method. The as-fabricated nanoparticle arrays display an intense plasmon band in the near-infrared region, which primarily arises from the interparticle plasmon coupling between adjacent nanoparticles. Such interparticle electromagnetic coupling produces enormous near-field enhancements at the junctions between neighboring nanoparticles, creating uniform periodic densities of well-defined "hot spots" which can be exploitable for large SERS enhancement. From the electromagnetic point of view, these nanoparticle arrays can be regarded as "inverse Van Duyne lattices", possessing similar but complementary near-field properties to the triangle arrays fabricated using nanosphere lithography. Moreover, the high periodicity of the arrays also provides a useful model for detailed studies of the correlations between localized near-field electromagnetic properties and spectroscopic enhancements. The SERS performance of the close-packed Au nanoparticle arrays is quantitatively and systematically evaluated by using para-mercaptoaniline (pMA) and dye molecules as the probing molecules.

Ra11.19/Rb11.19

Nanotubes in spray deposited Nanocrystalline HgTe:I thin films. Ranga Rao Arnepalli[1] and Viresh Dutta[1]; [1]Centre for Energy Studies, Indian Institute of Technology, Delhi, New Delhi, New Delhi, India; [2]Centre for Energy Studies, Indian Institute of Technology, Delhi, New Delhi, New Delhi, India.

Mercury Telluride is a narrow bandgap semiconductor, with a direct bandgap of -0.15eV at room temperature. The Bohr exciton radius of HgTe is 40 nm and it is possible to observe quantum confinement effects more easily. HgTe nanostructures may find wide applications in fabricating nanoelectronic devices for telecommunication, optoelectronic devices and sensors etc. Since as-prepared HgTe is p-type, making it n-type can help design novel nanosize devices. Iodine is known to be an n-type dopant in CdTe and Hg1-xCdxTe. Therefore, HgTe nanoparticles prepared using Solvothermal mehod have been doped with Iodine by adding trace amounts of iodine in addition to source materials (Hg and Te compounds) to yield HgTe: I nanoparticles. Thus prepared nanoparticles are dispersed in 1-Butanol for spray solution. The solution is sprayed on to the glass substrates kept at 200oC in air ambient for 20 min. The deposition is done without and with a voltage applied to the nozzle during this period. The films are characterized for structural, morphological and compositional properties. The thermo-voltage generated in the hot probe method shows that the hot end is positive compared to the cold end, which confirms that the electrons are the majority carriers in the films. In comparison, the undoped HgTe nanocrystalline films show a negative voltage at the hot end, since they are p-type. The surface morphology of the films (SEM and TEM images) shows the nanotubes morphology; in addition non-tubular nanostructures are also found. The TEM images of the films show the nanotubes with average diameter of 50 nm and upto several microns long. The SAD patterns recorded on the nanotubes show the cubic phase HgTe nanotubes, with lattice parameter a= 0.6452 nm. X-ray diffraction patterns of the films also show the cubic phase (111) HgTe dominant peaks in both the films. The EDAX spectra reveal the presence of Hg and Te in the ratio 51:49. In summary for the first time we report on the synthesis of HgTe nanotubes in spray deposited nanocrystalline iodine doped HgTe thin films. The role presence of iodine seems to be help in creation of the nanotubes. Reference Arnepalli RangaRao and Viresh Dutta, "Synthesis of mercury cadmium telluride nanoparticles by solvothermal method" Proceedings of Materials Research Society 2005, spring meeting (Symposium Y).

Ra11.20/Rb11.20

The Evolution of Vesicles from Bulk Lamellar Gels.

Anthony J. Ryan and Guiseppe Battaglia; Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom.

The remarkable ability of phospholipids to generate vesicles and lamellar morphologies has been recently mimicked by amphiphilic block copolymers. However, the formation of block copolymer lamellar structures in water has always been studied at low concentrations (vesicles) and at high concentrations (lamellae stacks). The self-assembly of the amphiphilic poly(ethylene oxide)-co-poly(butylene oxide) membrane former has been investigated mapping the different morphologies formed at different concentrations. In analogy with lower molecular weight membrane formers, phospholipids, at high concentration in water, phase progression from lamellae to sponge-phase has been observed. Particularly, the sponge phase has been found to have ordered domains with Im3m arrangements.At intermediate concentrations, when the system turn from gel to liquid, the sponge-Im3m phase breaks up into gel-cluster made of the regular packing of vesicles. Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM) have revealed that such clusters have an hexagonal-closed packed structure. Vesicles have therefore been observed to form when the copolymer-water systems have still long-ranged order. Eventually, at very low concentration, the packed vesicles separate generating very stable isotropic dispersions.

Ra11.21/Rb11.21

Electrospinning of Block Copolymers for Synthetic Muscle Fabrication. Anthony J. Ryan, Linge Wang, Paul Topham and Colin Crook; Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom.

We have previously demonstrated wholly synthetic muscles based on the coupling of a triblock copolymers comprising hydrophobic end blocks and a pH responsive mid-block with a chemical reaction that oscillates pH. Thus triblock copolymers have been used to produce self-assembled polymer gels where the responsive shape change deformation of the molecules can be used to covert chemical energy into mechanical force. The process can be followed directly by SAXS and a correlation between molecular shape change and macroscopic deformation has established. The deformation process is affine and the power output of these devices has been measured. Comparisons to molecular and macroscopic motors show that shape change polymers are diffusion control and therefore response-time (and power output) are limited by diffusion. The creation of responsive nanofibres by electrospinning allows faster equilibration and therefore greater power out-put. The processing technology required to produce aligned bundles of triblock copolymer nanofibres will be described and the response of such assembles to pH changes characterised.

Ra11.22/Rb11.22

Designing planar elastic sheets which self-assemble under electrostatic forces. Silas Alben and Michael P. Brenner; DEAS, Harvard, Cambridge, Massachusetts.

A recent work by Boncheva et al. (Proc. Nat. Acad. Sci. 2005 102: 3924-3929) has raised some basic issues about designable self-assembly within the context of planar elastic sheets which fold into 3D structures under magnetic forces. Among the important parameters are the geometry of the flat sheet, the configurations of the magnets, and the ratios of magnetic to elastic forces. We consider this problem using a numerical model of an elastic sheet, and restrict to the simpler case of electrostatic forces. We identify a simple algorithm for choosing configurations of electrostatic charges, and select ratios of charge strength to elastic energy using physical arguments. We then demonstrate our algorithm on unfoldings of a sphere and more general geometries.

Ra11.23/Rb11.23

A novel solvothermal pathway for synthesis of metal/bimetallic nanoparticles. Bratindranath Mukherjee and Ravishankar Narayanan; Materials Research Centre, Indian Institute of Science, Bangalore, India.

Synthesis of monodispersed metal/bimetallic nanoparticles and self assembly of these on different substrates is of particular interest for technological applications such as nanoelectronics, magnetic storage devices, SERS substrate fabrication, optical grating and antireflective coating. A general solvothermal synthetic method has been developed to prepare noble as well as transition metal and bimetallic nanoparticles in organic media. This is independent of the solubility of the salt or organometallic complexes used and nanoparticle can be produced in large scale. The nanoparticles produced are characterized using SEM, TEM, FTIR, VSM and XRD. Effect of temperature, duration of reaction, capping agent on nanoparticle size and shape has been studied in detail to understand the mechanism.

Ra11.24/Rb11.24

Multifunctional Self-Assembled Mesoporous Silica Films: Novel Nanostructures for MEMS Applications. Hae-Kwon Jeong[1], Ramesh Chandrasekharan[2], Mark A. Shannnon[2] and Richard I. Masel[1,3]; [1]Chemical and Biomolecular Engineering, Univ. of Illinois, Urbana, Illinois; [2]Mechanical and Industrial Engineering, Univ. of Illinois, Urbana, Illinois; [3]Electrical and Computer Engineering, Univ. of Illinois, Urbana, Illinois.

Chip-scale devices are of great interest mainly due to their portability and novel functionality.1 One of the key components in such devices is functional porous film nanostructure. Despite recent development in silicon-based microelectromechanical systems (MEMS) technology, with current top-down micromachining it is still a technological challenge to fabricate such porous functional nanostructure in cost-effective ways. Self-assembled mesoporous silica films can be an alternative to creating such nanostructure in a simple and controlled manner since they can be easily coated using conventional coating techniques2 (for instance, spin-coating and dip-coating), readily functionalized with functional organic groups, and are compatible with current silicon microfabrication technology.3 Self-assembled mesoporous silica materials (in the form of power or film) have drawn a great deal of research interest over the last decade.4,5 Their unique pore structures of nanometer dimension enable them to find applications in separation, catalysis, encapsulation, chemical/biological sensing, low-dielectric coatings, and optical thin films. In order to use the mesoporous films for MEMS applications as novel nanostructures, one has to solve several challenging problems. Such problems include: 1) to deposit continuous films of thickness of several micrometers in a facile way and 2) to fabricate self-standing films by microfabrication techniques for certain MEMS applications such as micro fuel cells. In this talk, we will introduce a new way to prepare continuous mesoporous films of 2-3 micrometer thick using a lamp-based rapid thermal processing technique. We will also talk about the preparation of self-supporting mesoporous films on a silicon wafer using standard microfabrication techniques. The characterization of the microstructures of the mesoporous films will be presented. The functionality of the self-supporting mesoporous films will be demonstrated by fabricating direct formic acid micro fuel cells and measuring performance. 1. Madou, M. J. Fundamentals of Microfabrication: The Science of Miniaturization (CRC Press, New York, 2002). 2. Edler, K. J. & Roser, S. J. Growth and characterization of mesoporous silica films. International Reviews in Physical Chemistry 20, 387-466 (2001). 3. Brinker, C. J. & Scherer, G. W. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic Press, San Diego, 1990). 4. Beck, J. S. et al. A New Family of Mesoporous Molecular-Sieves Prepared with Liquid-Crystal Templates. Journal of the American Chemical Society 114, 10834-10843 (1992). 5. Soler-illia, G. J. D., Sanchez, C., Lebeau, B. & Patarin, J. Chemical strategies to design textured materials: From microporous and mesoporous oxides to nanonetworks and hierarchical structures. Chemical Reviews 102, 4093-4138 (2002).

Ra11.25/Rb11.25

Super composites of metallic carbon nanotubes exhibiting dielectric constant enhancement. Jakub Rybczynski[1], Yang Wang[1], Glynda Benham[3], Maciej Olek[2], Michael Giersig[2], Krzysztof Kempa[1] and Zhifeng Ren[1]; [1]Physics Dept., Boston College, Chestnut Hill, Massachusetts; [2]CAESAR Institute, Bonn, Germany; [3]Megawave Corp, Boylston, Massachusetts.

We studied dielectric properties of composites made of isolated, aligned metallic carbon nanotubes distributed in a dielectric matrix, in the radio-THz frequency range. We find that properties of these composites depend crucially on the shape and orientation of nanotubes. Therefore, the elongated nano-particles (carbon nanotubes) produce composites with an enhanced real part of the dielectric function, and a moderate loss. Studies of dielectric properties of such composites will be presented.

Ra11.26/Rb11.26

Self-assembly in solutions of monodisperse cylindrical macromolecules. Nicolynn E. Davis[1], Michael A. Zhuravel[2], SonBinh T. Nguyen[2] and Ilya Koltover[3]; [1]Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois; [2]Chemistry Department, Northwestern University, Evanston, Illinois; [3]Laboratoire de Physique des Solides, Universite Paris Sud, Orsay, France.

Molecular self-assembly is a promising tool for creating and controlling order at the nanoscale. Its utility depends on availability of macromolecules with well-defined nanoscale shapes and sizes. We have developed a biosynthetic strategy to prepare a new class of macromolecules, dendronized protein polymers (DPPs), that have well-defined cylindrical shapes with controlled molecular dimensions. The DPPs consist of an alpha-helical polypeptide core that determines the molecular length (L) surrounded by grafted wedge-shaped dendrons that control the diameter (D). The monodisperse polypeptides were expressed in *E.coli* from synthetic genes encoding polyglutamic acids glu$_n$ with five discrete lengths n = 38, 58, 76, 94, 112. Three different generations of wedge-shaped poly(benzyl-ether) dendrons were then grafted to the carboxylic acid side-chains along the peptide backbone. The DPPs are soluble in many organic solvents, and in concentrated solutions, self-assemble to form highly ordered liquid crystalline (LC) phases. Formation of these LC phases is driven by excluded volume interactions between the rigid and identically-shaped DPPs, and the type of LC ordering is controlled by DPP aspect ratio (L/D) and concentration. Using small-angle X-ray diffraction and polarized optical microscopy we have observed chiral nematic, smectic, and hexagonal columnar phases in DPP/m-cresol solutions. The well-defined and controlled ordering of the DPPs extends to the nanoscale the tools of entropically-driven colloidal self-assembly, and shows the potential utility of combining biological and chemical synthetic tools towards preparation of new macromolecular blocks for nanoscale engineering.

Ra11.27/Rb11.27

Measurements of Young's Modulus of Ultrathin Polyelectrolyte Multilayer Films via Strain-Induced Buckling

Instabilities. Adam J. Nolte[1], Michael F. Rubner[1] and Robert E. Cohen[2]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We have successfully adapted a recently-published buckling-instability method to measure the modulus values of polyelectrolyte multilayer (PEM) films over a range of film thicknesses from 20 nm to 180 nm. PEMs comprised of fully ionized poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) were deposited directly onto elastomeric poly(dimethylsiloxane) (PDMS) substrates. Lateral deformation of a PEM-coated substrate produced a buckled surface; measurement of the buckling wavelength, the PEM thickness, and the stiffness of the PDMS allowed determination of the Young's modulus. PAH/PSS films in the dry state exhibited a modulus of 4.4 ± 0.7 GPa. Measurements conducted in the wet state showed that water plasticized the film and led to a reduction in modulus to 590 ± 90 MPa. Adding 1 M sodium chloride to the water environment further plasticized the films, resulting in a still lower modulus of 300 ± 30 MPa. We also demonstrate strategies for extending the buckling technique to PEM systems that may not be amenable to assembly directly on PDMS due to its high hydrophobicity, and show that pH control of the dipping conditions of weak PEMs can lead to films with very different structures and mechanical properties. The buckling instability technique is also applicable to a wide variety of systems outside the PEM field, and may be an ideal method for testing the mechanical properties of many other types of nanoscale films and assemblies.

Ra11.28/Rb11.28

Electronic structure of helically coiled carbon nanotubes. Gian Giacomo Guzman-Verri[1], L. C. Lew Yan Voon[1], Morten Willatzen[2] and Jens Gravesen[3]; [1]Department of Physics, Wright State University, Dayton, Ohio; [2]Mads Clausen Institute for Product Innovation, University of Southern Denmark, Sonderborg, Denmark; [3]Department of Mathematics, Technical University of Denmark, Lyngby, Denmark.

The electronic structure of single-wall helical nanotubes is obtained by means of the effective-mass theory. The approach followed in this work is similar to the one used by Ando et al. [1] for the case of a single-wall straight nanotube, that is, first by solving the Dirac's equation, second, by imposing appropriate periodic boundary conditions to the envelope function, and third, by finding the eigenvalues of the effective-mass hamiltonian. The k.p method has been successfully applied in order to study the physical properties of straight carbon nanotubes. Ando and coworkers, for example, studied the spin-orbit interaction [2], the transport properties [3], the effects of impurities [4], the lattice instabilities [5], and the electron-phonon scattering [6] of these nanostructures within the k.p scheme. Moreover, k.p parameters provide a more direct way to compare with future experiments than the ones used in tight binding. For instance, whereas the transfer term in the tight-binding hamiltonian is difficult to measure, the effective-mass in the k.p method is not. Furthermore, sometimes more physical insight can be achieved by the effective-mass approach. Such is the case for the conductance of nanotube junctions [7]. The power of our theory also lies in allowing the inclusion of curvature effects in a natural fashion via differential geometric formulation. Therefore, this work could lead to a comparison of a more detailed study in which curvature effects can be taken into consideration. Examples of the calculated band structure will be presented. Work supported by an NSF CAREER award (NSF Grant No. 0454849), and by a Research Challenge grant from Wright State University and the Ohio Board of Regents. [1] T. Ando, H. Ajiki, J. Phys. Soc. Jpn. 62 1255-1266 (1993) [2] T. Ando, J. Phys. Soc. Jpn. 69 1757-1763 (2000) [3] T. Ando, J. Phys. Soc. Jpn. 73 1273-1280 (2004) [4] T. Ando, T. Nakanishi, M. Igami, J. Phys. Soc. Jpn. 68 3994-4008 (1999) [5] N.A. Viet, H. Ajiki and T. Ando, J. Phys. Soc. Jpn. 63 3036-3047 (1994) [6] H. Suzuura, T. Ando, Phys.Rev.B 65, 235412 (2002) [7] H. Matsumura, T Ando, J. Phys. Soc. Jpn. 67 3542-3551 (1998)

Ra11.29/Rb11.29

Optical Thin Films with Very Low Refractive Index Consisting of Array of SiO2 Nano-rods for Photonics Applications. Jingqun Xi[1], Jongkyu Kim[2], Dexian Ye[1], Jasbir S. Juneja[3], T.-M. Lu[1], Shawn-Yu Lin[1] and E. F. Schubert[2,1]; [1]Department of Physics, Applied Physics, & Astronomy, Rensselaer Polytechnic Institute, Troy, New York; [2]Department of Electrical, Computer, & Systems Engineering, Rensselaer Polytechnic Institute, Troy, New York; [3]Department of Chemical & Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York.

The refractive index contrast in dielectric multilayer structures, optical resonators and photonic crystals is an important figure of merit, which creates a strong demand for high quality thin films with a very low refractive index. SiO2 nano-rod layers with low refractive indices n = 1.08, the lowest ever reported in thin-film materials, is grown by oblique-angle e-beam deposition of SiO2 with vapor incident angle $\theta = 85$ degree. Scanning electron micrographs reveal a highly porous columnar structure of the low-refractive-index (low-n) film. The gap between the SiO2 nanorods is < 50 nm, i.e. much smaller than the wavelength of visible light, and thus sufficiently small to make scattering negligibly small. Optical micrographs of the low-n film deposited on a Si substrate reveal a uniform specular film with no apparent scattering. The unprecedented low index of the SiO2 nano-rod layer is confirmed by both ellipsometry measurements and thin film interference measurements. A single-pair distributed Bragg reflector (DBR) employing the SiO2 nano-rod layer is demonstrated to have enhanced reflectivity, showing the great potential of low-n films for applications in photonic structures and devices.

Ra11.30/Rb11.30

Computational study of tethered nanocube assembly. Charles X Zhang[1] and Sharon C Glotzer[2,1]; [1]Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; [2]Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Self-assembly of functionalized nanoscale building blocks is a promising strategy for developing novel nanomaterials. Cubic-shaped nanoparticles have recently been synthesized from a variety of materials, including silver, gold, and iron. To date there has been limited success in assembling these nanocubes into functional nanostructures beyond simple cubic superlattices, presumably due to the lack of selectivity in the interparticle packing. Anisotropic interactions can be introduced by tethering short polymer chains or DNA strands onto the nanocubes to create cubic "shape amphiphiles" and thereby create the possibility for more complex ordered assemblies. We have developed a predictive computer simulation model that demonstrates the feasibility of guiding nanocube assembly via the use of tethers. We present simulation results that indicate that the assembly process and resulting equilibrium nanostructures may be controlled by manipulating the shape parameters of the tethered nanocubes, including tether length, tether rigidity, number of junction points, and placement of junction points.

Ra11.31/Rb11.31

Abstract Withdrawn

Ra11.32/Rb11.32

A Phase-Field Model for Step Instabilities Mediated by Elastic Interactions and the Ehrlich-Schwoebel Barrier. Dong Hee Yeon and Katsuyo Thornton; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

In recent years, formation of nanostructures on surfaces gained attention due to the possibility for application in novel electronic materials. In particular, spontaneous formation of nanostructures on vicinal surfaces is increasingly recognized as an attractive alternative to high-cost lithographic methods. To understand the formation of nanostructures, a wide range of methods from molecular dynamics to continuum modeling has been applied. At the mesoscopic scale, modeling the surface as a collection of crystal steps separated by terraces is a powerful tool for studying surface morphologies because step motion is a predominant elementary process governing the crystal surface topography. Therefore, the understanding of morphological instabilities of steps, which can be thermodynamic or kinetic in nature, is crucial for self-assembled nanostructures on vicinal surfaces. Long-range elastic interactions among the steps stem from various sources such as applied strain, surface stress and the epitaxial strain, and affect adatom diffusion, the motion of the steps, and the step instabilities. Furthermore, the asymmetric incorporation of adatoms to steps due to an asymmetric kinetic barrier known as the Ehrlich-Schwoebel (ES) barrier at step edges also invokes step instabilities such as step bunching and step meandering instabilities. We will discuss a phase-field model for step instabilities, which incorporate elastic interaction between steps and the ES barrier. The phase-field model is applied to step instabilities such as a step bunching and step meandering instabilities. Linear stability analysis for the step bunching and step meandering are presented, and numerical calculations using the phase-field model are compared with the results of linear stability analysis. The competitions between elastic interactions and ES barrier effects for step instabilities and kinetics in the nonlinear regime are also investigated.

Ra11.33/Rb11.33

SWCNT-CdS Nanocomposite as Light Harvesting Assembly. Photoinduced Charge Transfer Interactions. Istvan Robel[1,2], Bruce A. Bunker[1] and Prashant V. Kamat[2,3]; [1]Department of Physics, University of Notre Dame, Notre Dame, Indiana; [2]Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; [3]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana.

Basic understanding of optical and photoelectrochemical properties of semiconductor-carbon nanotube composites is important for developing light-energy conversion devices. Deposition of CdS nanoparticles on single-walled carbon nanotubes produces a photoactive composite that undergoes charge transfer interactions following excitation with visible light. The luminescence of CdS is quenched by SWCNT. Ultrafast transient absorption experiments confirm the quick deactivation of excited CdS on the SWCNT surface as the transient bleaching recovers in about 200 ps. Excitation of CdS deposited on SWCNT films produces photocurrent with a maximum incident photon to current generation efficiency of 0.5% and thus provides evidence for the electron transfer pathway in the composite. The ability of the CdS-SWCNT nanocomposite system to undergo photoinduced charge separation opens up new ways to design light harvesting assemblies.

Ra11.34/Rb11.34

Templating Pattern Formation in Polymer Films with Dip-Pen Nanolithography. Joseph H. Wei[1], David C. Coffey[2] and David S. Ginger[3]; [1]Chemical Engineering, University of Washington, Seattle, Washington; [2]Physics, University of Washington, Seattle, Washington; [3]Chemistry, University of Washington, Seattle, Washington.

Controlling the nanoscale morphology of polymer blends is important for applications ranging from organic optoelectronics to alternative lithographic strategies. We show how nanoscale templates generated via Dip-Pen Nanolithography (DPN) can be used to control the phase separation in several polymer blends for a variety of applications. The ability to control pattern sizes, pattern chemistry, background chemistry, film thickness, and blend compositions are all shown to be important factors impacting the size and fidelity of the polymer patterns. Using scanning-probe microscopy, optical microscopy, x-ray photoelectron spectroscopy, and selective etching experiments, we contrast the templating effects of nanoscale DPN-patterns with those of larger-scale patterns generated by micro-contact printing. Optimized conditions for pattern replication in both conjugated, non-conjugated, and block-copolymer films are reported.

Ra11.35/Rb11.35

Proof-Reading and Error Removal in a Nanomaterial Assembly. Yi Lu, Juewen Liu and Daryl P. Wernette; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Recent progress in self-assembly of nanomaterials promises to revolutionalize a number of science and engineering fields such as molecular electronics, photonics and computations. A key hurdle to realizing such a potential is the presence of imperfect structures or errors in the assembly process. To overcome this problem, major efforts have focused on optimization of the assembly process to minimize errors or to design devices that can tolerate errors. We argue that it could be equally valuable to investigate proof-reading and error removal during and after assembly, as demonstrated beautifully in a number of processes in biology, such as in mRNA-templated protein synthesis. Here, we report the first experimental demonstration of proof-reading and error removal in nanomaterial assembly by using DNAzymes (DNA molecules with catalytic activities) to specifically locate and remove errors in DNA-templated gold nanoparticle assemblies. We showed that error particles can be specifically removed from the system. The concept demonstrated here can be applied to assembly of other nanomaterials using other bio- or biomimetic molecules.

Ra11.36/Rb11.36

Ionic Complex Formed by DNA and Asymmetric Discotic Triphenylene Salts. Lei Zhu and Li Cui; Chemical Engineering, University of Connecticut, Storrs, Connecticut.

A series of asymmetric triphenylene imidazolium salts with different spacer length (C5, C8, C11) were synthesized and their complexes with DNA were prepared by ionic interaction. The thermal behavior of these complexes were studied by differential scanning calorimetry (DSC), polarized light microscopy (PLM) and wide-angle X-ray diffraction (WAXD). It shows that complexation of the discotic salt onto the rigid DNA chain favors the liquid crystalline properties. WAXD shows that the complexes packed into lamellar structure: The complex with short spacer length (C5) packed into ordered lamellar structure with strong correlation between layers and those complexes with longer spacers (C8 and C11) show reduced correlation due to more mobility of the discotic molecules provided by the longer spacer.

Ra11.37/Rb11.37

Controlled alignment of single-walled carbon nanotubes and study of their electrical properties. Lifeng Dong[1], Vachara Chirayos[1], Jocelyn Bush[2] and Jiao Jun[1]; [1]Department of Physics, Portland State University, Portland, Oregon; [2]Department of Biology, Portland State University, Portland, Oregon.

We present a floating-potential dielectrophoresis method used for the first time to achieve controlled alignment of an individual semiconducting or metallic single-walled carbon nanotube (SWCNT) between two electrical contacts with high repeatability. This result is significantly different from previous reports, in which bundles of SWCNTs were aligned between electrode arrays by a conventional dielectrophoresis process, and where the results were only collected from the control electrode regions. In this study, our alignment focus is not only on the regions of the control electrodes, but also on those of the floating electrodes. Our results indicate that bundles of carbon nanotubes along with impurities were first moved into the region between two control electrodes, while individual nanotubes without impurities were straightened and aligned between two floating electrodes. The measurements for the back-gated nanotube transistors made by this method displayed an on-off ratio and transconductance of 10^5 and 0.3 μS, respectively. These output and transport properties are comparable with those of nanotube transistors made by other methods. Most importantly, the findings in this study show an effective way to separate individual nanotubes from bundles and impurities, and advance the processes for site-selective fabrication of single CNT transistors and related electrical devices.
Acknowledgements: This research was partially supported by the Intel Corp. and the National Science Foundation (DMR-220926).

Ra11.38/Rb11.38

Synthesis of Nanocomposites: $[(\mathrm{NbSe}_2)_m(\mathrm{CrSe}_2)_n]$ Formed from Modulated Elemental Reactants. Polly Berseth, Kristi Carlsen, Astrid Albertini, Ngoc Nguyen and David C. Johnson; Chemistry Department, University of Oregon, Eugene, Oregon.

Modulated elemental reactants were used to synthesize new nanocomposite superlattices, $[(\mathrm{NbSe}_2)_m(\mathrm{CrSe}_2)_n]$, containing layers of metastable CrSe_2. Preliminary magnetic measurements suggest the CrSe_2 layers are stabilized by electron transfer, presumably from the NbSe_2 layers. X-ray reflectivity measurements were utilized to study the reactant interfaces as a function of annealing temperature; the nanocomposites form with gentle annealing and are stable to about 500 °C.

Ra11.39/Rb11.39

Fabricating Ordered Nanoporous Thin Films Using Block Copolymers. Kevin A. Cavicchi[1], Thomas P. Russell[1] and Dorothea Buechel[2]; [1]Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; [2]Seagate Technology, Pittsburgh, Pennsylvania.

Ordered nanoporous thin films are useful as templates or scaffolds for addressable media applications. Block copolymers that self-assemble into periodic nanostructures are attractive for the bottom up fabrication of nanostructured materials. We have been studying thin films of poly(isoprene-b-lactide) (PI-b-PLA) copolymers where the PLA forms hexagonally packed cylinders in a PI matrix. In the ordered state, the PI can be crosslinked and the PLA degraded to generate a nanoporous material. These polymers are highly immiscible and therefore low molecular weight polymers with small domain sizes can be used for fabrication. For many applications, cylinders oriented perpendicular to the substrate are desirable. However, preferential interactions at the substrate and air interface can dominate the morphological behavior resulting in a parallel cylinder orientation. We have been using solvent vapor to swell the films and anneal the structure. The solvent mediates the interactions between the blocks and at the air and substrate interfaces. The effect of this is two-fold: it increases the chain mobility resulting in better long-range order and it allows control over the domain orientation in the film. We have found a complex relationship between the domain orientation and the choice of solvent, concentration of solvent, and thickness of the swollen film where both parallel and perpendicular orientations can be obtained. This technique is also attractive from the point of view of processing as the time needed for solvent annealing (30 min) is short.

Ra11.40/Rb11.40

Strong Charge Inversion and Layer-by-Layer Assembly of Flexible Polyelectrolytes from Self-Consistent Field Calculations. Qiang Wang, Department of Chemical Engineering, Colorado State University, Fort Collins, Colorado.

We have applied a continuum self-consistent field (SCF) theory to flexible polyelectrolytes on flat surfaces either uncharged or carrying opposite charges to the polyelectrolytes. We examined in detail the effects of various parameters on the polyelectrolyte adsorption and surface charge compensation by the adsorbed polyelectrolytes. The ground-state dominance approximation (GSDA) was used to explore the large parameter space involved, including the charge distribution and degree of ionization of the polyelectrolytes, surface charge density, short-range (non-Coulombic) surface-polymer interactions, solvent quality, and bulk polymer and salt concentrations. The numerical results under GSDA were also compared with full SCF calculations to examine the effects of molecular weight of the polyelectrolytes. Strong charge inversion is found for relatively long polyelectrolytes on oppositely charged, attractive surfaces in poor solvent at high salt concentrations. At the mean-field level, the adsorption behavior of polyelectrolytes at high salt concentrations can be understood by that of neutral polymers in good solvent. Based on the above results, we have further modelled the process of layer-by-layer assembly of flexible polyelectrolytes on flat surfaces. The multilayer has a three-zone structure. An exponential growth is found for the first several layers, followed by a linear growth for subsequent layers evolving towards a steady state. While adjacent layers are highly interpenetrating, stratification can be seen for every four or more layers. We have also examined the effects of surface charge density, bulk salt concentration, and solvent quality on the thickness and internal structure of the multilayer. Our results agree with most experimental findings on polyelectrolyte layer-by-layer assembly.

Ra11.41/Rb11.41

Abstract Withdrawn

Ra11.42/Rb11.42

Novel template-less Fabrication of Poly (ethyl-2-cyanoacrylate) Nanofibers. Pratik Mankidy, Henry Foley and Ramakrishnan Rajagopalan; Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania.

Nanomaterials such as nanowires and nanorods are typically fabricated by a template-based technique wherein the material is first filled or synthesized within the template and subsequently released by dissolution/destruction of the template. The dimension of the resulting nanomaterial is hence governed by the dimension of the template it was made in. In this work we report a novel, template-less technique to fabricate nanofibers of poly (ethyl-2-cyanoacrylate) {PECA}. PECA, best known as an instant adhesive or superglue, is formed by rapid anionic polymerization of cyanoacrylate on contact with a nucleophile. The nanofibers were grown on a substrate placed in a humidity chamber where it was exposed to monomer vapor. The humidity acts as the nucleophile for initiation of the polymerization. Interestingly, the polymer grows as a fiber where the diameter of the fiber is a function of the relative humidity in the chamber. Higher the humidity, thinner is the diameter of the fibers formed. Also as this polymerization has a living character the length of the fiber is a linear function of the time of polymerization and the amount of monomer in the vapor phase. Hence, the dimension of the nanofiber can also be controlled during the synthesis.

Ra11.43/Rb11.43

Addition of CeO2 nanoparticle dispersions to enhance flux pinning in Y-Ba-Cu-O superconducting thin films. Jianhua Su[1], Vamsee Chintamaneni[1], Pratic Joshi[1], Sharmila Mukhopadhyay[1], Suvankar Sengupta[2], R. R. Revur[2] and T. Pyles[2]; [1]Mechanical and Materials Engineering, Wright State University, Dayton, Ohio; [2]MetaMateria Partners LLC, Columbus, Ohio.

Nano-pinning centers are expected to enhance the critical current density (Jc) of high temperature superconducting films at high magnetic fields. In this study, CeO2 nanoparticles have been successfully introduced into YBa2Cu3O7-x (YBCO) thin films by dispersing a trifluoroacetate (TFA)-based clear colloid of CeO2 with particle size below 10 nm into TFA precursor solutions of YBCO. Precursor films were spin-coated onto (100) LaAlO3 single crystal substrates and then converted to epitaxial YBCO films through a two-step heat treatment. The pH value of CeO2 colloidal sol has been evidenced to be a key factor to avoid agglomeration of CeO2 nanoparticles. Microstructure analysis reveals well-formed YBCO films. An enhancement in the critical current density was observed with addition of CeO2. The relationship between the content of CeO2 and Jc-H behavior is being investigated and will be presented. Our study reveals that introducing nano-pinning centers by a solution-based method, i.e., a lower cost fabrication process, is a feasible solution to improve the performance of YBCO at high magnetic fields.

Ra11.44/Rb11.44

Internal Structure and Alignment of Peptide Amphiphile Nanofibers. Hongzhou Jiang[1] and Samuel I. Stupp[1,2,3]; [1]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]Department of Chemistry, Northwestern University, Evanston, Illinois; [3]Feinberg School of Medicine, Northwestern University, Evanston, Illinois.

Our laboratory has recently been studying the self-assembly of peptide amphiphile (PA) molecules into one-dimensional cylindrical nanostructures. Previous work using transmission electron microscopy with selective staining and infrared spectroscopy (IR) has established that the peptide segments assemble on the periphery of the nanostructure commonly with β-sheet architectures. In this work we report on the use of polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) to characterize the organization of β-sheets within the nanofibers. Based on the surface selection rules in PM-IRRAS and the controlled deposition of nanofibers running parallel to the surface, we demonstrate that β-sheets are oriented parallel to the long-axis of the nanofibers and packed radially from the nanofiber core. Based on this model, we also show that we can use polarization-modulation infrared spectroscopy in transmission mode to characterize the in-plane orientation of monolayer-thick nanofibers fabricated using controlled draining of peptide amphiphile solutions.

Ra11.45/Rb11.45

Controlled Synthesis of Heteropod-Structured Monodisperse Particles by Discontinuous Growth. Changdeuck Bae[1], Hyunjung Shin[1] and Jooho Moon[2]; [1]School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; [2]School of Advanced Materials Engineering, Yonsei University, Seoul, South Korea.

We designed and demonstrated a new class of monodisperse colloidal nano-building blocks possessing heteropod structures in a variety of coordination numbers on their surfaces. Our approach is based on sol-gel method for both particle synthesis and site-selective growth of additional heteropods. A series of processes were carried out: Firstly, monodispersed silica colloids were produced by StÖber process having the size and distribution of particles conformed with wavelengths we use; Secondly, synthesized colloids were controlled to crystallize into many different periodic structures, such as face-centered-cubic (FCC), body-centered-cubic (BCC), two-dimensional (2D) close-packed, and 1D chain structures; Thirdly, the entire area of colloid surfaces was coated with octadecyltrichlorosilane (OTS) - self-assembled organic monolayers (SAMs) by immersing the substrate with colloidal crystals into OTS molecules containing medium for several hours; then, the OTS-coated colloidal crystals were resuspended in aqueous solutions for the next step leaving the desired hole patterns in OTS-SAMs on their surfaces which is non-OTS regions created by physical, inter-particle contacts and negatively charged metal oxide surfaces; and, lastly, additional selective growth of desired materials, e.g. titania, rendered onto the exposed silica surfaces, not OTS-coated surfaces resistant to nucleation and growth, making heteropods of TiO2 less than 100-nanometers. SEM, EDX, and HR-TEM data testify successful synthesis of these novel building blocks. We are also under study on photonic properties of 3D colloidal crystals consisted of these heteropod-structured particles, and feasibility of selective bioconjugation on them.

Ra11.46/Rb11.46

Nano-patterned Liquid Metal Electrodes for Prussian blue Nanotube Synthesis. Sathyajith Ravindran[2], Chunglin Tsai[3] and Cengiz Sinan Ozkan[1]; [1]Mechanical Engineering, University of California at Riverside, Riverside, California; [2]Chemical and Environmental Engineering, Unviersity of California at Riverside, Riverside, California; [3]Electrical Engineering, Unviersity of California at Riverside, Riverside, California.

We report the fabrication of Prussian blue nanotubes via a novel technique wherein a liquid metal surface is nano patterned with a porous polycarbonate membrane used as a hard mask. Prussian blue as 1D nanowires and nanotube are excellent candidates for ultra low level sensing, optical wave-guides and model systems to test the one-dimensional Ising model. One of the most feasible techniques for nanowire fabrication is to use porous template. However, Prussian blue dissolves in strong acids and decomposes in strong bases. Conventional procedures, which use porous alumina with a backside metal contact, need strong acids and bases in the various steps of the nanowire fabrication. We report a novel technique, which will pave way for the facile synthesis of nanowires and nanotubes of materials that are sensitive to strong acidic or basic environment. Hence, nano patterning of a liquid metal (Hg that functions as a topside metal contact) with polycarbonate membrane instead of porous alumina membrane eliminates the use of both strong acid and base during the fabrication of nanowires. With this innovative technique, we report the synthesis of novel organic Prussian blue nanotubes and nanowires.

Ra11.47/Rb11.47

Abstract Withdrawn

Ra11.48/Rb11.48

Size Effects on the Stabilization and Growth of Tetragonal ZrO2 Crystallites in Nanotubular Structure. Bokyung Ahn[1],

Hyunjung Shin[1], Jaegab Lee[1], Jiyoung Kim[1], Pil-Ryung Cha[1] and Myung M. Sung[2]; [1]School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; [2]Department of Chemistry, Kookmin University, Seoul, South Korea.

Nanotubular oxide materials have especially promising physical properties and potential applications in nanoelectronics. Even though Zirconium dioxide (ZrO2) is an interesting functional material, there are only a few reports of ZrO2 nanotubes in the literature. We investigated Nanosize effects on the stabilization of ZrO2 polymorphs and the growth behavior of their crystallites in 1-D nanotubular structures. Polycrystalline nanotubular structures of ZrO2 with tetragonal nanocrystallites were fabricated using the nanoporous PC (polycarbonate) templates, AAO (anodic aluminum oxide) template and ALD (atomic layer deposition) processes. Characterization of the ZrO2 nanotubes is accomplished by X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HR-TEM). As-prepared ZrO2 nanotubes were all polycrystalline of stabilized tetragonal polymorph at room temperature. Wall thickness (5 $\sim$ 50 nm in thickness) of the ZrO2 nanotubes is extremely linear relative to the number of ALD cycles. Faster growth of the tetragonal nanocrystallites was observed in the nanotubes of 50 nm in outer diameter, compared to the one of 200 nm. Possibly, Gibbs - Thompson relation could explain the observed nanosize effects on the growth of the tetragonal ZrO2 nanocrystallites.

Ra11.49/Rb11.49

Advanced Photonic Crystals by Holographic Lithography and Atomic Layer Deposition.

Jeffrey S. King[1], E. Graugnard[1], O. M. Roche[2], D. N. Sharp[2], J. Scrimgeour[2], C. J. Summers[1], R. G. Denning[3] and A. J. Turberfield[2]; [1]Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]Physics, University of Oxford, Oxford, United Kingdom; [3]Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom.

Holographic lithography [1] and direct optical writing using two-photon excitation [2] are promising fabrication methods for 3D photonic crystals. Both methods create sub-micrometer periodic microstructure in polymeric photoresist that have relatively low refractive index contrast. Strategies to create negative replicas of these polymeric templates by deposition of high-index dielectric in their pores must make allowance for the low thermal decomposition temperature of the resist; limiting the range of materials that can be deposited by chemical vapor deposition. Low temperature ($< 100^\circ$ C) atomic layer deposition (ALD) of titania has been demonstrated for formation of single [3] and multi-component inverse opals [4]. This technique yields low porosity, conformal films with sub-monolayer control, making it an ideal technique for polymer template infiltration. Here we report successful realization of 3D titania photonic crystals formed by infiltration and subsequent removal of holographically-defined polymeric templates. Homogenous infiltration of amorphous titania (n = 2.3) was observed throughout a 20 μm thick sample, $\sim$ 22 unit cells deep. The polymer template was subsequently removed by O_2 plasma etching. We present optical spectra for titania/epoxy and titania/air photonic crystals and correlate them with calculated photonic band structures. These results demonstrate an exciting coupling of two powerful techniques yielding unprecedented control at the nanoscale, and enabling previously unattainable nanophotonic structures. The combination of these techniques with two-photon writing will provide a rapid and simple route to photonic circuit fabrication. [1] M. Campbell et al., Nature 404, 53 (2000). [2] M. Deubel, et al., Nature Materials 3, 444 (2004). [3] J. S. King, E. Graugnard and C. J. Summers, Adv. Mat. 17, 1110 (2005). [4] J. S. King, E. Graugnard and C. J. Summers, App. Phys. Lett., submitted.

Ra11.50/Rb11.50

Bi-functionality of TBP-1 (Ti-binding peptide-1) facilitates nano-fabrication of heterologous multi-layers composed of inorganic nano-particles.

Ken-Ichi Sano[1], Hiroyuki Sasaki[2] and Kiyotaka Shiba[1]; [1]Protein Engineering, The Cancer Institute, CREST/JST, Tokyo, Japan; [2]Div. Mol. Cell Biol., Inst. DNA Med., Jikei Univ. Sch. Med., Tokyo, Japan.

Controlled interfacing between bio-molecules and inorganic materials is fundamental to the development of bio-nano materials. Numerous peptide aptamers that recognize inorganic materials have been isolated using in vitro peptide evolution systems. We have isolated a peptide aptamer, TBP-1 (Arg-Lys-Leu-Pro-Asp-Ala-Pro-Gly-Met-His-Thr-Trp), that binds to the surface of titanium by using a peptide-phage display system (Sano and Shiba, JACS 125 p14234). With the TBP-1 displaying phage, we have investigated the binding specificity of the peptide, and found that TBP-1 bound to Ti, Si and Ag surfaces, but not to Au, Cr, Cu, Fe, Pt, Sn and Zn. We also investigated the biomineralization activity of the TBP-1, and observed that a synthetic TBP-1 peptide mediated mineralization of silica as well as Ag (Sano et al., Langmuir 21 p3090). Thus, TBP-1 is a bi-functional peptide; it is a peptide binder and is a catalyzer for biomineralization. These properties of TBP-1 have been further shown to be implantable to other molecules by genetic engineering. By modifying the gene for a subunit chain of ferritin, we constructed the artificial cage protein, ”minT1-LF” that displays the core region of TBP-1 on its surface with the multivalency of 24. In addition to the ability to store various inorganic materials in its interior space, the minT1-LF acquired two additional activities derived from the TBP-1. The minT1-LF bound to the surfaces of Ti with the Kd of 3.8 nM. It also bound to Ag, and SiO2 but not to Au (Sano et al., Small in press). Biomineralization activities of TBP-1 also recapitulated on the minT1-LF, i.e., silification was accelerated by the presence of minT1-LF. Thus, the minT1-LF is a novel type of inorganic-storage cargo that has a biomineralization activity on its surface and shows tight and specific binding. In this presentation, we will introduce our novel method for fabrication of multilayer of minT1-LFs, in which the alternant application of binding and mineralization activities of minT1-LFs enabled the layering of different minT1-LFs filled with distinct inorganic materials.

Ra11.51/Rb11.51

Functionalization of Dispersible Mesoporous Silica Particles with Magnetic Crystals.

Robert Peter Hodgkins[1], Petr Vasiliev[1], Anwar Ahniyaz[1], Nina Andersson[2,1], Peter Alberius[2] and Lennart Bergstrom[1]; [1]Physical, Inorganic and Structural Chemistry, Stockholm University, Stockholm, Sweden; [2]Institute for Surface Chemistry, Stockholm, Sweden.

Functionalized mesoporous spherical particles with a high surface area, mechanical rigidity and chemical inertness have a great potential for a number of applications, e.g. chromatography, bioseparation, controlled drug release, sensors and catalysts. There are several routes to produce these particles where the rapid single-step, aerosol-assisted method is able to give excellent control over the mesostructure, pore size and also offer facile and versatile approaches for functionalization. We will show how superparamagnetic iron oxide nanoparticles can be incorporated into the mesostructured colloids. The possibility to tune the magnetic susceptibility by the amount and type of the magnetic nanoparticles opens up many interesting applications, e.g. bioseparation. The large surface area and extremely well defined pore size of the mesoporous material together with the possibility to transport the particles by a magnetic field give us a very interesting possibility to investigate specific bioreactions in complex systems. The possibility to incorporate nanocrystals of variable size and surface functionalization by both a one-pot, direct synthesis route and via post-synthesis impregnation will be discussed. Characterization of the materials involves the use of diffraction, microscopy, gas adsorption measurements and magnetic susceptibility. The dispersability is evaluated using electrokinetic mobility measurements and rheology.

Ra11.52/Rb11.52

Incorporation of Magnetic Nanoparticles and Quantum Dots into Silica Microspheres.

Numpon Insin[1], Joseph B. Tracy[1], Hakho Lee[2], John P. Zimmer[1], Robert M. Westervelt[2] and Moungi G. Bawendi[1]; [1]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Physics and Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

Fluorescent and magnetic silica microspheres were prepared by the incorporation of maghemite (γ-Fe_2O_3) nanoparticles (MPs) and CdSe/CdZnS quantum dots (QDs) into the shells of silica core/shell microspheres. The MP- and QD-doped silica shells were grown on pre-made silica cores according to a method previously developed in our laboratory. Briefly, the MPs and QDs, featuring ligands with alkoxysilane moieties, were included in a mixture of silica microsphere cores, tetraethoxysilane, and water in ethanol. The addition of ammonium hydroxide resulted in the initiation of silica shell growth on the cores, with the alkoxysilane ligands on the nanoparticles enabling their incorporation into the silica matrix. The microspheres were characterized using a combination of TEM, magnetization measurements and fluorescence microscopy. MPs of 5- to 18-nm in size were incorporated into core-shell silica microspheres of 100- to 500-nm in diameter. The microspheres demonstrated approximately uniform incorporation of QDs and MPs into the shell, and were readily imaged under a fluorescence microscope. The magnetic moment of these microspheres allowed them to be manipulated by magnetic fields produced by a microelectromagnetic device while their fluorescence permitted real-time imaging of their motion.

Ra11.53/Rb11.53

Loading of Carbon Nanotubes with Magnetic Particles.

Gulya Korneva[1,2], Haihui Ye[2], Yury Gogotsi[2,4], Derek Halverson[3], Jean-Claude Bradley[1] and Gary Friedman[3]; [1]Chemistry, Drexel

University, Philadelphia, New Jersey; [2]Materials Science and Engineering, Drexel University, Philadelphia, New Jersey; [3]Electrical and Computer Engineering, Drexel University, Philadelphia, New Jersey; [4]Drexel University, Philadelphia, New Jersey.

In the poster, we show a relatively simple, inexpensive, reproducible, scalable and fast method of filling the carbon nanotubes with functional nanoparticles, in particular, with magnetic nanograins. This technique opens an opportunity for engineering magnetic nanotubes based on the phenomenon of spontaneous penetration of wetting fluids into capillaries. The magnetization of magnetic CNTs is controlled by the number of encapsulated nanograins, thus the tubes can be made very magnetic. In our experiments, for example, the number of magnetic grains in the tubes varies between N $\sim$ 10000-100000. The filled nanotubes follow the applied magnetic field, thus manifesting their magnetic nature. We showed that the yield of magnetic nanotubes after wet filling was close to 100%. Controllable manipulation of magnetic nanotubes with micromagnets points to a straightforward way for utilization of these nanoneedles in different nanofluidic and electronic devices. Generally, the paper provides a procedure of making nanotubes functional. Other particulate fluids, emulsions, and polymer solutions can be used to fill nanotubes and transform them into multifunctional nanostructures.

Ra11.54/Rb11.54
Fabrication of epitaxial perovskite nanostructures. Chang Chuan You[1], Nils Vidar Rystad[2], Yun Liu[2], Anne Borg[2] and Thomas Tybell[1,3]; [1]Department of Electronics and Telecommunications, Norwegian University of Science and Technology, Trondheim, South-Trondelag, Norway; [2]Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway; [3]NTNU Nanolab, Norwegian University of Science and Technology, Trondheim, Norway.

Perovskite oxides are attractive for a variety of electronic applications, for example ferroelectric non-volatile random access memories. In order to fully exploit their properties it is important to understand how size affects the materials as the components are scaled down, and to develop appropriate nanostructuring methods. Here we present data on the fabrication of epitaxial perovskite nanostructures. The structures were fabricated using a two-step process, with initial e-beam lithography and subsequent dry etching followed by scanning tunneling microscopy (STM) lithography in order to create structures with lateral dimension down to $\sim$5 nanometer. Data on how voltage bias, tunneling current, and scan speed effect STM etching of $SrRuO_3$ will be discussed in detail. Moreover, the possibility to grow epitaxial perovskites on top of pre-structured $SrRuO_3$ templates will be assessed, with focus on the fabrication of ferroelectric mesas.

SESSION Ra12: Semiconductor Nanostructures I

Chair: Eli Sutter
Wednesday Morning, November 30, 2005
Room 207 (Hynes)

8:00 AM *Ra12.1
Self-Organized Nanopatterning of Surfaces by Focused Ion Beam. Wei Zhou[1], Haixia Qian[1], Gnian Cher Lim[2], Lumin Wang[3] and Michael J. Aziz[4]; [1]Precision Engineering & Nanotechnology Centre, Nanyang Technological University, Singapore, Singapore; [2]Singapore Institute of Manufacturing Technology, Singapore, Singapore; [3]Dept. of Nuclear Engineering & Radiological Sciences, University of Michigan, Ann Arbor, Michigan; [4]Div. of Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts.

We aim to use 30-50 keV Ga+ Focused Ion Beam (FIB) as a tool to produce nanoscale periodic structures in Si, Ge, ZnO, SiO2, InP, GaAs, GaSb, GaN and metals for various applications. When the highly focused ion beam is programmed to erode materials in selected areas by sputtering, nanoscale surface structures may be fabricated directly. We demonstrate the successful use of bitmap to control FIB for one-step maskless nanofabrication of pillars, wells and gratings in some materials such as Si. However, use of the *directwriting* method in many other materials is affected by either anisotropic surface diffusion (in Sn and Ti), or ion-induced nano-explosion (in Ge and GaSb), or severe redeposition of sputtered materials (in GaAs, GaSb and GaN). One the one hand, we explored various ways to get over the problems. On the other hand, we managed to make use of the phenomena to produce self-organized ripples, nano-dots or nano-rods. It is noteworthy that we obtained convincing evidence, through monitoring evolution of the surface patterns using in-situ real-time secondary ion and secondary electron imaging, to show that ion beam dwell time has significant effect on surface pattern formation. The Ga-containing compounds are common in the sense that liquid-like droplets may form on the surfaces at high ion doses. EDS and TEM analyses showed the droplets to be amorphous Ga. We have found a way to control the Ga droplets to make them disappear or appear in certain orders on the surfaces.

8:30 AM Ra12.2
Directed Self-Assembly of Highly Periodic Arrays of SiGe Quantum Dot Molecules Via Heteroepitaxy on Patterned Si Substrates. Jennifer L. Gray[1], Robert Hull[1] and Jerrold A. Floro[2]; [1]Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; [2]Sandia National Laboratories, Albuquerque, New Mexico.

Heteroepitaxial growth of SixGe1-x on Si substrates patterned ex-situ using a focused ion beam (FIB) can result in the self-assembly of quantum dot molecules (QDMs) at precisely defined locations under specific growth conditions. Individual QDMs are composed of four self-assembled islands that cooperatively nucleate at the edges of pits that form in the film at the FIB modified sites. In order to obtain uniform, well ordered islands, the FIB milling parameters and Si buffer thickness must be tailored to produce pits in the strained SiGe film with dimensions equal to or smaller than the compositionally-dependent natural length scale of strain relieving morphology that forms intrinsically and randomly in strained films on un-patterned substrates. We obtain long-range periodic arrays of QDMs with uniform shapes and sizes when growth is done under kinetically limited conditions to suppress roughening from occurring at locations other than directly adjacent to the pre-patterned pit sites. We will show that FIB substrate patterns deeper than 5nm result in degraded nanostructure self-assembly, while too shallow patterns can result in missing features. The ability to produce island arrays at specific locations is important for applications such as quantum computing where quantum dots must be able to be arranged into logic structures. These methods provide a new route to hierarchical assembly of nanostructures with potential applications to novel nanoelectronic device architectures. This work was partially supported by the DOE Office of Basic Energy Sciences. Sandia is a multiprogram laboratory of the United States Department of Energy operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:45 AM Ra12.3
Step erosion during nucleation of InAs/GaAs(001) quantum dots. Ernesto Placidi, Fabrizio Arciprete, Violetta Sessi, Massimo Fanfoni, Fulvia Patella and Adalberto Balzarotti; Physics, University of Rome Tor Vergata, Rome, Italy.

We have investigated, by means of atomic force microscopy, the complete evolution of InAs/GaAs(001) quantum dots as a function of deposited InAs. Direct evidence is found for step erosion by quantum dots nucleated onto the step edge and an estimate of the eroded volume is provided. The analysis of quantum dots position shows that the step is a preferential site for nucleation at the beginning of 3D islands formation, while, after the step erosion, quantum dots are mainly located below the steps and in the flat regions of the sample. A further analysis shows that nucleation on step bunching starts in advance compared to nucleation on flat regions, due to different strain conditions on the surface. By studying the quantum dots volume as a function of InAs coverage, we show that the wetting layer contribution in quantum dots formation is confined within a narrow range of coverage around the 2D-3D transition.

9:00 AM Ra12.4
Surface Diffusion Processes and Nanostructure Growth. Jian Wang[1], Hanchen Huang[1] and Timothy S. Cale[2]; [1]MANE, Rensselaer Poly. Ins., Troy, New York; [2]Chemical Engineering, RPI, Troy, New York.

This paper reports a molecular statics study of Cu surface diffusion barriers, particularly the facet-facet and step-facet barriers, and explains the phenomena in nanostructure growth based on these kinetic processes. The study focuses on two high symmetry surfaces or facets, Cu{111} and Cu{100}. Our results show that these two barriers are distinct from conventional step barriers and are independent of facet size once it is beyond three atomic layers. Usually, the facet-facet barrier is substantially larger than diffusion barriers on flat surfaces or down monolayer steps, and the step-facet barrier is substantially larger than diffusion barriers along or across monolayer steps. Exceptions do exist. When two Cu{100} facets are involved, the two barriers decrease as the size of the ending facet increases from one layer to two layers, and then increase from two to three (or more) layers. As a result of the large facet-facet and step-facet barriers, surfaces of Cu thin films are on the order of 100 nm. The small facet-facet and step-facet barriers between two Cu{100} facets, when the ending facet is two to three layers, make it difficult to form another Cu{100} facet near one Cu{100} facet. For the same reason, nanowires along <100>/{100} on the Cu{100} is unlikely while nanowires along <110>/{111} are feasible. Based on the numerical results, we also explain the growth process of Cu <111> columns involving appear and disappear of (100) facets. Finally, we have presented a unified description of diffusion barriers at the steps of islands, by classifying the barriers as horizontal or vertical, and one dimension to three dimensions.

9:15 AM Ra12.5

Self-Assembled Germanium Quantum Dots: Carbon-induced Growth and Role of Silicon Interdiffusion. Alessandro Bernardi, Oriol Osso, Maria Isabel Alonso, Alejandro Richard Goni and Miquel Garriga; Icmab-CSIC, Barcelona, Spain.

In order to cope with prerequisites for opto-electronic applications, it is desirable to maximize the island density in the fabrication of quantum dots (QDs). Dot diameters can, in principle, be reduced by lowering the growth temperature but addition of carbon during the process of QD growth opens additional possibilities to control the size and the shape of the islands by modifying the strain field in the surface of the growing material. Several works aimed at understanding the dependence of the density of C-induced QDs with temperature of material deposition. The increased Ge surface diffusivity with temperature leads to the transformation from small and dense domes to larger islands. In the present work we especially focused on the role of a Ge wetting layer (WL) before carbon deposition on the subsequent growth of C-induced Ge dots, in order to clarify the dynamics leading to the dot density reduction observed in presence of a pre-deposited Ge WL, compared to the case of a bare silicon substrate. A study of morphology of the different samples revealed a clear trend with the growth temperature chosen for the Ge WL deposition. An increase of temperature leads to higher density of small dome shaped quantum dots, contrarily to the temperature dependence observed for Ge dots nucleation stage. At low temperature interdiffusion of silicon in the WL is kinetically quenched and carbon atoms deposited on the surface sense a Ge rich environment, characterized by Ge-C chemical repulsion leading to energetic instability of carbon clusters. Further studies are under way in order to achieve a complete understanding of surface dynamics and their correlation with observed morphology.

9:30 AM Ra12.6

Self-Assembly of Steps and Vacancy-Lines on Ge Films Grown on Si(001) Surface. Dhananjay Tulsiram Tambe and Vivek B. Shenoy; Solid Mechanics, Brown University, Providence, Rhode Island.

During initial stages of deposition of Ge on Si(001) surface, defects such as dimer vacancylines and steps self-assemble to create a structure which has higly correlated features [1]. Understanding the mechanisms for this correlation/order is necessary for the possible use of this patterned surface as a template for nanofabrication of 1D structures or to study the growth of pyramidal quantum dots. We have studied these structures with the help of atomic simulations using empirical potentials. In our simulations, we have studied correlation between the steps and the vacancy-line based on energetics arguments. Our study provides a theoretical basis for the interaction between vacancy-lines and steps and explains some very interesting statistical observations made by Sutter et.al[1]. [1] P.Sutter, I.Schick, W.Ernst and E.Sutter, Phys.Rev.Lett.,91(2003),176102.

9:45 AM Ra12.7

Real-time observation of self-assembling Ge nanostructures on clean and Ga patterned Si(113). Torben Clausen[1], Thomas Schmidt[1], Jan-Ingo Flege[1], Andrea Locatelli[2], Tevfik Onur Mentes[2], Stefan Heun[2], Fangzhun Guo[3] and Jens Falta[1]; [1]Institute of Solid State Physics, University of Bremen, Bremen, Germany; [2]Sincrotrone Trieste, Trieste, Italy; [3]SPring-8/JASRI, Hyogo, Japan.

We report on a systematical temperature dependent low energy electron microscopy (LEEM) study of Ge nucleation and island growth on clean and Ga patterned Si(113), providing a detailed insight into the growth kinetics and the resulting surface morphology. The in-situ sample preparation and the measurements were performed in an UHV system equipped with a spectroscopic photoemission and low energy electron microscope (SPELEEM) at the undulator beamline 1.2 at ELETTRA. During Ge deposition on clean Si(113) a strong temperature dependence of the Ge island shape is observed. Starting from a rather circular appearance at 380°C it changes to a cigar-like shape for temperatures of 440°C to 590°C, elongated in [33-2] direction. With increasing temperature the Ge islands become more elongated and the average island size increases up to about one to five microns in length whereas the density decreases. From the arrangement of the islands, no indication for a strongly anisotropic diffusion is found, most likely poiting towards an anisotropic strain relaxation. However, if Ge is deposited on a Ga saturated Si(113) surface the shape and the arrangement of the Ge islands changes drastically. Ga pre-adsorption leads to the formation of substrate facets with a periodicity of about 40 nm in [33-2] direction. Ge deposition on this surface leads to Ge islands which are arranged at the Ga facets and elongated in [1-10] direction. A strongly anisotropic diffusion is observed, which may explain the Ge island shape and arrangement. Thus, using a Ga pre-patterned surface, the growth of small and aligned Ge nanoislands in the order of about 100 nm in length with high density is enabled.

SESSION Rb12: Alternative Nanofabrication Techniques IV

Chair: Younan Xia
Wednesday Morning, November 30, 2005
Room 208 (Hynes)

8:30 AM *Rb12.1

Integration of Top-Down and Bottom-Up Nanofabrication Schemes. Jurriaan Huskens, [1]Supramolecular Chemistry & Technology, University of Twente, MESA+, Enschede, Netherlands; [2]Strategic Research Orientation "Nanofabrication", University of Twente, MESA+, Enschede, Netherlands.

Nanotechnology deals with enabling technologies for the fabrication and study of materials (atoms, molecules, particles, etc.) on the nanoscale. In order to study nanoobjects, the preparation of nanoobjects is not enough: careful study of their individual properties usually requires anchoring to a substrate, and preferably to targeted or prepatterned areas of a substrate. Nanofabrication is the subdiscipline that deals with the development of general fabrication methodologies for the preparation of nanoobjects as well as of patterned substrates and of assembly methods for the anchoring of the objects to the patterned areas. In general, nanofabrication methods fall into two classes, which are called top-down and bottom-up. The integration of top-down and bottom-up nanofabrication schemes is considered a key issue for the advance of nanotechnology. In this paper, we will show an elaborate example of such an integration attempt. We chose to use nanoimprint lithography (NIL) as the top-down technique [1], because it is a technique that allows sub-10 nm resolution in pattern replication and has recently been put forward by the semiconductor industry as the most promising technique to be implemented in future chip fabrication processes. As the bottom-up technique, we chose layer-by-layer (LBL) assembly [2], since this allows the control over layer thicknesses with a nm accuracy. The full integration of these methods is therefore envisaged to lead to the fabrication of 3D nanoobjects of arbitrary shapes on substrates, where the x,y dimensions are determined by NIL and the z dimension by the LBL assembly. For the LBL assembly, we have used a supramolecular approach [3], based on host-functionalized substrates (molecular printboards [4]) and nanoparticles [5] in combination with guest-functionalized dendrimers [6]. The whole procedure is shown to result in a multistep, high-fidelity process yielding 3D objects with all dimensions on the nanoscale. [1] P. Maury, M. Peter, V. Mahalingam, D. N. Reinhoudt, J. Huskens, Adv. Funct. Mater. 2005, 15, 451. [2] G. Decher, Science 1997, 277, 1232. [3] O. Crespo-Biel, B. Dordi, D. N. Reinhoudt, J. Huskens, J. Am. Chem. Soc. 2005, 127, 7594. [4] J. Huskens, M. A. Deij, D. N. Reinhoudt, Angew. Chem. Int. Ed. 2002, 41, 4467; T. Auletta, B. Dordi, A. Mulder, A. Sartori, S. Onclin, C. M. Bruinink, C. A. Nijhuis, H. Beijleveld, M. Peter, H. Schoenherr, G. J. Vancso, A. Casnati, R. Ungaro, B. J. Ravoo, J. Huskens, D. N. Reinhoudt, Angew. Chem. Int. Ed. 2004, 43, 369; S. Onclin, A. Mulder, J. Huskens, B. J. Ravoo, D. N. Reinhoudt, Langmuir 2004, 20, 5460. [5] O. Crespo-Biel, A. Jukovic, M. Karlsson, D. N. Reinhoudt, J. Huskens, Isr. J. Chem. 2005, in press. [6] Michels, J. J.; Baars, M. W. P. L.; Meijer, E. W.; Huskens, J.; Reinhoudt, D. N. J. Chem. Soc. Perkin Trans. 2 2000, 1914.

9:00 AM Rb12.2

Nanomolding high-aspect-ratio nanostructures from polymers and their nanocomposites. Chi-Wei Lo[1], Ying Zhang[1], J. Ashley Taylor[2] and Shu Yang[1]; [1]Material Science and Eng., U. of Penn, Philadelphia, Pennsylvania; [2]Bell Lab, Lucent Tech., Murray Hill, New Jersey.

Abstract High-aspect-ratio responsive polymeric nanostructures are receiving increasing interests for potential applications in biomedical devices, tissue engineering, MEMS, sensors, and micro-optical elements. However, it is challenging to fabricate polymeric nanostructures with high aspect ratios. When the aspect ratio is greater than 5 and the pitch is small, polymer nanostructures collapse because of the surface adhesive forces. The molded sharp corner deforms due to the equilibrium between surface tension and Young's modulus of the cured polymer. Here we demonstrate the fabrication of high-aspect-ratio nanopost arrays (diameter of 350nm to 1μm) with an aspect ratio up to 20 using nanotransfer molding (nTM) technique. We investigate several parameters that affect the fidelity of nanopatterns, including the feature dimension, pitch, viscosity of the precursor liquids, and the mechanical strength of the cured polymers. When the aspect ratio is as high as 20 and the pitch is 1μm, the Si master with sharp corners are faithfully replicated in the rigid epoxy resins without deformation, while those from soft materials, such as PDMS and Norland collapse. Using the same technique, we incorporate carbon nanotubes and magnetic nanoparticles, respectively, into the nanoposts as nanoactuators in response to external fields. Further, we observe a much improved mechanical properties in carbon nanotube loaded PDMS nanocomposites, which may lead for broader applications of PDMS nanostructures.

9:15 AM Rb12.3

Sub Micron-Scale Cubic Patterning of Surfaces. Suresh Gupta and Thomas P. Russell; Polymer Science and Engineering, University of Massachusetts, Amherst, Amherst, Massachusetts.

Micron-scale patterns can be generated by the application of electric field across two fluid interface making use of result of electrohydrodynamic instabilities. These patterns are generally hexagonally packed features on the polymer surface. Patterns can also be generated with various symmetries on fluid surfaces when they are forced to vibrate normal to surface by means of Faraday instabilities. But, when ultrasonic vibrations are used with single frequency, cubic patterns are generated on the surface that are dynamic. These structures, observed using an optical microscope, were produced by vibrations upto 100 KHz in frequency. Kelvin's equation can be used to predict the wavelength of the pattern as a function of frequency where with increasing frequency the wavelength of the pattern decreases. This process is used widely in atomization of fluids. But beyond 100 KHz, there is a controversy regarding the mechanism of atomization in fluids. It is argued that cavitation produces the fine mist of spray or that the droplets are formed at the crests due to surface waves. Here, we have used an electric field to stabilize the pattern on thin polymer films using different vibration frequencies in the MHz range and found that the cubic packed patterns are produced. These features are sub-micron in size and the size can be varied by the frequency of vibrations. This provides evidence that surface waves are generated at frequencies higher than 100 KHz and that may cause the formation of droplets or a fine mist.

9:30 AM Rb12.4

Edge-Spreading Lithography: A Versatile Technique for Nanoscale Patterning. Joseph M. McLellan, Matthias Geissler and Younan Xia; Chemistry, University of Washington, Seattle, Washington.

We recently developed a simple and versatile technique for nanoscale patterning over large areas, which we call edge-spreading lithography (ESL). A typical ESL process utilizes a planar PDMS stamp to deliver ink molecules to a surface via a guide. Upon reaching the surface the ink molecules form a self-assembled monolayer (SAM) around the footprint of each guide. With a continuous supply of ink molecules the SAM can expand laterally until all areas not blocked by the guides are covered. In our initial demonstrations, we utilized monolayer arrays of silica beads on gold and silver substrates as the guides and alkanethiols as the inks. The circular footprints of the beads resulted in the formation of an array of SAM rings with a lattice constant that was consistent with that of the bead array. After lift-off of the beads, the SAM could then be used as an ultra-thin resist in order to transfer the pattern into the underlying gold or silver through a wet chemical etch process. Features generated by ESL may find use in a variety of applications such as substrates for surface enhanced Raman scattering (SERS). I will give an overview of our ESL experiments including some limitations of the process, how we characterized the patterns, and how we were able to tune the widths of the resultant SAM rings down to range of 30 nm. I will also discuss the formation of arrays of concentric rings, with several different functional groups (e.g. methyl, carboxyl, hydroxyl, or amine) next to one another through consecutive steps of ESL. Patterns generated through successive ESL are quite versatile in that the dimensions and order of the different functional groups can be varied independently. Finally I will discuss how we have overcome the geometric limitations imposed by bead arrays by using photoresist features as guides, enabling us to fabricate patterns of much higher geometric complexity.

9:45 AM Rb12.5

Directed Assembly of Nanoparticles onto Polymer Imprinted or Chemically Patterned Templates Fabricated by Nanoimprint Lithography. Pascale Maury, Maryana Escalante, Maria Peter, David Reinhoudt and Jurriaan Huskens; university, Enschede, Netherlands.

Several unconventional techniques have been employed to direct the deposition of nanoparticles in order to produce colloidal patterns that fulfill the requirements of order, generic design and functionality necessary for a wide range of applications. One method makes use of topographical templates, made up of silicon or a polymer, to confine non-functionalized particles within the pattern. Another employs self-assembled monolayer (SAM) templates to fabricate chemically patterned substrates. Here, we report on a novel multistep process for preparing chemically directed nanoparticle arrays by combining top-down and bottom-up techniques, namely nanoimprint lithography (NIL) with self-assembly of silanes on silicon oxide in the mm-and sub-mm range1. The nanoparticles are assembled by vertical deposition employing the meniscus method to allow versatile patterning of nanoparticles on different types of substrates. In NIL, a thin polymer layer on a substrate is patterned by means of compression molding of the polymer with a hard stamp at a temperature above the glass transition temperature of the polymer. After a residual layer removal step, the substrate consists of a polymer relief pattern with exposed and unexposed regions of the substrate. Subsequently, a SAM is formed on the exposed areas of the substrate. Furthermore, these substrates can be converted to truly chemically patterned substrates by removing the polymer template and covering the bare silicon oxide areas with SAMs of a different functionality. Both types of substrates are used to attach functionalized nanoparticles. Hexagonal close packing on mm-size features, and typical confined particle geometries on sub-mm features will be demonstrated in this work. It will be shown that this process is able of a resolution down to 60 nm for single particle-wide lines of functionalized nanoparticles topographically confined on 60 nm imprinted aminoalkyl SAM lines and of 300 nm on chemically confined substrates. 1P. Maury, M. Peter, V. Mahalingam, D. N. Reinhoudt, J. Huskens. Adv. Funct. Mat. 2005, 15, 451.

SESSION Ra13: Semiconductor Nanostructures II

Chair: Kohei Itoh
Wednesday Morning, November 30, 2005
Room 207 (Hynes)

10:30 AM *Ra13.1

Self-Assembly of Electrically Isolated Epitaxial Ge Quantum Dots on Ultrathin Silicon-on-Insulator (100). Eli Sutter, W. Ernst, Percy Zahl, Young-suk Choi and Peter Sutter; Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

Mainstream microelectronics has been based predominantly on bulk silicon substrates. Silicon-on-insulator (SOI), a composite material in which a thin monocrystalline Si 'template' is bonded to a conventional Si 'handle' wafer via a layer of amorphous SiO_2, has recently been developed into a viable substrate for very-large scale integrated circuits. As a result of these efforts, which were largely driven by the promise of substantial advantages of depleted SOI in high-speed and low-power applications, a first generation of state-of-the-art SOI-based microprocessors has become available commercially. The growth of heteroepitaxial materials on engineered composite substrates such as SOI opens a new route for controlling the structural and electronic properties of materials at the nanoscale. Lattice strain induced by Ge quantum dots grown coherently on SOI causes significant local distortion in the ultrathin Si template ($<$ 8 nm) and can be used as a tool for nanoscale band structure engineering of the Si substrate [1]. The Ge islands themselves form on SOI initially as huts and then transform into domes, similar to the sequence of epitaxially constrained shapes they assume on bulk Si (100). In the case of Ge growth on the ultrathin Si template, the transformation from huts to domes initiates the breakup of the template followed by nanostressor induced dewetting. We use a combination of atomic force microscopy, transmission electron microscopy, and in-situ low-energy electron microscopy to study the morphological evolution of the dewetting which in turn leads to the controlled formation of an array of free-standing Ge quantum dots. We identify the microscopic mechanisms underlying both the nanostressor induced dewetting and the spontaneous formation of the electrically isolated epitaxial Ge quantum dots. [1] P. Sutter, E. Sutter, P. Rugheimer, and M. G. Lagally, Surf. Sci. 532, 789 (2003).

11:00 AM Ra13.2

Self-assembled Nanoline Template for Growth of Nanoparticles and Nanowires on Si(001). James Hugh Gervase Owen[1,2] and Kazushi Miki[2]; [1]International Centre for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Long, straight Bi nanolines have been used as a 1D atomic-scale template for the deposition of metals on Si(001). Bi nanolines are ca. 1.5 nm wide, and up to 500 nm in length, limited only by the substrate terraces[1]. We describe the method for formation of these templates, demonstrate strongly preferential adsorption of several different metals onto the Bi nanoline templates, and show examples of both non-wetting and wetting behaviour, which produce nanoclusters and nanowires respectively. Deposition of noble metals such as Ag produces arrays of metal nanoclusters with size distributions sharply peaked at 0.7 nm, 1.1 nm and 1.4 nm, which correspond roughly to magic-cluster dimensions. Cluster formation suggests a weak interaction with the nanoline template. For Group III metals such as In, we form highly uniform nanowires with single-nm lateral dimensions, which have an epitaxial relationship with the underlying nanoline, indicating a strong template interaction. [1] J. H. G. Owen, K. Miki, H. Koh, H. W. Yeom, and D. R. Bowler, Phys. Rev. Lett. 88 (2002), 226104.

11:15 AM Ra13.3

Nucleation of Semiconductor Quantum Dots on Nanomesas: Role of Stressors and Early Stages of Capping Process. Cyril Meynier and Catherine Priester; ISEN, Epiphy, IEMN, Villeneuve D'Ascq, France.

The use of an array of nanomesas has proved to be an attractive way to obtain, for adequate design parameters of the mesas, the growth of one quantum dot per mesa. This has been recently investigated, for Ge deposited on an array of Si nanomesas, from both experimental [1] and theoretical [2] points of view. The first part of the work reported here focuses on mesas of the order of one hundred nm wide, obtained by classical lithography methods. Such InP mesas can include a stressor, either tensile (Ga rich InGaAs layer) or compressive (In rich InGaAs layer)which can modify InAs dots nucleation at the top of the mesa. By making use of continuous elasticity, and takin into account surface energy, some tendencies are investigated, in order to determine an optimal set of design parameters (thickness, location of the stressor, within a given panel of mesa sizes) for the best efficiency of the stressor. A very interesting result is that for too narrow mesa the elastic relaxation is so efficient that 3D boxes will never nucleate and InAs will keep covering the top of the mesa. For wider mesas transition to 3D growth mode on the top of the mesa will occur, but will be either advanced or delayed, depending on the type of the stressors. Either the stressor is compressive or tensile will also rule the place 3D island will preferentially nucleate (edges or center of the considered square nanomesa). Whereas the mesas studied in the first part are of the order of one hundred nm wide, the second part of the work reported here focuses on mesas smaller than a few tens of nanometers and result from the selective etching of a layer twist-bonded to its substrate. In this case the quantum dots one gets are square base pastills that cover the top of the mesa. We address here, from the theoretical point of view and by making use of an atomistic description, the question of capping such an array of nanodots: where will Si atoms preferentially deposit? We point out completely different behaviors for pure Si capping or SiGe capping. How long it tooks for recovering a flat surface stongly depends on Ge availibility during capping process. References [1] F. Leroy, J. Eymery, P Gentille, F. Fournel, Surf. Sci. 545 (2003) 211 [2] M. Bavencoffe, E. Houdard and C. Priester J. Growth 275 (2005)305

11:30 AM Ra13.4

MOCVD Growth of GaN and GaMnN Multifunctional Nanostructures. Shalini Gupta[1], Hun Kang[1], Martin Strassburg[1,2], Ali Asghar[1], Matthew Kane[1,3], William E. Fenwick[1], Nikolaus Dietz[2] and Ian T. Ferguson[1,3]; [1]Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia; [3]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Quantum dots (QDs) are known improve the efficiency and optical properties of opto- electronic devices as compared to two dimensional quantum wells in the active region. The formation of self-assembled GaN nanostructures on aluminum nitride (AlN) by MOCVD was explored to take advantage of QD structures in the UV spectral range. Further, this paper reports the first studies on the effect of in-situ activation in N2 atmosphere on MOCVD-grown GaN nanostructures. The introduction of silane and, for the first time, manganese as an antisurfactant was studied. Manganese is of great interest as it introduces ferromagnetic properties into the material, enabling the formation of multifunctional nanostructures. GaN nanostructures on AlN buffer layers were grown by MOCVD on sapphire substrates. The growth temperature and notably the V-III ratio were found to strongly influence the growth mode of the deposited GaN nanostructures. A low deposition temperature of 815C and an extreme V/III ratio of less than 20 were determined to favor nanostructure formation. An 'activation' step in N2 ambient was employed after GaN deposition in order to tailor the formation of nanostructures, as surface kinetics provides an avenue for controlling island growth. The strong impact of the activation temperature on the nanostructure density and dimensions is confirmed by nucleation studies applying temperatures ramps between 820 and 970C. The smallest island dimensions and highest island densities occurred at activation temperatures above 850C. Nanostructures with lateral dimensions of 40nm and a height of 2nm were obtained with a typical V/III ratio of 4.5 followed by an activation step. AFM images show a transition from 2D to 3D growth above an initial critical thickness of 2 monolayers (ML). Ripening of these structures was observed above a second critical thickness of 12ML. The density of the nanostructures is determined to be a function of the amount of deposited material. The above results depict Stranski-Krastanow like growth for these structures. The crystalline quality of the GaN/AlN nanostructures was confirmed by micro-Raman spectroscopy that showed the presence of the GaN A1(LO) mode despite the extremely metal-rich growth conditions at relatively low deposition temperatures. The intensities of the GaN-related Raman modes increase with deposition time. Initial nucleation studies on GaMnN grown on AlN epilayers were performed to achieve multifunctional nanostructures that combine the advantages of quantum dots and diluted magnetic semiconductors,. The AFM analysis revealed that Mn acts as an antisurfactant (similar to the behavior of Si) and eliminates the need for an annealing step at a deposition temperature of 815C. Activation temperatures above 880C contributed to ripening processes that lead to islands of infinite size reflected by increased island dimensions and smaller island densities.

11:45 AM Ra13.5

Self-Assembled GdSi$_2$ Nanostructures Grown on Si(001) Studied by TEM and STM. Gangfeng Ye[1], Martin A. Crimp[1] and Nogami Jun[2]; [1]Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan; [2]Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

Rare-earth (RE) metal silicides have attracted recent interest because they can form self-assembled nanowires in the initial stages of epitaxial growth on the Si(001) surface. In general, two classes of nanostructures are seen: monolayer high nanowires, and multiple atomic layer thick 3D islands. Some of the 3D islands have large aspect ratios that are usually in excess of 10:1 and can also be described as nanowires. Nanowire formation is due to an anisotropy in the lattice mismatch between the hexagonal form of the RE silicide and the substrate. Transmission electron microscopy (TEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM) are used to study the crystal structure and morphology of GdSi$_2$ 3D islands grown on Si(001). Cross-sectional TEM shows that both hexagonal and orthorhombic polymorphs of the silicide co-exist in these nanostructures. Moiré fringes observed in plan-view TEM shows that the morphology of the silicide islands is correlated with the crystal structure; the hexagonal phase forms islands with large aspect ratios (nanowires) while the orthorhombic phase forms islands with small aspect ratios. Nano-beam diffraction results support this observation. This behavior can be understood in terms of the difference between the lattice constants of the two silicide polymorphs. STM and AFM were used to study the morphology of the silicide nanostructures versus growth conditions. It was found that by adjusting the deposition conditions it was possible to control the ratio of nanowires to 3D islands, with nanowires becoming predominant at higher evaporation rates.

SESSION Rb13: Alternative Nanofabrication V

Chair: Cengiz S. Ozkan
Wednesday Morning, November 30, 2005
Room 208 (Hynes)

10:30 AM *Rb13.1

Soft Lithography and Nanofabrication. George Whitesides, Qiaobing Xu and Brian Mayers; Department of Chemistry, Harvard University, Cambridge, Massachusetts.

Soft lithography has provided a range of simple methods useful in fabricating small systems (for fluidic, optical, and electronic applications) with dimensions down to $\sim$ 1 micron; below this size, fabrication by soft lithography (and other lithographic techniques) becomes more complicated. This talk describes a series of techniques based on sectioning of polymers and formation of cracks in crystals that allow the formation of simple nanostructures. It thus extends soft lithography into new areas of nanofabrication.

11:00 AM Rb13.2

Synthesis and Characterization of Multifunctional Nanopatterned Surfaces Via Silica Imprinting. John D. Bass and Alexander Katz; Chemical Engineering, UC Berkeley, Berkeley, California.

A key capability for enabling several technologies and applications in the future is the nanoscale organization of two different chemical functional groups on a solid surface, such as silica. Covalent silica imprinting in principle offers a solution to this problem by using a molecular template for organizing chemical functional groups on silica surfaces, on length scales that are in general too small to achieve with conventional lithographic approaches ($<$ 2 nm). The imprinting process consists of immobilizing the imprint molecule, which consists of protected chemical functional groups, and subsequently deprotecting these groups after immobilization has been accomplished, thus leaving behind the desired chemical functional group organization on the surface. Although imprinting has been used for more than sixty years for the preparation of patterned surfaces, it has mainly been limited to organizing one type of functional group per site. We demonstrate the first covalent imprinting of two different types of functional groups per site, consisting of an amine and thiol spaced apart by approximately 1 nm, both of which are connected to the silica surface via a propyl tether, but are not connected to each other in any other fashion. This has been accomplished by developing an imprinting approach that relies on thermally labile protecting groups for the amine and thiol. We have successfully synthesized imprints containing a protected thiol-amine pair and have implemented them in both surface-functionalized and bulk imprinted silica synthetic approaches. The nanoscale organization in both surface-functionalized and bulk materials is compared by using a molecular probe that is able to covalently bind to the thiol-amine pairs and thereby produces a chromophore, which is highly specific for the imprinted organization. The results of our studies demonstrate the difficulty of achieving site isolation when using a surface-functionalized synthetic strategy, and the importance of a bulk silica synthesis strategy when imprinting silica with multiple different chemical functionalities. The resulting materials can be used as a versatile scaffold for selective nucleation and preparation of materials with higher levels of organization by utilizing orthogonal coupling strategies, and some of these are demonstrated for materials characterization purposes.

11:15 AM Rb13.3

Deposition of J-aggregate Thin Films via Stamping for Use in Optoelectronic Devices. M. Scott Bradley, Jonathan R. Tischler, Steven K. LaiHing and Vladimir Bulovic; Laboratory of Organic Optics and Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Thin film J-aggregates of cyanine dyes enable the observation of strong coupling between light and matter at room temperature, potentially allowing for the development of an entirely new class of optoelectronic devices [1]. Previously, J-aggregate deposition methods have required the exposure of a device in fabrication to the solvents of a J-aggregate solution, which can potentially damage other optically or electrically active materials and restrict the process steps involved in fabricating devices. In this work, we present a new stamping technique for depositing J-aggregate thin films that decouples the formation of J-aggregates from the placement of J-aggregate thin films into device structures. Combining research in polyelectrolyte layer-by-layer deposition of J-aggregates with stamping of polyelectrolyte thin films, we show how to form thin films of J-aggregates on a stamp and then dry-stamp those films into device structures. We show the optical and morphological properties of stamped J-aggregate films and calculate the optical constants of the films, which we use to determine the density of J-aggregated dye molecules in the final thin film. Additionally, we investigate device structures enabled by stamping of J-aggregate thin films, including J-aggregate organic light-emitting devices and patterned J-aggregate devices made via stamp pattern transfer. Lastly, we explore the extension of J-aggregate thin film stamping to other methods of depositing J-aggregate thin films, including Langmuir-Blodgett-type deposition methods. [1] Tischler *etal.*, Phys. Rev. Lett. (**2005**).

11:30 AM Rb13.4

Writing with Molecules: Supramolecular Nanolithography on Glass. Bart Jan Ravoo, Steffen Onclin, Alart Mulder, Jurriaan Huskens and David N. Reinhoudt; MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

Nanotechnology aspires to create functional materials with characteristic dimensions of the order 1-100 nm. One requirement to make nanotechnology work is to precisely position molecules and nanoparticles on surfaces, so that they may be addressed and used for bottom-up construction of nanoscale devices. Here we present the concept of a molecular printboard on glass. A molecular printboard is a monolayer of host molecules on a solid substrate on which guest molecules can be attached with control over position, binding strength, and binding dynamics. To this end, cyclodextrin molecules were immobilized on silicon wafers and on glass. Guest molecules (for example, adamantane derivatives) bind to these host surfaces through supramolecular, hydrophobic inclusion interaction. Multivalent interactions are exploited to tune the binding strength and dynamics of the guest molecules to the printboard and competition with host molecules in solution can be used to remove guest molecules from the printboard. Molecules can be positioned onto the printboard using supramolecular microcontact printing and supramolecular dip pen nanolithography due to the specific interaction between the ink (guest molecules) and the substrate (host surface). In this way, nanoscale patterns can be written and erased on the printboard. The potential of the molecular printboard will be illustrated with recent examples of (1) nanoscale fluorescent patterns printed, written and erased on glass surfaces, and (2) microscale patterns of dendrimers that function as molecular boxes that can be filled, emptied and refilled. References: Onclin, S. et al Langmuir 2004, 20, 5460-5466. Mulder, A. et al Small 2005, 1, 242-253.

11:45 AM Rb13.5

Capillary force lithography for fabrication of functional polymer templates. Christiaan M. Bruinink[1], M. Peter[1], P. A. Maury[1], M. de Boer[2], L. Kuipers[3], J. Huskens[1] and D. N. Reinhoudt[1]; [1]Supramolecular Chemistry and Technology (SMCT), MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; [2]Transducers Science and Technology (TST), MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; [3]FOM Institute for Atomic and Molecular Physics (AMOLF), Amsterdam, Netherlands.

The development of low-cost, high-throughput lithographic techniques for the fabrication of high-resolution patterns has taken a very dominant position in nanofabrication during the last decade. Although state-of-the-art lithographic techniques will remain the main technology for the semiconductor industry, several non-photolithographic techniques e.g. soft lithography[1] and nanoimprint lithography (NIL)[2] have made enormous progression in several areas of exploratory and scientific research (in terms of sub-100 nm resolution, reproducibility, and uniformity over large areas). In this contribution we illustrate the use of capillary force lithography (CFL)[3] for the fabrication of functional, high-resolution polymer templates. CFL is the patterning of polymer layers at a temperature above the glass transition temperature by capillary forces within the confinement of an elastomeric stamp. At thin polymer film thicknesses, i.e. with respect to the dimensions of the elastomeric stamp, the polymer structures only outline the feature edges of the stamp resulting in high-resolution polymer templates. By incorporation of different types of polymers and substrates in this general CFL procedure, the physical properties of these templates were modified in order to meet the diverging requirements for application as (i) masters for soft lithography[4], (ii) molds for NIL,[5] and (iii) etch masks for wet etching of metals.[5] Our template fabrication results demonstrate that CFL is a convenient and inexpensive technique for the fabrication of high-resolution polymer templates with high fidelity and excellent uniformity. Gold patterns on silicon of sub-150 nm resolution were fabricated by subsequent use of the polymer templates in any of the three pattern transfer techniques. The diversity of these techniques to replicate the template structure as well as the excellent feature definition of the resulting metal patterns at the 100 nm scale demonstrate the potential of CFL templates as tools for high-resolution lithography. Keywords: soft lithography, capillary force lithography, nanoimprint lithography, polymer templates, high-resolution pattern fabrication [1] Y. Xia, G. M. Whitesides, Angew. Chem. Int. Ed. 1998, 37, 550. [2] S. Y. Chou, P. R. Krauss, P. J. Renstrom, Science 1996, 272, 85. [3] K. Y. Suh, Y. S. Kim, H. H. Lee, Adv. Mater. 2001, 13, 1386. [4] C. M. Bruinink, M. Péter, M. de Boer, L. Kuipers, J. Huskens, D. N. Reinhoudt, Adv. Mater. 2004, 16, 1086. [5] C. M. Bruinink, M. Péter, P. A. Maury, M. de Boer, L. Kuipers, J. Huskens, D. N. Reinhoudt, Adv. Funct. Mater. 2005, submitted.

SESSION Ra14: Molecular Electronics I
Chair: Fabio Cicoira
Wednesday Afternoon, November 30, 2005
Room 207 (Hynes)

1:30 PM *Ra14.1

Forces, Current, Molecules. Peter H. Grutter, Physics, McGill University, Montreal, Quebec, Canada.

One of the crucial factors in molecular electronics is to understand the structure-property relationship: how does the structure of the molecule and the contact electrodes relate to the measured electronic properties? In this talk I will present some of our efforts to control, characterize and understand the details at the atomic scale of systems interesting from a molecular electronics point of view. In the first part, I will present some recent results describing the details of atomically defined contact formation using a combined ultrahigh vacuum scanning tunneling, atomic force and field ion microscope to study the a W tip-Au(111) sample interactions in the regimes from weak coupling to strong interaction and simultaneously measure current changes from picoamperes to microamperes. Close correlation between conductance and interaction forces in a STM configuration was observed. In particular, the electrical and mechanical points of contact are determined based on the observed barrier collapse and adhesive bond formation, respectively. These points of contact, as defined by force and current measurements, coincide within measurement error.

Ab initio calculations of the current as a function of distance in the tunneling regime is in quantitative agreement with experimental results. In the second part I will describe various experiments under way in our lab to construct an atomically defined three terminal device on an insulating substrate. We use UHV AFM to investigate nucleation and growth of different molecules (such as C60 and PTCDA) and metals (such as Au, Pd and Ta) as well as several patterning approaches spanning millimeter to nanometer length scales as first steps towards this goal. A major problem is the large diffusion lengths (of several 100 microns) observed at room temperature on insulating substrates. We find that molecules however readily attach to metal islands predeposited. Furthermore, we are able to confine and control the number of molecules to a region only a few nanometer in size by creating pits on the insulating substrate KBr(001) surface. Finally, we learn from our first molecular manipulation experiments that not every desired structural pattern can be achieved. In particular, the line tension of a 2D C60 island allows only shapes minimizing this line tension to be stable and thus obesrvable.

2:00 PM Ra14.2
SWNT-PNA-SWNT Conjugates: Synthesis, Characterization and Modeling. Krishna Veer Singh[1], Xu Wang[1], Rajeev R. Pandey[2], Roger Lake[2], Cengiz Ozkan[3] and Mihrimah Ozkan[2]; [1]Chemical & Environmental Engineering, UC Riverside, Riverside, California; [2]Electrical Engineering, UC Riverside, Riverside, California; [3]Mechanical Engineering, UC Riverside, Riverside, California.

Imparting molecular recognition to carbon nanotubes (CNTs) by conjugating them with bio-molecules has been an area of great interest as the resulting highly functionalized CNT-bioconjugates find their applications in various fields like molecular level electronics, pharmaceuticals, drug delivery, novel materials and many others. In this work we demonstrate the synthesis of functionally engineered single walled carbon nanotubes (SWNTs)-peptide nucleic acid (PNA) conjugates especially for nanoelectronic applications. Here we exploited the exceptional structural and chemical advantages of PNA (an artificial analogue of DNA) to join SWNTs ropes. SWNT-PNA-SWNT conjugates were synthesized using carbodiimide coupling chemistry and characterized by host of techniques like scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The results from different techniques confirm the formation of these conjugates. To further study these conjugates for electron transfer, models of SWNT-PNA interface were simulated using the PM3 semi-empirical package in Gaussian03 RevB.03 program suite. Simulations show that the highest occupied molecular orbital lies on the glutamate linker and indicate that this interface state will align closely to the valence band of the extended SWNT facilitating charge transfer. The unique electrical and structural properties of these conjugates make them a potential candidate for application in CNT based nanodevices.

2:15 PM Ra14.3
Multi-valued analog information storage using self-assembled nanoparticle films. Yoshinori Suganuma and Al-Amin Dhirani; Chemistry, University of Toronto, Toronto, Ontario, Canada.

Digital computers use binary states, typically represented by 0 and 5 V, to store and process information at all stages of a calculation. If more states (ideally a continuum) were available in between, density of information could be dramatically increased. Here we show that self-assembled nanoparticle films can feature such continuous state or analog information storage. Nanoparticle films were prepared on gate oxides by alternate immersion in solutions of gold nanoparticle and dithiol linker molecules. These films afford microlithography-free fabrication bridging nanometer to micrometer length scales as well as a layer-by-layer assembly yielding three-dimensional functional structures. Information provided by an arbitrary gate voltage was 'written' by trapping charges in local, gate-modified potentials when films were cooled below 175 K. The information was 'read' using the film's built-in ability to sense charge via Coulomb blockade. Application of a time-dependent, multi-step writing gate voltage generates conductance maps corresponding to multi-valued analog information. As a proof of concept, we exploited this technique to store 'UT' in Morse code.

SESSION Rb14: Nanowires V
Chair: Mihri Ozkan
Wednesday Afternoon, November 30, 2005
Room 208 (Hynes)

1:45 PM Rb14.1
Homo-Epitaxial Growth of ZnS Cross Nanowires Array and Its Photoluminescence Properties. Yang Jiang[1,2], Jiansheng Jie[1], Wenjun Zhang[1] and Shout-Tong Lee[1]; [1]Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, Hong Kong; [2]School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui, China.

Homo- or hetro- pitaxial growth of semiconductor naowires, quantum wells, dots on silicon wafer has emerged as potential basis of a large part of the active devices in modern optoelectronic information sensing and communication systems. Herein, we report a novel ZnS cross nanowires array homo-epitaxially grown on micro-scale ZnS single crystal, and present a though analysis of their morphology, characteristics and photoluminescence. The single crystal ZnS used as epitaxial substrate was obtained via hydrogen-assisted thermal evaporating ZnS powder, which have [120] growth direction, (-2 1 0) top surface and (001) side surface. The epitaxial ZnS cross nanowires array was grown on the surface of the gold coated single crystal substrate at lower temperature from tens minutes to one hour in the same way. On the top surface, the ZnS nanowires grow along [210] and [1-1 0] directions, one of <210> group, respectively, construct the cross nanowires array with 60 degree respect to each other and the epitaxial substrate (-2 1 0) surface. As for the side surface, the ZnS nanowires grow vertically to the side surface, and produce the nanowires array with [001] growth direction. Photoluminescence (PL) measurements of the cross nanowires array were obtained using the 4th harmonic of a Nd:YAG laser (266nm) as an excitation source. The results show lasing at band gap emission of 337nm and defects emission of about 540nm of Wurtzite ZnS.

Rb14.2
Transferred to Ra16.59/Rb16.59

2:00 PM Rb14.3
Growth of Epitaxial Inas Nanowires in a Simple Closed System. Hyun D. Park[1], Sharka M. Prokes[2] and Robert C. Cammarata[1]; [1]Materials Science & Engineering, Johns Hopkins University, Baltimore, Maryland; [2]US Naval Research Lab, Washington, District of Columbia.

InAs is a material with a high saturation velocity and an electron surface accumulation layer. Due to these properties, InAs nanowires would make an ideal electronic material for high performance large area TFTs on flexible substrates. Several methods of InAs nanowire and whisker growth have been reported previously, including metalorganic vapor phase epitaxy (MOVPE), chemical beam epitaxy (CBE), laser-assisted catalytic growth (LCG) and a vapor method using In metal and a GaAs substrate, with a growth time of 36 hours. We report on a very simple and inexpensive method to grow InAs nanowires epitaxially on a InAs(111) substrate. Our method, which utilizes the temperature gradient that exists inside the furnace, is comprised of evaporation inside the sealed quartz tube using bare InAs substrate as a source and a gold-colloid coated InAs substrate. This growth technique results in high quality, stoichiometric InAs wires, and there is no need to prefabricate complex target materials, use toxic gases or solid As sources, nor subject the sample to lengthy growth times. A similar growth process can also be used to grow stoichiometric InAs nanowire networks on non-crystalline, large area substrates.

2:15 PM Rb14.4
SiO_2 Nanowires with Embedded Au/Si Nanoparticle Chains. Florian M. Kolb, Andreas Berger, Herbert Hofmeister, Eckhard Pippel, Margit Zacharias and Ulrich Goesele; MPI of Microstructure Physics, Halle (Saale), Germany.

Silicon nanowires are potential building blocks for nanotechnology applications. In order to successfully utilize the nanowires, all aspects of nanowire growth need to be fully understood. During the growth of silicon nanowires by combining SiO evaporation with the VLS mechanism [1] on gold-coated silicon substrates, frequently amorphous nanowires with chains of embedded nanoparticles are observed. Using energy-dispersive X-ray spectroscopy (EDXS), electron energy-loss spectroscopy (EELS) and high-resolution transmission electron microscopy (HRTEM) we demonstrate that our nanowires consist of pure SiO_2 with embedded Au/Si nanoparticles. Experimental results suggest that oxygen plays a vital role in the formation of nanoparticle chains. Based on the SiO-VLS mechanism we propose a model for the formation mechanism of this special nanowire morphology, where the nanoparticles originate from the Au/Si alloy droplet on the nanowire tip. Based on the experimental results and the proposed model we investigate how to influence the formation of the nanoparticle chains and discuss their possible applications. [1] F. M. Kolb, H. Hofmeister, R. Scholz, M. Zacharias, U. Gösele, D. D. Ma, S.-T. Lee, J. Electrochem. Soc. **151** (7) G472 (2004).

SESSION Ra15: Molecular Electronics II
Chair: Peter Grutter
Wednesday Afternoon, November 30, 2005
Room 207 (Hynes)

3:30 PM *Ra15.1
Development of femtosecond time-resolved scanning tunneling microscopy for nanoscale science and technology. Hidemi Shigekawa, Institute of Applied Physics, CREST, 21st COE, University of Tsukuba, Tsukuba, Japan.

Smaller and faster are the key words in the progress of current nanoscience and technology. Thus, a method of exploring the ultrafast transient dynamics of the local quantum functions in organized small structures is eagerly desired. Ultrashort optical pulse technology has allowed us to observe transient phenomena in the femtosecond range, which, however, has the drawback of a relatively low spatial resolution due to the electromagnetic wavelength used. In contrast, scanning tunneling microscopy and its related techniques, although having a time resolution limited by the circuit bandwidth (~100kHz), enable us to observe spatial dynamics at the atomic level in real space. Our purpose is to combine these two techniques to achieve a new technology which will advance the pursuit of future nanoscalse scientific research in terms of the ultimate temporal and spatial resolutions. We proposed a promising new design for achieving ultimate spatial and temporal resolution, by combining a short-pulse laser and STM. Using this method, time-resolved tunneling current measurement in the subpicosecond range was successfully demonstrated. Namely, shaken-pulse-pair-excited STM (SPPX-STM) satisfies the requirements for exploring the ultrafast dynamics of the local quantum functions occurring in organized small structures. We hope this new technology can advance the development of future research on the nanoscale. (http://dora.ims.tsukuba.ac.jp/)

4:00 PM Ra15.2
Optoelectronic properties of sublimed and solution processed thin films of dithienothiophene oligomers. Fabio Cicoira[1], Clara Santato[2], Manuela Melucci[1], Laura Favaretto[1], Massimo Gazzano[1] and Giovanna Barbarella[1]; [1]Istituto per la Sintesi Organica e la Fotoreattivita, Consiglio Nazionale delle Ricerche, Bologna, Italy; [2]Istituto per lo Studio dei Materiali Nanosrutturati, Consiglio Nazionale delle Ricerche, Bologna, Italy.

We have successfully employed the oligomer 2,6-Bis-(5'-hexyl-[2,2']bithiophenyl-5-yl)-3,5-dimethyl-dithieno[3,2-b;2',3'-d]thiophene (DTT7Me) to fabricate light-emitting field-effect transistors based on vacuum evaporated and drop cast active layers. Atomic Force Microscopy images of films sublimed on SiO2 show their good adhesion on the substrate. With a deposition flux of 0.4nm/s, continuous films are already formed at a nominal thickness of 6nm. X-ray diffraction reveals that films are polycrystalline. Organic Field-Effect Transistors (OFETs), fabricated on bottom-contact SiO2/n-Si substrates, work in p-type accumulation mode. OFETs based on sublimed active layers show hole FET mobility of 0.01-0.02 cm2/Vs and threshold voltage of ca. 10V. Optoelectronic measurements reveal that DTT7Me films are able to generate electroluminescence in transistor configuration. Similar results are obtained depositing the active layer by drop casting. Our results suggest that dithienothiophene derivatives are very promising candidates for all-plastic optoelectronic applications.

4:15 PM Ra15.3
Field Effect Transistors based on Self-Organised Molecular Nano-stripes. Massimiliano Cavallini[1] and Fabio Biscarini[1]; [1]ISMN, CNR, Bologna, Italy; [2]ISMN Bologna, CNR, Bologna, Italy.

We present an application of combined Micromolding in Capillaries[1] (MIMIC) and Lithographically-Controlled Wetting[2] (LCW) for the fabrication of connected nanostructures of organic semiconductor in between electrodes of field effect transistors (FET) and on to flat surfaces. We demonstrate FET where current flows through an array of stripes, whose height is two-monolayers and width 180 nm, made of well-ordered semiconductor molecules, viz. oligofluorene. The stripes are formed across the channel of the transistor by self-organisation driven of the molecules in a solution confined under the protrusions of a stamp by the capillary forces. Each stripe is formed by two / three coherent domains and it is electrically connected to the electrodes. The charge mobility in the stripes is at least two orders of magnitude larger than that measured on solution-cast thin film devices, and one order of magnitude larger than that measured in high-vacuum-sublimed thin films. Acknowledgements This work was supported by the European Commission, under project NMP-IP NAIMO and the European Science Foundation under Eurocore SONS programme FUNSMARTS. References [1] E. Kim, G.M. Whitesides Nature 376, 581-584, (1995). [2] M. Cavallini, F. Biscarini, NanoLetters 3(9), 1269-1271, (2003)

4:30 PM Ra15.4
Positioning Molecular Nanostructures between Microfabricated Electrodes. Sarbajit Banerjee, James H. Dickerson, Mark L. Bushey, Thuc-Quyen Nguyen, Louis Brus, Colin Nuckolls and Irving P. Herman; Nanoscale Science and Engineering Center, Columbia University, New York, New York.

Controllably positioning low-dimensional nanostructures in prefabricated circuitry is essential for evaluating their suitability in molecular electronics. Here, we present a method to grow stacks of hexa-substituted arenes between microfabricated electrodes by applying a voltage across the electrodes during drop casting of a solution of these arenes. Growing molecular nanostructures in nanogaps requires the optimization of conditions including molecule concentration, solvent, applied voltage, gap size, height of electrodes, and the resistance of the load resistor. The molecular nanostructures are seen to grow via an electrocrystallization mechanism in which some current flow is required, rather than through pure electric field directed assembly of stacks or individual molecules. This work was supported primarily by the NSEC Program of the National Science Foundation under Award Number CHE-0117752 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

4:45 PM Ra15.5
Site-Selective Positioning of Nanoparticles on DNA Templates for Nanoelectronics. Gary Braun[1], Michael Diechtierow[3], D. K. Wood[2], Stephanie Wilkinson[1], Katsuhiko Inagaki[4], Elmar Weinhold[3], A. N. Cleland[2] and Norbert Reich[1]; [1]Department of Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, California; [2]Department of Physics, UC Santa Barbara, Santa Barbara, California; [3]Department for Organic Chemistry, University of Heidelberg, Aachen, Germany; [4]Department of Applied Physics, Hokkaido University, Sapporo, Japan.

The ability to position nanoparticles and semiconductor nanocrystals onto molecular scaffolds with nanometer control has potential applications for biosensors, optical waveguides, molecular electronics, and studies of surface enhanced Raman spectroscopy (SERS). We are developing approaches for site-specific placement of NP at predetermined positions within thousands of base pairs. Our approach utilizes bacterial DNA methyltransferases, which normally methylate a specific base pair within a recognition sequence, however in this application transfer a biotin by way of a modified enzyme substrate. Recently we have shown by AFM that biotinylated gold nanoparticles can be directed by streptavidin to unique positions designed into 300-1000nm DNA. Using these biotin sites we have also constructed three and four-way DNA junctions with nanoparticles positioned at the central site. This capability is combined with methodologies for nonspecific DNA metallization employed on electrode-patterned Si/SiO2 surfaces for electronic characterization of tunneling junctions, and we are currently creating repeating nanomaterial patterns on these templates for energy transfer and SERS studies.

SESSION Rb15: Nanowires VI
Chair: Li Chyong Chen
Wednesday Afternoon, November 30, 2005
Room 208 (Hynes)

3:30 PM Rb15.1
Nanoparticle-Nanowire Assemblies based on Complementary Protein Interactions. Nicholas A. Kotov[1], Jaebeom Lee[1] and Alexander Govorov[2]; [1]Chemical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Physics, Ohio State University, Athens, Ohio.

Nanoparticle/nanowire assemblies with a degree of radial organization were prepared around luminescent semiconducting CdTe nanowires using bioconjugation with streptavidin and D-biotin linkers. Red-emitting nanowires (diameter 6.62 nm, length 512 nm) and green-emitting nanoparticles (diameter 3.2 nm) were surface-modified with biotin, while orange-emitting nanoparticle (diameter 4.1 nm) were decorated with streptavidin. CdTe nanocrystals produced two fuzzy layers around the nanowires in which the diameter of CdTe nanoparticles decreased with the distance from the nanowire axis. F?rster resonance energy transfer (FRET) from the outside layer of nanoparticles to the central nanowire was observed for NW conjugated with 4.1 nm CdTe. Addition of 3.2 nm CdTe resulted in a red-orange-green optical progression with bandgaps of CdTe decreasing toward the axis of the superstructure. In this case, four-fold luminescence enhancement of the nanowire luminescence was observed and was attributed to multi-step FRET. This observation indicated the accumulation of photogenerated excitons in the cascade terminal. A simple model of multi-conjugated superstructure with cascade energy transfer is developed and used to describe and understand the experimental data. From the comparison of theory and experiment, we obtained the rates for exciton transfer between the building blocks separated by the very common SA-B linkers. They were determined to be 1/12 s-1 and 1/16 s-1 for the transfer from 3.2 nm to 4.1 nm nanoparticles and from 4.1 nm nanoparticles to 6.6 nm CdTe nanowires, respectively. Experimental data and theoretical model suggest the possibility of utilization of the prepared superstructures with radial symmetry in several classes of optoelectronic devices. They can also be a convenient model object for the investigation of methods of energy funneling in nanoscale assemblies.

3:45 PM Rb15.2
Metal Oxide Nanowires: Growth, Applications and Devices. Sanjay Mathur, Sven Barth, Thomas Ruegamer and Hao Shen; Leibniz Institute of New Materials, Saarbruecken, Germany.

One dimensional (1D) inorganic materials are gaining increasing attention because of their unique structural features and interesting functional properties. Given the structural stability, they show promising application potential in vacuum as well as in oxidizing atmospheres, which provides them a competitive edge over their carbon-based counterparts. A number of synthetic procedures have been developed and demonstrated for 1D nanostructures that have led to intriguing morphological variations (wires, tubes, belts, rods, etc.), however the control over radial and axial dimensions remains a continuing challenge. In addition, the choice of material is rather limited. We have developed a generic approach for the size-selective and site-specific growth of nanowires by combining vapor-liquid-solid (VLS) approach with the chemical influence of molecular precursors. The synthesis of nanowires (NWs) is based on the decomposition of discrete molecular species in the liquefied metal (Au, Ag, Ni, Sn), which allows growing nanowires at low-temperatures with a precise control over their diameter and length. The precursor chemistry can be tuned to facilitate the stripping of organic ligands and to achieve complete decomposition that is critical for maintaining the gas phase super-saturation necessary for 1D growth. High-yield synthesis of NWs of tin, vanadium and iron oxides was performed by the chemical vapor deposition of appropriate metal-organic precursors. Axial and radial dimensions of the NWs were varied in the ranges 50-1500 nm and 25-40 um, respectively by adjusting the precursor feedstock, deposition temperature, and catalyst size. We have investigated the device potential of these building blocks as photo- and gas sensors. For instance, illuminating tin oxide NWs with UV photons triggers interesting photo-conductance, which can be modulated by tuning the wire diameter as demonstrated for samples possessing radial dimensions in the range 50-1000 nm. The stable photo-response over several on-off cycles demonstrated their potential for applications in UV detectors or optical switches, where the NWs can act as resistive elements whose conductance changes by charge-transfer processes. In addition, tin oxide NWs were grown on sensor platforms and their response towards CO was compared with nanostructured tin oxide films. This talk will address the generic feature of our approach for the synthesis of oxide nanowires of various compositions and present the results obtained on device applications.

4:00 PM Rb15.3
Fabrication of Novel Semiconducting Nanowire Heterostructures. Jun-Qing Hu, Yoshio Bando, Jin-Hua Zhan and Dmitri Golberg; International Center for Young Scientists, National Institute for Materials Science, Tsukuba, Japan.

More recently, one-dimensional (1D) nanostructures having heterojunctions are of particular interest with respect to potential applications in nanoelectronics and nanophotonics.[1] If one-dimensional heterostructures with a well-defined compositional profile along the wire radial or axial direction can be realized within semiconductor nanowires, new nano-electronic devices, such as nano-waveguide and nano-capcipator, might be obtained. Here, we report the novel semiconducting nanowire heterostructures: (1) Si/ZnS and Si/ZnSe side-to-side biaxial nanowires and ZnS/Si/ZnS sandwich-like triaxial nanowires, [2], (2) Ga-ZnS metal-semiconductor nanowire heterojunctions uniformly sheathed with very thin silica nanotubes,[3] and (3) hierarchical heterostructures composed of Si core microwires and SiO2 nanowires covering them and thus forming multiple junctions to the cores.[4] The 1D semiconducting nanowire heterostructures are interesting objects with respect to physical properties and applications in the blocks of advanced semiconducting nanodevices. [1] S. M. Sze, Physics of Semiconductor Devices (Wiley-Interscience, New York, 1981). [2] J. Q. Hu, et al., J. Am. Chem. Soc. (2003) 125, 11306. [3] J. Q. Hu, et al., Adv. Mater. (2005) in press. [4] J. Q. Hu, et al., Adv. Mater. (2005) 17, 971

4:15 PM Rb15.4
Self-catalyzed Growth of Ge and Core-Shell Ge/Si-C-N Nanowires. Sanjay Mathur, Hao Shen, Thomas Ruegamer, Vladimir Sivakov and Sven Barth; Leibniz Institute of New Materials, Saarbruecken, Germany.

Semiconductor materials (Ge, Si) in confined 1D (nano)geometries display interesting electronic and optical properties due to the partial quantization of electronic states, which has led to the proposed use of Ge nanowires as building elements in future nanoscale electronic devices, in particular due to the high carrier mobilities. However, implementation of bottom-up concepts for the fabrication of functional devices demands synthetic methods offering precise control over the size and composition of nanowires. In addition, means for the chemical passivation of nanowires surface are currently required to provide them the necessary insulation. We have performed catalyst-free and high yield synthesis of single crystalline Ge and Ge/Si-C-N core-shell nanowires by employing thermally labile molecular precursors. The chemical vapor deposition (CVD) of precursor [Ge(C5H5)2] with weak Ge-C interactions produced Ge nanowires at extremely low temperatures (275 degree). Whereas the decomposition of [Ge{N(SiMe3)2}2] resulted in core-shell morphology in which single crystalline Ge core is wrapped with a Si-C-N amorphous overlayer. The nanowires could be grown on both single and polycrystalline substrates without performing any surface treatment or application of catalysts. In contrary to the popular VLS technique, nanowires in our case grow through an auto-catalytic mechanism, which is initiated by a defect-assisted diffusion of precursor species and tendency for a 3D growth. The growth model was supported by following experiments: (i) preferable growth on artificial defects created by nano-indenting a sapphire substrate and (ii) cross-sectional HR-TEM of a single nanowire to reveal the nucleation stages of nanowires on the substrate. The microstructure, morphology and chemical composition of pure Ge and Ge/Si-C-N core-shell nanostructures were characterized by XRD, SEM, TEM and XPS analyses. The EDX line scan on Ge/Si-C-N system, revealed a Ge-enriched crystalline core whereas Si was locally distributed in the shell. A comparison of Si 2p binding energy proved that Si exists in the Si-C-N composition and not in the elemental form. In comparison to bulk Ge ($\sim$ 300 cm-1), the micro-Raman spectra of both systems revealed a low field shift (< 300 cm-1) which excluded the possible formation of GeSi alloy in the later case.

4:30 PM Rb15.5
Growth control and self-assembly of ZnO nanowires using sol-gel technique. Mezy Aude[1,2,3], Suwanboon Sumetha[1], Ravot Didier[1], Tedenac Jean-Claude[1], Gerardin Corine[2], Tichit Didier[2], Bretagnon Thierry[3] and Lefebvre Pierre[3]; [1]Univ. Montpellier 2, LPMC-UMR CNRS 5617, Montpellier, France; [2]ENSCM, LMC3O-UMR CNRS 5618, Montpellier, France; [3]Univ. Montpellier 2, GES-UMR CNRS 5650, Montpellier, France.

Zinc Oxide is a II-VI semiconductor with an hexagonal wurtzite crystal structure, which presents a direct wide band-gap of 3.37 eV at room temperature and a large exciton binding energy of $\sim$ 60 meV. ZnO exhibits a large variety of nanoscale behaviours among all materials, both in terms of structural and physical properties. Much attention has been paid to nanostructured ZnO materials, due to their potential use for electronic, photonic, catalytic, sensoring, etc applications. Among semiconductors having a low dimensionality (1D), ZnO nanowires are of special interest for short wavelength optoelectronic nanodevices having a high efficiency because of their large excitonic binding energy and high mechanical and thermal stabilities. Due to their physical and chemical properties, ZnO nanowires have a great commercial stake. Many methods have been employed for the growth of ZnO nanomaterials, such as sputtering, chemical vapour deposition, molecular beam epitaxy, metal-organic chemical vapour deposition, which greatly improve the crystalline quality, etc. However, low cost and simplicity of the synthesis processes are required for commercial applications. The wet chemical synthesis route seems to meet these requirements, enabling the preparation of high crystal quality and proper growth orientation of ZnO nanowires. Seeded growth process involving a low temperature solution allows us to prepare mono dispersed ZnO nanowires of high quality, which is useful for the study of physical (optical, electrical, etc) properties of isolated ZnO nanowires. Control of the ZnO size, morphology, dimensionality, and self-assembly is a very important stake, due to their tight influence on ZnO properties. Efficient control of both nanostructure dimensionality and assembly is obtained by adding appropriate polymers at different step of the growth process. In the future, this preliminary work could lead to coax uniform nanoparticles associated for the formation of 3D supra-crystals. Furthermore, functionalization of the substrate seems to be very promising for forming well aligned and uniformly dispersed ZnO nanowires after a sol-gel growth step. Thus, the present method provides a convenient route to obtain high quality and low cost aligned arrays of ZnO nanowires with lasing properties at room temperature.

4:45 PM Rb15.6
LaB6 nanowires and their field emission properties. Han Zhang[1], Qi Zhang[2], Jie Tang[3,2], Gong-Pu Zhao[2], Guang Yang[2], Jian Zhang[2], Otto Zhou[1,2] and Lu-Chang Qin[1,2]; [1]Curriculum of Applied and Materials Sciences, University of North Carolina at

Chapel Hill, Chapel Hill, North Carolina; [2]Dept. Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; [3]National Institute for Materials Science, Tsukuba, Japan.

Lanthanum hexaboride (LaB6) has a boron octahedron based stable 3-D network embedded with La atoms. This unique arrangement allows a combination of properties including low work function, low resistivity, low volatility at high temperature, high melting point and high chemical resistance. They have been proved to be and utilized as the best thermionic electron emission materials for the past 50 years. On the other hand, field induced electron emission can offer a brightness 100 times higher than the thermionic electron source. The two factors that enable high field emission density at low applied voltages are (a) low work function of the emitter material and (b) sharpness of the emitter tip. We have developed and applied a chemical vapor deposition method to synthesize single-crystalline LaB6 nanowires. The crystallographic orientation of the grown nanowires can be controlled by the catalysts used in synthesis and their typical diameter is ranged from below 20 nm to over 100 nm. The nanowires' tip is either hemispherical or flat top with rectangular cross-section depending on the catalyst being utilized. Field emission properties have also been measured from the single nanowire emitters made of the nanowires and results will be presented and discussed in connection with applications as point electron sources used in high performance electron optical instruments such as transmission electron microscopes and scanning transmission electron microscopes.

MEDAL AWARD
TALK PRESENTATION

Wednesday Evening, November 30, 2005
5:05 PM
Room 210 (Hynes)

Inorganic Nanotubes and Inorganic Fullerene-Like Materials–From Concept to Applications. Reshef Tenne, Weizmann Institute, Israel.

"For realizing that nanoclusters of layered compound materials (e.g., MoS2, WS2) can be made to fold into hollow cage structures, in analogy to graphitic carbon; these structures, known as 'inorganic fullerenes,' constitute a materials class with exciting new properties" Inorganic Nanotubes and Inorganic Fullerene-Like Materials–From Concept to Applications

In 1992, we proposed that nanoparticles of layered compounds will be unstable against folding, and close into fullerene-like structures and nanotubes (IF). Initially this hypothesis was realized in WS2, MoS2 and the respective diselenides. Subsequently, nanotubes and fullerene-like structures were prepared from numerous compounds with layered, and recently, also non-layered, structure by various groups. Much progress has been achieved in the synthesis of inorganic nanotubes and fullerene-like nanoparticles of WS2 and MoS2, as well as many other metal dichalcogenides over the last few years. Synthetic methods for the production of multiwall WS2 nanotubes by sulfidizing WO3 nanoparticles have been described, and further progress is under way. A fluidized-bed reactor for the synthesis of up to 100 g/day of fullerene-like WS2 nanoparticles has been established in our lab, and the scaling-up of the synthesis to 100 kg/day and beyond is under way. The detailed mechanisms for the synthesis of fullerene-like WS2 and MoS2 nanoparticles and nanotubes of these compounds have been elucidated.

Substantial progress has been accomplished in the use of such nanoparticles for tribological applications, and lately as nanocomposites, e.g., impact-resilient materials for self protection. Numerous testing programs, undertaken jointly with different laboratories and major industrial partners have clearly indicated the usefulness of the fullerene-like WS2 (MoS2) as solid lubricants in various products. These tests indicated that IF-MoS2 and IF-WS2 are heading for large-scale applications in the automotive, machining, aerospace, electronics, medical, and numerous other industries. This technology was licensed to the company NanoMaterials, which is currently involved in many collaborative development programs.

Novel applications of inorganic nanotubes and fullerene-like nanoparticles in the fields of catalysis, microelectronics, Li rechargeable batteries, medicine, and optoelectronics will be presented.

SESSION Ra16/Rb16: Poster Session III
Chair: Cengiz S. Ozkan
Wednesday Evening, November 30, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra16.1/Rb16.1

Rolling behavior of a elastic micro cylinder analyzed by finite element method for micro-manipulation. Toshihiro Ochiai[1], Shigeki Saito[1] and Kunio Takahashi[2]; [1]Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, Tokyo, Japan; [2]Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Recently, micro-manipulation techniques such as mechanical micro-manipulation by a single probe are required for assembly of micro-electro-mechanical systems and highly functional micro devices. Mechanical micro-manipulation is often used to pick and place a micro-object by mechanical interaction between the probe and the micro-object. The micro-object, however, adheres to the probe, because the effect of adhesional force becomes dominant as the size of the object decreases. Therefore, to achieve high precision and repeatability in micro-manipulation, it is necessary to analyze the mechanics of the micro-object, especially the rolling behavior of the micro-object, which has not been well-known to date. In this study, we investigate the rolling resistance of an elastic micro-cylinder in the adhesive contact with a rigid surface. We estimate the total energy of this system as a numerical function of a contact area between the elastic micro-cylinder and the rigid surface when an external moment is applied to rotate the elastic micro-cylinder. The total energy is defined as the sum of three terms: the elastic energy stored in the elastic micro cylinder, the interfacial energy within the contact area, and the mechanical potential energy of the applied external moment. The interfacial energy is obtained from multiplication of a work of adhesion and the contact area; the elastic energy and the mechanical potential energy are obtained numerically by finite element method. To simplify the problem, we adopt the plane strain assumption. In view of the energy balance, we define the rolling resistance as the external moment that critically causes the micro cylinder to rotate. We calculate the rolling resistance of a polystyrene micro cylinder with radius of one micro-meter.

Ra16.2/Rb16.2

Abstract Withdrawn

Ra16.3/Rb16.3

Phase Transition Approach to Supply a Micro-volume of Water on the Probe-tip for Micromanipulation by Capillary Force. Shigeki Saito[1], Osamu Katsuda[2] and Kunio Takahashi[2]; [1]Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, Tokyo, Tokyo, Japan; [2]Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Tokyo, Japan.

The size of an object has decreased in the electrical and mechanical engineering field for fabricating highly functional micro-electro-mechanical systems and photonic crystals. In micromanipulation, even if we can pickup micro-objects, it is very difficult to detach the micro-objects because adhesional force is dominant. To date, some research groups have tried to manipulate micro-objects by using a micro-drop of water because capillary force has been considered effective in micromanipulation. How to supply a micro-volume of water, however, is still a difficult problem to develop the reliable system of micromanipulation. Thus, in this study, our group manipulates micro-objects with capillary force by condensing water from the atmosphere. This condensed water forms a water bridge. The volume of a water bridge can be controlled by evaporation and condensation. A Peltier device is used for temperature control in order to achieve water phase transition. By using this method, we have achieved repeatable micromanipulation with simple equipments. This experimental result shows the feasibility of this method for automated micromanipulation by capillary force.

Ra16.4/Rb16.4

Abstract Withdrawn

Ra16.5/Rb16.5

Si(001) Surface Self-Organization under Strain Field Influence. 2d Monte Carlo Simulation. Florin Nita[1,2], Alberto Pimpinelli[3] and Hiroo Omi[4]; [1]INFM and Genova University - Physics Department, Via Dodecaneso 33, Genova, I16146, Italy; [2]Institute of Physical Chemistry - Romanian Academy, Spl. Independentei 202, Bucharest, Romania; [3]LASMEA, UMR 6602 CNRS / Blaise Pascal University, Clermont 2, 63177 Aubiere Cedex, France; [4]NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa, 243 - 0198, Japan.

The morphology of vicinal and flat Si(001) surfaces during relaxation and during growth in the presence of a strain field is studied by kinetic Monte Carlo simulation. The same model was already used to study the decay of pyramidal nanostructures on Si(001) surface [1]. In the model we have taken into account the deposition, evaporation and diffusion events. The activation energy for the diffusion event is given by: $E_d = E_D + n_\parallel E_{a\parallel} + n_\perp E_{a\perp}$, where $E_{a\parallel}$ and $E_{a\perp}$ are the lateral interaction energies in parallel, respective perpendicular direction relative to the dimer rows direction in the plain, and $n_\parallel$ and $n_\perp$ are the numbers of nearest neighbours in these two directions. E_D is the energy barrier due to the interaction with the substrate and can have two different values, $E_{D\parallel}$ or $E_{D\perp}$, that depending on the dimer diffusion direction relative to the dimer rows direction on the substrate. We performed simulations using different strain field distributions taking into account different possibilities to produce such strain fields (ion implant or local surface deformation). For all cases we compare our simulation results with experimentally data. [1] Scaling and crossovers in nano-island decay : a kinetic Monte Carlo study Florin Nita, Alberto Pimpinelli, Surface Science **551** (2004) 31 - 38

Ra16.6/Rb16.6

Direct-Assembly of Nanofluidic Channels from a Buckling Patterning Method of Compressive Stressed Films.

Myoung-Woon Moon[1], Seok Chung[2], Kwang-Ryeol Lee[3], Kyu Hwan Oh[4], Jun Keun Chang[5], Thomas Ward[1], Howard A. Stone[1] and John W. Hutchinson[1]; [1]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; [2]Biological Engineering Division, MIT, Cambridge, Massachusetts; [3]KIST, SEOUL, South Korea; [4]School of Materials Sciences and Engineering, Seoul Natl Univ, SEOUL, South Korea; [5]School of Electrical Engineering and Computer Science, Seoul Natl Univ, SEOUL, South Korea.

Channels created by buckling delamination have been demonstrated for pathway networks of fluidic flow for compressed films on substrates. Microfluidic channels for controlled fluid flow have been created using buckling patterning method [1]. The method exploits buckle delamination of a thin compressed film of a Diamond like Carbon (DLC) film bonded to a Si substrate. A low adhesion layer coinciding with the desired layout of the channel network is laid down on the substrate prior to deposition of the film. Once triggered under condition that the elastic strain energy of the film exceeds the interface adhesion energy, the buckle delamination propagates along the low adhesion pathways due to the release of the elastic energy stored in the film; thus the entire channel network is created. Depending on the width of the low adhesion region, the buckled film displays either the common telephone cord morphology or a straight-sided morphology for more narrow regions. Control of the compressive film thickness (15nm to 260nm) and the width of the low adhesion regions (200nm to several microns) enables the cross-sectional area of the channels to be defined quite precisely with opening heights determined by the buckle amplitude and ranging from 40nm to 500nm. Channels having lengths of several millimeters are created. Channel networks have been developed with varying degrees of intricacy: straight strips; sequenced zig-zag channels; rectangular grids; and hexagonal grids. The channel network has been integrated with an micro-fluidic interface employing a polydimethylsiloxane (PDMS) layer on buckling channel network of DLC film. Fluid flow in the system is demonstrated with pure water. The velocity profile of the fluid inside the buckling channel on straight pattern, having telephone cord morphology, has been analyzed. Exploratory efforts are underway to study the potential of these networks with Y-shaped junctions to act as nano-scale mixers. Filters and sieves for sorting submicron particles in a fluid are also potential applications on tapered patterns, having different cross-sections. References [1] M.-W. Moon, K.-R. Lee, K. H. Oh, J. W. Hutchinson, Buckling delamination on patterned substrates, Acta Mater., 52(2004), 3151.

Ra16.7/Rb16.7

DNA based photosensitive nanocomposites for nanolithography.

Przemyslaw P. Markowicz, Preeti Gupta, Koichi Baba, Jim M. O'Reilly and Paras N. Prasad; Institute for Lasers, Photonics and Biophotonics, State University of New York at Buffalo, Buffalo, New York.

This talk will focus on application of DNA based nanocomposites for microfabrication of high quality photonic structures. We will show that the two-photon lithography method can be used for fabrication of 2-D photonic crystals and beam splitters from a photosensitive organic-inorganic hybrid resin highly loaded with DNA The resin, which was used in our studies contains polymerizable methacrylate groups. We will also demonstrate the intensity distribution of Raman signal attributed to the DNA surfactant to prove that the fabricated structures were of high quality. Furthermore, we will demonstrate that the DNA/hybrid films cast on glass substrates are of high enough quality to support amplified spontaneous emission from dyes intercalated in the DNA molecules. The last part of this presentation will deal with possible applications of these kinds of nanocomposite materials in optics and optoelectronics. Advantages of using DNA molecules will be discussed.

Ra16.8/Rb16.8

Templated growth of nanostructures using block-copolymer lithography for application in nanocrystal memories.

Rosaria A. Puglisi, Salvatore Lombardo, Manuela Rapisarda and Piero La Fata; Istituto per la Microelettronica e i Microsistemi, Consiglio Nazionale delle Ricerche, Catania, Italy.

The usage of nanodots as discrete storage nodes in non volatile memories has been extensively demonstrated to be a successfull approach due to the numerous potential advantages associated with the discrete-trap structures. In order to obtain very low fluctuations in the device electrical characteristics it is very important to precisely control the coverage of the gate area with the nanodots, i.e. to control the dots size and position. Presently the templated growth is believed to be one of the more promising routes for fabrication of nanostructures controlled in size and position. Self-assembling of diblock copolymers offers a simple and low cost method to produce a nanomask with circular pores of about 10 nm in radius, assembled in a close-packed hexagonal configuration. However, depending on the mask process conditions, self-assembled block-copolymer thin films typically present many hexagonal arrays of pores, with different sizes and randomly aligned between them. The size of these hexagonal domains exhibits a finite dispersion, and this indicates the level of long range order obtained. In order to control the size and the position of the dots in the final memory device it is extrememly important not only to measure the dot positions but also to measure the size and the number of the hexagonal domains present in the nanomask. In this work we present results on self-assembling of Poly(Styrene-b-MethylMethacrylate) diblock-copolymer with several molecular weights. The annealing conditions inducing the microphase separation are also varied to investigate the optimal conditions for long range order. The self-assembled thin polymer films are then used as nanomasks for the deposition of silicon or metals and the formation of the nanostructures after a lift-off process. The samples, either after the mask formation and after the lift-off process, are observed through AFM and SEM equipped with field emission gun. From the surface topographical characterization of the nanomasks and by means of a suitable image elaboration technique, the position of the pore centers are obtained. The data are then elaborated by means of a computer code written in order to identify the size and the number of the several hexagonal domains.

Ra16.9/Rb16.9

A statistical investigation of optimum and robust process conditions for large scale synthesis of cdse nanostructures.

Tirthankar Dasgupta[1], Christopher Ma[2], Roshan Joseph Venghazhiyil[1], Zhong Lin Wang[2] and C. F. Jeff Wu[1]; [1]School of Industrial and Systems Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Research in synthesizing semiconducting nanostructures is a forefront area in nanotechnology due to their applications in nanoelectronics, photonics, data storage, and sensing. The II-VI semiconductors, more specifically cadmium selenide (CdSe), have been investigated over the past decade for optoelectronics, luminescence, lasing materials and biomedical imaging. Cadmium selenide is the most extensively studied quantum dot material, and is therefore regarded as the model system for investigating a wide range of nanoscale process and phenomenon in zero-dimensional nanostructures. In spite of numerous studies on CdSe quantum dots, there exist only a few papers reporting the synthesis and properties of one-dimensional (1D) CdSe nanostructures. In particular, one-dimensional nanostructures present the ability to experimentally address the fundamental issues of reduced dimensionality and quantum confinement in one-dimensional system. A control on the size and size distribution of CdSe nanocrystals is extremely important for CdSe quantum dots. For 1D nanostructures, CdSe has been found to exhibit morphologies of nanowires, nanobelts and nanosaws. To meet the requirements of large scale, controlled and designed synthesis of nanostructures, it is essential to find process conditions under which the desired nanostructures are synthesized reproducibly, at large quantity and with controlled morphology. In this paper, an effort is made to systematically investigate the underlying mechanisms that determine the morphology and dimensionality of 1D CdSe nanostructures. Through a designed experiment and rigorous statistical analysis of experimental data, statistical models linking the probabilities of obtaining specific morphologies to the process variables are developed. The optimum process conditions that maximize the above probabilities and, at the same time, make the synthesis process less sensitive to variations of process variables around set values are derived from the fitted models.

Ra16.10/Rb16.10

Reflectance spectroscopy of single photonic crystal island fabricated by ink-jet printing. Dake Wang[1], Minseo Park[1], Jungho Park[2] and Jooho Moon[2]; [1]Department of Physics, Auburn University, Auburn, Alabama; [2]School of Advanced Materials Engineering, Yonsei University, Seoul, South Korea.

Photonic crystal is a material that possesses a periodic modulation of refractive index, and exhibits a photonic band gap where certain ranges of frequency of the light cannot propagate. In the present investigation, a micro-reflectance spectroscopy was performed on a single island of photonic crystal array. An array of islands of photonic crystal with colloidal polystyrene beads was assembled on Si using ink-jet printing. Three different sizes of the polystyrene colloids (190 nm, 210 nm, and 270 nm in diameter) were used and the polystyrene colloidal particles were self-assembled to form fcc lattices with three different lattice spacing. It was observed from the reflectance spectra that the position of the optical stop band shifts as the size of the colloidal particle changes. Effective medium approximations were used to model the dielectric properties of the colloid/air composite. The theoretically expected reflectance peak position agrees well with those of the experimentally observed peaks.

Ra16.11/Rb16.11

Formation of Sr-Si ordered monolayers for atomic templates using SrF2. Francisco Santiago, Kevin A. Boulais, Victor H. Gehman and Karen J. Long; Dahlgren Division Naval Surface Warfare Center, Dahlgren, Virginia.

This work explores the fundamental chemical reactions between strontium fluoride (SrF2) and silicon (Si) when the vapor flux of the reactant gas (SrF2) is below 10E11 molecules per cm2 per sec and the gas is highly directed toward the substrate (Si). These reactions are done inside a molecular beam epitaxy (MBE) system kept with a residual pressure below 4X10E-12 torr using substrates temperatures above 600oC. The SrF2 vapor is generated from a Knudsen cell kept at a temperature slightly above the sublimation temperature of SrF2. Previous results from the exposure of BaF2 to Si using the conditions above shown that BaF2 dissociates and react with Si to from a perfectly ordered monolayer of Ba linked to Si. This monolayer was used as a template to grow epitaxial films of BaF2 and other materials like PbTe and CdTe with lattice constants greater than Si. Sr features an atomic diameter very similar to Ba but it has 18 fewer electrons. This may bring an opportunity to develop ordered monolayers that could host epitaxial layers of materials with lattice constants smaller than Si. Results of analysis using x-ray photoelectron spectroscopy (XPS) done in vacuo show total decomposition of SrF2 on the Si surface leaving a monolayer of Sr on Si in manner similar to our Ba results. Reflective high-energy electron diffraction (RHEED), and low energy electron diffraction (LEED), results show that as in the case with Ba, the Sr monolayer is highly ordered. We will report results from exposures done at different conditions and their implication in the development of a new class of compliant substrates.

Ra16.12/Rb16.12

Colloidal Silver Nanoparticle Induced Photoluminescence Quench on the Surface Functionalized Planar Si. Li-Lin Tay[1], Nelson Rowell[1], Rabah Boukherroub[2] and David Lockwood[1]; [1]National Research Council, Ottawa, Ontario, Canada; [2]Interdisciplinary Research Institute, Villeneuve d'Ascq, France.

The indirect bandgap nature of the bulk Si renders it an inefficient material for light emission. Planar Si, however, does exhibit weak luminescence signature in the infrared region. This is produced from conduction and valence band carrier recombination. This room temperature bulk Si photoluminescence (PL) can be excited with Ar laser excitation and the signal detected with a sensitive Ge detector. Planar Si acts as a versatile growth surface for a host of nanostructured materials, e.g. as a template for carbon nanotube growth. Furthermore, metal nanoparticles are often deposited on the planar Si surface as possible catalytic materials. Here we examine the change in the PL of a surface functionalized planar Si due to an in-situ deposition of colloidal Ag nanoparticles. The planar Si (100) was first degreased in acetone and then cleaned in a piranha bath at an elevated temperature. The cleaned wafer was then dipped into 5% of HF to remove its surface oxide and to passivate its surface with Si-H bonds. By exposing the hydrogen passivated wafer surface to UV radiation while immersed in a degassed undecylenic acid solution, a radical initiated hydrosilylation reaction cleaved the Si-H bonds and replaced them with more stable Si-C bonds. This process produced a monolayer of undecylenic acid molecules self-assembled on the Si(100) surface. A single bounce attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic technique was developed to monitor the vibrational spectra of such monolayer layer film. The observed vibrational spectrum showed clear carbonyl stretch at 1714 cm-1 from the undecylenic acid on the Si (100) surfaces. Colloidal Ag solution was prepared by reducing silver nitrate with sodium borohydride.(Suh et al., J. phys. Chem., 87, 1540, 1983) It was necessary to work with surface functionalized Si (e.g. Si-C terminated surface) to avoid the rapid surface oxidation reaction. The surface functionalized Si wafer was immersed in the colloidal Ag sol while illuminated with 457.9 nm of Ar-laser radiation. The light not only excited PL of the bulk Si but also destablized the colloidal Ag nanoparticles causing them to form small aggregates, at the same time depositing them on the surface of the Si. In this presentation, we will present the exponential quenching data of the bulk Si PL in the presence of colloidal Ag sol. We will also attempt to explain this quenching mechanism with the formation of electron depletion region at the silicon-nanoparticle junction. We will also compare our observation of PL to the measurements of reduced conductance observed for nanoparticle and semiconductor nanowire devices.

Ra16.13/Rb16.13

Silicon Bragg Reflectors and Microcavities with Artificial Birefringence. Irina V. Soboleva, Elena M. Murchikova, Andrey A. Fedyanin and Oleg A. Aktsipetrov; Physics Department, M.V. Lomonosov Moscow State University, Moscow, Russian Federation.

One-dimensional anisotropic photonic crystals, single and coupled microcavities based on porous silicon with birefringence optimized for the control of the nonlinear-optical response are designed and fabricated. Silicon crystal is isotropic due to cubic lattice structure, but porous modification of silicon (110) can possess strong in-plane anisotropy of the dielectric function due to form anisotropy of porous media. This dielectric function anisotropy gives a reliable way for the control of optical and nonlinear-optical response of photonic crystals and microcavities based on anisotropic porous silicon. Photonic crystals, single and coupled microcavities are multilayered structures formed from heavily doped silicon (110) wafer etched in the fluoric acid solution. The refractive indices of adjacent porous silicon layers are n_1=1.81 and n_2=2.18. The optical anisotropy values are Δn_1=0.03 and Δn_2=0.04 for the wavelength of 860 nm. The reflectance spectra demonstrate presence of the photonic band gap (PBG) and the microcavity mode located in the center of PBG. Their spectral position is tuned upon the sample rotation around its normal and/or rotation of incident light polarization plane. The dependence of mode spectral position shift on polarization of the electromagnetic wave orientation relative to the sample optical axes is obtained. The microcavity mode shift increases for oblique angles of incidence and achieves 1.2 of half-width at half maximum (HWHM) of the microcavity mode. The enhancement by approximately 10^2 and 10^3 times, respectively, of second- harmonic (SHG) and third-harmonic (THG) generation intensity is achieved in photonic crystals and microcavities at the PBG edge due to fulfilment of phase matching condition. The angular positions of SHG and THG peaks are shifted by half and one of peak HWHM, respectively, for various polarizations of the fundamental wave. The 10 times changes of the THG intensity are attained for the switch of fundamental wave from ordinary to extraordinary one due to anisotropy of the dielectric functions of porous silicon layers. The shift of the angular position of SHG and THG peaks corresponds to changing of the PBG spectral position detected at reflectance spectroscopy.

Ra16.14/Rb16.14

Layer-by-Layer Self-Assembly of Ceramic Particles for Oxidation and Corrosion Resistant Coating Synthesis. Yi-Feng Su, Hongwei Qiu and Woo Y. Lee; Stevens Institute of Technology, Hoboken, New Jersey.

We investigated layer-by-layer self-assembly (LBLSA) as a non-line of sight technique for coating complex shape high-temperature materials such as Si3N4 and Ni-based superalloys in order to improve the environmental stability of these materials for use in advanced gas turbines. In this technique, the substrate surface is electrostatically charged by employing multilayered polyelectrolytes (PE), which are used: (1) as "electrostatic glue" to assemble a single layer of small ceramic particles onto the substrate surface at a time and (2) to provide a layer-by-layer mechanism for controlling thickness and coverage uniformity. We prepared a thin alumina layer using this LBLSA method on a Ni-based superalloy substrate. An aluminum hydroxide sol was used as a precursor in this work. Dynamic laser scattering (DLS) was used to determine the average length of aluminum hydroxide (boemite) platelets in the sol to be $\sim$100 nm and its ζ-potential to be +25 mV. The charged boehmite platelets were electrostatically attracted and assembled to the alloy surface whose top surface was pretreated with negatively charged polyelectrolyte ions. Subsequently, the assembled boehmite platelets were dried at 100°C and annealed at 1100°C to produce a $\sim$50 nm-thick alumina layer. Similarly, we prepared various structural assemblies of rare-earth silicate particles on Si3N4. We compared the assembly characteristics observed with the boehmite and rare-silicate particles to those observed for model SiO2 particles, and identified key parameters that control the morphological quality of the assembled structures for our coating applications.

Ra16.15/Rb16.15

Self-Organizing Nanoscale Electrochemical Junctions and Devices Using Controlled Surface Forces. Young Kyu Cho, Ryan Wartena, Matthew E. Spencer and Yet-Ming Chiang; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We are developing a colloidal scale self-organization approach whereby repulsive forces between dissimilar materials are used to form in-situ electrochemical junctions in dense particle arrays, while attractive forces between like materials are used to form continuous electronically conductive networks, resulting in bipolar devices. Specifically we focus on lithium storage compounds in which short-range surface forces due to solvent interactions can induce both self-assembly of like materials and self-separation of dissimilar materials. In this work, direct force measurements are performed by atomic force microscope (AFM) to characterize the attractive and repulsive material systems. Careful selection of the solvent medium introduces a repulsive vdW force between dissimilar electronically conductive device materials, enabling the formation of a resistive junction by inserting a nonconductive barrier layer. Impedance spectroscopy and various electrochemical tests are then used to demonstrate the creation of junctions and particle networks where needed, and device functionality. This work was supported by U.S. AFOSR Grant No. F49620-02-1-0406. YKC was supported by the Korea Science Foundation. RW was supported by a DCI Postdoctoral Fellowship.

Ra16.16/Rb16.16

Strong, Transparent Multifunctional Carbon Nanotube Sheets Made at Commercially Useable Rates. Mei Zhang[1], Shaoli Fang[1], Anvar Zakhidov[1], Sergey B. Lee[1], Ali E. Aliev[1], Christopher D. Williams[1], Ken R. Atkinson[2] and Ray Henry Baughman[1]; [1]Nanotech Institute, University of Texas at Dallas, Richardson, Texas; [2]CSIRO Textile & Fibre Technology, Belmont, Victoria, Australia.

We demonstrate a new process that enables the demonstrated production of five-centimeter-wide, meter-long transparent carbon multi-walled nanotube sheets at rates above 7 m/min. These self-supporting nanotube sheets, having fundamentally unlimited width and length, comprise a novel state of matter: a highly anisotropic electronically conducting aerogel with a density of $\sim$0.0015 g/cm3 that can be densified into strong sheets that are as thin as $\sim$50 nm. Experimental results suggest application for transparent, highly elastomeric electrodes; low-noise electronic devices; planar sources of polarized broad-band radiation; two-dimensionally reinforced composites; welding agents for microwave bonding of plastics; conducting appliques; and hole injecting electrodes for flexible organic light-emitting diodes.

Ra16.17/Rb16.17

Fabrication and Defect Designs on DNA Linked 2-D Colloidal Photonic Crystals Using a Nd:YAG Pulsed Laser. Ramazan Asmatulu[1], Robin M. Bright[1], Phillip P. Yu[1], Sejong Kim[1], Fotios Papadimitrakopoulos[1] and Harris L. Marcus[1]; [1]Institute of Materials Science, University of Connecticut, Storrs, Connecticut; [2]MSE, IMS, Storrs, Connecticut.

Controlled defects were created on DNA linked 2-D colloidal photonic crystals using a Nd:YAG pulsed laser in the presence and absence of an ethidium bromide (EB) dye. The 2-D photonic crystals were self-assembled using 1.8 mm polystyrene (PS) microspheres on functionalized glass substrates. To synthesize the hexagonal close packed crystalline samples, both substrate and particles attached single-strand DNA, sequence A on the substrate and sequence B on the particles. The DNA was hybridized using the DNA linker with complementary single-strand A'B' that anchored the particles to the substrate during self-assembly. The 532 nm second harmonic of the pulsed Nd:YAG laser (1064 nm) with a pulse width of 10 ns was used for the removal of individual colloidal particles from the self assembled photonic crystals. Diameter of the laser beam was optically reduced from 7 mm to 1.8 mm. Controlled line defects and geometrical shapes (e.g., hexagonal, triangle and diamond) were created on the glass substrates under a medium containing EB dye in 0.1 M NaCl solution.

Ra16.18/Rb16.18

Role of Composition on Structural Stability of Heteroepitaxial Islands: A Phase Field Study. Ramanarayan Hariharaputran and Vivek B. Shenoy; Division of Engineering, Brown University, Providence, Rhode Island.

We model the role of compostion in determining structural stability of nanostructures in thin films using phase field model. Evolution in two typical experimental categories namely phase mixing systems (eg. Si-Ge) and phase separating systems (III-V alloys) are taken for study by tuning the model features. In Si-Ge systems, elastic stresses gives rise to quantum dots where composition variations determine the final structure of the system. In this work we study the effect of stresses arising due to misfit formed because of difference in composition on the morphological changes arising due to Asaro-Tiller-Grinfield (ATG) instability. We also study the evolution of the quantum islands during deposition and during annealing leading to additional stress relieving mechanisms like formation of trenches. Our study also attempts to explain the recent experimental observations in III-V systems where lateral composition modulation is observed along with surface undulations. In this case, we study the interaction between morphological instability due to elasticity and the thermodynamically driven compositional instability in dictating the final microstructure. We model the alloy system using a ternary phase field model with A rich α phase as the film, B rich β phase as the substrate and a vapour phase. Thermodynamics of intermixing or unmixing characteristics of the free energy determining the growth as well as degradation of the nanostructures plays an key role in our simulation studies. Here we have attempted to characterize the evolution as a function of kinetic parameters such as surface and bulk diffusion coefficients of different species, material parameters such as elastic properties and operational parameters like deposition rate.

Ra16.19/Rb16.19

Simultaneous Complete Phononic and Photonic Band Gaps in Periodic Structures. Martin Maldovan and Edwin Thomas; Materials Science and Engineering, MIT, cambridge, Massachusetts.

We found "deaf and blind" structures having simultaneous complete phononic and photonic band gaps. These composite materials can control the flow of light and sound at the same time. The existence of complete photonic/phononic gaps can lead to the simultaneous localization of light and sound. These structures can be used to design a new class of acoustic-optical devices that can integrate the management of sound and light. We also study the dependence of the complete gaps on material parameters to provide design guidelines to create photonic-phononic crystals.

Ra16.20/Rb16.20

Directed Formation of Silver Nanowires and Nanoloops by Electroless Deposition. Jiajie Diao[1], Ke Wang[1], Yong Chen[2], Akos Vertes[2,3] and Mark E. Reeves[1,3]; [1]Physics, George Washington University, Washington, District of Columbia; [2]Chemistry, George Washington University, Washington, District of Columbia; [3]Institute for Proteomics Technology and Applications, George Washington University, Washington, District of Columbia.

We present a method for depositing high-density silver nanowires by electroless deposition on nonconductive glass and weakly conducting carbon substrates. The process we have developed does not require catalytic seeding, templating, or surface-capping reagents. Moreover, substrate conditioning can control the morphology and growth direction. On glass surfaces, straight silver nanowires are formed that are typically 20 to 50 nm in diameter and can be as long as $\sim$100 μm. On weakly conducting substrates like thin ITO or granular carbon, nanoloops are formed that are several microns in outer diameter and about 100 nm in thickness. Our results indicate that surface charges play a significant role in the deposition process. Data are presented on the effect of pH, surface preparation, and electric fields on the directed formation of silver nanostructures.

Ra16.21/Rb16.21

Aligned Millimeter-Long Carbon Nanotubes Arrays Grown on Single Crystal Magnesia. Guangyong Xiong, Dezhi Wang and Zhifeng Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

Single crystal magnesium oxide (MgO) was found to be very beneficial to the growth of aligned carbon nanotubes (CNTs) arrays as long as 2.2 mm by chemical vapor deposition. Before growth, a thin film of catalyst was always coated on the MgO by magnetron sputtering. Scanning electron microscopy was used to study the alignment and length, and transmission electron microscopy was used to exam the wall numbers, diameter, and graphitization. It was found that the number of walls as few as two can be controlled by the catalyst film thickness, whereas the length is a combined result of gas pressure, temperature, and time during growth.

Ra16.22/Rb16.22

Electrostatically Controlled Monolayer of M13 Virus on Polyelectrolyte Multilayer. Pil Jin Yoo[1], Ki Tae Nam[2], Angela M. Belcher[2,3] and Paula T. Hammond[1]; [1]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Materials Science and Engineering, Massachusetts Institute of

Technology, Cambridge, Massachusetts; [3]Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A novel means of incorporating ordered bio-functional viral assemblies into an electrostatic thin film nano-assembly has been demonstrated. We used negatively-charged engineered M13 bacteriophage (virus) as the adsorbant species on a weak polyelectrolyte multilayer support consisting of a cationic linear polyethyleneimine (LPEI) and anionic polyacrylic acid (PAA). Due to a unique phenomenon of interdiffusion, the LPEI/PAA multilayer provides full mobility to the M13 virus, and the adsorption process drive self-assembly and entropically-driven ordering. The resulting monolayer formation of M13 virus can be tuned for its packing density and directional alignment. Packing density can be modulated via the degree of electrostatic repulsion between M13 viruses by varying the pH of virus solution and a simple flowing process within a microfluidic channel gives the viruses directional order due to their liquid-crystalline-like behavior. Furthermore, we demonstrate the two-dimensional biomineralization from this monolayer template of M13 virus for nanoparticle and nanowire assembly. Electrostatic binding of cationic gold nanoparticles to the capsid body of a negatively charged M13 generates a well-ordered one-dimensional quantum dot array and nucleation of cobalt ions at the surface of M13 virus enables the two-dimensional assembly of cobalt nanowires on the surface. This technique can be a versatile tool for ordering and processing various biomolecules and nanomaterials, because many materials in nature are charged and exist in the solution phase. This approach may open up new pathways for bottom-up based biochemistry and nanotechnology.

Ra16.23/Rb16.23

Abstract Withdrawn

Ra16.24/Rb16.24

Morphological Evolution of Nanoporous Gold Membranes and Thin Films. Totka Ouzounova[1], Christopher Umbach[1], Keith Rekczis[2] and Daniel Henkel[2]; [1]Materials Science & Engineering, Cornell University, Ithaca, New York; [2]Pall Corporation, Cortland, New York.

Selective dealloying of silver is used to create nanoporous gold membranes from rolled Au/Ag alloy sheet. Similar nanoporous gold can be fabricated as a thin film by the sputtering of the alloy onto suitable substrates followed by dealloying. Nanoporous gold has potential for catalysis, filtration of nano-objects and sensitive detectors with high surface area. During dealloying, redistribution of gold results in a nanoporous network with openings on the order of 10 nm. The initial pore dimensions depend on alloy composition and can be subsequently coarsened after dealloying by the diffusion of the gold. The evolution of the pore morphology has been studied as a function of the annealing conditions and the ambient atmosphere. We show that the temperature-dependent coarsening rate also depends on the gas environment. Here, we present the morphological evolution of 200 μm thick membranes when annealed in the range of temperatures from 50 ^{o}C to 300 ^{o}C in vacuum at 10^{-7} Pa; in vacuum at 10^{-3} Pa; 1 atm O_2; and 1 atm Ar. We compare the evolution for bulk membranes with that for deposited thin films of porous gold.

Ra16.25/Rb16.25

Single Molecule Spectroscopy of Conjugated Polymers Embedded in a Functioning Organic Diode. Young Jong Lee, So-Jung Park, Andre J. Gesquiere and Paul F. Barbara; Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas.

A strong correlation was observed between current-voltage (I-V) and fluorescence-voltage (F-V) measurements of MEH-PPV single molecules imbedded in a functioning organic diode. The correlation allows to optically estimate hole density at the hole injection interface as a function of applied bias voltage. Comparison of the hole densities estimated from the F-V data and from the measured I-V using bulk charge transport models reveals important roles of injection barriers and traps in the local hole transport process at the interface.

Ra16.26/Rb16.26

Atomistic Simulations of Crystalline Orientation Selection in Nanofabrication. Longguang Zhou and Hanchen Huang; Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

During nanostructure fabrication, nanorods of different crystalline orientations compete. As a result, nanorods of particular orientation may dominate, and such dominance affects the nanorods properties. Using recently implemented atomistic simulator ADEPT, we investigate the orientations competition process at the nanoscale. The simulations take Cu as the prototype; the deposition are carried out at three different incident angles (45°, 60°, and 75°) with fixed azimuth; the deposition rate varies from 1 to 10 micron/min and the substrate temperature is 300K. Our studies show that the nanorods with <111> texture dominate if the incident angle is large (more shadowing effects) and there is sufficient diffusion. Otherwise, some other orientations such as <100> may appear and compete with <111> oriented nanorods.

Ra16.27/Rb16.27

Controllable Self-Assembly of Diblock Copolypeptides into Hydrogels, Fibrils, or Single Crystals. Lisa M. Pakstis[1], Andrew Nowak[2], Timothy Deming[2] and Darrin Pochan[1]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Bioengineering, University of California, Los Angeles, California.

Controlling the kinetics of diblock copolypeptide self-assembly leads to the formation of various materials. The amphiphilic diblock copolypeptides are 200 amino acids in length with a hydrophilic lysine (K) block and a hydrophobic leucine (L) block. When assembled quickly in pure water, the polypeptides form rigid hydrogels with bulk mechanical properties that are tunable based on molecular design, i.e. chain length and lysine to leucine block ratio, and solution conditions such as salt concentration. Alternatively, when assembled from miscible organic/water mixtures, block copolypeptiode nanoscale assembly morphology can be altered. Prior suspension of the block copolypeptides in organic cosolvent enabled greater copolypeptide chain mobility that, after water addition and subsequent removal of the organic via evaporation, provides for a more regular packing of the copolypeptide molecules. At the fastest organic evaporation rate ($\sim$6 hours), the copolypeptides assembled into weak hydrogels with a homogeneous microstructure and interconnected fibrillar nanostructure. Slowing the evaporation rate to $\sim$24 hours, and hence the kinetics of assembly, produced regular, noninterconnected fibrils. Longer evaporation times, $\sim$2 days, led to the formation of hexagonal single crystal-like assemblies. Interestingly, copolypeptides with a racemic copolymer leucine block did not assemble into any regular nanostructures, indicating that the secondary structure of the leucine block is critical for assembly. In all assemblies, regardless of the resulting nanostructure, the secondary structure of the hydrophobic block remains an α helix, as shown with circular dichroism (CD). Characterization of the hydrogels, fibrils, and single crystals using laser scanning confocal, atomic force, and transmission electron, and cryo-transmission electron microscopies indicate that assembly is dictated by the hydrophobic block association with hierarchical microscale assembly controlled through assembly pathway.

Ra16.28/Rb16.28

Synthesis and Characterization of Polymer Brushes using Anchored Organometallic Catalyst. Krishna Dronavajjala[1], Ramakrishnan Rajagopalan[1,3], Seong H. Kim[1,3], David L. Allara[2,3] and Henry C. Foley[1,2]; [1]Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania; [2]Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania; [3]Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Modification of inorganic substrates with organic coatings is an effective way of tailoring their surface properties. These polymer thin films play an important role in various fields such as surface modification, microfluidics, microelectronics, and novel biomaterials. In this work, a long chain of cyano alkane thiol Self-Assembled Monolayer (SAM) is formed on gold. The tail group (-CN) of SAM ligates with an organometallic catalyst [Pd(CH3CN)4](BF4) [1]. This catalyst is very well known to polymerize olefins carbocationically. In this investigation, we demonstrated surface initiated polymerization of p-methoxy styrene, polynorbornene using the anchored catalyst. The as grown polymer thin film was characterized using Ellipsometry, Reflection Absorption Infrared Spectroscopy, X-Ray Photoelectron Spectroscopy. This technique is a promising tool to develop patterned polymeric thin films of desired thickness. AFM was done on the patterned polymer brush to determine the surface roughness. [1] Sen, A. Accounts of Chemical Research. 1988, 21, 421.

Ra16.29/Rb16.29

Electric Field-Guided Growth of Mesoscopic Silica Thin Films at the Air-Water Interface. Kevin Jared Tatum, Jaehun Chun, Dudley A. Saville and Ilhan A. Aksay; Department of Chemical Engineering, Princeton University, Princeton, New Jersey.

A key goal in the design of materials is to improve performance by controlling structure across multiple length scales. Nature combines inorganic and organic components to produce composite materials, such as bone and nacre, with structures controlled down to the nanometer length scale. These natural materials have inspired the use of surfactant supramolecular entities in the development of self-assembled mesostructured organic/ceramic composites. The organic material can be subsequently removed by calcination or solvent-extraction, leaving behind a continuous ceramic matrix with a pore-structure that mirrors the configuration adopted by the surfactant during self-assembly. One such ceramic material system is mesoscopic silica formed by mixing a dilute acidified surfactant (cetyltrimethylammonium chloride, CTAC) solution with a small amount of inorganic precursor, in this case, tetraethoxysilane (TEOS). Thin films spontaneously "grow" at the air-water interface. Researchers have previously shown that the films have a disordered mesophase of hexagonally-packed surfactant tubules that meander in 2-D with their axes parallel to the plane of the film [1]. The ability to use these films for separation processes or as catalyst supports is hindered by both the disordered meandering and the in-plane orientation of the mesochannels, demonstrating a key limitation of self-assembly. The driving force of our research is to develop techniques for imparting long-range order to self-assembled materials in order to enhance their applicability. In this work we demonstrate the use of electric fields applied parallel to the film surface in controlling both the 2-D micrometer- and nanometer-level structure of free-standing mesoscopic silica thin films synthesized at the air-water interface over large areas, on the order of several square centimeters. A combination of polarizing optical microscopy, scanning electron microscopy, transmission electron microscopy, and small-angle x-ray diffraction is used to probe orientation in the films. We find that films synthesized under the influence of electric fields display a high degree of micrometer- and nanometer-level orientation parallel to the field lines compared to control samples synthesized in the absence of an applied field. This technique could be used to tailor self-assembled materials to specific applications and, thus, increase a material's usefulness. [1] N. Yao, A.Y. Ku, N. Nakagawa, T. Lee, D.A. Saville, I.A. Aksay, *Chem.Mater.* **12**, 1536 (2000).

Ra16.30/Rb16.30

Multifunctional nanocomposite transparent UV-blocking films sythesized by sol-gel process for optical, automotive and aeronautic applications. Phani Ratna Ayalasomayajula, Luca Lozzi and Sandro Santucci; Physics, CASTI-INFM Regional Laboratory, L'Aquila, Abruzzo, Italy.

Development of UV blocking thin films with effective cut-off features with steep edges and high transmission in the visible and IR region have been developed. The unique optical, mechanical and chemical properties of silica and ceria nanocomposites with surface functional groups making them most promising candidate for applications in opto-electronic, automotive and aeronautic industries. On the other hand, highly hydro and oleophobic films are being actively considered in optical, automotive and aeronautic industries to increase adhesion and scratch, abrasion resistance properties. In order to fill the gap, and fulfil the requirements to meet both ends, it could be proved that morphological changes in the nanometer range influences the water contact angles and their hystersis of low-surface energy materials. Nanocompsite films of SiO_2 and CeO_2 with surface functionalisation with decafluorooctyl-triethoxy silane itself forms nano-hemispheres (similar to lotus leaf) at and above 100C favoring an increase in the water contact angle from 122 (25C) to 145 (400C). The structural, optical, compositional properties have been examined by employing X-ray diffraction, UV-visible spectroscopy, X-ray photoelectron spectroscopy, respectively. On the other hand, mechanical and scratch and abrasion resistance, hydro-oleophobic, properties have been measured by nanohardness and nanoscratch tester, contact angle instruments, respectively. The cut off behavior of the deposited and annealed nanocomposite thin films has been tuned by varying different amounts of CeO_2 in SiO_2 has also been investigated.

Ra16.31/Rb16.31

Exploring the potential to introduce carbon nanotube probes into bacterial cells by atomic force microscopy. Minhua Zhao[1], Haoyan Wei[1], Ismael U. Nieves[2], Sang-Yong Ju[1], Kenneth M. Noll[3], Harris Marcus[1], Fotis Papadimitrakopoulos[1] and Bryan D. Huey[1]; [1]Materials Science & Engineering, University of Connecticut, Storrs, Connecticut; [2]Department of Civil and Environmental Engineering, University of Connecticut, Storrs, Connecticut; [3]Department of Molecular and Cell Biology, University of Connecticut, Storrs, Connecticut.

A variety of biological applications of carbon nanotubes are emerging, including the potential to pierce biological membranes with functionalized single wall carbon nanotubes (SWNTs) for possible applications in sensing intracellular activities. In this study, SWNT bundles are first assembled onto the apex of commercial atomic force microscopy (AFM) probes using dielectrophoresis. Using these tips, the mechanics of the surfaces of bacterial cells, Escherichia coli, suspended in phosphate-buffered saline (PBS) solution are studied by AFM via force-distance curves. These results are compared to similar measurements made with standard and sharpened AFM probes.

Ra16.32/Rb16.32

Bulk enrichment of particular single-walled carbon nanotube indices within a distribution. Timothy J. McDonald[1,2], Jeffrey L. Blackburn[1], Chaiwat Engtrakul[1], Marcus Jones[1], Garry Rumbles[1] and Michael J. Heben[1]; [1]National Renewable Energy Lab, Golden, Colorado; [2]Applied Physics, Columbia University, New York, New York.

Finding methods to obtain homogenous collections of a single nanotube type through purification of as-produced samples is an active area of nanotube research. We have been successful in applying laser-assisted selective oxidation of single-walled carbon nanotubes (SWNTs) to remove a particular nanotube type. Also, removal of surfactant followed by centrifugation has been shown to affect the distribution of nanotubes present in a suspension. Nanotube density of states have quantum wire features composed of sharp peaks. Transitions between peaks are strongly allowed, and nanotube indices have strong absorption at these energies. It is possible to select a laser energy such that most of the absorption of the beam takes place with a single nanotube type. Applying such a laser to a SWNT suspension in the presence of H2O2 allows for the selective oxidation of a single nanotube index. Other nanotubes in the sample remain unharmed. The detection of photoluminescence from surfactant suspended SWNTs allows for the study of individual nanotubes with a known index within a distribution[1]. We have performed photoluminescence excitation spectroscopy on SWNT-H2O2 suspensions before and after laser treatment. We observe a selective quench of the luminescence from the particular nanotube type with a transition in resonance with the laser. We will discuss this procedure which, in contrast to studies done on solid materials[2], has the potential to more completely remove individual tube chiralities from bulk samples. The excess hydrogen peroxide can be removed with a platinum catalyst, leaving the SWNT suspensions stable for at least many days. We will also discuss other methods for narrowing the distribution of nanotubes, such as the slow removal of surfactant to promote the selective bundling of a particular tube, alternative selective oxidation techniques, and suspensions with surfactants that do not have interactions with certain nanotube indices. 1. O'Connell, M.J., et al., Science, 2002. 297(5581): p. 593-596. 2. Maehashi, K., et al., Applied Physics Letters, 2004. 85(6): p. 858-860. The U.S. Department of Energy (DOE) Solar Photochemistry program funded by the Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences supported this work.

Ra16.33/Rb16.33

Synthetic Helical Nanostructures with Controlled Pitch and Their Application as Chemical Sensors. Liang-shi Li, Hongzhou Jiang and Samuel Stupp; Department of Chemistry, Northwestern University, Evanston, Illinois.

The systematic control of nanometer-scale architectures by encoding the structural information on the molecular level is of great importance for fundamental understanding and applications. It allows the molecular information to be amplified over a much longer length-scales and can therefore may be used for sensing purposes. Herein we describe a synthetic approach to self-assembled helical nanostructures whose pitch can be tuned systematically by varying the bulkiness of molecular monomers. When incorporated with conjugated polymers, these nanostructures show responsive behavior to external environments.

Ra16.34/Rb16.34

Carbon Cones- a Different Form of Carbon Structure with Unique Properties. Arne Skjeltorp, Henning Heiberg-Andersen, Geir Helgesen, Kenneth Knudsen, Jean Patric Pinheiro and Eldrid Svaasand; Physics, IFE, Kjeller, Norway.

It is possible to make perfect conical carbon nanostructures fundamentally different from the other nanocarbon materials, notably buckyballs and nanotubes. Carbon cones are realized in five distinctly different forms. They consist of curved graphite sheets formed as open cones with one to five carbon pentagons at the tip with successively smaller cone angles, respectively. Ge & Sattler at the Univ. of Hawaii first produced it in minute amounts in 1994 using a CVD technique [1]. Soon after, large-scale production was achieved in the so-called Kvaerner Carbon Black & Hydrogen Process, with pyrolysis of hydrocarbons using an exclusive torch plasma process [2]. The physics of carbon cones has been relatively little explored up until now. Recent ad-hoc model calculations show that the structural and functional properties of carbon cones appear to be dramatically different from those of the other forms of nanocarbon, due to fundamentally different topology and symmetry [3,4]. This will very likely result in unprecedented electronic-, chemical- and mechanical properties and open up possible applications like hydrogen storage [5]. In this presentation, we will primarily review the ongoing research on carbon cones performed in Norway. The work was supported in part by the Research Council of Norway Grants No. 14935/431, No. 163570/S10 and No. 158541/431. References: [1] M.Ge and K. Sattler, Observation of Fullerene Cones. Chem. Phys. Lett. 220, 192(1994) [2] A. Krishnan, E. Dujardin, M. M. J. Treacy, J. Hugdahl, S. Lynum and

T. W. Ebbesen, Graphitic Cones and the Nucleation of Curved Carbon Surfaces, Nature 388, 451-454 (1997) [3] H. Heiberg-Andersen, Carbon Nanocones, Handbook of Theoretical and Computational Nanotechnology (American Scientific Publishers, 2005) [4] H. Heiberg-Andersen and A. T. Skjeltorp, Stability of Conjugated Carbon Nanocones(Accepted for publication in J.Math.Chem.) [5] A.T. Skjeltorp and A.Maeland, US patent No. 6,290,753 in 2001, EPO Patent No. 1051530 in 2004 (Hydrogen storage in carbon material).

Ra16.35/Rb16.35

Tailoring 'Air' Defects in Self-Assembled Photonic Band Gap Crystals. Yoonho Jun and David J. Norris; Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Colloidal microspheres can be used to "self-assemble" novel structures known as photonic band gap crystals. The optical properties of these materials can be manipulated by introducing micron-scale structural defects into the structure. However, there have been no successful attempts to incorporate intentional defects into self-assembled photonic band gap crystals. Here we demonstrate a promising strategy to tailor such defects without disturbing the lattice around the defects. We use photoresists and multiphoton photopolymerization to draw patterns inside the photonic crystal with a laser scanning confocal microscope. Because high temperature processing steps are required to obtain the photonic band gap, conventional organic photoresists are not suitable. Instead, we utilized organic-inorganic hybrid materials (silsesquioxanes) that are converted to silica during the subsequent steps. Confocal and electron microscopies were then used to observe the patterned feature inside the 3-D structure. The intentional defects maintained their shape without cracking even at the elevated temperatures necessary for further processing of the photonic crystal.

Ra16.36/Rb16.36

Nanofluidic capillaries produced via femtosecond laser induced delamination of thin thermal oxide films from Si(100) substrates. Joel P. McDonald[1], Katherine E. Ray[2], Vanita R. Mistry[3], Neville R. Moody[5] and Steven M. Yalisove[4]; [1]Applied Physics, University of Michigan, Ann Arbor, Michigan; [2]Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan; [3]Mechanical Engineering, University of Michigan, Ann Arbor, Michigan; [4]Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; [5]Sandia National Laboratory, Livermore, California.

Highly selective and repeatable delamination of thermal oxide films from Si(100) substrates has been performed using single and multiple femtosecond laser pulses forming bubbles or blisters. By overlapping the bubbles laterally, tubes or capillaries can be formed with a range of volumes suitable for nanofluidics. By scanning the sample through the laser using an automated translation stage, patterns of tubes with arbitrary complexity can be formed, while the scan velocity can easily control the volume of the tubes. The production time for capillaries in this fashion is considerably less than with other lithographic techniques, while the proximity of the tubes to the underlying silicon substrate yields the possibility for integrated devices. The mechanism responsible for the delamination will be discussed and the optimal laser and sample translation conditions will be presented which provide the most uniform tubes. Atomic force microscopy and optical microscopy of capillaries with a range of volumes will be presented, as well as examples of complex patterns applicable to nanofluidics.

Ra16.37/Rb16.37

Novel Optical Properties Observed from Functional, Nanostructured Hybrid Glasses; 'Acoustically Coupled Photorefraction'. Lisa S. Brown, University of california, Irvine, Irvine, California.

This talk will present a fundamental challenge in nanotechnology by developing nanostructured optical device materials, which are shown a novel optical phenomenon, "acoustically coupled photorefraction". TEM analysis reveals novel nano-structured fringe patterns due to its nano-aligned structure. The hybrid laser material exhibits a novel optical property, photorefraction modulated by acoustic waves. The most striking observation is the transient acoustic grating, which is phase shifted by p/2 from the optical grating, and which leads to a diffraction efficiency as high as 80 % of the probe beam. The properties of these materials including the near theoretical limited diffraction achieved without applied fields and very fast response time will be of interest to novel devices in nanotechnology. Additionally, the photorefraction that we report is in a centrosymetric material and does not require the application of static electric fields or polling during material synthesis. While both photorefractive and acoustic grating can be separately demonstrated in different materials, we do not know of examples in which the two effects are coupled. Implicit in such behavior is fast response photorefraction, which is ascribed to the density-controlled mobility of electrons trapped in aligned nano domains of the hybrid sol-gel hosts. Applications, such as light modulators that rely on electro-acoustic-optical response, acousto-optics, and dynamic holography, are suggested.

Ra16.38/Rb16.38

Facile Formation of Chemically Functional Nanoparticles. David Fleming, Christopher J. Thode and Mary E. Williams; Chemistry, The Pennsylvania State University, University Park, Pennsylvania.

A library of chemically functionalized noble metal and magnetic nanoparticles has been prepared using a straightforward reaction strategy. In particular, Au, CoFe$_2$O$_4$ and various Iron Oxides have been functionalized through ligand place exchange and the pendant groups further reacted in a single step with redox active, fluorescent, or chemically active moieties. Particle synthesis, as well as characterization via transmission electron microscopy, UV-Visible spectroscopy, NMR, cyclic voltammetry, and fluorescence, will be discussed. The presented functionalization scheme represents a generalized method of nanoparticle surface modification amenable to the synthesis of several classes of functional nanoparticle materials.

Ra16.39/Rb16.39

In-situ Synthesis, Characterization, and Applications of Boron-doped Single Wall Carbon Nanotubes. Jeff Blackburn[1], Yanfa Yan[1], Kim Jones[1], Thomas Gennett[2,1], Michael Heben[1] and Anne Dillon[1]; [1]National Renewable Energy Laboratory (NREL), Golden, Colorado; [2]chemistry, Rochester Institute of Technology, Rochester, New York.

Control of the electronic properties of carbon nanotubes (CNTs) is highly desirable for a variety of applications. Specifically, the ability to produce large quantities of highly pure n- and p-type nanotubes would allow the fabrication of sensors, storage media, and opto-electronic materials. CNTs may be doped analogously to solid state semiconductors, with boron doping leading to p-type materials and nitrogen doping leading to n-type materials. For the doping of single-wall CNTs (SWCNTs), ex-situ doping (where dopant molecules are reacted with previously synthesized SWCNTs) has been the most successful path thus far. A wide variety of acceptors and donors have been studied, resulting in SWCNTs with tunable electronic properties. Efforts directed towards in-situ doping of CNTs (where boron and/or nitrogen are incorporated into the nanotube lattice via the synthesis) have generally produced multi-walled nanotubes with a variety of structures and morphologies, in addition to small yields of single-wall tubes. In particular, laser ablation syntheses utilizing boron reactants have produced small yields of SWCNTs with little or no incorporation of B into the nanotube lattice. Here we present a novel process to produce B-doped SWCNTs employing pulsed-laser-vaporization. This reaction produces a high yield of SWCNTs, with significant levels of boron doping. The nanotubes are characterized by TEM, small spot electron energy-loss spectroscopy, thermogravimetric analysis, Raman, absorption, and photoluminescence spectroscopy. We will also discuss potential applications for the B-doped SWCNTs, with preliminary results demonstrating progress towards such applications.

Ra16.40/Rb16.40

Thermally driven nanomechanical deflection of hybrid nanowires. Takashi Ikuno[1], Jung Goo Lee[2], Tatsuro Yasuda[1], Shin-ichi Honda[1], Kenjiro Oura[2], Hirotaro Mori[2] and Mitsuhiro Katayama[1]; [1]Dept of Electronic Eng, Osaka University, Suita, Japan; [2]Research center for UHVEM, Osaka University, Suita, Japan.

The building blocks for nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS) are being developed aggressively for a variety of applications. Recently, there have been advances in the miniaturization of NEMS and MEMS by adopting new nanomaterials. Among them, carbon nanotube (CNT) and nanowire (NW) are appropriate building blocks for the system due to the intriguing physical and chemical properties such as the unique geometry, the mechanical flexibility, the high Young's modules, the high electrical conductivity, and the chemical inertness. In general, to control the mechanical deflection of CNT/NW, electrostatic force, external mechanical force, or infrared radiation by has been used. However, to date, thermally driven-NEMS based on CNT/NW has not been performed. In this study, we observed the thermally induced nanomechanical deflection of the hybrid inorganic NWs, which were synthesized by pulsed laser deposition (PLD) of aluminum oxide (AlOx) and tungsten oxide (WOx) thin layers on a CNT template in a sandwich form. Multi-walled CNTs (MWNTs) used as a template for the hybrid NW synthesis have a diameter of 20 nm and a length of over 2 μm. To coat thin layers on the MWNT, the PLD was carried out by setting the angle between the surface of the target and the MWNT axis at 45°. First, the first layer (W) was deposited for 20 min at room temperature (RT). Second, to deposit the second layer

(Al) on the opposite surface of the first-layer-coated CNT, the specimen holder of the PLD was azimuthally rotated with 180°, and the deposition was carried out under the same condition for the first layer. After the deposition, each layer was naturally oxidized. The resultant product can be recognized as "thermostat" because it consists of two materials with different coefficients of thermal expansion. Utilizing the difference of the property, we performed in situ TEM observation of "thermostat" behavior; mechanical deflection by heating up. On initial stage at RT, the NW is almost straight. During the temperature elevation process, the NW bends gradually, and its shape becomes curved rather than straight. At 800 °C, the NW is obviously bent with a curvature. After cooling the specimen to RT, the NW returned to the straight shape. Moreover, we confirmed that this behavior of mechanical deflection was repeatable.

Ra16.41/Rb16.41

Nanoscale Assembly of Nanowires Templated by Microtubules. Jing Zhou[1], Yzy-Jiun Mark Luo[1], Yan Gao[2], Toshikazu Hamasaki[3], Evelyn Hu[2] and Bruce Dunn[1]; [1]Materials Science, UCLA, Los Angeles, California; [2]Materials, UCSB, Goleta, California; [3]Bioengineering, UCLA, Los Angeles, California.

Conventional top-down lithographic processes approach their practical and theoretical limits at dimensional scales less than 100 nm. Alternative bottom-up methods are being investigated to build nanoscale architectures. Many biosystems can self-assemble into regular structures of less than 100 nm and contain functional groups that bind to inorganic particles. There is increasing interest in using biomolecules as templates to construct nanoscale-achitectures. In this study, fabrication and alignment of microtubule-based nanowires are investigated. Microtubules are fibrous proteins found in nearly all eukaryotes. They are shaped like long hollow tubes about 25 nm in outer diameter and microns in length. These filaments are formed by polymerization of dimerized proteins called alpha- and beta-tubulins. To further stabilize the protein structure, polymerized tubulins are cross-linked with glutaraldehyde. Colloidal gold particles are bound to the surface of microtubules as nucleation sites for further particle growth. Dense coverage of Au particles is observed after electroless deposition. With electroplating, substrate bound microtubules are completely covered with Au particles. Ni coated microtubules are also fabricated by reducing Ni2+ to Ni0 on Pd activated microtubule surfaces. Focus Ion Beam is used to write metal contacts to these Ni patterned microtubule nanowires and DC conductivity values are obtained. Alignment of microtubules is observed when the microtubules are injected into microfluidic devices over amine-coated glass. Current investigation focuses on fabricating aligned nanowires on the substrate surface and forming nanowire arrays. These biotemplating approaches are the first steps towards more complicated 2D and 3D architectures.

Ra16.42/Rb16.42

Fullerenes as molecular templates in the formation of metal and semiconductor clusters. Petra Reinke[1], Hui Liu[1] and Helge Kroeger[2]; [1]Dep. of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; [2]2. Physikalisches Institut, Universitaet Goettingen, Goettingen, Germany.

Clusters with fewer than 100 atoms are envisaged as components in nanoelectronics, catalysis and in numerous other nanotechnology related applications. The cluster properties and reactivity change dramatically with the number of atoms. An important goal is to develop methods, which allow to tailor the cluster size and spatial arrangement, and create environmentally robust cluster arrays. C60 serves as a model system to explore the concept of molecular templates, where the presence of preferred adsorption/nucleation sites provide the template for self-organized cluster growth. The present investigation explores the synthesis of size-selected clusters exploiting the structured, corrugated surface and bulk of C60. The relatively large interstitial spaces can provide space for clusters with up to 20 atoms. An additional advantage of the fullerene-cluster system is the ability to create 2D and 3D arrangements by choosing a sequential or simultaneous deposition of the reactants. Scanning tunneling spectroscopy yields information on the geometric structure of the surface, photoelectron spectroscopy applied in the analysis of the core level and valence band spectra affords information on the cluster size, electronic structure of clusters and interface properties. The growth of the Si on the C60 surface begins with the formation of clusters in the interstitial sites between the C60 molecules. As the growth continues they coalesce and an a-Si overlayer forms. The interface contains no SiC covalent bonds and the electronic properties are deduced from the PES data. The analysis illustrates that the fullerene surface provides a suitable mold for the self-organized growth of Si clusters. In contrast the absorption of gold occurs at random surface sites and no preferential nucleation sites of Au clusters could be identified. The change in surface topography of thin Au-C60 films illustrates the influence of the metal atoms and indicates the transition to a layer-by-layer growth mode. The structure and properties of the 3D Si-C60 and Au-C60 were investigated with a wide range of methods and will briefly be summarized. The interaction between the template molecules and the cluster forming element is decisive for the successful implementation of this concept, which leads us to the second part of our investigation. The C60 layers grow on graphite as dendritic structures and their formation can be described by diffusion limited aggregation. The fractal dimension of the islands increases with time. The interaction of the fullerene island structure with metal atoms, the change in shape and growth mode will be described in detail and the consequences for the formation of spatially well-defined cluster arrays are discussed. Understanding the fundamental interactions within the adatom-C60 system and their impact on the resultant structure will enable us to develop a wider range of molecular templates.

Ra16.43/Rb16.43

Functionalization and Dielectrphoretic Manipulation of DNA-Modified Silicon Nanowires. Jeremy A. Streifer, Matthew S. Marcus, Beth M. Nichols, Heesuk Kim and Robert J. Hamers; Chemistry, University of Wisconsin, Madison, Madison, Wisconsin.

We have investigated the biomolecular functionalization of silicon nanowires with DNA and the assembly of silicon nanowires across electrode gaps as a step toward creation of arrays of nanowire biosensor devices based on electrical detection. Photochemical functionalization of H-terminated silicon nanowires with molecules bearing a reactive olefin (C=C) group was used to produce amine-terminated nanowires with no intervening surface oxide that were then covalently linked to DNA oligonucleotides. The biomolecular recognition properties of the nanowires were tested as they interacted with complementary and non-complementary biological molecules, showing good selectivity and reversibility. After removal of the nanowires from their growth substrate we assembled them into circuits using dielectrophoretic manipulation. Optical microscopy videos demonstrate the ability to dynamically control the position of individual ~50 nm diameter silicon nanowires near microelectrodes and to selectively capture single nanowires between microelectrode gaps for electrical characterization.

Ra16.44/Rb16.44

Micropatterns of Chiral Self-Assembled Monolayers: Toward Bistable Switching Between Right and Left Handed States. Jinchul Cho, Yo-Han Cho and Ji-Woong Park; Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea.

Micropatterned surfaces of chiral self-assembled monolyers(SAM) are fabricated using enantiomeric pair of 1,1-binaphthyl derivatives containing surface-reactive functional groups. (R) or (S)-2-binaphthol is reacted with 3-(triethoxysilyl)propylisocyanate to yield enantionmerically pure chiral molecules that are reactive to silica based substrates. A substrate surface is micro-patterned with the enantionmers of binaphthol derivatives with opposite chirality using microcontact printing and immersion method. Processing conditions are optimized to yield the micropattern that is racemic as a whole, but that is composed of enantiomerically pure domains in the micrometer scale. We discuss the interaction of the resulting chiral surface with small molecule or polymeric nematic liquid crystals on its surface, where the chiral molecules twist the nematic phase. The effect of chiral excess in the chiral monolayer on the phase behaviors of the liquid crystalline small molecules or polymers above the surface is discussed. Switching between two helical states of the induced chiral phases will be also investigated using external stimuli such as circularly polarized light.

Ra16.45/Rb16.45

Wafer-scale nickel imprint stamps based on interference lithography and their applications for perfectly ordered anodic aluminum oxide (AAO). Woo Lee, Ran Ji, Mato Knez, Ria Idris, Ulrich Goesele and Kornelius Nielsch; Max Planck Institute of Microstructure Physics, Halle, Germany.

In the last decade, anodic aluminum oxide (AAO) with hexagonally self-organized cylindrical nanochannel arrays has been intensively utilized as a template material for the fabrication of various nanowires and nanotubes, which have potential applications in advanced electronic, magnetic, and optical devices. For the synthesis of structurally and dimensionally well-defined nanowires and nanotubes, a perfectly ordered template is highly desirable, since a wide range of materials properties depend critically on the size, shape, and regularity of their substructure on the nanometer size scale. A combination of lithographic patterning and electrochemical oxidation of aluminum allows the preparation of perfectly ordered AAO templates. Surface pre-patterns defined by nanoimprint lithography have been utilized to guide the pore formation and to align the nanochannels. For the development of wafer-scale imprint stamps, first we fabricated photoresist patterns on silicon substrates by laser interference lithography (LIL), where the period and the square or hexagonal arrangement of the resist patterns can be modulated. The photoresist patterns were used as a master structure for the replication of Ni imprint stamps via electrodeposition technique. The Ni imprint stamps with a periodicity of 200 nm up to 500 nm were used to pre-pattern the surface of aluminum substrates. Subsequently, the pre-patterned Al substrates were electrochemically oxidized and the perfectly ordered AAO could be obtained. AFM and SEM analyses revealed that the present Ni imprint stamps can be used several times for the surface pre-patterning of aluminum with a high fidelity in pattern transfer. In this presentation, we will also present the practical applications of perfectly ordered AAO templates for the development of various multifunctional nanostructured materials, such as magnetic nanowires and nanotubes, TiO2 nanotubes, and Au nanotube membranes. Financial support from the German Federal Ministry for Education and Research (BMBF, Project No. 03N8701) is greatly acknowledged.

Ra16.46/Rb16.46

Template-Directed Growth of Nanoparticle-Mediated Colloidal Crystals on Large-Area Patterned Substrates. Ryan J. Kershner[1,2,3], Summer K. Rhodes[3,2], Florencio Garcia-Santamaria[3,2,1], Paul V. Braun[3,1,2], Jennifer A. Lewis[3,1,2] and Pierre Wiltzius[1,3,2]; [1]Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois; [2]Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois; [3]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Large-domain colloidal crystals were created by gravitational settling of microspheres onto patterned substrates. The large-area patterns were produced using multibeam interference lithography, facilitating templated epitaxial growth of single domain crystals with controlled crystallographic orientation. Colloidal crystals were produced from a binary suspension of microspheres (diamater $\sim$0.5 μm) stabilized through the addition of highly charged nanoparticles (Tohver et al., PNAS (2001)) followed by subsequent nanoparticle gelation (Lee et al., Langmuir (2004). Successful epitaxial growth was shown to depend on the periodicity of the substrate as well as on the chemistry of the binary suspension, the later allowing the interparticle spacing to be finitely controlled. Tuning both of these parameters allowed the crystals to be dried without disrupting their order. The resulting optical properties of the dried crystals are presented, as measured along the [111] and [100] directions.

Ra16.47/Rb16.47

Analysis of New Y-Junction Carbon Nanotube Transistors with Novel Three-Way Electrical Switching and Logic Capability. Chiara Daraio[1], Prab R. Bandaru[1], Sungho Jin[1] and Apparao M. Rao[2]; [1]Materials Science and Engineering Program, University of California, San Diego, La Jolla, California; [2]Physics, Clemson University, Clemson, South Carolina.

A dramatic electrical switching behavior in a nano-particle-containing Y-junction carbon nanotube (CNT) is demonstrated for the first time(1). An abrupt modulation of the current from the ON to the OFF state is observed as the field for the third branch is adjusted, most likely induced by the presence of catalyst nanoparticle and associated defects at the junction. The interactions of the electron currents in the three branches of the Y-junction synthesized by chemical vapor deposition using adherent, Ti-containing, catalyst nanoparticles(2) are shown to be the basis for a new, three-way logic device. Unlike previously reported CNT field effect transistors where the gate structure had to be separately fabricated, the Y-junction transistor has a built-in gate structure as one of the three branches serve as a natural gate. Furthermore, the transistor function can be effected by any combination of the three branches, thus allowing a three-way device operations. This is the first time ever that such switching and logic functionalities have been experimentally demonstrated in Y-junction nanotubes without the need for fabrication of an external gate, as only a diode like behavior was previously observed in Y-junctions. The new Y-junction transistor device can enable an entirely new class of nanoelectronic architecture and functionality extending well beyond conventional field effect transistor technologies. In this presentation, transmission electron microscopy and scanning electron microscopy analysis of the Y-junction nanotube microstructure, electrical transport and switching properties, various materials and device fabrication issues, and alternative structural arrangements for future advanced devices will be discussed. (1) P. R. Bandaru, C. Daraio, S. Jin, and A.M. Rao, "Novel Electrical Switching Behavior and Logic in Carbon Nanotube Y-junctions", Nature Materials 4, 2005 (in press). (2) N. Gothard, C. Daraio, J. Gaillard, R. Zidan, S. Jin, A.M. Rao, "Controlled growthof Y-junction nanotubes using Ti-doped vapor catalyst", Nanoletters 4, 213-217 (2004).

Ra16.48/Rb16.48

Abstract Withdrawn

Ra16.49/Rb16.49

Controlled Assembly of Nanoparticles. Lisa Dillenback[1], Glenn Goodrich[2] and Christine Keating[1]; [1]Chemistry, The Pennsylvania State University, State College, Pennsylvania; [2]Nanospectra Biosciences, Houston, Texas.

Nanoparticles are promising building blocks for the bottom-up assembly of high-density electronics and other functional materials due to their small size and tunable optical, electronic, and physical properties. Our current research involves the assembly of nanoparticles both in solution and at a 2-dimensional interface. In solution, temperature is used to control the order of assembly events of three types of particles to be linked by two different sets of complementary DNA. At higher temperatures, only the duplexes having higher thermal stability are able to form. By starting at a high temperature and then cooling the sample, these more stable sequences hybridize first, followed by the less stable sequences at lower temperatures. Temperature programming combines the selectivity of DNA directed assembly with the ability to control the order in which several complementary strands hybridize in a common solution, and could contribute to the synthesis of more complex nanostructured materials. Two-dimensional assembly is performed at the air/water interface using the Langmuir-Blodgett technique. The behavior of nanoparticles at the air/water interface, and the effect of surface chemistry (e.g. alkane thiols) is studied. The effect of forces between particles on the resulting assemblies is under investigation. This 2-dimensional technique can be used to create well-ordered arrays of nanoparticles.

Ra16.50/Rb16.50

Simultaneous Transport and Raman Spectroscopy on Single Walled Carbon Nanotubes. Hootan Farhat[1], Eduardo B. Barros[3,2], Hyungbin Son[2] and Jing Kong[2]; [1]Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [3]Departamento de Fisica, Universidade Federal do Ceara, Fortaleza, Ceara, Brazil.

Current saturation at high fields in micron length carbon nanotube devices is believed to be caused by electron scattering by high energy optical and zone boundary phonons. Scattering lengths calculated using theoretical electron-phonon coupling strengths, and assuming a thermally equilibrated phonon population[1][2], are an order of magnitude greater than those observed in transport experiments[1][3]. It has recently been proposed that this discrepancy can be attributed to presence of non-equilibrium phonons[2]. Raman spectroscopy is a useful tool for probing the phonon distribution because the intensity of each peak is closely tied to the population of the related phonon. We are performing simultaneous Raman spectroscopy and high field transport experiments to investigate the occupation of high energy phonons during electrical transport. We have fabricated electrically contacted suspended SWNT devices that are compatible with a tunable Raman spectroscopy setup, which has allowed us to obtain resonance Raman spectra over a wide range of nanotube diameters. Measuring the Stokes and antiStokes Raman intensities of biased nanotube devices, we calculate the phonon occupation as a function of applied field. [1] Z. Yao et al., Phys. Rev. Lett. 84, 2941 (2000). [2] M. Lazzeri et al., cond-mat/0503278 (2005). [3] J-Y. Park et al., Nano Lett. 4, 517 (2004).

Ra16.51/Rb16.51

Selective Electrostatic Self-assembly on Patterned Ferroelectric Surfaces. Jacqueline Nicole Hanson[1], B. J. Rodriguez[1], R. J. Petrie[2], J. Choung[3], C. B. Gorman[2], A. Gruverman[3] and R. J. Nemanich[1]; [1]Physics, North Carolina State University, Raleigh, North Carolina; [2]Chemistry, North Carolina State University, Raleigh, North Carolina; [3]Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

We present an approach for self-assembly which employs nanopatterned polar surfaces. Separating and controlling chemical and electronic properties of the surface is important for selective deposition. Ferroelectric templates for nano-patterning utilize the local surface electronic properties (bound polarization, surface dipole, and band bending), which can be controlled by switching the direction of spontaneous polarization with an external electric field, by heating (pyroelectric effect), and by UV-illumination. In this study, charged particles (toner) and molecules (evans blue dye) are deposited onto patterned ferroelectric LiNbO3 (lithium niobate). We found negatively charged toner particles adhered to negative domains and negatively charged evans blue molecules adhered to positive domains, the differences will be discussed. The results were verified using several techniques including atomic force microscopy (AFM), optical and fluorescence microscopy, and x-ray photoemission spectroscopy (XPS). Research supported by the NSF (Grant No. 0403871, NIRT on Nanopatterned Polar Surfaces).

Ra16.52/Rb16.52

Fabrication of Patterned Carbon Nanotube Arrays and Study of Their Electron Field Emission. Devon J. McClain[1], Lifeng Dong[1], Patricia Pan[1], Jun Jiao[1], Coralee M. McCarter[2], David F. Bahr[2], Cecilia D. Richards[2] and Robert F. Richards[2]; [1]Department of Physics, Portland State University, Portland, Oregon; [2]Electrical Engineering Department, Washington State University, Pullman, Washington.

We report on the study of electron field emission properties of aligned carbon nanotube (CNT) arrays. CNT growth was accomplished via chemical vapor deposition (CVD) on catalyst dot arrays created by photolithography. The specific procedure was as follows: (1) An iron nitrate sol gel catalyst was spun onto a silicon wafer (100) and patterned using standard photolithographic techniques; (2) Individual die cut from the wafer were placed in a horizontal tube furnace for multi-walled CNT growth; (3) Growth was achieved at 700 øC for 30 minutes with an admixture of H2 and C2H2 (385 sccm and 25 sccm respectively). The morphology of these arrays was characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The configuration of the CNT arrays is determined by the patterned catalyst dots. EDS spectra confirm that iron catalyst leads the growth of the CNTs. HRTEM analysis of an individual CNT revealed that the tube consists of 5-6 graphitic layers. Field emission analysis was performed utilizing a point-to-plane scanning anode-cathode apparatus at a base pressure of 1x10-8 Torr. The electron field emission properties, in terms of threshold field, turn-on field, field enhancement factor and emission current of various patterns are compared with other nanostructures such as ZnO nanowires. Acknowledgments: Financial support for this research was provided in part by the NSF under awards No. ECS-0217061, No. NIRT-0404370 and DMR-0353738.

Ra16.53/Rb16.53

Supramolecular assembly of surfactant-like peptides: characterization and study of peptide- membrane interactions. Isabella Miglioli[1], Salvatore Chessari[1], Martina Baumann[1], Shuguang Zhang[2] and Marcus Textor[1]; [1]Materials, Swiss Federal Institute of Technology, Zurich, Switzerland; [2]Biology, MIT, Boston, Massachusetts.

Surfactant-like peptides (peptide sequences with both hydrophobic and hydrophilic moieties in a single molecule) self-assemble in a variety of motifs to form pores, channels and tubules. Ion transport through cell membranes, and physical functions such as solubilizing difficult-to-dissolve molecules, are facilitated by the tubes that are formed by molecular assemblies [1]. Peptide nanostructures are constructed by highly convergent non-covalent processes, both intra- and inter-chain interactions, such as van der Waals, electrostatic and hydrophobic forces as well as hydrogen bonds [2]. In this study the supramolecular assembly of four different amphiphilic peptides is studied and preliminary results on peptide-cell interactions shown. Transmission electron microscopy (TEM) is used to study the supramolecular assembly of the samples in solution, complemented by conformational analysis as a function of concentration and pH-achieved by circular dichroism, and morphological studies of peptide assemblies based on atomic force microscopy (AFM). Peptide-lipid membrane interactions are studied by in situ QCM-D, as well as by AFM and TEM, while molecular mechanics calculations are performed to simulate the assembly of selected peptide sequences in aqueous media, and the comparison of such results with those experimentally obtained is also discussed. References 1. von Maltzahn, G., et al., Positively charged surfactant-like peptides self-assemble into nanostructures. Langmuir, 2003. 19(10): p. 4332-4337. 2. Schultz GE, S.R., Principles of Protein Structure, ed. Springer. 1979, Berlin Heidelberg New York.

Ra16.54/Rb16.54

Assembly of Binary Nanoparticles by Difunctional Molecular Mediators. Nancy N. Kariuki, Jin Luo and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

The ability to assemble nanoparticles with defined interparticle linkage and chemical properties is critical to the exploration of the nanoparticle-structured electronic, optical, magnetic, catalytic, and chemical or biological properties. While the assembly of monometallic nanoparticles has been studied extensively in recent years, little is known about assemblies of binary or ternary metal nanoparticle systems, which is in part due to the lack of strategies for controllable interparticle linkages. This presentation describes a new strategy towards the assembly of bimetallic nanoparticles via selective linkage of mediator/linker molecules at the nanoparticle surface. One goal is to understand the nanoscale properties of the nanomaterials for chemical/biological sensing and catalytic applications. Gold-silver alloy nanoparticles with different bimetallic compositions were studied as a model system, and the unique interparticle-linking chemistry of difunctional groups at Ag and Au sites are exploited for defining the interparticle chemistry. The mechanism for the molecularly-mediated assembly involves the selective mediating effect of the linker molecules at the silver sites and templating effect of the alkanethiolate capping molecules at the gold and silver sites. Implications of the findings to the exploration of binary nanoparticle-structured sensing and catalytic materials will also be discussed.

Ra16.55/Rb16.55

Novel synthesis method of gold nanoparticles in aqueous media. Abhilash Sugunan[1], Joydeep Dutta[1] and Jons Hilborn[2]; [1]Microelectronics FOS, Asian Institute of Technology, Pathumthani, Thailand; [2]Polymer Chemistry, Materials Chemistry, Uppsala University, Uppsala, Sweden.

One of the most widely used methods for the synthesis of gold colloids in water involves the reduction of an aqueous solution of gold salt (HAuCl4) by trisodium citrate. The colloidal nanoparticles are stabilized by a physical adsorption of excess citrate ions from the medium. In the past decade, several new techniques have been developed that are stabilized by an alkanethiol chemically bound on the particle surfaces and are often referred as monolayer-protected clusters (MPC). Synthesis of MPCs usually involves organic solvents, which can potentially degrade most bio-molecules, making them unsuitable for many applications like the solution-based biosensors. Although citrate capped nanoparticles have been widely studied and reduction of gold(III) salts with trisodium citrate is possibly the most commonly used technique for aqueous gold colloids, there are very few reports on alternative techniques for synthesis of gold nanoparticles in water, based on electrostatic stabilization. Recently, synthesis of aqueous gold colloid has been reported by reduction of aqueous solution of gold(III) chloride with aspartic acid (amino acid). However, it is suggested in the report that other amino acids were ineffective in reducing aqueous solutions of Au(III) salts. Size selective synthesis was not successfully carried out in that work, and variation of the concentration of precursors resulted in mostly agglomerated nanoparticles. We will report the synthesis of spherical gold nanoparticles with very high uniformity in size and shape by reducing aqueous solution of gold (III) chloride with monosodium glutamate (MSG). To the best of our knowledge this is the first report of the successful reduction of gold chloride by MSG to produce metallic gold colloids. The obtained nanoparticles are found to be comparable in size and shape to the nanoparticles obtained by the well known Turkevich process involving trisodium citrate. By varying the molar concentration ratio of reducing agent to gold salt in the precursor solution, uniform spherical particles ranging from 10 to 20 nm have been synthesized. The plasmon absorption band and the line-shape of the absorption spectra was found to be very similar for gold colloids obtained employing equal concentrations of monosodium glutamate and trisodium citrate (following the well documented Turkevich method) as reducing agent, due to similarity in morphology of the nanoparticles obtained by both methods. This suggests that the thermodynamically governed evolution of gold nanoparticles in both the synthetic methods follow a similar sequence of nucleation of gold seeds and subsequent Ostwald ripening of seeds to form larger nanocrystals. It can be further concluded that aqueous solution of gold salts can be reduced by acidic amino acids or their sodium salts.

Ra16.56/Rb16.56

Synthesis and Characterization of Tungsten Oxide Nanostructures by MPECVD. Uei-Shin Chen, Sen-Hung Hsueh and Han C. Shih; Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Tungsten oxides have been grown by microwave plasma enhanced chemical vapor deposition directly on silicon wafer without using any catalyst. Due to the unique property of the plasma system, tungsten oxide could be synthesized in just several minutes (3-5 minutes). It is very economic for saving time and cost. In this study, tungsten oxides have been fabricated in various morphologies, such as nano-rods (20-100nm in diameter), nano-slabs (30-100nm in thickness, 100-500 in width and 1-2 μm in length). Although the cause of different morphologies is still not very clear, from our preliminary observations analyses, the results suggest that the temperature and the gas flow rate play an important role in the growth of these nano-materials of differert morphologies. The crystal structure and chemical composition of these nano-rods and nano-slabs identified by the high-resolution transmission electron microscopy (HRTEM), energy dispersion spectrum and selective area diffraction patterns show that the nano-rods and nano-slabs are both single crystal. The results of X-ray diffraction and Raman spectra coincide with the analyses of HRTEM. The cathode luminescence spectra of these nanostructures reveal a red or orange emission. The vapor-solid growth mechanism is proposed for these tungsten oxide nanostructures.

Ra16.57/Rb16.57

Vibrational anharmonicity in single-walled carbon nanotubes: Raman linewidth of the radial breathing mode. rahul rao[1], Christian Poweleit[2], Jose Menendez[2] and Apparao Rao[1]; [1]Physics and Astronomy, Clemson University, Clemson, South Carolina; [2]Physics and Astrononmy, Arizona State University, Tempe, Arizona.

The electronic properties of carbon nanotubes are strongly affected by the quasi one-dimensional character of these materials, as demonstrated by a vast body of scientific literature produced over the past decade. Equally dramatic effects are to be expected on the vibrational properties, and in particular, on the anharmonic phonon-phonon interactions that determine phonon lifetimes and thermal expansion. Unfortunately, the notorious experimental difficulties associated with measurements at the single nanotube level have limited progress in this fundamental area. We report here what we believe is the first measurement of the intrinsic lifetime of the Raman-active Radial Breathing Mode (RBM) in carbon nanotubes. This quantity is of great interest because the so-called Klemens decay channel [1] (a zone center optical phonon decaying into two acoustic phonons of equal energy) is limited by dimensionality to a single pair of phonons. Therefore, one might expect very small RBM linewidths (the full width at half maximum (FWHM) of the Raman peak is the inverse of the phonon lifetime) in carbon nanotubes. However, the reported FWHMs are about 5-10 cm^{-1}, an order of magnitude larger than in tetrahedral semiconductors.[2] This suggests that the experimental data are strongly affected by bundling and defects. Recent experiments on isolated single-walled nanotubes (SWNT) on Si substrates yield a FWHM of ~ 3 cm^{-1} [3], still large compared with well-known semiconductors. For the present study, suspended SWNTs were synthesized by chemical vapor deposition on silicon substrates with 5 micron-wide trenches. The suspension over trenches should minimize nanotube/substrate interactions. Resonant micro-Raman spectra were obtained from several individual suspended SWNTs using 647.1 nm excitation. The spectra were collected with different Raman spectrometers with a resolution close to 1 cm^{-1}. Under these experimental conditions, the Raman line width was sensitive to the incident laser power, suggesting that it was indeed caused by anharmonic interactions. After deconvolution of instrumental effects, the Lorentzian FWHM of the measured RBMs were found to range between 1 cm^{-1} and 2 cm^{-1} at room temperature. Assuming that the decay is dominated by the Klemens channel, this implies zero-temperature linewidths between 0.25 and 0.50 cm^{-1}. These values represent an upper limit for the low-temperature linewidth, since the Klemens channel has a weaker temperature dependence than any other competing channel. Therefore, the Raman linewidth of the RBM is clearly smaller than the linewidth of Raman-active phonons in group-IV semiconductors including diamond, but larger than the observed line width for low-energy optical phonons in wurtzite materials.[4] 1 P.G. Klemens, Phys. Rev. 148, 845 (1966). 2 J. Menéndez and M. Cardona, Phys. Rev. B 29, 2051 (1984). 3 A. Jorio et al., Phys. Rev. B., 66, 115411 (2002). 4 C. Aku-Leh et al., Phys. Rev B 71, 205211 (2005).

Ra16.58/Rb16.58

The interparticle forces and organization of surfactant-coated ZnS nanoparticles in dodecane: effect of water,. Mustafa Akbulut, Anna Godfrey and Jacob Israelachvili; Chemical Engineering, UCSB, Santa Barbara, California.

The forces between surfaces with confined spherical ZnS nanoparticles coated with hexadecylamine surfactant (total diameter ~5 nm) in dodecane were measured in the absence and presence of trace amounts of water. The water molecules cause the nanoparticles to aggregate and adsorb on the (hydrophilic mica) surfaces, resulting in an initial long range exponentially repulsive force between the surfaces. After longer times (t>20 hr), water bridges form between the nanoparticles and surfaces, and attractive capillary forces then cause a long range attraction and a strong short-range adhesion. Clearly, as previously seen in non-aqueous bulk colloidal systems, even trace amounts of water have a profound effect on the interactions and structure of nanoparticle assemblies in thin films that in turn affect their physical properties. These effects should be considered in the design of thin film processing methodologies, and final structure of such films.

Ra16.59/Rb16.59

Fabrication of Free Standing Co/Pt Barcode Nanowires with Tunable Nanomagnetism via Programmable Barcode Layer Effect. Joon-rak Choi[1,2] and Jinwoo Cheon[1,2]; [1]Chemistry, Yonsei University, Seoul, South Korea; [2]Nano-Medical National Core Research Center, Yonsei University, Seoul, South Korea.

Free standing Co/Pt magnetic barcode nanowire structures with controllable layer thickness are fabricated through pulse-sequence electrodeposition of cobalt and platinum followed by subsequent nanowire isolation processes. All of such barcode nanowires display well-defined bamboo-like shapes with almost identical shape either inside or out of the templates. Magnetic properties of nanostructures obtained are fully elucidated by systematically controlling the aspect ratio of cobalt segments and thicknesses. Significant enhancements of the ferromagnetism of Co/Pt barcode nanowires are also feasible through the interfacial alloying processes produced by thermally induced phase transitions. These magnetism controlled free standing Co/Pt magnetic barcode nanowires can be used as versatile building blocks for the realization of 1-dimensional wire based magneto-electronic devices.

SESSION Ra17: Supermolecular Assemblies I

Chair: Peter Beton
Thursday Morning, December 1, 2005
Room 207 (Hynes)

8:30 AM *Ra17.1

Controling Matter at the Nanoscale through Supramolecular Engineering at Surfaces. Johannes V. Barth, [1]Chemisty and Physics & Astronomy, UBC Vancouver, Vancouver, British Columbia, Canada; [2]IPN, EPFL, Lausanne, Switzerland.

The adaptation of biologically inspired principles to artificial compounds and environments opens up intriguing vistas for the development of highly organized systems with molecular-level feature control. Here I focus on using well-defined surfaces as platforms to assemble supramolecular architectures from adsorbed molecular building blocks. Their evolution, order principles and structural characteristics are investigated in exquisite detail by temperature-controlled scanning tunneling microscopy. Complementary experimental studies with integral techniques and model simulations provide insight into the corresponding physicochemical properties and the nature of the underlying noncovalent interactions. In particular we explored hydrogen-bond mediated and metal-directed self-assembly to guide the formation and mesoscopic organization of mononuclear metal-complexes and arrays, one-dimensional molecular gratings and two-dimensional nanoporous layers. It is suggested that this design strategy provides a versatile rationale for engineering low-dimensional nanosystems with specific structure, composition and functionality, which bear promise for future technological applications.

9:00 AM Ra17.2

Self-Assembly and Molecular Recognition of Nucleic Acid Bases Studied by STM. Roberto Otero[1,2], Maya Schoeck[2], Luis Miguel Molina[2], Erik Laegsgaard[2], Ivan Stensgaard[2], Bjork Hammer[2] and Flemming Besenbacher[2]; [1]Dept. of Condensed Matter Physics, Universidad Autonoma de Madrid, Madrid, Spain; [2]Dept. of Physics and Astronomy, iNANO and University of Aarhus, Aarhus, Denmark.

Self-assembly and molecular recognition are two basic and related concepts from the emerging field of supramolecular chemistry. Both concepts are based on the ability of molecules provided with peripheral functional groups to interact in a selective manner with other molecules of the same (self-assembly) or complementary (molecular recognition) chemical species. Most of the forseeable applications for molecular systems on solid supports, such as molecular electronic devices or nanomechanical biosensors, are based on these two properties of organic species. This has motivated a very important effort towards the understanding and control of the self-assembled geometries of adsorbed species on different solid surfaces. In this respect, Biology is a continuous source of inspiration. From the replication of DNA to the way in which a virus particle anchors to a cell's membrane, everything is related to the concepts of self-assembly and molecular recognition. The capability of complementary DNA strands to steer the self-assembly of other elements attached to them has already been used in various occasions. Furthermore, by providing the DNA strands with surface-anchoring groups, 2D self-assembled architectures could be built. However, the 2D architectures built in this manner are still relatively large, since the larger the DNA strand the more selectively it binds its complementary strand, and they need a very particular environment for the DNA strands not to denature. In this talk we will present a number of experiments showing that nucleic acid bases (Adenine, Guanine, Cytosine and Thymine) can be deposited on single crystal Au (111) surface where, thanks to the weak interaction with the substrate, they self-assemble and recognize each other, forming very similar motifs to those found for DNA and RNA studies in solution. We will show that guanine molecules on Au (111) self-assemble into a hydrogen-bonded network of G-quartets with essentially the same structure as those found in in vitro studies of telomeric DNA. The large stability of this network to high temperatures can only be explained by a cooperative effect that strengthens the hydrogen-bonds within the quartets, as revealed by our DFT calculations. This constitutes the first evidence that cooperative effects might be basic to properly describe the hydrogen-bonding interaction between DNA strands. We have also investigated binary mixtures of complementary (G-C) and non-complementary (A-C) DNA bases. Our experiments show that whereas non-complementary base pairs completely break and seggregate upon gentle annealing, complementary pair are stronger and the mixture so formed cannot be separated by thermal treatments. A thourough inspection of STM images shows that the most probable reason for the enhanced stability of the G-C mixed network is the formation of Watson-Crick G-C pairs, with a similar geometry as those found in DNA.

9:15 AM Ra17.3

Self-organization of tetraphenylporphyrins on highly oriented pyrolitic graphite. Manuela Scarselli[1], Paola Castrucci[1], Donato Monti[2], Gianlorenzo Bussetti[1], Michele Russo[2], Claudio Goletti[1], Piero Chiaradia[1], Roberto Paolesse[2] and Maurizio De Crescenzi[1]; [1]physics, universita di roma "tor Vergata", roma, Italy; [2]chemistry, university of tor vergata, roma, Italy.

The preparation of thin films of porphyrin derivatives is of great interest due to their potential application in material science and for, among others, optical, chemical sensors, and solid state synthetic hemoproteins. One of the most compelling characteristics influencing the properties of porphyrin films is, undoubtedly, the geometry and orientation of the deposited mesostructure. In this work, we present a combined Scanning Tunneling Microscopy (STM), Reflectance Anisotropy Spectroscopy (RAS)(1), X-Ray photoelectron spectroscopy and Reflection Energy Loss Spectroscopy (REELS) performed in ultra high vacuum condition (UHV) at room temperature, on tetraphenylporphyrin (H2TPP) molecules sublimated on highly oriented pyrolitic graphite (HOPG). Once the presence of the molecule and its integrity after the deposition, has been verified by X-Ray and REELS spectroscopy, STM observation allowed obtaining the morphological characterization of the molecules deposited on the graphite and the RAS study revealed an anisotropy signal in the Soret band [1]. After very low sublimation rates, STM images show few isolated molecules on the HOPG and RAS is still unable to detect any anisotropy. When spontaneous aggregation of the molecules is visible in the STM, RAS measures a small anisotropy signal (about 0.18%) in correspondence of the Soret band region (l=433nm) of the H2TPP. Molecules are arranged in an highly ordered hexagonal lattice, where each bright structure corresponds to the porphyrin ring of diameter 1.8 nm and height 0.2nm and the distance between adjacent porphyrins is about 3.0 nm. Subsequent porphyrin sublimation cycles increase the RAS signal intensity and shift the energy position of the main peak towards lower energies, in agreement with a J-type interaction of H2TPPs. When STM images observe the formation of agglomerates randomly distributed on the surface, RAS can still measure an anisotropy peak of just reduced intensity. The interaction of porphyrins with the substrate plays an important role in determining the geometry of the ordered films [2,3], H2TPPs have an intrinsic four-fold symmetry but when spontaneously assemble on graphite, they give rise to an ordered film with hexagonal symmetry. The mechanism that determines this unpredictable symmetry is still under investigation in particular, theoretical studies together with some molecular modelling are in progress. These experiments show how the local morphological information obtained with STM can be linked with RAS study as a function of H2TPP deposition and aggregation on the graphite surface. References: 1. C. Goletti, G. Bussetti, P. Chiaradia, A. Sassella, A. Borghesi, Organic Electronics 5(1-3) 73-81 (2004) and references therein. 2. T. A. Jung, R. R. Schlitter & J. K. Gimzewski, Nature 386 696 (1997) 3. T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno & S. Mashiko, Nature 413 619 (1997)

9:30 AM Ra17.4

Patterning multilayers of molecules via self-organization. Wei Lu and David Salac; Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

The electric dipole interaction among adsorbate molecules may cause them to form regular nanopatterns. In a multilayer system, the self-organization of each layer is also influenced by the underlying layers. This paper extends our recent work (W. Lu and D. Salac, Phys Rev. Lett.94,146103,2005) to study the patterning of multiple layers of molecules via self-organization. Charge interactions have been utilized to construct functional multilayer systems by the approach of electrostatic self-assembly (ESA). ESA processing involves dipping a chosen substrate into alternate aqueous solutions containing anionic and cationic molecules or nanoparticles, such as complexes of polymers, metal and oxide nanoclusters or proteins. This leads to alternating layers of polyanion and polycation monolayers. Design of the precursor molecules and control of the order of the multiple molecular layers allow control over macroscopic electrical, optical, mechanical and other properties. While applications such as nano-filtration and photovoltaic devices have been demonstrated, the ESA process is limited to simple, laminar multilayer systems, with little or no lateral variation in the monolayer. We show that for molecules carrying electric dipoles, dipole interaction can induce self-assembled patterns within each layer in a multi-layer system. The capability is desired for making complex structures, especially the formation of nanointerfaces and three dimensional nanocomposites. We consider the presence of two types of molecules in each layer, which are characterized by different dipole moments. The patterns are characterized by the non-uniform distribution of the two molecules. A phase field model is developed to simulate the molecular motion and patterning under the combined actions of dipole moments, intermolecular forces, entropy, and external electric field. The model allows us to simulate arbitrary number of layers. The study reveals self-alignment, pattern conformation and the possibility to reduce the domain sizes via a layer by layer approach. Take a two layer system as an example. We show that the first layer determines the overall pattern, while the second layer follows the contour of the first layer pattern with a smaller feature size. It is also shown that the pattern in a layer may define the roadway for molecules to travel on top it. This combined with electrodes embedded in the substrate gives much flexibility to guide the molecular motion and patterning.

9:45 AM Ra17.5

Preparing Si Surfaces for Functionalization. Nelson Rowell[1], Li-Lin Tay[1], Jean-Marc Baribeau[1], Rabah Boukherroub[2] and David Lockwood[1]; [1]National Research Council Canada, Ottawa, Ontario, Canada; [2]Interdisciplinary Research Institute, Villeneuve d'Ascq, France.

Recently there has been a large increase of Si-based biosensor activity observed in the literature. Central to this technology is the ability to form self-assembled monolayer directly on the bare Si surface. This self-assembled organic layer on a bare Si surface will provide surface functionality and bio-specificity the subsequent molecular binding events. Prior to the formation of this first functional layer, a Si wafer must be subjected to a very stringent cleaning essay to remove whatever thin layers of organic contaminants and/or inorganic surface oxides are present. This is a crucial step which will then enable a subsequent successful growth of the functional monolayer being laid down on the wafer surface. Here we adapt the infrared vibrational spectroscopy in a new attenuated total reflection (ATR-FTIR) geometry to investigate the presence of organic and inorganic thin layers on Si-wafer surfaces. In this study, three different Si wafer cleaning processes were explored: (1) microwave plasma etching (2) UV-Ozone etching (3) piranha bath at an elevated temperature. We will compare and contrast the effectiveness of three different cleaning essays for surface contaminant removal. The CH vibrations appearing at 2928 and 2856 cm-1 that are characteristic of organic contaminants were monitored before and after each of the cleaning procedures to quantitatively determine how effectively the surface organic contaminants had been removed. We also found that the removal of the native oxide on the Si surface (via HF dip) should not be carried out until these cleaning essays were completed. Premature removal of the surface oxide exposes a hydrophobic bare Si surface, which then acts as a trap for whatever hydrophobic organic contaminants are present in the solution or air. This was clearly evident from the large increase of CH vibrational signature of the uncleaned wafer. Our results revealed that a combination of plasma cleaning followed by the UV-Ozone treatment on Si generated the most effective cleaning of Si wafer. In the ATR-FTIR measurement, there was 25 times less absorbance in the CH vibrational signature after such a treatment. Following this procedure with the ATR method, we are able to evaluate quantitatively the effectiveness of the cleaning methods and as well as monitor hydrogen surface passivation. We will show that subsequent functionalization can also characterized with the same method as can oxide regrowth.

SESSION Rb17: Nanoparticles I
Chair: Heinrich Hofmann
Thursday Morning, December 1, 2005
Room 208 (Hynes)

8:30 AM *Rb17.1

Hierarchical Design of Metal Oxide Multi-Dimensional Arrays from Solutions. Lionel Vayssieres, ICYS, National Institute for Materials Science, Tsukuba, Japan.

The hierarchical design of well-defined and highly oriented two- and three-dimensional arrays of conventional semiconductor nanomaterials and their large scale manufacturing at low cost remain a crucial challenge to unfold the very promising future of nanodevices. In addition to economical manufacturing of nanostructured semiconductors, better fundamental knowledge of their electronic structure, physical, interfacial and structural properties and stability, is required to fully exploit their fascinating potentials. To combine such essential requirements, the predictive creation of structurally well-defined and well-ordered functional and multi-functional materials is essential. As an attempt to achieve such ambitious goals, a novel strategy to thin film metal oxide semiconductor nanotechnology processing has been developed and investigated. A thermodynamic growth control concept based on the chemical and electrostatic minimization of the surface energy as well as a thin film growth technique have been developed. Such original approach allows the generation of nanomaterials with novel and functional morphologies. Advanced metal oxide nanostructures consisting of oriented multidimensional arrays featuring building blocks of controlled morphologies, sizes, aspect ratios and orientations at nano-, meso-, and microscale are genuinely fabricated directly onto various substrates of large physical areas without template, surfactant, undercoating or applied field from the hydrolysis-condensation of aqueous metal salts solutions at mild temperatures (below 100C). Recent innovative advances in the fabrication of highly oriented and functional nanostructure arrays of transition metal oxides will be presented.

9:00 AM Rb17.2

Nanocrystals as Precursors for Flexible Functional Films. Ludovico Cademartiri[1], Georg von Freymann[4], Andre C. Arsenault[1], Jacopo Bertolotti[2], Diederik S. Wiersma[2], Vladimir Kitaev[3] and Geoffrey A. Ozin[1]; [1]Department of Chemistry, University of Toronto, Toronto, Ontario, Canada; [2]European Laboratory for Non-linear Spectroscopy (LENS), Sesto-Fiorentino (Florence), Italy; [3]Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario, Canada; [4]Institute for Applied Physics, University of Karlsruhe, Karlsruhe, Germany.

The use of semiconductor chalcogenide nanocrystals as precursors for the one-step formation of flexible functional films will be discussed. By taking advantage of the surface chemistry of these "zero-dimensional" building blocks we obtain close-packed three-dimensional arrays of nanocrystals interconnected by oxide sheaths. The films are obtained by exposing oxidation-resistant nanocrystals to an air plasma treatment. This treatment does not significantly harm the photoluminescence of the individual nanocrystal building blocks but confers it resilience to bending as well as acidic environments, hot solvents, annealing, and UV irradiation. Chemical accessibility and selective etching of the nanocrystals allows for micron scale patterning of the film. Preliminary results on the tuning of the film composition will be presented.

9:15 AM Rb17.3

Fast and Efficient Fabrication of Gold Nanoparticle Networks using Double-Stranded DNA. Ulrike Rehn[1], Paul Tiberiu Miclea[2], Ralf B. Wehrspohn[2] and Ulrich Goesele[1]; [1]Max Planck Institute of Microstructure Physics, Halle/Saale, Germany; [2]Department of Physics, University of Paderborn, Paderborn, Germany.

The controlled integration of functional nanoparticles into superstructures is crucial for the fabrication of nanoparticle-based devices, but remains still a challenge. Short artificial DNA sequences may be used as linker molecules, since their chain length as well as the composition of the sequence can be customized. Particularly interesting is their combination with metal nanoparticles, because the resulting hybrid systems are promising candidates for sensing or photonics. The general objective is the fabrication of flexible, ordered 3D building blocks of DNA-conjugated nanostructures. To reach this, the detailed understanding of mechanisms behind the network formation and the interactions between DNA and the particles is a prerequisite. Thus, a method based on use of double-stranded DNA and a variation of available thiol-groups was exploited. Besides the unambiguous evidence for the guidance of the particle network formation by the dsDNA, the morphology of the hybrid materials as well as the reversibility of the network formation was investigated by uv-vis spectroscopy and transmission electron microscopy. The data have been cross-checked by theoretical calculations using Mie theory. The results show, that the double-stranded DNA is highly efficient due to less interactions with the particle surface. No additional stabilizing molecules like alkanethiols are necessary, and no unspecific aggregation occurs. The latter is one of the limiting factors for the DNA-hybrid generation and will be discussed from the viewpoint of electrostatic interactions between the particles [1]. I would be desirable to combine the advantages of double-stranded DNA with that of complementary single-stranded DNA for the directed coupling of particles. A method to combine the advantages of both double- and single-stranded DNA will be presented. [1] U. Rehn et al., Proc. Fourth IEEE Conference on Nanotechnology, WE-P 24, Piscataway. USA (2004).

9:30 AM Rb17.4

Alignment of Gold Nanoparticles along Mesoporous Nanofibers with Controlled Pore Architectures. Jianfang Wang[1] and Galen D. Stucky[2]; [1]Physics, CUHK, Shatin, N.T., Hong Kong; [2]Chemistry, UCSB, Santa Barbara, California.

Mesoporous silica materials with tunable pore diameters on the nanometer scale and varying pore organizations can function as robust and open scaffolds to create novel composites with active components embedded inside pores. Up to date, a variety of nanoscale building blocks with interesting electronic, magnetic, optical, and catalytic functionalities have been embedded inside mesoporous silica materials, the morphological shapes of which include thin films, spheres, and irregularly-shaped particles. We have used cationic surfactants as structure-directing agents to synthesize nanoscale mesoporous fibers and ribbons and incorporated gold nanoparticles inside mesoporous fibers along their length direction. These fibers and ribbons possess pore channels that are hexagonally packed and 2- 3 nm in diameter (Wang, J. F.; Zhang, J. P.; Asoo, B. Y.; Stucky, G. D. J. Am. Chem. Soc. 2003, 125,13966-13967; Wang, J. F.; Tsung, C.-K.; Hong, W. B.; Wu, Y. Y.; Tang, J.; Stucky, G. D. Chem. Mater. 2004, 16, 5169-5181; Wang, J. F.; Tsung, C.-K.; Hayward, R. C.; Wu, Y. Y.; Stucky, G. D. Angew. Chem. Int. Ed. 2005, 44, 332-336). The fibers have diameters ranging from 50-300 nm, and they possess either circular pore architectures with pore channels oriented perpendicular to the fiber axis or longitudinal pore architectures with pore channels oriented parallel to the fiber axis. The ribbons are 50-250 nm thick and 0.4-1.5 μm wide and they have running-track-like pore channels oriented perpendicular to the ribbon length direction. Remarkably, the fibers with two types of pore architectures and ribbons can all be synthetically controlled. Gold nanoparticles are incorporated into mesoporous fibers by hydrogen reduction of a gold salt. Their shape can be synthetically controlled to be either spherical or elliptical. Furthermore, the orientation of elliptical gold nanoparticles depends on the pore architecture of the fiber. The elliptical gold nanoparticles grown inside the fibers with longitudinal pore architectures have their long axes oriented parallel to the fiber axis, while those grown inside the fibers with circular pore architectures have their long axes oriented perpendicular to the fiber axis. Because gold nanoparticles exhibit unique plasmon resonance properties, the plasmon coupling between gold nanoparticles aligned inside mesoporous nanofibers makes these composite structures ideal candidates for nanoscale waveguides on length scales below the optical diffraction limit.

9:45 AM Rb17.5

Binary superlattices of nanoparticles with different size and shape. Elena V. Shevchenko[1,2], Dmitri V. Talapin[2], Christopher B. Murray[2] and Stephen O'Brien[1]; [1]Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York; [2]IBM T.J. Watson Research Center, Yorktown Heights, New York.

Colloidal synthesis allows producing nanoparticles with different functionality, size and shape. Monodisperse nanoparticles show a tendency to self-assemble into ordered structures. Self-assembly of several different materials into a periodic superlattice is a promising tool to create novel materials with unique properties originating from the interactions between nano-scale building blocks. Co-crystallization of nanoparticles from multi-component colloidal mixtures leads to the formation of ordered superlattices over tens square micron areas. The structure and the stoichiometry of binary superlattices consisting of quasi-spherical nanoparticles can be varied in a broad range. The most of nanoparticulate binary superlattices has analogous among atomic binary systems. Thus, we developed technique for controllable growth of superlattices isostructural with $NaZn_{13}$, AlB_2, NaCl, Fe_4C, $CaCu_5$, CuAu, Cu_3Au, etc. Control of particle shape provides an additional degree of freedom for designing binary superlattices with sophisticated structures. Several examples of superlattices formed by nanoparticles of different shape will be demonstrated. The diversity of experimentally observed nanoparticulate binary superlattices is inconsistent with the theoretical predictions made for hard non-interacting spheres. The role of particle-particle interactions such as dipolar, van-der-Waals, etc will be discussed.

SESSION Ra18: Supramolecular Assemblies II

Chair: S. De Feyter
Thursday Morning, December 1, 2005
Room 207 (Hynes)

10:30 AM *Ra18.1

Directed and spontaneous assembly of molecular nanostructures. Peter Beton[1], Luis Perdigao[1], Neil Champness[2], Paul Staniec[1], Jin Ma[1], Janine Swarbrick[1], Ben Rogers[1], James Theobald[1], Lev Kantorovich[3], Natalia Martsinovich[3] and Chris Hobbs[3]; [1]School of Physics & Astronomy, University of Nottingham,

Nottingham, United Kingdom; [2]School of Chemistry, University of Nottingham, Nottingham, United Kingdom; [3]Department of Physics, Kings College London, London, United Kingdom.

Molecular networks and nanostructures have been formed using two complementary approaches - self assembly and scanning probe induced manipulation. Firstly, hydrogen bonding between molecules adsorbed on silicon surfaces is used to provide a highly specific directional interaction which controls the placement of neighbouring molecules. Through appropriate choice of molecules it is possible to form an extended regular network of two dimensional pores. The pores have a diameter in the range 0.5 - 3.5 nm and may be used to capture further adsorbed molecules giving rise to novel ordered structures and growth phenomena. We discuss examples of bimolecular networks which are direct analogues of the melamine/cynauric acid array which has been studied widely in supramolecular chemistry and is stabilised by a triple hydrogen bond. The pore size and spacing is controlled through choice of component molecules. Specifically one molecule (eg melamine) is used as a molecular vertex with threefold symmetry which combines with a second 'edge' molecule (eg cynauric acid and related perylene derivatives) to form a honeycomb network. The formation of fullerene clusters within the pores is demonstrated including highly regular 'magic' C60 heptamers. For the higher fullerene C84 more complex structures are formed which undergo growth induced transitions induced by the addition of a single molecule. We also describe recent results showing that tip induced molecular manipulation of C60 adsorbed on Si(100) proceeds through a rolling motion. This leads to a long range periodicity in tip response and is caused by a coupling of bond breaking, translation and rotation. This model is supported by extensive ab initio calculations in which an adsorbed molecule is forced to move across the surface resulting in simulated bond breaking and rotation. More recent results based on alternative rolling paths, as well as the role of the tip in stabilising intermediate states through an attractive interaction, will be discussed. In addition we will show preliminary data which demonstrate that self-assembly and manipulation may be combined. In particular the component molecules of the network may be displaced , or, alternatively, the tip of an STM may be used to induce hopping of captured clusters from pore to pore within th network. These results show that the clusters stabilised by the supramolecular networks have sufficient cohesive energy to be displaced as a single coherent structure. We will discuss the possibility of the use of spontaneous assembly as a generic technology for templating on the 1-10 nm scale and consider in particular the stability of the networks, and their formation on a range of substrates which would be required for their widespread use.

11:00 AM Ra18.2

Surface Chirality from Enantioselective Co-adsorption of C$_{60}$ and ACA. Bo Xu, Chenggang Tao, Janice Reutt-Robey and Ellen Williams; Univ. of Maryland, College Park, Maryland.

Chiral surfaces are actively studied for heterogeneous enantioselective catalysis and chiral recognition. Adsorption of chiral molecules (or achiral molecules which become chiral due to broken symmetry after adsorption) provides a typical route to produce chiral surfaces. Here we demonstrate the surface chirality can also be introduced through the arrangement of achiral molecules. By co-deposition of acridine-9-carboxylic acid (ACA) and C$_{60}$ on room temperature Ag (111) substrate, an intermixed ACA and C$_{60}$ supramolecular structure is formed. Two distinct chiralities are identified with molecule-resolved STM images. The chirality stems from the ACA arrangement and C$_{60}$ position within ACA arrays. Inside the domain of this intermixed structure, each unit cell has two pinwheels (ACA trimers) with opposite rotational direction, namely a R trimer for clockwise and an S trimer for anticlockwise. C$_{60}$ molecules are enantioselectively located on top of the trimers with identical chirality throughout the domain. The chirality of the domain is then determined by the unoccupied ACA trimer. It is noted, because of the supramolecular arrangement, the distance between neighboring C$_{60}$ molecules is 2.65 nm, increased by 165% compared with that in the bulk C$_{60}$ crystal. Such mixed phase systems thus offer a new strategy for generating chiral surfaces with tunable physical and electronic properties, as needed for device applications. * This work is supported by NSF under grant DMR-00-80008 (MRSEC) and CHE-01-36401.

11:15 AM Ra18.3

Optimal control of molecular adsorption on surfaces. Petr Kral and Boyang Wang; Department of Chemistry M/C 111, University of Illinois at Chicago, Chicago, Illinois.

We design a new approach that allows to control adsorption of molecules on surfaces. The method requires to perform structural modifications of the surfaces in a predesigned fashion. We show that precise molecular docking can be achieved. The approach has numerous potential applications in material and bio-sciences.

11:30 AM Ra18.4

Self Assembly of Anisotropic Organic Molecules: Diffusion versus Sticking Anisotropy. Stephen Berkebile[1], Georg Koller[1], Gregor Hlawacek[2], Martin Oehzelt[3], Roland Resel[3], Falko P. Netzer[1] and Michael G. Ramsey[1]; [1]Institute of Physics, Karl-Franzens-University, Graz, Austria; [2]Institute of Physics, University of Leoben, Leoben, Austria; [3]Institute of Solid State Physics, Graz University of Technology, Graz, Austria.

The molecular/crystal orientation and morphology of active molecular structures is a key determinant for the function of nanoscaled organic devices. In π-conjugated systems, both charge transport and optical properties will strongly depend on the molecular orientation due to the highly anisotropic charge carrier mobility in these organic crystals and the anisotropic absorption and luminesence behavior of the molecules. Although the importance of organic on inorganic interface formation and thin film growth is widely acknowledged, little is known regarding the growth kinetics. A better understanding of the processes driving molecular self-assembly is necessary if the self-assembly process is to be controlled. Moreover, it is interesting as the anisotropy of the molecular building blocks presents a fundamental difference to what we know from inorganic growth. In this presentation we show that either sticking or diffusion anisotropy can control the growth depending on preparation conditions. This is illustrated by a detailed investigation into the growth of sexiphenyl (6P) on the anisotropic TiO$_2$(110)-(1x1) surface for temperatures between 80 K and 400 K using in-situ UHV photoemission, x-ray absorption spectroscopy, synchrotron x-ray diffraction and ex-situ atomic force microscopy. For 6P adsorption even at 80 K we found that the molecules orient parallel to the TiO$_2$ oxygen rows and form small crystallites. At 300 K this molecular orientation is retained and large micrometer sized 6P($20\underline{3}$) oriented needles running perpendicular to oxygen substrate rows are formed. In contrast, for growth at elevated temperatures the 6P molecular axis is near perpendicular to the surface and large islands elongated parallel to the substrate rows are formed. These differences in crystallite orientation and morphology can be explained by the domination of the growth kinetics by either sticking or diffusion anisotropy depending on growth temperature. The effect of these different geometric structures on the observed valence band structure will also be discussed. Supported by the Austrian Science Foundation (FWF).

11:45 AM Ra18.5

Nanohybrid Self Assembly via π-π and H-Bonding Interactions. Inna Karatchevtseva[1], Gerard Calleja[1], David J. Cassidy[1], Dunbar P. Birnie[2], Bruno A. Latella[1], David R. G. Mitchell[1], Darren J. Attard[1], John Hanna[1] and John Bartlett[1]; [1]Institute of Materials and Engineering Science, ANSTO, Menai, New South Wales, Australia; [2]Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Organic groups that form supramolecular architectures via well defined interactions such as π-π interactions, steric effects and H bonding can be used to control the structural evolution of nanohybrids, leading to control of the size and spatial orientation of organic and inorganic domains within the nanohybrids. Here we investigate the structural evolution of a series of nanohybrid powders and coatings incorporating self assembling organic species based on complexes between aromatic carboxylic acids and amine functionalised alkyltrialkoxysilanes. The structural evolution of conventional (non self assembling) nanohybrids based on methyltrimethoxysilane was also investigated for comparison. Self assembly in solution prior to initiating formation of the inorganic network was studied by vibrational spectroscopy, ^{29}Si MAS NMR, light scattering and small angle X ray scattering (SAXS), while the nanostructure and properties of the corresponding thin films and nanopowders were investigated by XRD, AFM, TEM, SAXS, X ray reflectometry and Raman spectroscopy. The mechanical properties of selected coatings were examined using nanoindentation and tensile testing. Coating solutions prepared by hydrolysing MTMS:TMOS mixtures under acidic conditions exhibited weak, flat SAXS patterns, consistent with the presence of small, structurally diverse species in solution. In contrast, the corresponding solutions prepared from the acid/amine complexes exhibited scattering patterns consistent with larger, more structurally defined species, suggesting that self assembled moieties were forming in solution prior to deposition of coatings and/or formation of nanopowders. Raman spectra indicated that the self assembled moieties remained intact during hydrolysis of the alkoxy groups and evolution of the inorganic network. The extent of cross linking and abundance of hydroxyl species within the nanohybrids (^{29}Si MAS NMR) could be modulated by controlling the amine:carboxylate mole ratio and by inclusion of additional silica source (either TEOS or TMOS) during synthesis. AFM and TEM images revealed the presence of well defined domains in the self assembled coatings (with dimensions of 20 to 100 nm), whereas the corresponding coatings produced from the MTMS:TMOS mixture were smooth and featureless. Tensile testing and nanoindentation studies indicated that the self assembled nanohybrid coatings were well adhered to the substrates, with hardness and Young's moduli of 0.65 to 1.7 and 15 to 26 GPa, respectively. These results clearly highlight the structure directing role of the self assembling organic species in such nanohybrid precursors that exploit H-bonding and/or π-π interactions, leading to well defined nanosegregation of organic and inorganic domains. Possible approaches for tailoring the structure of these organics to modulate the size and spatial orientation of the domains, and post functionalisation for control of surface chemistry, will be presented.

SESSION Rb18: Nanoparticles II

Chair: Bruce Lennox
Thursday Morning, December 1, 2005
Room 208 (Hynes)

10:30 AM *Rb18.1

Directed Self-Assembly of Multilayer Thin Films of Manganese Doped Zinc Sulphide Nanoparticles by a Modified Polyelectrolyte Deposition Technique. Joydeep Dutta[1], Syed Hassan Mujtaba Jafri[1], Sujira Promnimit[1], Chanchana Thanachayanont[2] and A. B. Sharma[3]; [1]Microelectronics, Asian Institute of Technology, Pathumthani, Thailand; [2]National Metal and Materials Technology Center, Pathumthani, Thailand; [3]Information & Communications Technology, Asian Institute of Technology, Pathumthani, Thailand.

Fabrication strategies that rely on mechanisms of self-assembly are now widely being recognized as inevitable tools in nanotechnology. By self-organization of nanoparticles, it may be possible to manufacture materials and devices by mimicking the nature. Such self-organised construction of advanced materials and devices could be carried out by tailor made nanoparticles as building blocks. A prerequisite to utilization of colloids in nanotechnology is that they remain in suspension and resist settling down. The stability of colloids can be achieved by two means: electrostatic stabilization, involving the creation of an electrical double layer arising from ions intentionally adsorbed on the surface of the particle and associated counter ions that surround the particle, and by Steric Hindrance, which can be achieved by the adsorption of large molecules such as polymers on the surface of the particles. The inherent necessity to introduce steric hindrance to avoid colloidal agglomeration can be utilized to induce self-assembly of multilayers applying similar concepts used for the layering of polyelectrolytes. Here we will report the development of a modified polyelectrolyte deposition technique for building multilayer thin films. Quantum dots of zinc sulphide nanoparticles have been synthesized by co-precipitation techniques and capped by chitosan that is extracted by alkaline deacetylation of chitin which stabilizes the colloid. The amide groups in the chitin monomer is deacetylized to form positively charged amine (NH_2) groups. We will report the fabrication of alternate stacks of monolayers of Mn doped ZnS nanoparticles [30 nm particles] followed by the deposition of a layer of anion, polyacrylic acid (PAA) or Poly (sodium 4-styrenesufonate) (PSS). Subsequent layers are attached by simply dipping alternately into PAA or PSS and ZnS:Mn^{2+} (chitosan capped) colloids with intermediate steps of washing. The intermediate washing step is necessary to remove all unattached excess particles (or polymer) from cross-contaminating the subsequent layers. We have utilized the modified polyelectrolyte deposition technique for the growth of multifunctional nanoparticulate ZnS thin films and fabricated Schottky diodes with aluminum and gold electrodes. The Schottky junction device exhibit diode-like behavior and this technique show promise for simple large area construction of diodes using wet-chemistry. The electronic properties of these diodes will also be presented and discussed.

11:00 AM Rb18.2

Large Arrays of Ordered 1 and 2 Dimensional Arrangment of Nanosized Particles. Heinrich Hofmann, Frederic Juillerat and Paul Bowen; Ecole Polytechnique Federal Lausanne, Lausanne, Switzerland.

Many potential applications in nanotechnology, like magnetic storage media, require virtually defect-free arrays of nanometer scale particles over large areas. Guided self-assembly of colloidal particles on patterned templates has been shown to produce ordered arrays of colloidal particles. However, there is a need to extend this technique to particles measuring much less than 50nm in size and to develop robust fabrication techniques that would lead to defect-free, large-area arrays. We report the production of one- and two-dimensional arrays on patterned templates over large surface areas of tens to hundreds of micrometers, using particles with mean diameters in the 15-50nm range. Substrates with arrays of grooves or holes were prepared by X-ray Interference Lithography. Dip-coating of the substrates in colloidal suspensions under adapted conditions. The results presented in this work show that by combining novel lithographic and colloidal methods, ordered arrays of sub-50nm particles can be achieved for areas of tens of microns. No inherent limitations of the self-assembly process were found that would restrict the quality or the size of the nanoparticle arrays. Dip coating on nanometer-scale grooved substrates is shown to be an effective method to create large area 1-D particle arrays. For 2-D patterned surfaces (e.g. arrays of holes) it was necessary to follow the dip-coating step by ultrasonic treatment to create low-defect particle arrays. We varied several process parameters in our experiments to mainly understand the relative influences of the forces that contribute to the assembly process. The quality of the obtained arrays without careful optimization testify to the robustness of the developed techniques. This combination of top-down method for topological structuring of surfaces as templates for the bottom-up assembly opens the way to produce large area defect-free ordered structures produced the desired nano-architectures. The observed assembly processes are shown to be in agreement with theoretical models that account for the relative influences of various forces. The techniques developed here have the potential for use in applications where controlled creation of large area nanoparticle arrays is needed. The results point to different ways of achieving defect-free arrays over arbitrarily large areas with no inherent limitations of the guided self-assembly process.

11:15 AM Rb18.3

Directed Assembly and Control of Nanoparticles. Ahmed A. Busnaina, Kaveh Bakhatri, Xugang Xiong and Prashanth Makaram; NSF NSEC for high-rate Nanomanufacturing, Northeastern University, Boston, Massachusetts.

Nano-particles can be used for a variety of applications and are considered as one of the building blocks of future nano devices. The use of nano-particles as building blocks requires scalable assembly strategies such as electrostatically addressable nanotemplates. The use of the templates for the directed assembly of nanoparticles is studied analytically, computationally and experimentally. Computational fluid dynamics is used to analyze the effect of different parameters such as electrostatic field, solution conductivity, particle charge, etc.. The results show the importance of having a secondary electrode that creates a uniform electric field similar to a capacitor. The experimental results verified the modeling results for the nanoparticle assembly. Defects generated during the assembly resulted from particles deposition on surface areas other than the nanowire patterns. Analytical studies have been used to find the right conditions for controlled assembly which involves directed assembly combined with selective removal. Results show that the controlled assembly approach is successful.

11:30 AM Rb18.4

Electronic Transport in Molecularly Linked Gold Nanoparticle Films Near the Metal-Insulator Transition. Jeffrey L. Dunford, Yoshinori Suganuma and Al-Amin Dhirani; Chemistry, University of Toronto, Toronto, Ontario, Canada.

We have investigated the temperature (T) dependence of the conductance (g) of 1,4-butane dithiol linked Au nanoparticle films. Over a wide range of temperatures (20 K to 300 K), the conductance behaves as $g = g_0 \exp(-(T_0/T)^{\frac{1}{2}})$. Qualitatively, this is consistent with an Efros-Shklovskii variable range hopping model based on a competition between Coulombic and inter-cluster tunneling processes. However, we find that hopping distances are too large (62 nm to 720 nm at 100 K) to be consistent with tunneling between clusters, and tend to scale with cluster size. We propose a modifed "quasi-localized hopping" model based on competition between single-electron cluster charging and intra-cluster electron backscattering to explain this temperature dependence.

11:45 AM Rb18.5

"Surface-Programmed Assembly" Method for Massive Nano-Assembly of Pristine Vanadium Oxide Nanowire-Based Devices. Sung Myung[1], Minbaek Lee[1], Gyu Tae Kim[2], Jeong Sook Ha[3] and Seunghun Hong[1]; [1]Physics, Seoul National Univ, Seoul, South Korea; [2]Electrical Engineering, Korea University, Seoul, South Korea; [3]Chemical and Biological Engineering, Korea University, Seoul, South Korea.

Nanowires have been drawing a tremendous attention due to their potential applications for various nanoscale devices. However, one major bottleneck for their practical applications is a lack of a high-yield mass-production method for such devices. Herein, we report a method named "surface-programmed assembly" for high-precision assembly and alignment of a large number of pristine vanadium oxide nanowires on solid substrates. In this method, positively-charged surface molecular patterns guide the 'assembly' and 'alignment' of negatively-charged vanadium oxide nanowires on solid substrates. Using this method, we demonstrated massive assembly of vanadium oxide nanowire-based transistors and confirmed their gating effects.

SESSION Ra19: Semiconductor Nanostructures III

Chair: Wei Zhou
Thursday Afternoon, December 1, 2005
Room 207 (Hynes)

1:30 PM *Ra19.1

Self-Assembly of Parallel Atomic Wires and Periodic Nano-Dots of Silicon and Germanium on a Vicinal Silicon (111) Surface. Takeharu Sekiguchi, Shunji Yoshida and Kohei M. Itoh; Applied Physics, Keio University & CREST-JST, Kanagawa, Japan.

We demonstrate that annealing of a vicinal Si(111) surface at about 800 C with a direct current in the direction that ascends the kinks results in the formation of atomically straight step edges over micrometer lengths while annealing with a current in the opposite direction does not. High resolution STM shows that every straight step edge has the same atomic configuration U(2,0), which is useful as a template for the formation of a variety of nanostructures.[1] Indeed, we show by STM that both Si and Ge atoms deposited onto such templates form regular arrays of either atomic wires or nano-dots depending on the substrate temperature during depositions.[2,3] For example, deposition of Ge at 250 C results in self-assembly of one-dimensional arrays of Ge dots, which nucleate exclusively at U-halves of 7x7 unit cells along every upper terrace edge. The resulting dots have uniform diameters ($\sim$2nm) and form one-dimensional simple lattice with the lattice constant 2.7 nm. To our knowledge, these are the smallest Ge dots ($\sim$2nm) forming ”one-dimensional” arrays, and are strikingly different from previously reported ”two-dimensional” orderings of Pb [4] and Ge [5] dots which nucleated preferentially at F-halves. Mechanisms leading to such distinct straight step-structures by kink-up annealing and Si and Ge nanostructures in the following deposition are discussed. [1]. S. Yoshida, T. Sekiguchi, and K. M. Itoh, ”Atomically straight steps on vicinal Si (111) surfaces prepared by step-parallel current in the kink-up direction,” Appl. Phys. Lett., in press. [2]. T. Sekiguchi, S. Yoshida, and K. M. Itoh, ”Self-assembly of parallel atomic wires and periodic clusters of silicon on a vicinal Si(111) surface,” submitted to Phys. Rev. Lett. [3]. S. Yoshida, T. Sekiguchi, and K. M. Itoh, ”Self-assembly of parallel atomic wires and periodic clusters of germanium on a vicinal Si(111) surface,” in preparation. [4]. S.-C. Li et al., ”Borderline Magic clustering: The Fabrication of Tetravalent Pb Cluster Arrays on Si(111)-(7x7) Surfaces”, Phys. Rev. Lett. 93, 116103 (2004). [5]. H.M. Guo et al., ”Formation of Ge nanoclusters on Si(111)-7x7 surface at high temperature”, Surf.Sci. 561, 227 (2004).

2:00 PM *Ra19.2

The Two- to Three-Dimensional Transition in InAs/GaAs(001) Heterostructure: The Role of Kinetics. Fabrizio Arciprete, Ernesto Placidi, Violetta Sessi, Massimo Fanfoni, Fulvia Patella and Adalberto Balzarotti; University of Rome Tor Vergata, Rome, Italy.

In the previous decade the Stranski-Krastanov growth mode has been the subject of many experimental and theoretical studies. In the case of semiconductor heterostructures characterized by a large lattice mismatch, the strain built up during the layer-by-layer growth may bring about a drastic and sudden change in the growth mode; atoms start self-organizing in three-dimensional islands called quantum dots (QDs). InAs/GaAs(001) heterostructure, with its lattice mismatch as large as 7%, is a paradigmatic example of these interfaces and undergoes the two- to three-dimensional transition for a deposition of InAs lower than 2 ML. Many attempts have been made to clarify the mechanisms underlying the growth mode transition, but many aspects are still little understood. In this paper we present an accurate investigation of the kinetics of QDs for the InAs/GaAs(001) heterostructure grown by means of molecular beam epitaxy. Because the system evolves within a narrow range of coverage around the critical thickness, we have grown a single sample where the InAs coverage varies in a continuous way along the sample surface. In this way the system can be studied for InAs coverage increments as low as 0.01 ML. The kinetics of the number density of three dimensional quantum dots evidences two transition thresholds at 1.45 and 1.59 ML of InAs coverage, corresponding to two separate families, small and large. According to the scaling theory analysis, such families result characterized by different mechanisms of aggregation, the transition from small to large dots being accompanied by the change of the critical nucleus size. We show that the scaling function change is coincident with the explosive nucleation of the large QDs and it is triggered by the large increase of the adatoms number density determined by the erosion of the step edges. Such findings demonstrate how kinetics drives the two- to three-dimensional growth mode transition and clarify a fundamental aspect of quantum dots formation.

2:30 PM Ra19.3

Kinetically driven patterning scheme for self assembly of nanocrystals in selected regions. Scott K. Stanley[1], Sachin V. Joshi[2], Shawn S. Coffee[1], Davood Shahrjerdi[2], Sanjay K. Banerjee[2] and John G. Ekerdt[1]; [1]Department of Chemical Engineering, The University of Texas Austin, Austin, Texas; [2]Department of Electrical & Computer Engineering, The University of Texas Austin, Austin, Texas.

Nanomaterials have much to contribute to the electronics industry. Current problems in the application of nanotechnology include arrangement of nanomaterials into significantly ordered patterns for use in devices. Modern flash memory architecture is well suited for nanomaterials integration. The continuous charge-storing layer in a flash memory device can be replaced by an array of nanocrystals that serve as discrete charge-storage elements. It is well documented in the literature that using nanocrystals in place of a continuous layer results in improved device characteristics for large arrays. For this nanocrystal-based memory to become industrially viable and scalable, we must address the issue of how to reliably arrange the nanocrystals into arrays for each device. This paper discusses a kinetically driven patterning scheme to marry top-down and bottom-up assembly of nanoparticle arrays. We explain how Si and Ge atoms interact with different dielectric surfaces to either etch the surface or to accumulate and self assemble into nanocrystals during chemical vapor deposition (CVD). By exploiting the different reactivity of these dielectrics, the accumulation of adatoms is controlled and the subsequent self assembly of nanocrystals is controlled. Physical vapor deposition (in the form of cracking GeH_4 over a hot filament) is used to deposit calibrated submonolayer to multilayer amounts of Ge atoms on surfaces. The chemistry of Ge on SiO_2 and HfO_2 enabling this kinetically driven patterning scheme is fully explained with X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) studies. We have achieved dense ($>10^{11}$ cm^{-2}) arrays of self assembled Ge nanocrystals within lithographically defined HfO_2 windows with no Ge deposition on the adjacent SiO_2 sacrificial mask region. Beyond this demonstration, we investigate the use of electron beam lithography and self assembled diblock copolymers to direct self assembly of Ge nanocrystals within the gate region of the device. We also explore capacitance-voltage characteristics of different preparations of Ge nanocrystals to determine how efficiency as charge storage elements changes.

2:45 PM Ra19.4

Shadowing Growth of Uniform 3D Nanostructures on Templated Substrates by a Novel Oblique Angle Deposition Technique. Dexian Ye[1], Catalin R. Picu[2], Gwo-Ching Wang[1] and Toh-Ming Lu[1]; [1]Department of Physics, Rensselaer Polytechnic Institute, Troy, New York; [2]Department of Mechnical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Shadowing effect during oblique angle deposition (also known as glancing angle deposition) on surfaces can physically self-assemble three dimensional (3D) nanostructures such as rods and springs. This shadowing growth on a templated substrate with regular arrays of seeds would give rise to a phenomenon referred as ”fan-out” growth in that the size of the nanostructures overgrow along the direction perpendicular to the incident deposition flux. The net result is that the size of the nanostructures cannot be controlled as they grow. In this talk we will present a back-forth substrate swing rotation method to overcome the ”fan-out” growth. By using this method, uniform slanted Si nanorods and square nanosprings were fabricated on templated substrates. A simple model based on decomposition of the deposition flux is used to describe qualitatively the effect of substrate swing rotation on inclined angle, uniformity, and the top-end shape of nanostructures. We also employ a Monte Carlo simulator to quantitatively predict the behavior of the swing rotation growth of the nanostructures. In addition, we will discuss possible applications of this technique for the fabrication of integratable, functionalized electromechanical and photonic nanodevices that are otherwise difficult to produce using advanced lithographic techniques.

SESSION Rb19: Carbon Nanotubes I

Chair: S.R.P. Silva
Thursday Afternoon, December 1, 2005
Room 208 (Hynes)

1:30 PM *Rb19.1

Control of Carbon Nanotube Geometry for Advanced Technical Applications. Sungho Jin, Materials Science & Engineering, University of California at San Diego, La Jolla, California.

The fascination and great technical promises associated with nanoscale materials are based on the significant changes in their fundamental physical and chemical properties. For eventual successful engineering applications of carbon nanotubes and other nanowires, an ability to control not only their intrinsic structures and properties but also their basic configurations is essential, for example, in terms of diameter, length, alignment, periodicity, spacing, geometry manipulations and appropriate placements on a substrate. In this talk, various synthesis techniques and microstructural analyses for controlling the nanotube geometry such as diameter, length, alignment, bending, branching, tip opening, cutting, and bonding will be discussed. Growth of patterned nanotubes or nanocone arrays, sharp bending of nanotubes for creation of 90o bent or zig-zag nanotubes, nano-scale shortening, thorough removal of catalyst metal particles for uncontaminated electrochemical reactions, tip opening and filling of nanotubes for nanocomposite formation, and coating of nanotubes with high-density Pt catalyst nanoparticles will be described in relation to their potential applications. The implications of such geometry controls for physical, electronic, chemical, mechanical, and bio-related properties and for technical applications including field emitters, chemical/electrochemical sensors, nanosprings, nanosolenoids, sidewall-probing tips or nanometer-resolution AFM probes, fuel cell electrodes, electronic circuit nano interconnections, nanocomposites, and bio-devices will also be discussed.

2:00 PM Rb19.2
Analysis of Defect-Assisted Double Resonance Raman features of Graphite and Carbon Nanotubes.

Eduardo Bede Barros[1,2], Ge. G. Samsonidze[2], H. B. Son[2], J. Jiang[3], R. Saito[3] and Mildred S. Dresselhaus[2]; [1]Departamento de Fisica, Universidade Federal do Ceara, Fortaleza, Ceara, Brazil; [2]Electrical Engineering and Computer Science, Massachusetts Institute of technology, Cambridge, Massachusetts; [3]Department of Physics, Tohoku University and CREST, Cambridge, Massachusetts.

Some of the most interesting properties of carbon nanotubes originate from the unique electronic and vibrational properties of graphite. The Double Resonance Raman Scattering (DRRS) process observed in both graphite and Carbon nanotubes is an important process that is related to the strong electron-phonon coupling observed for graphitic materials. The frequency and intensity of the Double Resonance Raman feautures depend strongly on excitation energy. Although the frequency dependence of these modes have been widely studied, little is known about their intensities. In graphite, the DRRS consists of an electron with wavevector k close to the K-point of the graphite Brillouin Zone being optically excited to the conduction band, which is then scattered to a state close to the K'-point and then back to the K-point, by either a two phonon (second-order) process or by a phonon and a defect (first-order) process. In the case of two phonons, the intensity of the DRRS features depends on the matrix elements of the phonon modes that are involved in the scattering and in the phonon density of states. For defect-assisted DRRS, the intensity will depend not only on the properties of the phonon, but also on the matrix element of the defects involved in the scattering process. Raman Spectroscopy experiments were performed in different defective regions of graphitic materials using a tunable Raman system. The defective regions were mapped using a contolled stage and the relative intensities of the Double resonance features in the different regions were compared. Based on the difference between the intensity dependence with excitation energy of the different defective areas, an estimative could be made of the electron-defect matrix element and its dependence on the localization of the defect in the lattice. Applications to carbon nanotube physics are discussed.

2:15 PM Rb19.3
SWNT Directed Assembly Using Nanotemplates.

Prashanth Makaram[1], Xugang Xiong[1], Kaveh Bakhatri[1], Ahmed Busnaina[1] and Glen Miller[2]; [1]The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, Northeastern University, Boston, Massachusetts; [2]The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, University of New Hampshire, Durham, New Hampshire.

The Center for High-rate Nanomanufacturing (CHN) is developing tools and processes that will enable high-rate/high-volume bottom-up, precise, parallel assembly of nanoelements (such as carbon nanotubes, nanoparticles, etc.) and polymer nanostructures. Nanotemplates are utilized to conduct fast massive directed assembly of nanoscale elements. Carbon Nanotubes have shown a lot of promise as next generation switches or interconnects in electronic applications. The negatively charged SWNTs are assembled onto a positively charged patterned nanowire electrophoretically or chemically. We have successfully demonstrated the assembly of SWNTs on micron and nano sized gold wires using both AC and DC voltage. The assembled SWNTs show good density coverage on the wires using DC voltage. It also shows alignment with respect to the nanowires when using AC voltage. The assembled patterns are then transferred to another patterned substrate to function as electronic device (such as nanotubes mechanical switches).

2:30 PM Rb19.4
Selective Dispersion of Single Walled Carbon Nanotubes in the Presence of Polymers: The Role of Molecular and Colloidal Length Scales.

Rachel Yerushalmi - Rozen[1,2], Igal Szleifer[3], Rina Shvartzman-Cohen[1], Ezhil Baskaran[3], Yael Levi-Kalisman[2] and Einat Nativ-Roth[1]; [1]Chemical Engineering Department, Ben-Gurion University, Beer- Sheva, Israel; [2]The Ilse Katz Center for Meso- and Nanoscale Science and Technology, Ben-Gurion University, Beer-Sheva, Israel; [3]Chemistry Department, Purdue University, West Lafayette, Indiana.

Dimensionality is known to play a key role in the solution behavior of nano and meso particles. In particular, the shape and the range of the attractive van- der Waals inter-particle potential are determined by the number of microscopic versus mesoscopic dimensions. For Single Walled Nano Tubes (SWNT) where two of the dimensions are nanoscopic and one is mesoscopic, the inter-tube attraction is relatively short ranged, albeit very steep. The very large attraction (compared to the thermal energy, KbT) among long SWNT leads to aggregation at different levels, and constitutes a major barrier for manipulation and utilization of SWNT. We demonstrate in a series of studies, that it is possible to shape the inter-tube potential by decorating SWNT with end-tethered polymers. Consequentially, stable dispersions of individual, well separated SWNT, can be prepared, and further used for preparation of CNT-polymer composites of low percolation thresholds. Investigation of different chain lengths and tethering densities of the polymers as well as the inter-particle potentials for nanometric versus mesoscopic particles suggests that polymer-induced steric stabilization provides a generic method for purification of SWNT from mixtures of colloidal species via dimensional selectivity.

2:45 PM Rb19.5
Site-specific Forest-assembly of Single-Wall Carbon Nanotubes on Electron-beam Patterned SiOx/Si Substrates.

Haoyan Wei[1], Sang Nyon Kim[2], Sejong Kim[2], Bryan D. Huey[1], Fotios Papadimitrakopoulos[2] and Harris L. Marcus[1]; [1]Department of Materials Science and Engineering, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; [2]Nanomaterials Optoelectronics Laboratory, Polymer Program, Institute of Materials Science, Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Based on electron-beam direct writing on the SiOx/Si substrates, favorable absorption sites for ferric cations were generated on the surface oxide layer. This allowed Fe3+-assisted self-assembly arrays of single-wall carbon nanotube (SWNT) probes to be produced. Auger investigation indicated that the energetic electrons used for direct writing depleted oxygen, creating more dangling bonds around Si atoms at the surface of the SiOx layer. This resulted in electrical trapping and a distinct difference in the frictional force from unexposed regions as measured by Electrostatic Force Microscopy (EFM) and Lateral Force Microscopy (LFM) respectively. After exposure both Auger chemical mapping and Atomic Force Microscopy (AFM) affirmed that the irradiated domains absorbed considerably more Fe3+ ions upon immersion into pH 2.2 aqueous FeCl3 solution. This rendered a greater yield of FeO(OH)/FeOCl precipitates, primarily FeO(OH), upon subsequent washing with lightly basic dimethylformamide (DMF) solution. Such selective metal-functionalization established the basis for the subsequent patterned forest-assembly of SWNTs as demonstrated by AFM and resonance Raman Spectroscopy.

SESSION Ra20: Supramolecular Assemblies III
Chair: Roberto Otero
Thursday Afternoon, December 1, 2005
Room 207 (Hynes)

3:30 PM *Ra20.1
Supramolecular Chemistry at the Liquid/Solid Interface.

Steven De Feyter[1], Jan van Esch[2], A. P. H. J. Schenning[3], Frank Wuerthner[4] and Frans De Schryver[1]; [1]Katholieke Universiteit Leuven, Leuven, Belgium; [2]University of Groningen, Groningen, Netherlands; [3]Eindhoven University of Technology, Eindhoven, Netherlands; [4]Universitaet Wuerzburg, Wuerzburg, Germany.

Self-assembly is a natural phenomenon, which can be observed in many biological, chemical and physical processes. In contrast to chemisorption, physisorption is not very suitable for making "permanent" architectures. Nevertheless, these physisorbed adlayers are model systems to investigate the interplay between molecular structure and the formation of ordered assemblies in two dimensions. The organic liquid/solid interface provides an interesting environment to perform self-assembly and to investigate the structure and properties of the self-assembled two-dimensional architectures by scanning tunneling microscopy (STM). a) Most systems reported up to date have only limited possibilities to include functionality and are not flexible with regard to size and symmetry. The observation that linear alkyl fragments featuring amide or urea groups form lamellar structures reminiscent of the beta-sheets found in nature upon adsorption at the solid-liquid interface of HOPG prompted us to introduce a beta-turn mimic in these systems as a next logic step. Here we report on the design of such a 2D turn mimic which is a first step in controlling the position/orientation of functional groups in 2D with the potential of being extended in 3D [1]. b) Tuning the intermolecular interactions by tailoring the non-covalent interactions such as hydrogen bonding indeed leads to control of the self-assembly process. Of special interest are those molecules which carry 'functional' moieties, such as conjugated oligomers. p-Phenylene vinylenes form such an important class. The self-assembly of three types of chiral p-phenylene vinylenes which differ in their hydrogen bond forming abilities will be reported, including the discussion on the effect of the molecular chirality on the 2D self-assembly [2,3,4]. c) Finally, by bias dependent imaging we have probed the molecular electronic levels involved in the tunneling process, for a unique p-phenylene vinylene containing system: (1) it combines an electron donor and electron acceptor part, covalently linked to each other and (2) the donor and acceptor parts are relatively large and well-separated in space, allowing addressing them individually [5]. [1] N. Schuurmans, H. Uji-i, W. Mamdouh, F. C. De Schryver, B. L. Feringa, J. van Esch, S. De Feyter J. Am. Chem. Soc., 2004, 126, 13884-13885 [2] P. Jonkheijm, A. Miura, M. Zdanowska, F. J. M. Hoeben, S. De Feyter, A. P.H.J. Schenning, F. C. De Schryver, and E.W. Meijer Angew. Chem. Int. Ed., 2004, 43, 74-78 [3] S. De Feyter, A. Miura, S. Yao, Z. Chen, F. Wuerthner, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, F. C. De Schryver Nanoletters, 2005, 5, 1, 77-81 [4] A. Miura, P. Jonkheijm, S. De Feyter, A. P. H. J. Schenning, E. W. Meijer, F. C. De Schryver Small, 2005, 1, 1, 131-137 [5] A. Miura, Z. Chen, S. De Feyter, M. Zdanowska, H. Uji-i, P. Jonkheijm, A.P.H.J. Schenning, E.W. Meijer, F. Wuerther, F.C. De Schryver J. Am. Chem. Soc., 2003, 125, 49, 14968-14969

4:00 PM Ra20.2

Supramolecule-Nanopattering and Related Dynamics at Liquid-Solid Interface. Krishna G. Nath[1], Jill Miwa[1], James D. Wuest[2], Antonio Nanci[3] and Federico Rosei[1]; [1]INRS-EMT, University of Quebec, Varennes, Quebec, Canada; [2]Department of Chemistry, University of Montreal, Montreal, Quebec, Canada; [3]Laboratory for the Study of Calcified Tissues and Biomaterials, Faculty of Dentistry, University of Montreal, Montreal, Quebec, Canada.

We are investigating a series of self-assembled monolayers (SAMs) by means of scanning tunneling microscopy (STM) at the solution-graphite interface, to establish tailor-made surfaces with bio-friendly functionalized molecules. The present study is a first step of our broader approach on supramolecule-nanopattering [1] for potential applications in novel biocompatible materials [2]. Here we show how the related dynamics of SAMs governs the shape and area of a specific self-assembled pattern as a function of time. All SAMs were prepared on freshly cleaved highly oriented pyrolytic graphite (HOPG) surfaces at room temperature. The dynamics of SAMs was observed by recording successive STM images from a same region over a certain period of time. Among several tecton [3] molecules under investigation, we present results for Trimesic acid (TMA). Depending on the nature of the solution two types of structures, namely the chicken-wire [4] and the flower-type [5] are observed on HOPG. In the case of the flower-type pattern, an additional droplet of 1-undecanol deposited prior to placing the TMA-Heptanoic acid solution induces a phase separation comprised of domains of the TMA flower-pattern and the 1-undecanol linear-pattern. The flower-pattern domain undergoes an Ostwald ripening-like phenomenon [6], where the region of flower-pattern is surrounded by 1-undecanol patterns of different orientation. We also observed the pathways of chicken-wire formation, where a network of organized Hydrogen-bonding through TMA molecules was developed followed by a scattered and diffused arrays of same molecules. References: [1] F. Rosei et al., Prog. Surf. Sci. 71, 95 (2003). [2] F. Rosei, J. Phys. Condens. Matter 16, S1373 (2004). [3] M. Simard et al., J. Am. Chem. Soc. 113, 4696 (1991). [4] S. De Feyter et al., Chem. Soc. Rev. 32, 139 (2003). [5] M. Lackinger et al., Langmuir 21, 4984 (2005) [6] Q. Guo, X. Sun, R. E. Palmer, Phys. Rev. B 71, 35406 (2005).

4:15 PM Ra20.3

Molecular Interactions of PTCDA on Si(100) and H-Si(100) Surfaces: Towards Self-assembled Molecular Nanocrystals. Didier Stievenard, Thibaut Soubiron, Francois Vaurette, Jean Philippe Nys, Bruno Grandidier and Xavier Wallart; Dpt ISEN, IEMN UMR 8520, Lille, France.

The interactions of PTCDA molecules with the Si(100) surface have been investigated by means of scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Among the large distribution of the adsorbates observed by STM for submonolayer coverages, around 20% show a distinct feature, which is interpreted as the product of the covalently linkage between PTCDA and Si atoms. The formation of this product through the anhydride groups is further supported by the XPS measurements. For coverage above 1 monolayer, there is the formation of a disordered initial layer, which nevertheless acts as a passivation layer and leads to the formation of islands. These islands have a common layer structure, similar to the molecular arrangement found in the (102) plane of PTCDA bulk phase. The growth mode is a Stranski-Krastanov one, with a 2D-3D transition. On the contrary, on a hydrogen passivated silicon surface (H-Si(100)), the formation of an initial molecule layer is not observed. The molecules have a low interaction with the surface and can easily migrate. Molecular nanocrystals are directly built, i.e. a Volmer-Weber growth mode is observed. The smallest nanocrystals have no commensurable position with the surface, according to a low interaction with the surface. By increasing the coverage and controlling the growth rate, an unidirectional growth of the nanocrystals is obtained. Taking advantage of this self-assembly process should favour the spontaneous growth of organic nanocrystals between electrodes in a vacuum chamber for future electrical characterization.

4:30 PM Ra20.4

Combining Conventional Lithography with Molecular Self-Assembly to Build Nanostructures and Pattern Surfaces. Mary E. Anderson[1], Charan Srinivasan[2], J Nathan Hohman[1], Mark W Horn[2] and Paul S Weiss[1]; [1]Chemistry and Physics, The Pennsylvania State University, University Park, Pennsylvania; [2]Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania.

Molecular self-assembly plays an essential role in the development of many nanolithographic techniques acting as a building block and/or an active component. In conjunction with conventional lithography, we have fabricated metal structures with precise proximal placement using self-assembled multilayers as lift-off resists (building blocks) and chemically patterned surfaces with functionalized films using self-assembled monolayers as the components. We have created metal electrodes with nanometer-scale separations using the selective placement and controllable dimensions of self-assembled multilayers. The thickness of this multilayer lift-off resist can be tailored defining the spacing between the electrodes with single nanometer resolution in the 10-50 nm regime.[1-4] Much effort has gone into developing the lithographic process steps to create nanogaps reproducibly with electrical integrity.[5] An important aspect of this process is a lithographic resist, which is robust enough to withstand the deposition of self-assembled multilayers without compromising their formation. This optimized lithographic method and resist compatible with self-assembly has opened a novel avenue for us to direct the chemical patterning of multi-component self-assembled films. For our process, photolithography is utilized to pattern our resist atop a self-assembled monolayer (SAM) on a gold substrate. Then the exposed region of the SAM is removed, another component SAM is inserted, and then the resist is removed maintaining the functionality that has been patterned onto the substrate. A major advantage of this technique is that the different components (SAMs) of the film are shielded by the resist against displacement and intercalation. Additional benefits of this process over other unconventional methods for chemical patterning are the ability to have multiple levels of alignment, reproducible one-to-one feature size transfer, and parallel processing. We present this research outlining our work developing methods for the integration of self-assembly with lithographic processing for future applications ranging from molecular electronics to sensor platforms. [1] A. Hatzor and P.S. Weiss, *Science* **291**, 1019 (2001). [2] M. E. Anderson *et.al.*, *JournalofVacuumScienceandTechnologyB* **20**, 2739 (2002). [3] M. E. Anderson *et.al.*, *JournalofVacuumScienceandTechnologyB* **21**, 3116 (2003). [4] M. E. Anderson *et.al.*, *submitted.* [5] M. E. Anderson *et.al.*, *MicroElectronicEngineering* **78 − 79**, 248 (2005).

4:45 PM Ra20.5

Bio-inspired self-decontaminating surfaces from polyelectrolyte multilayers. Xiaoxia Sheng, Zhi Li, Michael F. Rubner and Robert E. Cohen; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A self-decontaminating surface, as inspired by the self-cleaning lotus leaf and the fog-collecting Namib beetle, was developed by patterning hydrophilic regions on a superhydrophobic surface and filling the porous reservior beneath with antibiotics. The honeycomb-like porous structure was assembled from poly(acrylic acid) and poly(allylamine hydrochloride) followed by proper acid treatments. Molecules with long alkyl chains were reacted to the nanoparticles that were assembled onto this highly textured structure to render the surface superhydrophobic. The superhydrophobic, water repelling and hydrophilic, water collecting features were achieved by patterning the surface with hydrophilic polymeric molecules. Airborne tests demonstrated that a bacteria-carrying mist preferentially accumulated to the hydrophilic regions where the loaded antibiotics (e.g. Ag, penicillin) released to kill the bacteria upon contact. Addition of micron-sized particles to the substrate before multilayer assembly can be introduced to create a bumpy surface topography that facilitates the rolling of water droplets off the hydrophilic domains on the bump-tops, thereby substantially increasing the efficiency of surface self-decontamination.

SESSION Rb20: Carbon Nanotubes II
Chair: Singho Jin
Thursday Afternoon, December 1, 2005
Room 208 (Hynes)

3:30 PM *Rb20.1
Assembly, Manipulation and Chemical Bond Engineering of Single Walled Carbon Nanotubes. Zhongfan Liu, Zhuo Chen, Xiaojie Duan, Yingying Zhang, Bo Gao, Quan Qing, Liying Jiao, Jin Yang, Jingling Ao, Zhongyun Wu and Jin Zhang; Center for Nanoscience and Technology and College of Chemistry and Molecular Engineering, Peking University, Beijng, China.

Single-walled carbon nanotubes (SWNTs) have shown great potential for creating nanoelectronic devices because of the excellent electronic, mechanical, thermal and chemical performances. To fabricate such SWNTs devices, it is necessary to find an effective way to align the randomly-entangled or randomly-oriented nanotubes in a highly-controlled manner. We demonstrate here our recent studies along this direction based on chemical assembly, controlled CVD growth and AFM manipulation. The main topics include: (1) Vertical alignment on solid surfaces via chemical assembly. The self-assembled monolayer (SAM) technique conventionally used for small organic molecules was employed here for fabricating vertically aligned SWNTs assembly on solid surfaces. The CVD-grown SWNTs were cut into short tubes by chemical oxidation. The assembly was made on Au, Ag, and amine-terminated surfaces via Au-S bonding, Ag-COOH salt formation, and condensation reaction, respectively. It has been shown that the "giant" carbon nanotubes can be self-assembled on a suitably designed surface, forming a well-aligned assembly. The assembling kinetics, the electric-field enhanced assembly effect, and a number of applications of these assemblies will be discussed. (2) Lateral alignment and interconnection using dielectrophoresis force. A dipole moment can be induced for the large π-conjugated SWNTs by applying electric field. Such polarized carbon nanotubes would undergo a directional movement along the electric field gradient under the inhomogeneous AC electric field. Using this so-called dielectrophoresis force, SWNTs have been successfully aligned and interconnected in-between the electrode gaps. With nanofabricated gap arrays and optimized experimental conditions, well-controlled lateral alignment of SWNTs has been achieved. (3) Controlled surface growth and AFM manipulation. By predesigning the growing surface, a controlled CVD growth of SWNTs has been achieved, including site-specific growth and directional growth. We also tried to use AFM tips to align, bend and stretch the surface-grown SWNTs. By suitably designing the growth surface and by employing the nanowelding phenomenon, we have created various deformed nanotube structures having different bending angles and stretching degrees on surfaces. Because the energy band and chemical reactivity strongly depend on the deviation degree of carbon nanotube from its original sp^2 equilibrium structure, this approach, called chemical bond engineering provides an alternative way for tuning the physical and chemical properties of SWNTs. The mechanical deformation performance of individual nanotubes will also be discussed. Single-walled carbon nanotubes (SWNTs) have shown great potential for creating nanoelectronic devices because of the excellent electronic, mechanical, thermal and chemical performances. To fabricate such SWNTs devices, it is necessary to find an effective way to align the randomly-entangled or randomly-oriented nanotubes in a highly-controlled manner. We demonstrate here our recent studies along this direction based on chemical assembly, controlled CVD growth and AFM manipulation. The main topics include: (1) Vertical alignment on solid surfaces via chemical assembly. The self-assembled monolayer (SAM) technique conventionally used for small organic molecules was employed here for fabricating vertically aligned SWNTs assembly on solid surfaces. The CVD-grown SWNTs were cut into short tubes by chemical oxidation. The assembly was made on Au, Ag, and amine-terminated surfaces via Au-S bonding, Ag-COOH salt formation, and condensation reaction, respectively. It has been shown that the giant carbon nanotubes can be self-assembled on a suitably designed surface, forming a well-aligned assembly. The assembling kinetics, the electric-field enhanced assembly effect, and a number of applications of these assemblies will be discussed. (2) Lateral alignment and interconnection using dielectrophoresis force. A dipole moment can be induced for the large p-conjugated SWNTs by applying electric field. Such polarized carbon nanotubes would undergo a directional movement along the electric field gradient under the inhomogeneous AC electric field. Using this so-called dielectrophoresis force, SWNTs have been successfully aligned and interconnected in-between the electrode gaps. With nanofabricated gap arrays and optimized experimental conditions, well-controlled lateral alignment of SWNTs has been achieved. (3) Controlled surface growth and AFM manipulation. By predesigning the growing surface, a controlled CVD growth of SWNTs has been achieved, including site-specific growth and directional growth. We also tried to use AFM tips to align, bend and stretch the surface-grown SWNTs. By suitably designing the growth surface and by employing the nanowelding phenomenon, we have created various deformed nanotube structures having different bending angles and stretching degrees on surfaces. Because the energy band and chemical reactivity strongly depend on the deviation degree of carbon nanotube from its original sp2 equilibrium structure, this approach, called chemical bond engineering provides an alternative way for tuning the physical and chemical properties of SWNTs. The mechanical deformation performance of individual nanotubes will also be discussed.

4:00 PM Rb20.2
Nanoscale Integration of Nanocarbons Based on Ultrananocrystalline Diamond and Carbon Nanotubes. Xingcheng Xiao[1], Chao Liu[1], Orlando Auciello[1,2] and John A. Carlisle[1,2]; [1]Materials Science Division, Argonne National Laboratory, Argoone, Illinois; [2]Center for Nanoscaled Materials, Argonne National Laboratory, Argonne, Illinois.

Nanocarbons, or nanostructured carbon materials have attracted extensive research interest during the past decade, especially after the emergence of carbon nanotubes. Another form of nanocarbons, ultrananocrystalline diamond (UNCD) developed at Argonne National Laboratory, has been demonstrated to possess many desirable properties for fabrication of MEMS/NEMS devices, electron field emission devices, biosensors and biomedical devices, due to its unique nanostructure. In this presentation, we will report the selective but simultaneous growth of UNCD and carbon nanotubes using hydrogen poor plasma chemistry in a microwave plasma CVD system. A self-assembled monolayer of polystyrene spheres (PS) is used as the shadow mask for patterning the catalyst on a substrate for growing carbon nanotubes. Then the mask is etched by toluene and the wafer is seeded with nanodiamond powder for growing UNCD. The relative fraction and arrays of carbon nanotubes and UNCD are controlled by the diameter of PS and the thickness of the catalyst. The carbon nanotubes grown in hydrogen poor plasma (99% Ar/ 1% CH4) are a mixture of single walled and multi walled carbon nanotubes, which are dependent of the thickness of catalyst. By controlling the diameter of the PS and growth time, nanocomposite coatings were obtained, in which carbon nanotubes are embedded into the UNCD matrix. We will report results from measurements of mechanical and tribological properties of this novel nanocomposite.. We will also discuss results from studies of the electronic contact between sp2-bonded carbon nanotubes and mostly sp3-bonded UNCD. This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

4:15 PM Rb20.3
Carbon Nanotube-Zinc Oxide Core-Shell Composite Nanowires for Optoelectronics. Sathyajith Ravindran[2], Yu Zhang[1], Senthil Andavan G. T.[1] and Cengiz Sinan Ozkan[1]; [1]Mechanical Engineering, University of California at Riverside, Riverside, California; [2]Chemical and Environmental Engineering, University of California at Riverside, Riverside, California.

The focus of this work is to investigate the electrical and optical properties of semiconducting ZnO shell formed over single walled and multi walled carbon nanotubes. We use electrostatic coordinative affinity of Zn atoms towards the oxygen of the carboxylic groups in oxidized carbon nanotubes to coat ZnO axially around the nanotubes. Owing to high operating temperatures during chemical vapor deposition, the MWCNTs burn out leaving the ZnO shell. In case of SWCNTs, they form stable heterostructures and other interesting 3D structure. We show characterization of the MWCNT-ZnO and the SWCNT-ZnO structures with SEM, TEM, electron diffraction, EDS, XRD and Photoluminescence. We also report their electrical and optical characterization. In addition, we report a simple technique for the SWCNT patterning and the selective and controlled growth of ZnO structures over the patterned SWCNTs for devices. Effect of the growth temperature of the morpgology of the ZnO heterostructures formed on the CNTs are also discussed.

4:30 PM Rb20.4

Substrate Effects on the Mechanism for Carbon Nanotube Growth. Xuesong Li[2], Anyuan Cao[2], Pulickel M. Ajayan[2], Stephen J. Kilpatrick[1] and Matthew H. Ervin[1]; [1]Sensors & Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland; [2]Department of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Vertically aligned multi-walled carbon nanotubes, grown using vapor phase catalyst delivery techniques, are known to grow well from some substrate materials, like SiO_2, while growth does not appear possible from others, such as Si. The mechanism for this selective growth on patterned SiO_2/Si substrates has been elucidated in previous work [1]. It was concluded that this was due to strong metal (catalyst particles)-substrate (Si) interactions resulting in new phase formation and inhibiting nanotube growth compared to no metal-substrate (SiO_2) interactions allowing nanotube growth. In the present work, we study an extended series of useful substrates such as SiC, AlN, Al_2O_3, and MgO, which all exhibit dense nanotube growth. This will be contrasted with a study of Si_3N_4 and diamond-like carbon substrates, from which no or few nanotubes could be grown. The same growth conditions as reported previously were used, namely a thermal chemical vapor deposition chamber with a mixture of xylene and ferrocene vapor at 770 °C. The near-surface regions of these substrates are exposed using cleaving or focused ion beam cross-sectioning techniques and analyzed by SEM and/or TEM. The mechanism of selective growth on these new substrate materials, while not on others, will be postulated and compared to the results for SiO_2/Si. These studies were largely motivated by the anticipated use of carbon nanotubes for on-chip thermal management on wide bandgap high-power semiconductor devices, optical devices, MEMS structures, and nanoscaled electronics. [1] Y-J Jung, B. Wei, R. Vajtai, P.M. Ajayan, Y. Homma, K. Prabhakaran, and T. Ogino, Nano Letters 3(4), 561 (2003).

4:45 PM Rb20.5

Thin Silicon Dioxide Layers as Diffusion Barriers During the CVD Growth of Carbon Nanotubes. J. M. Simmons[1], Beth M. Nichols[2], Matthew S. Marcus[2], O. M. Castellini[1], R. J. Hamers[2] and M. A. Eriksson[1]; [1]Department of Physics, University of Wisconsin - Madison, Madison, Wisconsin; [2]Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin.

Chemical vapour deposition (CVD) of carbon nanotubes utilizes the catalytic decomposition of hydrocarbon feedstock on the surface of transition metal nanoparticles to form metal carbides, and subsequent carbon precipitation to form nanotubes. Controlling the kinetics and thermodynamics of the catalyst feedstock interaction allows for tunable growth, in both yield and diameter, of single- or multi-walled carbon nanotubes. Since nanotube growth is a high temperature process (700 °C-900 °C), interfacial reactions between the substrate and the catalyst are extremely important. Indeed, the growth of single-walled nanotubes on clean silicon or silicon with a native oxide is inhibited due to the formation of a catalytically inactive metal silicide, though growth on thick oxide layers is straightforward. We show that metal diffusion through the silicon dioxide limits the minimum thickness of silicon dioxide capable of permitting high-yield growth of carbon nanotubes. Using X-ray photoelectron spectroscopy (XPS), we have probed the interaction between iron and nickel single-walled nanotube catalysts and Si/SiO_2 substrates with a range of oxide thickness. At low temperatures on substrates with thin SiO_2 layers, the metal oxide particles are reduced through bonding exchange with the silicon substrate. As we heat the substrate further, there is a shift in the atomic core levels of the catalyst on thin oxides due to the formation of a metal silicide. Most importantly, the silicide formation occurs while the oxide layer remains, indicating that metal diffusion through the silicon dioxide layer is responsible for the silicide formation. We show that oxides as thin as 4 nm are effective diffusion barriers and allow high yield nanotube growth.

SESSION Ra21: Nanostructures for Biology and Medicine III

Chair: Amy Blum
Thursday Evening, December 1, 2005
Room 207 (Hynes)

6:15 PM Ra21.1

Surfactant-like peptides: Supramolecular assembly and peptide-membrane interaction to engineer novel drug delivery systems. Salvatore Chessari[1], Isabella Miglioli[1], Martina Baumann[1], Shuguang Zhang[2] and Marcus Textor[1]; [1]Materials, Swiss Federal Institute of Technology, Zurich, Switzerland; [2]Biology, MIT, Boston, Massachusetts.

In the last few years, significant advances have been made in the use of peptides as building blocks to produce biological materials for a wide range of applications [1]. Thus, synthesis and characterization of short peptides that can adopt a stable three-dimensional structure in solution are crucial for the construction of bio-active and bio-inspired de-novo polypeptides. Selected peptides and hybrid peptides (combinations of peptide sequences with organic moieties in a single molecule) self-assemble in a variety of motifs to form pores, channels and tubules. Various physiological functions, such as ion transport through cell membranes, and physical functions such as solubilizing difficult-to-dissolve molecules, are facilitated by the tubes that are formed by molecular assemblies [2]. Peptide-lipid membrane interactions play a critical role in the regulation of several biological phenomena, including the insertion and folding of membrane proteins, the translocation of polypeptides through membranes and the cytolytic action of antimicrobial peptides. However, a systematic study of the interaction of different peptide assemblies with membranes is still missing [3]. The aim of the present study is the systematic design and synthesis of cationic surfactant-like peptides, the structural characterization of spontaneously formed supramolecular entities, and the evaluation of their interactions with supported bilayers serving as a model for cell membranes. The development of such biologically inspired delivery vehicles should fulfill several criteria that are important for the envisaged application such as biodegradability, cell-membrane transit promotion and lack of cytotoxicity. To assess the approximate size of the peptide assemblies, transmission electron microscopy (TEM) will be used to study the supramolecular assembly of the samples in solution as a function of concentration and pH, complemented by morphological studies of peptide assemblies at surfaces based on atomic force microscopy. Molecular mechanics calculations are performed to simulate the assembly of selected peptide sequences in aqueous media, and the comparison of such results with those experimentally obtained is also discussed. References 1. Santoso, S., et al., Self-assembly of surfactant-like peptides with variable glycine tails to form nanotubes and nanovesicles. Nano Letters, 2002. 2(7): p. 687-691. 2. von Maltzahn, G., et al., Positively charged surfactant-like peptides self-assemble into nanostructures. Langmuir, 2003. 19(10): p. 4332-4337. 3. Mozsolits, H., et al., The interaction of bioactive peptides with an immobilized phosphatidylcholine monolayer. Biophysical Journal, 1999. 77(3): p. 1428-1444.

Ra21.2

Abstract Withdrawn

6:30 PM Ra21.3

Nano-Confined Polymer Hydrogels For Drug Delivery System Using Radiation Synthesis. Jung Chul An, Lourdes Guadalupe Salamanca-Riba, Joseph Silverman and Mohamad Al-Sheikhly; Materials Science and Engineering, University of Maryland, College Park, Maryland.

We have synthesized polymer nanohydrogel for Drug Delivery System (DDS) applications by nano-confined radiation methods. Both high energy electron beam and gamma ray were used as radiation sources. The synthesis conditions (total dose, dose rate, and pulse repetition rate) and the concentration of the solution, control the size and molecular weight of the nanohydrogels. The diameter of the nanohydrogel is in the range of 100 - 200 nm as measured from static light scattering experiments. Irradiation of solutions with dilute concentrations results in intra crosslinking within a single chain rather than inter crosslinking under high dose rate and high repetition rate of electron beam irradiation. Alumina nanoporous templates with 200 nm diameter pores were also used to synthesize polymer nanohydrogels in the low dose rate gamma irradiation for comparison. The alumina template gives spatial isolation of single polymer chain by the confinement within the channels resulting in preferred intra crosslinking. Hydrogels with diameters of 100 - 200 nm were synthesized within the capillary channels of the nanoporous template. Environmental Scanning electron microscopy and atomic force microscopy are used to investigate the morphology of the nanohydrogels after irradiation. Various approaches to produce nano hydrogel with radiation synthesis will be presented in this study. This work was supported by the DOE/Industry Matching Grants Program under contract number DEFG0702ID14356.

6:45 PM Ra21.4

Hydroxyapatite/Collagen Self-Organized Nanocomposite for Bone Tissue Regeneration Scaffold. Masanori Kikuchi[1], Shinichi Sotome[2], Yoshinori Asou[2], Yoshihisa Koyama[3,1], Kazuo Takakuda[3,1], Kenichi Shinomiya[2] and Junzo Tanaka[1]; [1]Biomaterials Center, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]Orthopedic Surgery, Tokyo Medical and Dental University, Bunkyo-ku, Tokyo, Japan; [3]Institute for Biomaterials and Bioengineering, Tokyo Medical and Dental University, Chiyoda-ku, Tokyo, Japan.

We have already reported the hydroxyapatite/collagen (HAp/Col) self-organized nanocomposite in the previous meeting of MRS. The nanocomposite has bone-like nanostructure and ability to incorporate into regular bone remodeling metabolism. In the present paper, the authors prepared the HAp/Col sponge-like porous body and paper-like membrane using its long fiber, and carried out the first trial to apply for bone tissue engineering. The HAp/Col long fibers with bone-like nanostructure were synthesized by the simultaneous titration method previously reported under fine control of starting material concentrations. For the sponge-like porous body, the fiber obtained were vacuum dried and mixed with pure water and 1 wt% of collagen. Then, sodium chloride and phosphate buffered saline were added to promote fibrillogenesis of collagen, mixed well and incubated at 37°C. The HAp/Col gel was lyophilized and crosslinked. For the membrane, the dried HAp/Col fibers were dispersed in pure water and flatly filtrated. The filtered sheet was vacuum dried and crosslinked. The sponge-like porous body showed viscoelastic property in wet condition. The membrane has paper-like softness at 200 μm in thickness and cardboard like rigid at 500 μm. The tensile strength at wet condition of the sponge-like porous body and cardboard-like membrane is 80 kPa and 1 kPa, respectively. The strength was enough to handle at both cell culture and material/cell hybrid transplantation. The MG-63 cells, derived from human osteosarcoma, were used for cell culture test. From the preliminary test, the composite adsorb large amounts of Ca and Mg from culture medium and inhibit cell proliferation; therefore, the materials were soaked in the Dulbecco's modified Eagle's essential medium (DMEM)supplemented with 10 % fetal bovine serum and 1% penicillin and streptomycin to allow ions (and proteins) adsorption onto the material. The cells were seeded onto the material and cell proliferation was measured. Although initial attachment of cells was reduced by the surface roughness in comparison to tissue culture polystyrene (TCPS), the growth of cells were similar to that of TCPS. The porous body and membrane expected to be useful for bone tissue engineering. Acknowledgement: A part of this study was supported by Research Promotion Bureau, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan under the contract No.17-83.

7:00 PM Ra21.5

Interpenetrant Nanostructured Composites Mimicking Bone. Sang Soo Jee[1], Rajendra K. Kumar[1], Matthew J. Olszta[2,1] and Laurie B, Gower[1]; [1]Materials Science & Engineering, University of Florida, Gainesville, Florida; [2]Materials Science & Engineering, Pennsylvania State University, State College, Pennsylvania.

Bone is a hierarchically-structured natural composite material, which at the primary level, consists of an interpenetrating network of hydroxyapatite nanocrystals dispersed within the interstices of self-assembled collagen fibrils. In fact, the structure is so unique and different than synthetic materials, it is difficult for the materials engineer to define: Is it a collagen fiber-reinforced bioceramic-matrix composite; or is it a nanoparticle-reinforced collagen-matrix composite? This intrafibrillar mineralization that is achieved during bone formation has eluded scientists who seek to duplicate this nanostructured architecture using conventional synthetic techniques. We have been able to achieve intrafibrillar mineralization of collagen using a polymer-induced liquid-precursor (PILP) process, in which acidic polypeptides transform the solution crystallization process into a precursor process by sequestering ions and generating liquid-liquid phase separation within the crystallizing media. This fluidic mineral precursor can then be drawn into the gaps and grooves of the collagen matrix by capillary forces. The PILP phase is highly metastable, so the thermodynamic driving force to form the more stable crystalline phase drives off the waters of hydration, leaving the collagen fibrils embedded with mineral crystals. Using this capillary action mechanism, we have generated a collagen-hydroxyapatite nanocomposite with diffraction patterns matching natural bone, demonstrating that highly specific epitaxial nucleating proteins are not needed to duplicate the orientation control found in bone formation; instead the unique structure of collagen provides the appropriate template for regulating crystallographic control. This has potential application in terms of hard-tissue biomaterials applications, but from a materials science perspective, the exciting ramifications are that this is a non-specific process, suggesting that this mechanism could be means of generating interpenetrating organic-inorganic nanostructured composites for a variety of materials.

7:15 PM Ra21.6

Nanostructured Ceramic Film Formation on Self-Assembled Monolayers via a Biomimetic Approach. Guangneng Zhang and Junghyun Cho; Mechanical Engineering, State University of New York, Binghamton, New York.

A biomimetic approach is employed to deposit ceramic films on organic self-assembled monolayers (SAMs) coated substrates. Specifically, zirconia (ZrO_2) films are grown in a zirconium sulfate precursor solution at near room temperatures ($< 80°C$). This process, directed by the nanoscale organic template, mimics the controlled nucleation and growth of the biominerals such as bones and teeth. The phosphonate-terminated SAMs are prepared through a vapor phase method in an attempt to avoid the polymerization often found in a solution method. The resultant zirconia films consist of nanosized particles ($\approx$ 5-10 nm) that are precipitated out in a supersaturated precursor solution. The underlying mechanisms of generating the nanostructured films are systematically studied by tailoring solution chemistry and SAM functionalities. Cross-sectional, high-resolution TEM and STEM works are performed to quantitatively analyze the film structure and chemistry, as well as interfacial region of the ceramic - SAM films. Further, the dynamic nanoindentation testing is developed to assess the thickness and 'film-only' properties for direct comparison among the films processed with different processing parameters and microstructures. This ceramic film growth mechanism can be sufficiently general that it may be applicable to other oxide systems.

7:30 PM Ra21.7

Colorimetric Sensors Based on Chemically Controlled Disassembly of Nanoparticle Aggregates Linked by Catalytic DNA, Aptamers, and Aptazymes. Juewen Liu and Yi Lu; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

DNA-functionalized nanoparticles have been demonstrated to be programmable building blocks for directed nanomaterial assembly. Taking advantage of the distance-dependent optical property of metallic nanoparticles, the resulting novel materials can be used as highly sensitive colorimetric sensors for sequence-selective DNA detection. A DNA can recognize its complementary DNA, which forms the basis for DNA detections. To apply the nanoparticle-based detection method to a broad range of analytes beyond DNA, we employed functional DNA to assemble nanoparticles. Three classes of functional DNA were pursued: metal-specific catalytic DNA, DNA aptamers, and aptamer-regulated catalytic DNA (aptazymes). Catalytic DNA are DNA molecules with catalytic activities. Most catalytic DNA molecules require metal cofactors for their activities. Therefore, they are ideal for metal ion sensing. DNA aptamers are DNA molecules that can bind target analytes with high affinity and specificity. Since its first discovery in the early 1990s, DNA aptamers have been selected to bind a broad range of analytes, ranging from small organic molecules to proteins and even anthrax spores. First, a Pb(II)-specific catalytic DNA and its substrate were employed to assemble gold nanoparticles. The catalytic DNA can cleave its substrate DNA in the presence of Pb(II), and the substrate DNA was physically responsible to assemble nanoparticles. As a result, the nanoparticle aggregates disassembled in the presence of Pb(II) with a blue-to-red color transition observed. We demonstrated that an aggregate containing $\sim$10000 nanoparticles can be disassembled in less than 5 minutes in the presence of Pb(II). To apply the detection method to more analytes beyond metal ions, DNA aptamers and aptazymes were also employed to assemble nanoparticles. The resulting functional materials can detect metal ions, small organic molecules and proteins. While most people are interested in controlled assembly of nanomaterials, we demonstrate here that chemically controlled disassembly is equally interesting and useful.

7:45 PM Ra21.8

Selective Placement of Templated DNA Nanowires Between Microstructured Electrodes. Joseph Kinsella[2] and Albena Ivanisevic[2,3]; [1]Purdue University, West Lafayette, Indiana; [2]Biomedical Engineering, Purdue University, West Lafayette, Indiana; [3]Chemistry, Purdue University, West Lafayette, Indiana.

We report the deposition of polyelectrolyte films between microfabricated electrodes as a selective guide for DNA templated nanowire structures. Dip-pen nanolithography (DPN) was first used to fabricate a layer of the positively charged polyelectrolyte, poly(allylamine hydrochloride) (PAH), on a spin-on silicon oxide surface between gold electrodes. The PAH films were further modified using the DPN procedure to deposit a negatively charged polyelectrolyte film, poly(styrene sulfonate) (PSS), on top of the PAH film. The functionalized was used as a scaffold to stretch DNA templates coated with positively charged magnetic nanoparticles. To verify the deposition of the polyelectrolyte films between the microfabricated gold electrodes Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, Force Volume Imaging, and Adhesion Mapping were used. From these experiments we have concluded that the selective deposition of the polyelectrolyte films can be effectively incorporated into microfabricated devices for the guided assembly of DNA templates. Prototype device structures were tested and the formation of nanometer scale gaps of the DNA templated wires was explored using restriction enzyme digests. This work can become the basis for novel architectures for (bio)sensors.

SESSION Rb21: Carbon Nanotubes III
Chair: R. Ramesh
Thursday Evening, December 1, 2005
Room 208 (Hynes)

6:00 PM *Rb21.1

Effects of Self-Organisation on Charge Carrier Mobility in Poly(3-Hexylthiophene)-Carbon Nanotube Nanocomposites.

Roland Ghim Siong Goh[1], Eric Rolf Waclawik[2], Nunzio Motta[1] and John Marcus Bell[1]; [1]Centre for Built Environment and Engineering Research, Queensland University of Technology, Brisbane, Queensland, Australia; [2]School of Physical and Chemical Sciences, Queensland University of Technology, Brisbane, Queensland, Australia.

There has been much excitement generated by organic photovoltaic (OPV) devices in recent years, following the demonstrated success of the "bulk heterojunction" concept, in which a composite film of two interpenetrating phases is used as the photoactive layer. We now know that the degree of molecular order of a material can profoundly affect device performance in organic electronic technological applications. In blends of poly(alkyl-thiophene) and fullerene derivatives, increasing the percentage of fullerene derivatives in P3HT have been shown to destroy the self-organized structure in P3HT[1]. It has also been demonstrated that the reduced self-organization of P3HT with high amounts of fullerene leads to decreased external quantum efficiencies in organic solar cells made from composites of these materials[2]. Moreover, hole mobilities of p-type conjugated polymers have been known to decrease with increasing fullerene content[3]. In this work, we observe that when nanotubes are substituted for the fullerenes, a high degree of organization of the P3HT fraction is achieved at low nanotube concentrations nearing the percolation threshold. To achieve a better understanding of this issue we have studied by STM the structural properties and the details of poly(alkylthiophene) self-assembly and organization on single-walled carbon nanotubes (SWNTs). Monolayers of regioregular poly(3-hexylthiophene) (rrP3HT) on SWNTs have been imaged for the first time using scanning tunneling microscopy (STM). The microscopic images show polymer chains wrapped around individual carbon nanotubes and allow the measurement of interchain spacing. The polymer chain-to-chain distance is approximately 1.68nm, compared to the measured interchain distance for rrP3HT absorbed on highly-ordered pyrolytic graphite (HOPG) of 1.4nm. This disparity in interchain distances between rrP3HT deposited on SWNTs and on HOPG indicates that the assembly of polymer onto SWNT is not as simple as absorption on HOPG; the substrate curvature and electronic effects plays an important role in assembly of ordered domains. UV-visible spectroscopic data are also presented, which provides strong evidence for increased interchain interactions in composites of rrP3HT and SWNTs compared to the pure polymer[4]; this shows that adding nanotubes to the polymer results in increased interchain order. The STM local-probe studies of the native polymer as well as the composite confirmed that the polymer interacts with nanotubes to produce a highly ordered material at the molecular level. Finally, current-voltage characterisation of hole-only sandwich-type devices built from these composites shows a clear field dependence of the hole current. At low bias, current density increases by an order of magnitude, whereas at high bias, the increase amounts to 3 orders of magnitude. In the latter case the transport regime changes from a space charge limited conduction model (SCLC) to a trap filling model with exponential trap distribution[5]; this shows not only that the nanotubes have the effect of increasing the hole conductivity, but that hole trap density is increased, possibly because of defect sites on the acid-treated nanotubes. We propose that increased hole mobility is due to an increased degree of order induced in the polymer by the presence of nanotubes. This and other issues pertaining to using these composites in devices will be discussed. We propose that increased hole mobility is due to an increased degree of order induced in the polymer by the presence of nanotubes. This and other issues pertaining to using these composites in devices will be discussed. [1] Kim, Y. C., S.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C. *Chem.Mater.* **2004**, 16, 4812. [2] Chirvase, D. P., J. Hummelen, J. C.; Dyakonov, V. *Nanotechnology* **2004**, 15, 1317. [3] Choulis, S. A.; Nelson, J.; Kim, Y.; Poplavskyy, D.; Kreouzis, T.; Durrant, J. R.; Bradley, D. D. C. *AppliedPhysicsLetters* **2003**, 83, 3812. [4] Brown, P. J. T., D. S.; Köhler, A.;ö Wilson, J. S.; Kim, J-S; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys.Rev.B* **2003**, 67, 064203. [5] Chiguvare, Z.; Dyakonov, V. *PhysicalReviewB*(*CondensedMatterandMaterialsPhysics*) **2004**, 70, 235207.

6:30 PM Rb21.2

Crystallization driven, periodical patterning on individual carbon nanotubes.

Christopher Y. Li, Lingyu Li, Bing Li and Michael J. Birnkrant; Materials Science and Engieering and A. J Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania.

We report herein a unique means to periodically pattern polymeric materials on individual carbon nanotubes (CNT) using controlled polymer crystallization. One dimensional (1D) CNTs were periodically decorated with polymer lamellar crystals, resulting in nano hybrid shish-kebab (NHSK) structures. The periodicity of the polymer lamellae varies from 20 - 100 nm. The kebabs are approximately 5 nm thick (along CNT direction) with a lateral size of $\sim$ 20 nm to micrometers, which can be readily controlled by varying the crystallization condition. Both polyethylene and Nylon 6,6 have been successfully decorated on multi-walled as well as single-walled CNTs. The detailed mechanism of forming this periodic structure on CNTs will be discussed. Since the polymer kebabs can be easily removed, using 1D lithographic technique, these unique NHSKs can serve as templates to fabricate a variety of CNTs-containing hybrid materials with controlled pattering on the CNT surface. This method thus opens a gateway to periodically patterning on CNTs or similar 1D nanowires in an ordered and controlled manner, an attractive research field that is yet to be explored. It also directly leads to the synthesis of polymer/CNT nanocomposites with controllable tube-to-tube distance. *Supported by NSF DMR-0239415, ACS-PRF, 3M and DuPont.

6:45 PM Rb21.3

Preparation of Mesoporous CN, BN, and BCN.

Ajayan Vinu, International Center for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

We report here the preparation of the highly ordered mesoporous carbon nitride material, designated as MCN-1, having uniform pore size distribution through the simple polymerization reaction between ethylenediamine and carbon tetrachloride. The ordered mesoporous carbon nitride MCN-1 structure was investigated by powder X-ray diffraction and nitrogen gas adsorption measurements. The XRD pattern of MCN-1 material shows three, clear peaks, which can be assigned to (100), (110), and (200) diffractions of two dimensional hexagonal lattice (space group p6mm) with a lattice constant a100 = 9.52 nm, similar to the XRD pattern of parent mesoporous silica template SBA-15 which consists of the hexagonal arrangement of cylindrical pores and the pores are interlinked by the micropores present in the walls. Such materials with one dimensional mesopores are arranged in a hexagonal net are defined as two dimensional because the diffraction peaks pattern shows two dimensional p6mm symmetry. The powder diffraction pattern of MCN-1 also shows a single broad diffraction peak (inset) near 25.8 , corresponding to interlayer d spacing of 3.42 A, which is almost similar to the d spacing obtained in the nonporous carbon nitride spheres. This indicates the presence of turbostratic ordering of the carbon and nitrogen atoms in the graphene layers of MCN-1. The MCN-1 material exhibits high specific surface area, specific pore volume and uniform mesopores size distribution, could offer great potential for the applications, such as catalytic supports, gas storage, lubricants, biomolecule adsorption and drug delivery. We have also successfully prepared mesoporous boron nitride and boron carbon nitride for the first time using mesoporous carbon as template at a very high temperature. These materials were extensively characterized by TEM, XRD, EELS, and N2 adsorption. Detailed characterization of those materials will also be discussed in the presentation.

7:00 PM Rb21.4

Self-assembled monolayers of carbon nanotubes.

Vladimir Samuilov[1,3], Jean Galibert[2], Vitaly Ksenevich[3], Laszlo Forro[4], Jaseung Koo[1], Jonathan Sokolov[1] and Miriam Rafailovich[1]; [1]Materials Science, SUNY@SB, Stony Brook, New York; [2]Laboratoire National des Champs Magnetiques Pulses, Toulouse, France; [3]Department of Physics, State University of Belarus, Minsk, Belarus; [4]Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Electronic transport properties of carbon nanotubes are of particular interest due to their potential use as components in nano electronics applications. Applications of the individual nanotubes, such as nanotube -based transistors and chemical sensors or aligned by growth arrays of nanotubes are progressing rapidly. However, the electrical transport properties of the regular 2-D layers still fall far short of the properties of the individual carbon nanotubes. We have developed: 1) a controlled method of self-assembly of functionalized carbon nanotubes into 2-D layers with highly regular structure and unique electronic properties. In contrast to the standard morphologies of the samples of arrays of nanotubes involving definitions of bundles (ropes) mats, networks, etc., based on non-controlled deposition from an organic solvent dispersion of pristine nanotubes, we use the Langmuir-Blodgett (LB) technique of self-assembling of functionalized and highly solvable in the organic solvents carbon nanotubes. 2) a method of alignment carbon nanotubes in the self-assembled 2-D arrays. The method we propose offers a radical departure from the existing methodology due to the capability to cover large surfaces with dense, molecularly ordered ultra-thin films of nanotubes of controlled thickness and orientation. The electrical and magneto-transport properties of the monolayers (arrays) of multi-wall and single-wall carbon nanotubes in the temperature range 1.8-300K and in magnetic fields up to 35 T have been tested.

7:15 PM Rb21.5
Properties of Chemically Modified Carbon Nanotubes. Ryotaro Kumashiro[1], Hirotaka Ohashi[1], Masahiro Yamashita[1], Takeshi Akasaka[3], Yutaka Maeda[4], Shinya Takaishi[1], Shigeo Maruyama[5], Takeshi Izumida[1], Rikizo Hatakeyama[1] and Katsumi Tanigaki[1,2]; [1]Tohoku University, Sendai, Japan; [2]JST, CREST, Kawaguchi, Japan; [3]University of Tsukuba, Tsukuba, Japan; [4]Tokyo Gakugei University, Tokyo, Japan; [5]The University of Tokyo, Tokyo, Japan.

From the viewpoint of nano structure materials, fullerenes, carbon nanotubes (CNTs), and their related ones are very interesting due to their unique electronic properties. Especially CNTs are expected to be used for applications in the near future. In order to introduce intriguing electronic properties to CNTs, two techniques of chemical and physical doping can be adopted. In the case of chemical doping, various atoms and molecules have been used as dopants. The resulting solids have exhibited various kinds of interesting properties depending on the doping level. Physical doping, in contrast, is a method of using field effect transistors (FETs) for carrier doping. The FET technique is a very useful method not only for studying the fundamental properties but also for device applications in the future. Both techniques are also very essential for understanding the electric properties from the fundamental aspects point of views. As for CNTs, chemical carrier doping has been reported so far for controlling carrier concentration like graphite intercalations. Two major techniques are generally possible; One is endohedral doping and the other the exohedral chemical modifications of CNTs. It has been exemplified that doping with alkali metals can introduce electron carriers into CNTs. Furthermore, the electrical transport properties of CNTs were reported to be controlled by the endohedral insertion of organic molecules inside the CNTs. A similar carrier doping could exohedrally be possible when the CNTs surface is chemically modified. With such chemical modifications, the charge transfer from the substituent groups to CNTs will be expected and this could modify the electronic properties of CNTs. We have made a chemical modification of CNTs using a Si-containing molecule of $\mathrm{Si(ph)_2{}^tBu}$ showing relatively strong electron donation, and have examined how the FET properties of these chemically modified CNTs will change. In order to investigate the FET properties, the chemically modified CNTs were dispersed on a $\mathrm{SiO_2/Si}$ FET substrate with Au/Ti electrodes on its surface, and the measurements were carried out at ambient temperature using a conventional method for CNTs-FET studies. As a reference, the experiments were also made in the same manner on chemically non-modified CNTs, It will be demonstrated in the conference that p-type pristine CNTs can be converted to n-type ones by this modification and this could be interpreted in terms of the electronic states produced as a result of hole carrier injections generated by the $\mathrm{Si(ph)_2{}^tBu}$ modifications. These results show the possibility for the accurate control of the electric properties of CNTs by exohedral modifications, by changing the type as well as the concentration of substituent groups that can be adopted to the surface chemical modifications on CNTs.

7:30 PM Rb21.6
High Thermal Conductivity of Carbon Graphite and Realization of Very Low Heat Resistance. Yoichi Taira and Kuniaki Sueoka; Tokyo Research Lab, IBM, Yamato, Japan.

For cooling of future high power chips, the thermal conductivity of the thermal interface material (TIM) between the back of the chip and the heatsink or heat spreader is one of the main thermal limitations in the package stack. As a part of this program we included carbon based materials as the possible candidate thermal solution material. Although many people have been discussing the thermal applications of carbon nanotube (CNT) system to take advantage of their high thermal conductivity, little information is known on the attainable thermal resistance using CNTs. The thermal conductivity of CNT molecule itself was reported to be as high as 1900 W/mK for single wall CNT by laser probing method but its relationship to the attainable heat resistance as a TIM is still unclear. Therefore, we prepared a 100-micron thick aligned CNT film deposited by CVD, where CNTs are standing perpendicular to the substrate and evaluated the system thermal resistance. In the measurement both CNT surfaces are thermally connected to the copper blocks of our heat resistance measurement system using a liquid heat conductor. The resulting thermal conductivity of the film was 4.4-4.7 W/mK, which can be translated to single molecule CNT value of about 1300 W/mK, roughly consistent with the reported CNT values, when two factors are taken into account. First, the CNTs in the deposits fill only 1% of the volume as determined by cross-sections of polymer-impregnated samples; and second, the CNT are approximately three times longer than the nominal 100-micron thickness of the deposit. Based on these results, it is concluded that CNT deposits could give useful TIMs if the volume filling could be increased to 5%. A film of such 5% CNT with 100-micron thickness is expected to have a heat resistance of 0.01-0.04 cm2 C/W. Although increasing the volume filling factor may require further effort, the result also indicates a use of other carbon materials. If we can interpret this result as the usefulness of graphene structure, we can utilize other forms of continuous graphene structure for TIM applications. The material system has to be compliant as well as thermally conductive for the TIM applications. Although high packing of nanotubes and maintaining compliance may be a tradeoff relationship, we expect that reasonable compliance can be achieved by padding soft polymer material among the aligned nanotubes.

7:45 PM Rb21.7
Fast and Position-Controlled Growth of Single-Walled Carbon Nanotubes. Zuqin Liu[1], David Styers-Barnett[1], Alex A. Puretzky[2], Christopher M. Rouleau[3], Hongtao Cui[3] and David B. Geohegan[1,3]; [1]Center for Nanophase Materials Sciences, Oak Ridge National Lab, Oak Ridge, Tennessee; [2]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; [3]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Fast-heating chemical vapor deposition is a proven efficient approach for the growth of long individual single walled carbon nanotubes (SWCNTs). However, obtaining insights into the growth mechanism of how fast a carbon nanotube can grow is still of both scientific and technical importance for designing future experiments to achieve better control of the nanotube growth. In this paper, we describe a new laser-irradiated CVD technique to synthesize SWCNTs using laser irradiation as a source of heat. A high power industrial Nd:YAG laser (600 W average power, 1-500 Hz repetition rate, 0.5-10ms pulse width) was employed. The heating time can be precisely controlled by choosing the proper laser power, repetition rate, pulse width and numbers of laser pulse. Scanning electron microscopy (SEM), microRaman scattering spectroscopy, transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to characterize the nanomaterials produced at different regions within the laser-irradiated zone. The lengths of the nanotubes produced were compared with the thermal treatment of the catalyst films as measured in situ by optical pyrometry. Growth rates, single wall nanotube yield, and diameter distributions of SWCNTs are estimated for various thermal treatments for different hydrocarbon feedstock gases. Growth rates for carbon nanotubes vary dramatically depending on catalysts and parameters of the heating profile, indicating laser-CVD technique may provide local control over growth conditions and may pave a way for investigating the growth mechanism of fast-heating carbon nanotubes. Research on Functional Nanomaterials at the Center for Nanophase Materials Sciences is supported by the U. S. Department of Energy, Division of Materials Science, Basic Energy Sciences.

SESSION Ra22/Rb22: Poster Session IV
Chair: Zhong Wang
Thursday Evening, December 1, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra22.1/Rb22.1
Template fabrication for the ordered growth of semiconductor nanowires. Bodo Fuhrmann[1], Hartmut S. Leipner[1], Hans-Reiner Hoeche[1], Peter Werner[2], Margit Zacharias[2] and Ulrich Goesele[2]; [1]Center of Materials Science, Martin-Luther-University Halle, Halle/ Saale, Germany; [2]Max-Planck-Institute of Microstructure Physics, Halle/ Saale, Germany.

Due to their importance in fundamental research and possible applications, semiconductor nanowires are of great interest. Different growth techniques are used for the growth of semiconductor nanowires, e.g. pulsed laser deposition, metal-organic chemical vapor deposition or molecular beam epitaxy. While the length of the wires mainly depends on the growth conditions, size and location of the nanowires are strongly related to the deposition of metal particles used as mediators of nanowire growth. Beyond the nanowire growth itself, the control of position and the tuning of the dimensions is a main point of interest in present research. The obvious way to do this is the preparation of ordered metal particle arrays by a suitable lithographic method. Optical lithography on the one hand is not applicable because the desired dimensions lie in the nm range. Electron beam lithography on the other hand would be suitable in point of resolution, but is cost intensive and hardly available. We have used in our work nanosphere lithography to fabricate ordered arrays of metal nanoparticles. In nanosphere lithography, hexagonal closed packed monolayers or bilayers of monodisperse particles are used as a shadow mask for the subsequent processing of the substrate, which is in our case the metal deposition by thermal evaporation. In a subsequent thermal annealing step the triangular shaped metal islands are transfered into semispheres. Size and distance of the metal particles depend mainly on the size of the particles used for the mask. We have used suspensions of monodisperse polystyrene particles with diameters in the range 287 nm to 1.32 μm. The spectrum of applicable substrates could be extended to hydrophobic substrates like GaAs and GaN by applying a mask transfer technique. In this technique firstly the mask of polystyrene spheres is deposited on a hydrophilic substrate, then stabilized by deposition of a metal layer and finally transfered onto the desired substrate. The advantage of this technique is that the holes between the spheres become smaller by increasing the thickness of the stabilization layer. This opens the possibility to control the size of the metal particles independently from their distance, which is mainly determined by the diameter of the polystyrene particles. On this basis ordered arrays of gold particles with diameters in the range 25 nm to 100 nm were fabricated for the growth of arrays of nanowires of ZnO on GaN and sapphire, GaAs on GaAs (-1-1-1)As, and Si on Si (111).

Ra22.2/Rb22.2

Fabrication of Three-Dimensional Dendritic Nanostructures of Titanate and Titania Nanowires. Yuanbing Mao[1] and Stanislaus S. Wong[1,2]; [1]Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York; [2]Materials Sciences Department, Brookhaven National Laboratory, Upton, New York.

There have been innumerable reports on the synthesis and characterization of nanotubes, nanorods, nanowires, and nanoparticles, due to their interesting size- and shape-dependent properties. What is now a relevant area of focus in nanoscience involves the preparation of higher-order assemblies, arrays, and superlattices of these various, individual nanostructures. In this presentation, we will present that micron-scale three-dimensional (3-D) dentritic structures of sodium hydrogen titanate nanowires have been generated using a modified hydrothermal technique in the presence of sodium hydroxide and hydrogen peroxide. These assemblies of sodium hydrogen titanate nanowires then have been transformed into their hydrogen titanate analogues by neutralization and finally into those of anatase nanowires by annealing at ~400 °C in air without destroying the 3-D hierarchical structural motif. This in-situ one-pot assembly process for the controlled synthesis of nanostructures of titanates and anatase can readily be used to attain mesoscopic-sized 3-D assemblies and can be easily scaled up to achieve gram quantities of products in a simplistic manner, while maintaining dimensional monodispersity without the use of sacrificial templates to give spatial confinement. The as-prepared assemblies of anatase nanowires demonstrate reasonable photocatalytic activity. The detailed investigation of the growth mechanism will be presented. Based on our experimental data, it is plausible to postulate that the growth mechanism of the 3-D dendritic assemblies of sodium hydrogen titanate nanowires is the result of a two-step mechanism involving the initial formation of primary nanowires that subsequently self-assemble. The subsequent acid leaching and neutralization exchange the Na^+ with H^+ to form the assemblies of hydrogen titanate nanowires. A high-temperature treatment and accompanying dehydration process transform these assemblies of hydrogen titanate nanowires into their anatase TiO_2 analogues.

Ra22.3/Rb22.3

NiSi Nanowires and Nanobridges Formed by Metal-Induced Growth. Joondong Kim, Dongho Lee and Wayne A. Anderson; Electrical Engineering, University at Buffalo, Buffalo, New York.

Nanowires are attractive entities as one-dimensional building blocks to use in nanoelectronics and nanoscale connections. This approach is a breakthrough to overcome the difficulty in scaling down of integrated circuits. We will present a unique method to grow NiSi nanowires (NWs) and form nanobridges (NBs) by metal induced growth (MIG). Additionally, the processing temperature is below 600 ^{o}C reducing potential damages on fabricated structures. Ni as a catalyst layer was thermally deposited on SiO2-coated Si wafers. During dc magnetron sputtering of the Si from a 2 inch diameter target, Ni atoms react with sputtered Si nanoparticles. The solid state reaction of Si and Ni reduces the processing temperature and produces linearly grown nanowires. The nanowires were 2~8 μm in length and 30~80 nm in diameter. Dry etching and metal lift-off procedures made different sized trenches and revealed that the longest NBs could reach to the NW length. A field emission scanning electron microscope (FESEM, Hitachi S-4000 accelerated by 20 ~ 30 kV) was used to observe the nanowires and nanobridges. X-ray diffraction (XRD) analysis showed the presence of NiSi peaks as a key factor to grow NWs. The MIG method provides advantages of lowering processing temperature as well as self-assembled characteristics of nanowires, which has a potential to alter the conventional lithographic techniques to provide an easier, simpler, and more reliable contact scheme in nanoelectronic applications.

Ra22.4/Rb22.4

Carbon nanotube/V2O5 nanowire hetero-film actuator. Kang Ho Lee[1], Seong Min Yee[1], So Jeong Park[1], Jung Hwan Huh[1], Gyu Tae Kim[1], Sung Joon Park[2] and Jeong Sook Ha[2]; [1]Electrical Engineering, Korea University, Seoul, South Korea; [2]Chemical and Biological Engineering, Korea University, Seoul, South Korea.

Hetero-film actuator composed of carbon nanotubes and V2O5 nanowires were demonstrated in a bimetal configuration. The successive filtration of V2O5 nanowire solution followed by carbon nanotube dispersed water solution in the same way produced a dark-gray colored sheets. A significant actuation was observed in sodium chloride electrolyte solution with a bending direction to the carbon nanotube side at the positive bias voltage against the copper counter-electrode. As the frequency of the applied voltage increased up to 50Hz, the amplitudes decreased, indicating a rather slow response of the hetero-film actuator in the electrolyte solution. The hybrid structure enabled an easy fabrication of the film actuator with the enhanced efficiencies.

Ra22.5/Rb22.5

Self-Organization of a Curable Ferrofluid - Characterization and Applications. Richard Lloyd Carroll, Dan B. Blum and Rich Superfine; Physics and Astronomy, University of North Carolina - Chapel Hill, Chapel Hill, North Carolina.

Ferrofluids demonstrate self-organized spikes in response to a strong magnetic field. These "spikes", needles, or rods arise as a result of dipole-dipole interactions (both attraction and repulsion) of the nanoparticles comprising the ferrofluid, balanced by the surface tension of the liquid phase. Examples of extensive rod structures have been reported in the literature, in systems where the structures that formed dissipated without the constant application of an organizing magnetic field. In these cases, the organized rods were free in solution, rather than attached to a substrate or platform. These types of systems could show utility in a number of areas, including as polarizers, birefringent filters, and dichroics. For such applications, it may be advantageous to have stable, substrate-bound devices that show response to magnetic fields, but do not dissipate or degrade without a magnetic field present. We present a unique curable ferrofluid that shows self-organization into arrays of rods that may then be cured into stable surface bound arrays. The rods are uniform, as small as 320 nm in diameter, and hexagonally packed with spacings as small as 2.4 microns. The uniform packing extends over hundreds of square microns with very high crystallinity. Spacing and rod diameter are dependent on a number of factors, including field shape and strength, magnetic composition, and spatial confinement. We will present the results of experiments to understand the formation of the rods and their spacing, as well as characterization by multiple techniques. Finally, we will describe possible applications for the rod arrays, and early efforts to study them.

Ra22.6/Rb22.6

Abstract Withdrawn

Ra22.7/Rb22.7

Sub-micrometer patterning of quantum dots and nano-rods. Peter Karageorgiev[1], Renata Jarzembinska[1], Joel van Embden[1,2], Maciej Olek[1], Nicolas Pazos Perez[1], Thomas Buesgen[1], Paul Mulvaney[1,2] and Michael Giersig[1]; [1]Center of advanced European studies and research (c a e s a r), Bonn, Germany; [2]School of Chemistry, University of Melbourn, Melbourn, Australian Capital Territory, Australia.

We present a method for fabrication of 2D structures consisting of different type nanoparticles ordered in nanometric domains. The confinement and deposition of the nanoparticles in domains is based on the using of cantilevered nano-pipette as an atomic-force-microscopy sensor, which directs a flow of a particle solution to the substrate surface. An advantage of the approach is that it allows a deposition without any chemical modification of the particles. The size of the domains depends on the solvent, the concentration of particles, the applied force, and the affinity of the sample surface and can be controlled up to dimensions comparable with the aperture of the pipette (100-300 nm). Structural and scanning near-field optical characterization of patterns comprising elongated particles show the existence of a orientational order, which can be attributed to pre-orientation of the particles by the narrow aperture and orientation due to scanning of the pipette.

Ra22.8/Rb22.8

Metal Nanoparticle Formation Directed by a Radiation-synthesized Copolymer Template. Alia Paige Weaver, Joseph Silverman, Lourdes Guadalupe Salamanca-Riba and Mohamad Al-Sheikhly; Materials Science and Engineering, University of Maryland, College Park, Maryland.

Metal particle nanostructures are an area of intense research interest due to their possible role as building blocks for next generation electronic and magnetic components, and for sensor applications. In order for these materials to be useful, the particles must be positioned in a strategic manner such that their dispersion is controlled. A variety of synthetic methods have been developed for the formation of these types of structures, and a great deal of effort is currently being focused on the use of organic templates to mediate the nucleation density of these particles. In this presentation, we report a procedure utilizing a radiation-synthesized copolymer as a directing agent for the production of iron nanoparticles. Cobalt-60 gamma irradiation was used to synthesize a 2-ethylhexyl acrylate/acrylic acid copolymer which serves as a molecular template for the fabrication of metal nanoparticles. The morphology of this polymer produces local changes in the energy barrier for nucleation of the iron, thus providing greater control of the distribution of the particles. The particle size produced has been investigated as a function of total dose, dose rate, and concentration of acrylic acid. This work was supported by the DOE/Industry Matching Grants Program under contract number DEFG0702ID14356.

Ra22.9/Rb22.9

Simulation of the Assembly of Acene-Functionalized Nano Building Blocks. Feng Qi[1], Murat Durandurdu[2] and John Kieffer[1]; [1]Materials Science and Engineering, the University of Michigan, Ann Arbor, Michigan; [2]Physics, University of Texas - El Paso, El Paso, Texas.

We use multi-scale simulations, including ab initio quantum mechanical calculations, molecular dynamics (MD) simulations, Monte Carlo (MC) and constrained molecular dynamics simulations to study a series of novel acene-functionalized polyhedral oligomeric silsesquioxane (POSS) assemblies as nano building block. The conformations and electronic properties of individual functionalized molecules were first determined using ab initio calculations. Then the equilibrium structures of those molecules that exhibit the most promising electronic properties were determined by simulating their assembly using MC, MD, and constrained MD methods. Of the self-assembled structures, which include both amorphous and crystalline configurations, the most likely to develop were predicted based on energetic considerations. Finally, these assemblies were characterized in terms of their electronic, thermal, and mechanical properties. Accordingly, acene functionalized POSS assemblies in crystal form have similar band gaps than pure acene molecules, but have superior thermal and mechanical bulk properties. Moreover, the predicted crystal form shows parallel stacking of acene groups, which provides for increased pi-orbital overlap, and thus, better electronic conductivity. The self-assembled amorphous structures show thermal and mechanical properties comparable to crystalline ones. The packing of acene molecules can also be affected by the presence of templating surfaces.

Ra22.10/Rb22.10

Templated Deposition of Polyelectrolyte-Functionalized Colloids. Marianne S. Terrot and Paula T. Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The selective adsorption behavior of polyelectrolytes and polyelectrolyte multilayers is of great importance to the production of nano and micro-scale features within organic thin films; such patterned films are of interest for use in electrochromic devices, proteomic arrays, and sensors based on molecular recognition. In previous work, our group has demonstrated the use of chemical templating of surfaces for in-situ patterning of polyelectrolyte multilayers. This approach has recently been extended to polyelectrolyte-functionalized colloids, making possible the assembly of multi-component colloidal arrays via selective adsorption. Chemical motifs capable of multiple hydrogen bonding are of particular interest for such selective systems as their interactions are both highly specific and readily tuned. In our current work, we explore the use of RNA homopolymers as guides for selective adsorption. Polyadenylic, polycytidylic, polyguanylic, and polyuridylic acid were layered onto the surface of microspheres as well as printed by soft lithography to create chemically patterned surfaces and the ability of the adenine-uracil and cytidine-guanine pairs to direct deposition of the functionalized colloids on the patterned surfaces was studied. We have also explored the self-assembly properties of colloids asymmetrically functionalized with two complementary polybases.

Ra22.11/Rb22.11

Microwave-assisted single-step functionalization and $in-situ$ derivatization of carbon nanotubes with metallic nanoparticles. Raghuveer S. Makala, S. Agrawal, A. P. Singh, Q. Y. Yan and G. Ramanath; Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Functionalizing carbon nanotubes (CNTs) is of widespread interest for separating CNTs of different chiralities, assembling and interconnecting CNTs, and tailoring the matrix-CNT interactions in nanocomposites. Derivatizing CNTs with nanostructures with other low dimensional structures (e.g., nanoparticles and biomolecules) is also attractive for new CNT-based hybrid device concepts that harness the unique properties of the constituent nanostructures. Many current functionalization methods employ multiple steps such as heating and aggressive refluxing with strong acids, often in combination with ultrasonication. These can cause problems such as tube shortening due to bond fissure, and high impurity concentrations due to prolonged residence times, resulting in low yields. The use of non-invasive and non-thermal excitations is attractive for obviating such shortcomings, and for enabling the maturation of simpler and more readily scalable functionalization and derivatization methods. Here, we demonstrate the use of microwaves to rapidly functionalize and derivatize CNTs with metallic nanoparticles formed by reduction of metal ions, all in a single processing step. Raman and infrared spectroscopy results indicate that the defects generated during microwave exposure increase the chemical reactivity of the CNTs and enable its functionalization by reaction with water and oxygen at the defect sites. For example, microwave exposure of CNTs dispersed in a solution mixture of chloroauric acid and ethylene glycol renders the nanotubes hydrophilic. Preferential microwave-activated reduction of chloroauric acid by ethylene glycol at the functionalized sites results in the uniform decoration of nanotubes with gold nanoparticles while preserving the overall structural integrity of the CNTs, as confirmed by transmission electron microscopy and diffraction. To illustrate the flexibility of our approach, we have also derivatized CNTs with magnetic and electrically functional nanoparticles such as CoPt, Cu and CuO. This strategy of harnessing microwave-assisted functionalization coupled with in situ nanoparticle synthesis provides a rapid and efficient method to attach a variety of nanostructures onto CNTs for applications in future devices and composites.

Ra22.12/Rb22.12

Nanostructure fabrication through template directed multi-layer atomic layer deposition: non-close-packed inverse opals. Elton Graugnard, Jeffrey S. King and Christopher J. Summers; Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

We present a powerful, flexible and unique concept for fabricating nanoscale devices based on multi-layer atomic layer deposition (ALD) in patterned template structures. The ultra-conformal nature of ALD allows the nanoscale features of almost any template to be faithfully maintained during film growth. The proper selection of coating precursors can yield the desired material properties, such as high index, luminescent, or magnetic films. Likewise, the number and sequence of materials can augment the template in varying degrees from a slight tuning of the shape or feature size to complete inversion or replication. Thus, multi-layer ALD allows patterned templates to be used as scaffolding for fabricating a device whose structural properties are defined by the template, while the material properties are controlled independently by the choice of films grown by ALD. Although this concept has application to many areas of materials science, we demonstrate the specific application of engineering enhanced photonic crystal structures. The multi-layer ALD technique provides a controllable method for fabrication of high quality non-close-packed inverse opals with the widest possible photonic band gap. Additionally, with this method, the inverse opal pore size can be increased to allow for a high degree of dielectric backfilling. Here we report using multi-layer ALD of ZnS, Al_2O_3, and TiO_2 to fabricate non-close-packed inverse opal films. We observed Bragg peak tuning of over 600 nm and enhancement of the Bragg peak width by >150%. The optical properties of the non-close-packed inverse opals are discussed and a model is presented for characterizing the controlled fabrication of optimized photonic crystal structures using multi-component conformal film deposition. Using this flexible technique we have extended the inverse opal architecture to create NCP structures that have enhanced photonic properties, including wider photonic band gaps for a given dielectric constant. Thus, it should be possible to fabricate optimized structures (NCP or otherwise) with a lower minimum dielectric contrast requirement, potentially making a full photonic band gap in the visible a reality. Beyond photonic crystals, this technique allows materials with different electric, magnetic, and optical properties to be patterned and combined at the nanoscale, creating new composite materials. Taking advantage of the large number of materials that can be conformally deposited by ALD either individually or in multi-layers, and combining them with the large number of template fabrication techniques allows a nearly infinite number of new photonic and electronic device structures to be fabricated.

Ra22.13/Rb22.13

Simulated Self-Assembly of Functionalized Silsesquioxane Building Blocks. Jinhua Zhou, Feng Qi and John Kieffer; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

We have developed a computational framework for the simulation of structural assembly in Polyhedral oligomeric silsesquioxane (POSS) nanocomposites, by combining computational techniques ranging from ab initio quantum mechanical calculations to molecular dynamics simulations to coarse-grained mesoscale modeling methods. Using ab initio calculations we predict the inherent properties of molecular building blocks. Using large-scale molecular dynamics simulations we reproduce the transport, reaction, and microphase evolution processes that occur during nano-assembly, and thereby generate realistic models that serve to establish structure-property-processing relationships for these materials. In this presentation the general approach taken with our the computational framework will be outlined and results from two representative materials simulation studies will be discussed. One example details the self-assembly behavior of POSS cubes attached to a polymer backbone in pendant fashion. The other one describes the peculiar amphiphilic behavior of mono-tethered POSS that causes nano-phase separation and can be exploited for pattern formation at this scale.

Ra22.14/Rb22.14

Self-assembly of nanoparticles and polymer into "patchy" microspheres. Vinit Murthy[1] and Michael Wong[1,2]; [1]Chemical and Biomolecular Engineering, Rice University, Houston, Texas; [2]Chemistry, Rice University, Houston, Texas.

A new mode of assembling charged nanoparticles and polyamines to give three dimensional functional constructs such as microcapsules was reported recently (Rana et al., Adv. Mater. 17 (9), 2005, 1145). Briefly, upon addition of multivalent anions (e.g., citrate3-), polyamines (e.g., poly(L-lysine)) form metastable aggregates via charge interactions. Contacting these spherical aggregates with negatively charged nanoparticles (e.g., silica, $d \sim 15$ nm) leads to the formation of stable thick-shelled microcapsules. The shell comprises the nanoparticles intercalated with the oppositely-charged polymer chains, and the core interior contains polymer (or water, depending on the formulation). For the first time, we report the synthesis of microcapsules that contain smaller, discrete polyamine domains within the shell wall, on the shell wall exterior, and in the polymer-filled core interior. We will provide optical microscopy evidence for such structures, and will discuss their synthesis and formation mechanism. The "patchy" microcapsule structure provides for spatially controlled surface functionalization, suggesting the possibility of guided formation of three-dimensional microcapsular assemblies.

Ra22.15/Rb22.15

Materials and Processes for High Resolution Nanostructure Fabrication using Thermal Cantilever Array Lithography. Yueming Hua[1], Shubham Saxena[2], William P. King[2] and Clifford L. Henderson[1]; [1]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The long term goal of our work is to develop a revolutionary nanofabrication technology based on the use of arrays of heated atomic force microscope cantilevers for nanoscale thermal manufacturing. In the processes being investigated, patterning of various materials is performed using thermal cantilever arrays in which heated cantilever tips having nanometer-scale sharpness write structures onto a surface. This writing can be performed using various operational modes ranging from thermal dip pen or tDPN deposition of materials from the cantilever tip to the direct thermal decomposition and removal of material from a surface. Since this fabrication method requires no mask or template, it is potentially a very low cost alternative to other existing nanopatterning technologies. Also, since the cantilever array can be easily scaled to large numbers of cantilever tips, the throughput of such a multi-tip system can be large using highly parallel writing strategies. This parallel writing capability overcomes the major limitation to the other primary existing maskless nanofabrication technology, namely the single beam serial writing nature of electron beam lithography. Finally, the thermal cantilevers fabricated thus far can already access a wide temperature range from ambient to $\sim$700C. This large temperature range enables the use of a variety of thermally activated processes for the direct patterning, deposition, or removal of materials. In order to design such thermal cantilever array systems and processes, significant research on the fundamental issues which control the performance of these systems and the materials used with them is required. Preliminary work in our labs at Georgia Tech has already shown the feasibility of directly depositing conductive metal patterns using a thermal cantilever tip. We have also shown the basic feasibility of using the local thermal decomposition of polymers to form polymer micro- and nanostructures. This paper will focus on our work directed at designing and optimizing "thermally sacrificial polymers" which can be used as the analog of conventional photoresists for such a thermal cantilever array lithography system. Such sacrificial polymers are designed so that they cleanly decompose to gaseous byproducts when heated to a well defined temperature. Thus local heating of a thin film of such a polymer allows for the clean removal of the heated area to produce polymer physical relief structures. The impact of the polymer structure and physical properties on the thermal imaging process will be discussed and illustrated using results from our polymer synthetic and image testing work. Additional imaging modes for polymers will also be presented and compared to the sacrifical polymer imaging approach.

Ra22.16/Rb22.16

Growth of Self Assembled Metal Nano-Particles and Ultra-Thin Films Observed with In-Situ Ellipsometry and Resistance Measurements. Luke Ryves[1] and Tom W. H. Oates[2]; [1]School of Physics, University of Sydney, Sydney, New South Wales, Australia; [2]Forschungszentrum Rossendorf, Dresden, Germany.

Thin coatings of metal nano-particles have the potential for use in bio-sensor applications, whereas ultra-thin continuous films are required for electronic devices and nano-laminate hard coatings. Coatings were deposited in a high current pulsed vacuum arc. In-situ spectroscopic ellipsometry has been used calculate the substrate coverage of nano-particles during growth, to find the percolation threshold, and to monitor post deposition changes in the coatings. These results are compared with in-situ measurements of resistance and substrate temperature, and ex-situ electron microscopy.

Ra22.17/Rb22.17

Optical Trapping for Agile Nanoassembly and Testing. Thomas LeBrun and Arvind Balijepalli; NIST, Gaithersburg, Maryland.

Despite the rapid advance of tools to make and characterize structures at the nanoscale a key gap remains: we are still largely unable to manipulate individual nanocomponents to build functional nanodevices and test their performance. Optical trapping can offer a agile tool for nanoassembly, and we will describe the development of Optical Tweezers (OT) for efficient nanoassembly and testing. OT presents a number of advantages for manipulating nanocomponents, including full six-degree-of-freedom manipulation, compatibility with a range of materials and shapes, and simultaneous manipulation of multiple particles in real-world environments such as biological media in-vitro and in-vivo. We will outline the physics that determines the capabilities and limitations of optical tweezers for nanoassembly, and describe the engineering that allows some of the limitations to be overcome. We will also describe the development of a graphical user interface and an architecture for the instrument control system to transform the tool from a simple trap to an agile tool that allows an inexperienced operator to manipulate nanocomponents in six degrees of freedom and prototype functional nanodevices in a CAD/CAM-like environment. These nanoassembly tools will be demonstrated with examples including nanowire device fabrication and control of biological nanoparticles such as liposomes for detection and treatment of cancer.

Ra22.18/Rb22.18

Capillary Growth of Oriented Composite Mesostructures under Nanoscale Confinement. Rong Kou, Donghai Wang and Yunfeng Lu; Department of Chemical and Biomolecular Engineering, Tulane university, New Orleans, Louisiana.

Cooperative assembly of silicate/copolymer replicates liquid crystalline mesophase of copolymer resulting in highly ordered mesostructures of inorganic/organic composite (e.g. cubic, hexagonal, lamellar structure). The self-assembly process always shows non-preferred orientation within the mesostructured composite. Oriented composite mesostructure will be of great interest due to favorable orientations that may provide enhanced device performance. However, fabrications of such oriented and highly ordered mesostructured composite still remain a challenge. In this presentation, we will show capillary-induced growth of oriented silicate/copolymer composite nanowire within nanoscale cylindrical alumina pores. Morphology of the oriented composite nanowires were studied using XRD, TEM and SEM. The liquid crystalline silicate/copolymer mesophase is driven into cylindrical alumina pores to form wire-like structure by capillary force. Shearing force within the liquid crystalline mesophase induced by interfacial capillary force aligns the composite mesostructure for both hexagonal and lamallar structure. Lamellar silicate/surfactant layers grow along curved pore wall surface resulting in oriented concentric lamellar mesophase. The corresponding mesoporous silica wires with oriented hexagonal tubular and concentric lamellar pore channels were obtained after removal of surfactants. As-generated hexagonal mesoporous silica nanowires possess desirable oriented nanopore channels along cylindrical alumina pores. The diameter of the oriented mesoporous silica nanowires are controlled by the diameter of cylindrical alumina pores, i.e. number of the oriented tubular mesopores within the mesoporous silica wire is tunable. The novel structured nanowires and corresponding mesoporous silica/alumina composite are expected in membrane based application such as separation, templating synthesis, etc. This work also will bring the insight of nanoscale confiment effect on self-assembly process.

Ra22.19/Rb22.19

Atomistic Study of the Mechanical Properties of One-Dimensional Nanomaterials. Kazuhito Shintani, Shunji Kameoka, Shuhei Sato and Yusuke Kometani; Dept of ME & Intelligent Sys, Univ of Electro-Comm, Chofu, Tokyo, Japan.

One-dimensional nanomaterials such as metallic nanowires and carbon nanotubes are suited for nanoscale building blocks in opto-electronic devices and micro/nano-electromechanical systems (MEMS/NEMS). Understanding their mechanical properties is essential for such applications. In this study, we first address the structural dependence and size effect of the Young's modulus of Au nanowires by using the molecular dynamics (MD) method with the modified embedded atom method (MEAM) potential. Ten kinds of nanowire models with helical multi-shell structures and the fcc structures are created. The uniaxial tensile forces are imposed on the atoms at the both ends of the nanowire models. The stress-strain curves yield the Young's moduli of the nanowires. Their dependences on the structure, size, and temperature are discussed. Next, we investigate the Young's modulus of carbon nanotubes by using the MD with the reactive empirical bond order(REBO) potential. Six kinds of nanotubes with different chiralities are prepared. The stress-strain curves derived from the uniaxial tensile and compressive simulations yield the Young's moduli of the nanotube models. Their chirality dependences are discussed.

Ra22.20/Rb22.20

Three Dimensional Nanotextured Opal-Like Silica Foams. Florent Carn, Pascal Masse, Serge Ravaine, Hassan Saadaoui and Renal Backov; Centre de Recherche Paul Pascal (UPR-CNRS 8641), Pessac, France.

Designing new porous materials in a monolitic form with framework involving hierarchical pore system and tailored macroscale form is an emerging area of technological interest toward heterogeneous catalysis, separations, artificial bone structure, thermal and/or acoustic insulation, ion-exchange operation. In addition to the micro- and/or meso-structure organisation, shapping porous solids in the form of monolith with tailored macropore morphologies associated with a tunable surface roughness are also important factor that influence the suitability for potential applications. In this context, such materials with higher order architecture can be obtained by using soft matter macroscopic template such as biliquid[1] or air-liquid foam[2]. We describe here a low cost and effective way of preparing hierarchically organised porous silica monolith arising from an air-liquid foam structure transcription by colloidal cristallisation. The opal-like skeleton provide a tunable surface roughness by using different size of silica colloidal particles while the macropore morphology (i.e. pore wall thickness, pore wall length) can be tune by a continuous control over the foam's liquid fraction and the gas bubble size during the mineralization process. Moreover open or closed pore structure can be reached upon the foam's liquid fraction and the colloidal particle size involved during the foaming process. This work[3] extends the recently reported study[4] on the preparation of SiO_2 foam using molecular precursor. This time by mimicking natural microstructure of super-hydrophobic leaves, the use of colloidal particle allow the surface roughness shaping leading to amplified surface hydrophobic chraracter. Furthermore, predominantly closed cell materials are needed for thermal insulation and open interconnected materials are required for uses involving fluid or gas transport such as filters and catalysts. 1- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, E. Sellier, M. Birot, R. Backov *J.Mater.Chem.*, 2004, 14, 1370. 2- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, C. Sanchez, R. Backov *Adv.Mater.*, 2005, 17, 62. 3- F. Carn, P. Masse, S. Ravaine, H. Deleuze and R. Backov *Langmuir* (submitted). 4- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, R. Backov *Adv.Mater.*, 2004, 6, 140.

Ra22.21/Rb22.21

Thioacetate Deprotection Using Catalytic Tetrabutylammonium Cyanide. Brian T. Holmes and Arthur W. Snow; Chemistry, US Naval Research Laboratory, Washington, District of Columbia.

While investigating thiol deprotection methods for a polymer with pendant aliphatic thioacetate groups, we successfully explored the use of tetrabutylammonium cyanide (TBACN) as a catalyst on a series of model compounds. Routine thioacetate deprotection methods utilizing several strong bases and acids proved inadequate whereas the initial studies of TBACN catalyst and solvent conditions were promising on three model compounds. Particularly attractive are the mild reaction and workup conditions, reduced byproduct formation typically seen using literature methods, and yields of greater than 80% for the free thiols. Consequently, a series of compounds were selected to analyze the scope and range of the method using various conditions including protic solvents, co-solvents, and catalyst quantity. Background work, synthesis, yields and limitations of this new method are presented.

Ra22.22/Rb22.22

Abstract Withdrawn

Ra22.23/Rb22.23

Nano Organic-Inorganic Hybrid Materials as Corrosion Protective Layers on Aluminum surface. Yuung-Ching Sheen, Chih-Kwuang Chen, Chih Kuang Chang and Shi-Min Shau; Union Chemical Laboratories, ITRI, Tainan, Taiwan.

Chromates and its salts like hexavalent chromium and chromium oxide (Cr2O3) have been used as effective corrosion inhibitors on steel, aluminum and aluminum alloys for many years. Traditional chromate-based surface treatments for the corrosion resistance purposes, such as chemical conversion and anodizing treatment, are very efficient and offer many valuable coating properties like durability, hardness and adhesion power because the dense passivation layer was formed on metal surfaces. Moreover, chromates especially the hexavalent chromium have self-healing ability which makes coatings possess an extra long-term work time and avoid the fracture of metal. The hexavalent chromium does not been considered as an environmental friendly material because of its toxicity and carcinogenic danger even though it has superior corrosion resistance properties on various metals. These properties of hexavalent chromium have caused European Union will prohibit to import it totally from 2007. Thus, searching for a new replacement material or an approach for corrosive protection as effective as hexavalent chromium is a momentous topic under these restrictions of law. In this study, we developed a new approach which without chromium component to enhance the corrosion resistance after the surface coating on metals. In the organic/inorganic (O/I) hybrid systems, the epoxy resins and silica particles were treated as the organic parts and inorganic parts, respectively, and they were considered as barrier layers to prevent the permeation of water, air and electrolyte like chloride ions. Furthermore, the efficient organic and inorganic corrosion inhibitors were incorporated in these O/I hybrid coatings as passivation layers when they had reacted with the metal surface to form a continuous and dense thin film at the interface between coating and metal surface. Besides, the organic corrosion inhibitors were composed of phosphate like phenylphosphonic acid or sulfur like 2-mercaptobenzimidazole(2-MBI), and the nano-sized inorganic corrosion inhibitors were manufactued by grinding processes from zinc phosphate and had been well dispered in our resin solutions. Finally, the O/I hybrid materials which incoporated with corrosion inhibitors were coated on the alumiun plates, and their anti-corrosion properties had been examined by salt spray testing and potentiodynamic polarization analyses. The O/I hybrid coating films were found to pass the 1000 hr salt spray testing and have much lower corrosion currents (0.9 nA/cm) compared with the bare aluminum (2742 nA/cm) based on the polarization curve. Both salt spray testing and electrochemical analyses showed that the O/I hybrid coatings which incoporated with corrosion inhibitors had provided excellent corrosion protection by forming a physical barrier layer and a continuous passivation film on aluminum surface simultaneously and independently.

Ra22.24/Rb22.24

Selective Deposition of Polymer Nano-Particles on Silicon Microfabricated Substrate. Manabu Tanaka[1], Hiroyuki Nishide[1], Naonobu Shimamoto[2], Takashi Tanii[2] and Iwao Ohdomari[2]; [1]Department of Applied Chemistry, Waseda University, Tokyo, Japan; [2]Department of Electrical Engineering and Bioscience, Waseda University, Tokyo, Japan.

Recently, there is great interest in arrangements of nano-particles (nanometer-sized homogeneous particles with diameters from a few nanometers to sub-micrometers) on substrates. Several approaches have been studied to arrange nano-particles on substrates, including laser manipulation, ink-jet printing, nanoprobe lithography, and a nano-particle arrangement using the substrate as a template. Among them, the template-assisted procedures are simple and feasible without any special equipments and techniques. This report describes the selective deposition of polystyrene nano-particles in various nano- or micro-sized recessed patterns on silicon substrates by using a simple dipping and pulling-up procedure. A Nano-particle array dot, the zero-dimensional arrangement, was first achieved on the silicon nano-etchpit array substrate which possesses a nanometer-sized recessed cylindrical etchpit (a pit formed through the etching) at the lattice points with a constant interval on the silicon substrate as an array. "Particle-packing" and "particle chain", the two- and one-dimensional particle arrangement, by using other types of silicon microfabricated substrates were similarly realized. In addition, as an example of functional nano-particles, nanometer-sized and monodispersed polymer particles bearing stable radicals (unpaired electrons) was newly synthesized. Magnetic properties of the radical nano-particles and their arrangement on the silicon microfabricated substrate are also described.

Ra22.25/Rb22.25

Selective Chemical Vapor Growth of Carbon Nanotubes for Application of Electronic-Measuring Nano-Probes. Hiroki Okuyama, Nobuyuki Iwata and Hiroshi Yamamoto; College of Science and Technology, Nihon University, Chiba, Japan.

It is necessary to prepare nano-scaled probes and to control accurate approaching toward specimen for measuring electronic properties of nano-structured specimen. Carbon nanotubes (CNTs) have many unique characteristics, for example, high mechanical strength, flexibility and high electric conductivity. Furthermore CNTs grow from only fine particles of catalyst by using chemical vapor deposition (CVD). Those characteristics are applied to prepare novel CNT probes that are easy to prepare and to handle. In this work, we demonstrate the process for selective growth of CNTs on patterned metal layers. A Ni catalyst and a Mo metal layer were deposited on a quartz substrate through a mask. The boundary of the metal pattern was prepared to become thin gradually. The Ni / Mo films were prepared by RF magnetron sputtering equipment. The growth conditions (substrate temperature, sputtering power and growth time) were 120 °C, 50 W and 1 min for Mo, 70 °C, 20 W and 1 min for Ni respectively. The CNTs were grown by Thermal-CVD method. The reactor tube of the CVD equipment was heated up to 600 °C. The flow of H_2 / Ar (5 ccm / 200 ccm) was introduced into the reactor tube during heating. The background pressure was 0.1 Pa, the total pressure was fixed at 5 kPa. When the temperature of the furnace reached a growth temperature, the 10 ccm of ethylene (C_2H_4) was fed into the reactor for 30 min for the CNTs growth. From results of SEM observations, CNTs with 15 nm diameters grew up near the boundary where the surface of the Mo films was rough and porous. The amount of CNTs reduced gradually from boundary to inside of the metal pattern. The width of the CNT grown region was about 30 μm. In contrast the smooth Mo surfaces resulted in no growth of CNTs. Particles of the Ni catalyst were not observed in the resolution of SEM. The reason why CNTs grew up near by the boundary is that the Ni catalysts formed fine particle at the grown region. The Ni catalysts didn't become fine particle on the smooth surface of Mo. Rough morphology of the Mo underlayer promoted the Ni catalyst to become fine particles. The Mo thickness of the rough region was thinner than that of the smooth region. Conclusively it was demonstrated that a selective growth of CNTs was realized by controlling the thickness of the underlayer. The results of electronic property measurements by the probes, which are prepared by this method, will be reported.

Ra22.26/Rb22.26

Nanotube Coalescence Inducing Mode: A Novel Vibrational Mode in Carbon Systems. Morinobu Endo[1], Mauricio Terrones[2], Yoong-Ahm Kim[1], Takuya Hayashi[1], Hiroyuki Muramatsu[1], Riichiro Saito[3], Federico Villalpando[4], Shin Grace Chou[5] and Mildred Dresselhaus[6]; [1]Faculty of Engineering, Shinshu University, Nagano, Japan; [2]Advanced Materials Department, IPICYT, San Luis Potosi, Mexico; [3]Department of Phyiscs, Tohoku University, Aoba Sendai, Japan; [4]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [5]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; [6]Department of Physics, and Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We inspected a new resonant Raman mode located at 1855cm-1 which is attributed to vibrations of linear carbon chains located between double-walled carbon nanotubes (DWNT). This mode has now been termed the "coalescence induced mode" (CIM) because it signals the onset of the nanotube coalescence process. In order to understand this phenomenon, high purity DWNT bundles were thermally treated at various temperatures, ranging from 1000°C to 2000°C. For each temperature step, Raman spectra were taken at different excitation energies and compared with HRTEM images. A separate section of the sample was mixed with elemental boron at 0.05% and the same experimental procedure was repeated to understand the effect of boron doping in the coalescence process. It was observed that the CIM feature appears in the Raman spectra just before the tubes begin to coalesce. The intensity of the CIM mode reaches a maximum at a critical temperature and disappears once the adjacent tubes start to merge. The CIM vibration is provoked by 1D carbon chains (3-7 atoms-long) established covalently between adjacent tubes. These chains induce a zipper action while the tubes coalesce, and the process is enhanced in boron doped samples. Once coalescence is initiated, the CIM disappears and a new Radial Breathing Mode (RBM) appears, which corresponds to larger diameter carbon nanotubes. The effects were confirmed using high-resolution transmission electron microscopy (HRTEM). The CIM mode could now be used to identify sp hybridized carbon in various systems such as irradiated graphite, polymerized C_{60} molecules, functionalized fullerenes and nanotubes, carbynes, etc.

Ra22.27/Rb22.27

"Smart" Defects in Colloidal Photonic Crystals. Friederike Fleischhaker[1,2], Andre C. Arsenault[1], Nicolas Tetreault[1], Zhuo Wang[1], Vladimir Kitaev[1], Frank C. Peiris[1], Agustin Mihi[3], Hernan Miguez[3], Georg von Freymann[1], Ian Manners[1], Rudolf Zentel[2] and Geoffrey A. Ozin[1]; [1]Department of Chemistry, University of Toronto, Toronto, Ontario, Canada; [2]Department of Chemistry and Pharmacy, University of Mainz, Mainz, Germany; [3]Centro de Tecnologia Nanofotonica, Universidad Politecnica de Valencia, Valencia, Spain.

We present a bottom-up approach for the construction of "Smart" active defects in colloidal photonic crystals (CPCs). These structures incorporate polyelectrolyte multilayer (PEM) planar defects embedded in silica CPCs through a combination of evaporation induced self-assembly and microcontact printing. We show how the enormous chemical diversity inherent to PEMs can be harnessed to create chemically active defect structures responsive to solvent vapor pressures, light, temperature, enzymes as well as redox cycling. A sharp transmission state within the photonic stopband, induced by the PEM defect, can be precisely, reproducibly and in some cases reversibly tuned by these external stimuli. These materials could find numerous applications as optically monitored chemical sensors, adjustable notch filters and CPC-based frequency tunable laser sources.

Ra22.28/Rb22.28

Abstract Withdrawn

Ra22.29/Rb22.29

Fabrication of Arrays of Hollow Metal Pillars Using Nanosphere Lithography. Jang Se Gyu[1], Dae-Geun Choi[2] and Seung-Man Yang[1]; [1]Biochemical Eng., KAIST, Dae-jeon, South Korea; [2]Intelligent Precision Machine, KIMM, Dae-jeon, South Korea.

Arrays of nano-pillars and nano-rings of metals have attracted great attention due to their potentially important properties including superconducting and magnetooptical properties, tuning of the localized surface plasmon resonance, enhancement of raman scattering, fast switching capability as magnetic media, and field emission performance. Recently, several fabrication methods by the metallization of the anodic aluminum oxide (AAO) template were reported for the fabrication of nano-ring and nano-pillar array. However, the control of the feature sizes and aspect ratios is not easy because the feature sizes are limited by the employed AAO template. Consequently, AAO templates with controllable dimensions have to be prepared to fabricate the nanostructure arrays of various feature sizes. In addition, the thickness of the pillar is limited to some degree because the top pores of an AAO membrane can be blocked by the excessive metal deposition. Here, we report a novel approach for the hexagonally ordered nano-pillar array using reactive ion etching (RIE) through the nanosphere arrays self-organized over a polymeric film. First, RIE through the colloidal mask produced polymeric nano-cylinder array, and subsequently various metals were sputtered over the nano-cylinder arrays. Then, the colloidal particles on the nano-cylinder arrays were removed, and finally the nanopillar array was fabricated by removing the polymeric cores. The height and diameter were controlled by simply adjusting the polymer film thickness and the RIE conditions during the formation of nano-cylinders. Moreover, the thickness of the resulting nano-pillars was controlled by the variation of the sputtered thickness of metals. UV-NIL absorption spectra showed that our nano-pillar array was suitable for the detection of biomolecules with red-shift of the absorption peaks.

Ra22.30/Rb22.30

Flexible anti-reflection coatings from layer-by-layer assembled nanoparticles. Zhizhong Wu[1], Adam Nolte[1], Joe Walish[1], Lei Zhai[1], Robert Cohen[2] and Michael Rubner[1]; [1]Materials Science and

Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

In biological vision systems, lenses are often flexible and fluidic, therefore the focal lengths can be tuned through a change in the refractive index and (or) lens shape. For example, crystalline fisheye lenses possess a varying index of refraction via an inhomogeneous gradient of protein/water, which, when deformed, allows for a variable field of view. Recently, much attention has been directed to the fabrication of deformable lenses that mimic the fisheye's dynamically controllable field of view. However, at certain wavelengths these deformable lenses (such as PDMS) reflect the incoming light due to their high refractive index relative to air. This work demonstrates the fabrication of anti-reflection coatings on PDMS flexible substrates using the layer-by-layer assembly of silica nanoparticles and poly(diallyldimethyl ammonium chloride) (PDAC). The coatings showed good anti-reflection properties on the flexible substrates. The maximum transmittance of the PDMS substrates was improved to as high as 99%. SEM and AFM images showed that the porous nature of the film, a structural feature that lowers the film's refractive index, originated from the random packing feature of silica nanoparticles on PDMS substrates. Preliminary results show that the coatings can be used on a deformable PDMS lens.

Ra22.31/Rb22.31

Joining Techniques for Template Synthesized Nano-components. Jordan S. Peck[2,1], Jonathan J. Mallett[4], Andras E. Vladar[3], Jon R. Pratt[1], Daniel Josell[4] and Gordon A. Shaw[1]; [1]Manufacturing Metrology Division, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Mechanical Engineering, Binghamton University, Binghamton, New York; [3]Precision Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland; [4]Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Template Synthesized nanocompontents of various Ni, Co and Pt alloys have been fabricated and characterized. These components are grown in the pores of an aluminum-oxide membrane which is then dissolved leaving free standing high aspect ratio nanowires 200 nm in diameter and up to 50 μm long. The morphology, composition, structure, and mechanical properties of these wires were studied using scanning electron microscopy, atomic force microscopy, x-ray diffraction, and instrumented indentation. Electrochemical deposition is utilized to pursue joining the nanowires to macroscopic wires as well as atomic force microscope tips. Once understood, this joining technique can then be used in the creation of functional nanodevices.

Ra22.32/Rb22.32

Synthesis and Characterization of BaZrO3 Perovskite Nanocrystal. Hongjun Zhou[1], Yuanbing Mao[1] and Stanislaus S. Wong[1,2]; [1]Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York; [2]Materials and Chemical Sciences Department, Brookhaven National Laboratory, Upton, New York.

Single-crystalline perovskite nanostructures of reproducible shape have been prepared in large quantities using a simple, readily scaleable solid-state reaction in the presence of salt mixtures such as NaCl, NaOH, and NaOH/KOH. The mechanism of synthesizing pristine, single-crytalline BaZrO3 nanostructures has been systematically investigated. Different experimental processing parameters such as the type and amount of salt, temperature, and reaction time appear to affect the resulting product characteristics (including morphology) in the molten salt method. We have determined that the type of salt utilized is the most important parameter governing the reaction and growth environment. Extensive characterization of these nanostructures has been performed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

Ra22.33/Rb22.33

Patterning of Single-Walled Carbon Nanotubes Using Wet Chemical Self-Assembling and Photolithographic Technique. Myung-Sup Jung[1,2], Sung-Ouk Jung[1], Jung-Na Heo[1], Hee-Tae Jung[2] and Jingyu Hyeon-Lee[1]; [1]Materials and Devices Research Center, Samsung Advanced Institute of Technology, Suwon, South Korea; [2]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

Single-walled carbon nanotubes (SWNTs) have been chemically attached with high density onto a pre-patterned substrate. In order to form the SWNT pattern, the substrate was treated with acid-labile group protected amine, and an amine pre-pattern was formed using a photolithographic process with a novel polymeric photo acid generator (PAG). The polymeric PAG has triphenylsulfonium salt moieties on its polymer backbone and moderate molecular weight. In contrast to photoresists or monomeric PAGs, the polymeric PAG is more useful for simple and efficient selective surface modification due to its improved spin-coating properties. The SWNT monolayer pattern was then formed through the amidation reaction between the carboxylic acid groups of carboxylated SWNTs (ca-SWNTs) and the pre-patterned amino groups. High-density multilayer was fabricated via further repeated reaction between the carboxylic acid groups of the ca-SWNTs and the amino groups of the linker with the aid of a condensation agent. The formation of covalent amide bonding was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. SEM and UV-vis-NIR results show that the patterned SWNT films have uniform coverage with high surface density. Unlike previously reported patterned SWNT arrays, this ca-SWNT patterned layer has high surface density and excellent surface adhesion due to its direct chemical bonding to the substrate. Also, The resolution of the SWNT pattern is very high compared to those of patterns obtained with conventional methods. Further, the high-density structure of the ca-SWNT film has good electrical conductivity and electron emission properties, and the strong adhesion of the patterned SWNT layer should improve the reliability of devices using such films. We found that the high-density multilayer SWNT patterns emit electrons under an applied electrical field. The electrical resistivities of the SWNT layers were found to be 5 ∼10 W cm, with a turn-on electric field of about 3 V/mm at an emission current density of 10 mA/cm2. This approach enables the formation of micro-patterned ca-SWNT arrays on solid substrates at mild temperatures. Also, this patterning method provides strong adhesion between the SWNTs and the substrates, resulting in high surface density structures on various substrates, which is critical to their practical applications such as solar cells and batteries, flat panel displays, transistors, chemical and biological sensors, and semiconductor devices.

Ra22.34/Rb22.34

Synthesis and optical properties of manganese-doped ZnS nanoribbons by post-annealing. Yanqing Li, Juan Antonio Zapien, Yue Yue Shan, Yingkai Liu and Shuit-Tong Lee; Dept. of Physics & Materials Science, COSDAF, Hong Kong, Hong Kong.

ZnS doped with manganese (Mn) exhibits significant light-emitting properties, and can be applied as efficient phosphors. In this work we demonstrate a simple method for Mn doping of ZnS nanostructures by post-annealing treatment. ZnS nanoribbons synthesized by thermal evaporation are doped with manganese (Mn) by simple annealing in MnS powder. The morphology of single-crystal ZnS nanoribbons of a uniform hexagonal wurtzite 2H structure remains unchanged after Mn incorporation at an annealing temperature below 700 oC. The photoluminescent characteristics show the intrinsic ZnS emission is gradually replaced by a Mn2+?induced feature with increasing annealing temperature, which is attributed to increasing incorporation of Mn2+ ions.

Ra22.35/Rb22.35

Self-Organization of Colloidal Particles in Monodisperse Aqueous Emulsions. Shin Hyun Kim[1], Gi-Ra Yi[2], Jong-Min Lim[1] and Seung-Man Yang[1]; [1]Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; [2]Corporate R&D Center, LG Chem Research Park, Daejeon, South Korea.

Over the years, confined geometries such as emulsions, aerosols, capillaries, and patterned substrates have been introduced to self-organization of colloid particles by several research groups. Using these confining geometries, we are able to create controlled structures of colloid crystals with specific photonic properties. Especially, emulsion droplets are of potential importance as confined geometries for the evaporation-induced self-organization of the colloidal particles to produce colloidal clusters or crystals. In particular, colloidal crystals in spherical symmetry (or photonic balls) possess photonic band gaps for the normal incident light independently of the position all over the spherical surface, unlike usual colloidal crystals. In this paper, we report a fabrication method of monodisperse spherical colloidal crystals using water-in-oil emulsion droplets as confining geometries. For monodisperse photonic balls, we controlled the size of aqueous emulsion droplets by a drop break-off mode in a coflowing stream of oily hexadecane. In this case, we obtained the photonic balls dispersed in hexadecane and subsequently redispersed in other solvents easily. After a heat treatment of the emulsion droplets at 70°C for several hours, photonic balls began to exhibit an iridescent color, and the reflection spectra were responding readily and precisely to any change in physical properties including the size of the constituting colloidal particles, refractive index mismatch, and angle of the incident beam. For better photonic structures, inverted photonic balls, in which air cages were packed in a dielectric medium, were also prepared by colloidal templating. In doing this, we first obtained the composite colloidal crystals in which the silica nanoparticles were filled at the interstices between the polystyrene microspheres, and then removed the polystyrene microspheres by thermal decomposition leaving behind well-ordered air cages in silica matrix.

Ra22.36/Rb22.36

Fabrication of One-dimensional Colloidal Assemblies via Electrospinning. Jong-Min Lim[1], Jun Hyuk Moon[1,2], Gi-Ra Yi[3] and Seung-Man Yang[1]; [1]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; [2]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [3]Corporate R&D Center, LG Chem Research Park, Daejeon, South Korea.

The self-assembled structure of monodisperse colloidal particles has attracted great interest due to their wide range of applications such as photonic crystals, chemical and biological sensors and catalytic supports. Recently, several methods were suggested to fabricate the one-dimensional (1D) colloidal assemblies including growth of 1D structures in patterned substrates. However, these methods require additional procedures to make the patterned substrates and it is usually difficult to transfer the assembled structures to other substrates. In this work, we developed a simple and highly efficient electrospinning process to fabricate one-dimensional colloidal assemblies. To do this, we first prepared a mixed solution of colloidal particles and polymeric liquid, and then, the mixture solution was introduced into a capillary needle which was under a high electric field. As the electrospun fiber became thinned due to the formation of the instability region of whipping, the colloidal particles embedded inside of the electrospun fibers began to arrange into pearl-necklace structures by shear-induced self-assembly. A designed collector, which was composed of two copper plates with a constant gap, was used to fabricate aligned colloidal assemblies. Finally, we determined the optimal conditions such as field strength, throughput rate, particle loading and types of polymers for the stable electrospinning process to produce well-ordered colloidal structures. The self-assembled structures were easily transferred to other substrates required for various applications.

Ra22.37/Rb22.37

Structure of carbon nano-particles by novel template method. Toshifumi Shiroya[1], Hiroyuki Aikyou[1], Masaki Yamamoto[1] and Takashi Kyotani[2]; [1]Soft Materials Science Laboratory, Mitsubishi Chemical Group Science and Reserach Center, Yokohama, Japan; [2]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan.

Many researches for the synthesis of nano-carbon materials with precisely controlled nano-structures have been carried out. For example, to control the lengths and diameters of carbon nanotubes (CNTs), the template carbonization method using an anodic oxide film have been proposed (1). In addition, controlling graphene layer orientation is also important for the application of nano-carbon materials. For example, CNTs are concentric structure in which the curved graphene planes lie parallel to the tube axis. Platelet nanofibers, however, have graphene layers which lie perpendicular to the fiber axis (2). As a result, they are suitable for the different applications, respectively. Furthermore, the dispersibility of nano-carbon materials into solvents is the important subject for applications of them. We will report the new template method for preparing novel carbon nano-particles using polymer nano-particles, which were elongated beforehand, and heat-resistant materials as templates. By using this method, one elongated polymeric nano-particle could be converted to one hollow carbon nano-particle. Therefore, we can easily control the shapes and size of carbon nano-particles. Further, two types of carbon nano-particles which had different graphene layer orientations could be prepared by changing the template synthesis condition. In the present work, we will also show the dispersibility of the carbon nano-particles into water. References: (1) T.Kyotani, L.Tsai, A.Tomita, Chem.Mater. 1995, 7, 1427. (2) K.Jian, H.-S.Shim, A.Schwartzman, G.P.Crawford, R.H.Hurt, Adv.Mater. 2003, 15, 164

Ra22.38/Rb22.38

Low-threshold lasing in a dye-doped low molecular cholesteric LC layer sandwiched by polymeric cholesteric LC films. Myoung Hoon Song[1], Natsumi Tomoe[1], Yoichi Takanishi[1], Ken Ishikawa[1], Suzushi Nishimura[2], Takehiro Toyooka[2], Timothy M. Swager[3] and Hideo Takezoe[1]; [1]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan; [2]Central Technical Research Laboratory, Nippon Oil Corporation, Yokohama, Japan; [3]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

People have intensively studied organic lasers, since organic materials are easy to be fabricated for devices and to be modified to realize a variety of attractive properties by changing the substituted groups. Particularly, continuous wave lasing is desired for practical devices. However, it has not been realized yet because of the thermal effects and high threshold properties. Many researchers demonstrated the lasing action of dye-doped CLCs. Fluorescence emission is suppressed inside the photonic band gap (PBG), but enhanced at the band edges. Moreover, by introducing defect(s) into a periodic structure, additional resonant modes appear inside the PBG. Photons are localized at the defect position, thus low-threshold lasing would be expected to occur. In this work, we will introduce a new type of defect mode structure that exhibits low threshold property. The helical pitch of low molecular weight CLC mixture was controlled by changing the ratio of a chiral dopant (MLC6247 Merck Co.) and a nematic liquid crystal (ZLI2293 Merck Co.) The CLC was doped with a laser dye of 2 wt%. Polymeric CLCs (PCLCs) were mixtures of chiral and achiral aromatic polyesters (Nippon Oil Corporation). The PCLC films were fabricated by spin coating onto glass substrates coated with a polyimide alignment layer (AL1254,JSR). The dye-doped CLC is sandwiched between glass substrates coated with PCLCs, and we call it g3-layer cellh. Low molecular weight CLC has a helical structure with left-handedness, which is opposite to that of PCLCs. Due to the difference between optical pitches and handedness of two kinds of CLCs, a defect mode lasing was observed. For comparison, we prepared three types of cells; a simple DFB type cell using only a low molecular weight CLC (single-layer cell), a glass sandwich cell of low molecular weight CLC in which one of glass substrates is coated with the PCLC (2-layer cell) and the 3-layer cell mentioned above. An optical parametric oscillator (Surelite OPO: Continuum) pumped by third-harmonic light of a Nd:YAG laser (Surelite II: Continuum) was used as a light source for lasing experiments. The laser emission from the cell was detected by a spectrometer (HR2000: Ocean Optics). The single and 2-layer cells exhibit almost the same threshold energy (500 nJ/pulse). In contrast, it is found that threshold energy of the 3-layer cell is much lower than the other cells; i.e., 180 nJ/pulse. Moreover, to our surprise, lasing emission from the 3-layer cell contains both of circularly polarized lights while only circularly polarized light with the same sense as the CLC helix is observed in the single-layer cell. The intensity of a left-circularly-polarized light is stronger than that of a right one. This phenomenon is consistent with the calculation using a 4X4 matrix method, indicating that the lasing emission from the 3-layer cell is caused by the defects.

Ra22.39/Rb22.39

HRTEM and EELS Studies of GdSi$_2$ Nanostructures Grown by Self-Assembly. Jiaming Zhang[1], Martin A. Crimp[1] and Jun Nogami[2]; [1]Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan; [2]Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

Rare-earth metal silicide nanowires are candidates for low resistance interconnects in future nanometer scale electronic devices. Since the formation of self-assembled silicide nano-wires by deposition of rare earth (RE) metals on Si (001) was first discovered, intense interest has been focused on the epitaxial growth of RE silicides on silicon surfaces. In order to expand our understanding of the heteroepitaxial growth mechanisms of gadolinium silicides on Si (001), plan view and cross-sectional high-resolution transmission electron microscopy (HRTEM) are used to investigate the crystal and interfacial structures at the atomic scale. Complementary information from electron energy loss spectroscopy (EELS) is used to provide spatially resolved information about the electronic structures of these silicide nanostructures by analyzing the energy-loss near-edge fine structure (ELNES). Comparisons of the Gd EELS M$_{45}$ edge of metallic Gd, bulk GdSi$_2$ and Gd-silicide nanostructures will be presented.

Ra22.40/Rb22.40

Metal Hollow Nanoparticles Derived by Bio-Templating. Jae-Woo Kim[1], Sang H. Choi[2], Peter T. Lillehei[2], Sang-Hyon Chu[3], Glen C. King[2] and Gerald D. Watt[4]; [1]STC/NASA LaRC, Hampton, Virginia; [2]NASA LaRC, Hampton, Virginia; [3]National Institute of Aerospace, Hampton, Virginia; [4]Chemistry and Biochemistry, Brigham Young University, Provo, Utah.

There has been great interest in the synthesis and characterization of hollow metal nanostructures due to their surface plasmonic properties and catalytic activities, which are different from their solid counterparts. Most of the previous works utilize large hollow nanostructures of several hundreds of nanometers. Very recently, a couple of research groups demonstrated the preparation of hollow nanostructures on the scale of tens of nanometers by a replacement reaction with a solid Ag template and a nanoscale Kirkendall effect, respectively. However, the fabrication process is complicated and requires organic solvents. In this work, ferritin is used as a biotemplate to produce hollow nanoparticles and as a separator between the hollow nanoparticles. The protein cage of ferritin is very stable and robust which allows constrained material synthesis. Previous studies using the ferritin cage were focused on demonstrating the fabrication of solid nanoparticles through reconstitution of the ferritin iron core with different metals rather than investigating the mechanism of the metal growth. We will propose on a mechanism of cobalt oxide and iron oxide growth in apoHoSF (Sigma), which has a protein shell without a core, and the fabrication of hollow nanoparticles by controlling the number of metal atoms in the ferritin. When the ferritin has 200 Co atoms in the interior, several nanoparticles of cobalt oxide with mean diameters of 1.8 nm are formed in the interior. Scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM) imaging allows us to see only the metal cores inside the ferritin cage due to the relatively low density of the protein shell. The metal ions enter through the hydrophilic channels along the three fold symmetric axis of the protein and combine with the carboxylate groups of glutamic acid residues on the ferritin interior wall, forming discrete nanoparticles during the oxidative reaction. Once these seeds of metal oxide nanoparticles form inside the ferritin, they grow auto-catalytically along the ferritin interior wall and then merge together upon further addition of Co(II) and H2O2. When the ferritin contains over 1000 Co atoms, the cobalt oxide forms a hollow nanoparticle. When 2000 Co atoms are contained in the ferritin, a clear circle with a hollow core is observed indicating merging between the nanoparticles. The size of hollow nanoparticle is around 6 nm, which is smaller than the inner diameter of the ferritin core. We will present the first fabrication of hollow cobalt oxide and iron oxide nanoparticles using a bio-template in aqueous solution and describe the metal oxide growth mechanism in the ferritin interior. This growth mechanism facilitates the preparation of hollow metal oxide nanoparticles by controlling the number of metal atoms inserted in the ferritin interior.

Ra22.41/Rb22.41

Process structure and properties of quantum dot nanofiber composite. Heejae Yang[1], Hui Li[2], Wei-Heng Shih[2] and Frank Ko[2,1]; [1]School of Biomedical Engineering, Science & Health Systems, Drexel University, Philadelphia, Pennsylvania; [2]Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

A new type of fluorescent fibrous composite material ranging several hundred nanometers to less than less than a micrometer consist of quantum dots and polymer has been successfully processed by the electrospinning process. The quantum dots are single crystals that posses unique electrical and optical properties. Especially quantum dots offer several advantages over organic dyes traditionally used for cell labeling. Unlike fluorescent dye, the emission and excitation wavelength of quantum dots do not overlap and the optical properties is controllable by changing the size of quantum dots. The emission light intensity is higher than the dye. Also, it is very stable over a period of time. Electrospinning is the process to produce ultra fine fibers from solution or melt polymer. When high voltage is applied to polymer solution, the charged polymer solution forms a jet and travels to grounded target. While the solution traveling, solvent evaporates and fine fibers are collected on the target. The various concentrations of aqueous CdS quantum dot solutions were prepared. Resulting in quantum dots with 5nm in diameters was found to be well suspended and stable for over several months on the shelf. 5wt% of Polyethylene Oxide (PEO, Mw 600,000) were dissolved in prepared CdS solution then magnetically stirred for 24 hours. The prepared CdS-PEO solutions and collected fibers were characterized by optical fluorescent and electron microscopy. The design of this new hybrid quantum dot/nanofiber technology opens the door to many applications including drug delivery, scaffold for tissue engineering and security device.

Ra22.42/Rb22.42

Self Assembled Nanostructure in Metal Thin Films on Single Crystalline Substrates. Zhuopeng Tan[1,2], Albert Davydov[2,1], Alexander Shapiro[2], Leonid A. Bendersky[2], Julia Slutsker[2] and Alexander L. Roytburd[1,2]; [1]University of Maryland, College Park, Maryland; [2]NIST, Gaithersburg, Maryland.

The goal of our study is to engineer a self-assembled two-phase nanostructure as a result of eutectic decomposition of metallic film on a single crystal substrate. As a model system, AgCu films were grown on hydrogen terminated Si(111) using electron beam deposition system under high vacuum. A structure consisting Ag particles of 200∼300nm embedded in a Cu matrix was obtained during deposition at 873K with 1:1 composition ratio. The average distance between the particles is about 200nm. X-ray shows a good epitaxial relationship between the two phases and the substrate. Effects of growth temperature and composition on nanostructure formation have been studied. The experimental results were interpreted adequately by the thermodynamic theory and phase field modeling.

Ra22.43/Rb22.43

Synthesis of hierarchically porous materials using colloidal and amphiphilic templates. Petr Vasiliev[1], Zhijian Shen[1], Robert Hodgkins[1], Erik Sundstrom[1], Peter Alberius[2] and Lennart Bergstrom[1]; [1]Department of Physical, Inorganic and Structural Chemistry, Stockholm University, Stockholm, Sweden; [2]Institute for Surface Chemistry, Stockholm, Sweden.

The possibility to control the pore size and pore structure resulting in a material characterized by a high surface area, accessible monodisperse pores, hydrothermal- and mechanical stability is of interest in various applications, e.g. as membranes, sensors, catalyst support , slow release agents, chromatography and ground water treatment. We will show how hierarchically porous bulk materials can be produced by two different approaches. Mesoporous spherical particles, prepared by a recently developed spray-drying technique, have been fused (initial stage of sintering) together into cylindrical disc shaped materials with the use of the spark plasma sintering (SPS) technique. SPS can simultaneously subject powder bodies to a rapid temperature increase and a compressive stress. By keeping the temperature low (from 600 to 800 C), and the holding time below 10 minutes, it was possible to form a continuous body where the particles were connected by necks formed at the surface of the particles, while the mesoporous structure was retained within the particles. The structure, porosity, necking and mechanical properties of the fused mesoporous particles are strongly dependent on the applied pressure and temperature. It will be discussed how bulk materials with a hierarchical porosity can be prepared, where the inter-granular pore size is mainly determined by the particle size and the inter-granular (mesoporous) structure is controlled by the conditions in the particle synthesis step. Polymeric particles have also been used as templates to produce cellular silica materials that display micro- or meso-porosity. It will be shown how the pore size as well as the thickness of the ceramic walls within the final cellular structure can be varied independently by choosing different templates and reaction conditions.

Ra22.44/Rb22.44

Silated acidic polymers for nanoimprint lithography on flexible substrates. Wenchang Liao and Steve Lien-chung Hsu; National Cheng Kung University, Tainan, Taiwan.

A series of new silated acidic resists have been prepared for nanoimprint lithography on flexible plastic substrates. The resists were synthesized by copolymerization of several acrylic monomers including at least one acidic and one silated monomer. For use on flexible plastic substrates, the glass transition temperatures of these resists were adjusted to a range of 20-40°C. They were easily removed by environmental friendly aqueous base solution during the stripping process without using reactive ion etching (RIE) process or an organic solvent which is used in conventional imprint process. They can enhance the throughput and save cost during the stripping process, and also have good etching resistibility. Replications of high-density line and space patterns with resolution of 100 nm were obtained on a flexible ITO/PET substrate. The subsequent ITO etching patterns were also achieved.

Ra22.45/Rb22.45

Structural Studies of Inorganic Metal Oxides Encapsulated in Single Walled Carbon Nanotubes. Pedro M. F. J. Costa[1,2], Steffi Friedrichs[1,2], Jeremy Sloan[2] and Malcolm L. H. Green[2]; [1]Materials Science, University of Cambridge, Cambridge, United Kingdom; [2]Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom.

The seminal report by Sumio Iijima describing the observation of carbon nanotubes has been key to the immense body of research carried out on these structures. Behind the scientific enthusiasm lies the potential of revolutionary technological applications which span from nanoelectronic computer circuitry to miniaturised and highly-efficient gas sensors. One particular area that has seen interesting advances recently is the encapsulation of substances in the internal tubular structure of carbon nanotubes. Working as test-bed composite materials for electron microscopy techniques development or as 1D templates for the synthesis of nanowires, filled carbon nanotubes offer a new window of opportunities for the study of the physical properties and chemistry of confined structures. The first successful and controlled filling of carbon nanotubes was performed using Pb3O4 and Multi Walled Carbon Nanotubes in Ar atmosphere. Other studies soon followed which dealt with oxide systems ranging from first row transition metal oxides (V2O5, NiO) to lanthanide metals (Sm2O3). Nonetheless, the filling of lower numbered walls carbon nanotubes (Single and Double) with inorganic oxides has been scarce. This may be due to several factors such as the reactivity of the metal oxides and the fact that commonly being refractory, their melting points are too high to enable melt-phase nanotube fillings.

Furthermore, the wide range of chemical and physical properties of these systems renders more difficult a consistent study in contrast to other system families such as the metal halides. Some of the few encapsulated metal oxides reported for SWNTs include Sb2O3 and CrO3. One of the main tools used in the characterisation of nanomaterials is undoubtedly the Transmission Electron Microscope, which allows structure imaging with very high resolution. This, however, is impaired by the inherent limitations of the equipment such as lens aberrations. Recently, this area of structural analysis has seen important progress with the introduction of software-based approaches to aberration corrections. It follows that using a series of images taken at different defoci it is now possible, after performing the restoration of the exit surface wavefuntion, to obtain super-resolved images of the materials within the carbon nanotubes. We would like to report the successful filling of Single Walled Carbon Nanotubes with various inorganic metal oxides. Depending on the oxide used, the filling behaviour differs and structures obtained range from clusters (RexOy) to well-defined wires (PbO, Te2O). These composites were studied using a state-of-the-art phase-restoration technique which results in High Resolution TEM images free of aberrations. Additionally, it is also shown how chemistry can be performed inside the restricted environment represented by the inner tubule of SWNTs (partial washing of encapsulated material, reduction of oxides to metal).

Ra22.46/Rb22.46

Mechanical Behavior of Functionalized Multi-Walled Carbon Nanotube Thin Films. Shin-ichi Ogino[1], Yoshinori Sato[1], Kenichi Motomiya[1], Balachandran Jeyadevan[1], Kenichiro Sasamori[2], Hisamichi Kimura[2], Rikizo Hatakeyama[3] and Kazuyuki Tohji[1]; [1]Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; [2]Institute for Materials Research, Tohoku University, Sendai, Japan; [3]Graduate School of Engineering, Tohoku University, Sendai, Japan.

Multi-walled carbon nanotubes (MWCNTs) are composed of strong graphene sp^2 bonds that hinder their functionalization. Consequently, the preparations of MWCNTs solid bodies have been found to be difficult. However, we believe that the preparation of MWCNTs solid bodies could be realized by making the surfaces of MWCNTs active by forming defects that facilitate the functionalization as well as binding between tubes. In this paper, we report the synthesis of thin films using chemically functionalized MWCNTs, and their mechanical properties. The as-grown MWCNTs were air oxidized and treated with hydrochloric acid to remove amorphous carbon and catalytic metal particles respectively. Then, the samples thus obtained were treated with nitric acid at 373 K for 16 hours to induce defects on the surface of the tubes. As a consequence, the surface becomes fuctionalized with carboxyl and hydroxyl groups [1]. Then, these functionalized tubes were polymerized to prepare MWCNT thin films using the following steps. Firstly, the functionalized MWCNTs were ultrasonicated for an hour in N, N-dimethylformamid (DMF), and the solution was stirred for 24 hours. Finally, MWCNT thin films with different thickness were prepared by filtering dispersion with varying MWCNT concentrations. However, the mechanical strength of these MWCNT films is too weak as there was no chemical bonding between tubes. Therefore, it is believed that the formation of chemical bonds between tubes is vital to obtain robust films. Here, we attempted to reinforce the films by using the polymerizing effect. The MWCNT films were soaked (dispersed) in N, N-dicyclohexylcarbodiimide (DCC) dissolved DMF solution [2] to facilitate the formation of ester bond between MWCNTs, whose surface is modified with carboxyl and hydroxyl groups. And the above treatment was carried out at 333 K for 16 hours under nitrogen atmosphere. As a result, the mechanical strength of the MWCNT films was reinforced. In this presentation, we will discuss the results of Vickers hardness and tensile test. [1] S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis, and R. C. Haddon, *Acc.Chem.Res.*, **35**, 1105, 2002. [2] M. Sano, A. Kamino, J. Okamura, and S. Shinkai, *Science*, **293**, 1299, 2001.

Ra22.47/Rb22.47

The Effect of Electric Field on the Morphology of Poly(styrene-b-ferrocenyldimethylsilane) Langmuir-Blodgett Films. Arielle Jolan Galambos[1], Benjamin Eghbali[3], G. Julius Vancso[4], Jonathan Sokolov[2] and Miriam Rafailovich[2]; [1]Wellesley College, Stony Brook, New York; [2]Mat. Sci. Eng., Stony Brook University, Stony Brook, New York; [3]DRS High School, Cedarhurst, New York; [4]Faculty of Chemical Engineering, University of Twente, A E Enschede, Netherlands.

Poly(styrene-b-ferrocenyldimethylsilane) (PS-b-PFS, NPS:NPFS= 54:52) and Poly(styrene-b-2-vinylpyridine) (PS-P2VP, NPS/NP2VP= 1k/1k) block copolymer mixtures have previously been shown to produce a high degree of order.[1] Here we explored mixtures of PS-b-PFS with either Polystyrene-polymethylmethacralate (PS(100)-PMMA(165)) copolymer or homopolymers of PS (N=10000) or PMMA(Mw=120K). Solutions of different ratios of the PS-b-PFS co-polymer with the other components were spread at the air/water interface, lifted onto hydrophilic Si wafers and imaged with a DI-3000 Scanning probe microscope in the contact mode. Different morphologies were shown to result as a function of the film composition. Electrodes were placed normal to the air/water interface and electric fields up to 175V/cm were applied during the spreading. Polarization of the micelles was observed which resulted in fusing of the patterns and production of a mesh-like structure at higher fields. The results were interpreted in terms of the relative magnitude of the dielectric constant of the respective polymers. Supported by the NSF-MRSEC Program [1] Young-Soo Seo, et. al., Nano-Wire and Mesh Conformations of Diblock Copolymer Blends at the Air/Water Interface, Nano Letters, 4 (3) 483-486 (2004).

Ra22.48/Rb22.48

Synthesis of a Novel Nanocomposite Material: Covalent Linking of Carbon Nanotube and Polylactide. Donghui Zhang[1,2], Madhuvanthi A. Kandadai[2] and Seamus Curran[2]; [1]Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico; [2]Physics Department, New Mexico State University, Las Cruces, New Mexico.

Carbon nanotubes (CNT) have exhibited many unique physical properties. Notably, it has unusually high tensile strength and modest to high conductivity. So CNT can be used as filler for strengthening polymer materials as well as enhancing conductivity. However, to maximize effects of CNT filler and enhance overall performance of a CNT / polymer composite, a good interfacial interaction is normally required. This can be achieved through covalent linking of CNT with polymer matrix. Poly(L-lactide) (PLLA) is a biodegradable polyester derived from ring-opening polymerization of L-lactide or condensation of L-lactic acid. It has been traditionally used as biomedical implant material due to its high production cost until very recently. Cargill Inc. developed a procedure for manufacturing poly(L-lactide) in large scale using corn or sugar beet as raw materials. For the first time, poly(L-lactide) production became competitive with conventional petroleum-based plastics in term of price and overall performance and is considered as the new generation of green thermoplastic. Despite of its high tensile modulus and tensile strength, it is inherently brittle. Different approaches can be taken to improve polymer toughness, addition of filler being one of the common tactics. In this regard, we describe the preparation of covalently linked CNT and polylactide nanocomposite through ring-opening polymerization of lactide directly off the pre-modified CNT surface. The nanomposites are characterized by NMR, Raman and fluorescence spectroscopy as well as SEM and AFM. The conductivity of the nanocomposite as well as its mechanical properties will also be discussed.

Ra22.49/Rb22.49

Transition metal nanoparticles spontaneously aligned on chemically tuned single walled carbon nanotubes with conjugated molecules. Yoonmi Lee and Hee Cheul Choi; Chemistry, Pohang University of Science and Technology, Pohang, South Korea.

Recent observation of spontaneous reduction of noble metal ions on the sidewalls of single-walled carbon nanotubes (SWNTs) has opened a window to understand fundamental knowledge about surface chemical properties of SWNTs as well as to apply for innovative hybrid systems such as hybrid junction nanoelectronics and metal-nanotube composites. The spontaneous formation of novel metal nanoparticles on SWNT is guided by thermodynamically favorable electron transfer from SWNTs to noble metal ions. In the case of transition metal ions, however, this would not occur because of the unfavorable energy relation between SWNTs and the standard reduction potentials of transition metal ions. In order to overcome this issue, we have introduced a smart anchoring molecule, 2,2′:6′,2″-terpyridine (Terpy) to interact with both SWNTs and transition metal ions, resulting in the spontaneous nucleation of transition nanoparticles on the sidewalls of SWNTs. Terpy has been non-covalently functionalized on SWNTs grown by chemical vapor deposition (CVD) method, and their successful functionalization has been characterized by UV-visible spectroscopy. Transition metal nanoparticles such as Ru, Cu, Zn and Sn are formed spontaneously on Terpy-SWNTs at room temperature in aqueous solution and are confirmed by Atomic Force Microscopy (AFM). Spontaneous electron transfer phenomena occurring after Terpy functionalization and Ru nanoparticle formation are clearly observed by measuring conductance changes and threshold voltage shifts using SWNT field effect transistor (FET) devices. X-ray photoelectron spectroscopy (XPS) also has confirmed the electron transfer during the reaction processes by observing Ru species having lower oxidation states.

Ra22.50/Rb22.50

Novel Tree-shaped Macromolecular Amphiphiles: Self-assembly and Applications. Lu Tian and Paula T. Hammond; Department of Chemical Engineering, Massachusetts Institute of

Technology, Cambridge, Massachusetts.

In this work, we report a novel amphiphilic biocompatible linear-dendritic block copolymer rationally designed to serve as a "tree-shaped" self-assembly building block for advanced biomedical applications. Consisting of poly (ω-n-dodecyl-L-glutamate) as a hydrophobic comb-like linear block and polyester dendron modified with poly (ethylene glycol) (PEG) as a hydrophilic dendritic block, these macromolecular amphiphiles incorporate the advantages of properties of traditional spherical dendrimers and diblock copolymers. Utilizing the principles of amphiphilic block copolymer self-assembly, micellar systems containing hydrophilic dendritic exteriors and hydrophobic comb-like linear chain interiors are created, resulting in colloidal nanoparticles with outstanding stability and the unique exterior multivalent functionality of a dendrimer. These polymeric micelles are being studied for hydrophobic drug delivery and stabilization of gold nanoparticles in aqueous solution. Multi-angle dynamic light scattering, UV-Vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) were performed to characterize these micellar aggregations. In addition, some interesting self-assembly behaviors of these macromolecular amphiphiles at high concentrations will be presented.

Ra22.51/Rb22.51

Organic-Inorganic Hybrid Nanocomposites Prepared by the Incorporation of Silicon Oxide into Polymers. Il-Jin Kim, O-Sung Kwon, Jae-Bum Park and Ho Joo; Research Institute of Chemical & Electronic Materials, Samsung-Cheil Industries Inc., Uiwang, Gyeonggi, South Korea.

Organic-inorganic nanocomposites have been attracting much attention due to their potential applications, such as colloidal stabilizers, electro-optical devices, and nanocomposite materials. Recently, we have developed a new class of organic-inorganic hybrid nanocomposites incorporating spherical silica nanoparticles (10~20nm diameter) into acrylonitrile-butadiene-styrene copolymers (ABS) using a strong acid-base interaction between hydroxyl groups of silica surfaces and cyano-groups of ABS. Encapsulation of ABS particles with silica nanoparticles was taking place in situ during ABS coagulation process, resulting in the formation of colloidal nanocomposites with a core-shell morphology. Interestingly, the resulting nanocomposites with 1.0~1.8 wt.% silica nanoparticles exhibit the improvement of impact strength by 30~45%, without sacrifice of elastic modulus, hardness, and tensile strength. The interfacial interaction between the silica and the ABS phases plays a major role in controlling the microstructures and the properties of the composite materials. The morphology and properties of nanocomposites were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), differential scanning calorimet (DSC), tensile tests, impact strength tests, and thermogravimetry. TEM studies showed good dispersion of silica nanoparticles regardless of particle size and SEM analysis revealed that silica nanoparticles resided both in the SAN matrix and on the surface of g-ABS domain of the polymer.

Ra22.52/Rb22.52

Low Temperature Synthesis of FePt Nanoparticles by using Polyol Process. Daisuke Kodama, Yoshinori Sato, Kozo Shinoda, Balachandran Jeyadevan and Kazuyuki Tohji; Graduate School of Environmental Studies, Tohoku University, Sendai, Japan.

Structural phase transition in Fe-Pt system from a disordered fcc to ordered fct results in a strong increase in magnetic hardness of the alloy, which make them suitable for magnetic applications. However, the transition temperature (T_t) is high to be used in any industrial applications. The phase transition being a thermally activated process and the transition mainly proceed by growth of the as-prepared nucleation sites, the T_t depends on experimental conditions. As the solution reactions are often controlled kinetically rather than thermodynamically, leading to the initial trapping and growth of metastable phases, metals and alloy particles with different crystal structures can be synthesized by controlling the reaction kinetics [1-2]. Though the mechanism for the direct formation of fct-FePt nanoparticles are yet to be understood, the authors believe that milder synthesis conditions could promote the formation of the ordered phase. Thus, in this paper, we explored the possibilities of the synthesis of FePt nanoparticles at temperatures less than 400 K. When synthesizing alloy nanoparticles, two types scenarios can be envisaged. In the first case, one type of metal is reduced easily compared to the other and this acts as a catalyst for the reduction of the second type and consequent formation of alloy is realized. This was the case in our previous reports [2]. In the second case, both types metal ions are coreduced to form the alloy. To attempt the synthesis of alloy under the latter case, the synthesis of Fe at low temperature is a prerequisite. We attempted the synthesis of iron by polyol and succeeded in synthesizing Fe nanoparticles by using as the metal precursor in TMEG at temperatures lower than 400 K. Thus, we attempted the synthesis of FePt through coreduction of Fe and Pt. $FeCl_2 \cdot 4H_2O$ was used as the source of Fe. The phases formed during the reaction were a function of platinum salt type, reaction temperature, Fe/Pt ratio, concentration NaOH, and type of polyol. Synthesis of $Fe_{35}Pt_{65}$ was realized when the $FeCl_2 \cdot 4H_2O$ and $H_2PtCl_6 \cdot H_2O$ were reduced in TMEG at 393 K under Fe/Pt and hydroxide/metal ratios were 1 and 20 at 393 K. Along with other results obtained under various experimental parameters listed above, the magnetic properties of FePt synthesized at 393 K will also be reported. [1] O. P. Perales-Perez, et al. RAIM, Editors, D. Bahadur, S. Vitta and O. Prakash, *NarosaPublishingHouse*, p. 9-15, 2004. [2] B. Jeyadevan, et al., *Jpn.J.Appl.Phys.* **42**, L350, 2003.

Ra22.53/Rb22.53

Exploring Applications of Size-, Shape- and Composition-Controllable Nanoparticles in Biology. I-Im Stephanie Lim[1], Lingyan Wang[1], Susannah Gal[2] and Chuan-Jian Zhong[1]; [1]Chemistry, State Univ. of New York at Binghamton, Binghamton, New York; [2]Biological Sciences, State Univ. of New York at Binghamton, Binghamton, New York.

Various nanoparticles have attracted growing interests in chemistry, biology and materials science because of enormous potential applications in chemical/biological sensing, catalysis, drug delivery, and medical imaging. One of the important applications involves the exploration of DNA-anchored nanoparticles assembly. The key to such application requires the ability to control the size, shape and interparticle spatial properties at a nanoscale level. This presentation describes our recent results in constructing size-, shape- and composition-controllable nanoparticles (e.g., Au, Ag, Pt, Alloy, Fe2O3, Fe3O4, etc.) as core-shell nanostructures tagged with bio-affinitive molecules. While many types of DNA-nanoparticle network structures are known to assemble and disassemble via altering temperatures, other physical, chemical and biological stimuli are exploited for manipulating the nanostructures. Various enzymes are used for targeting sequence specific sites, and the reactivities of assembly and disassembly are probed using spectroscopic, TEM, and QCM techniques. Implications of our findings to the potential application of the nanostructures in detecting pathogenic or biohazardous organisms will also be discussed.

Ra22.54/Rb22.54

Assembly of Nanomaterials using Polymers and Biomaterials: Sensing and Electronic Applications. Jaebeom Lee[1], Alexander O. Govorov[2] and Nicholas A. Kotov[1]; [1]Chemical, Material Science and Engineering, and Biomedical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Physics and Astronomy, Ohio University, Athens, Ohio.

This paper presents theoretical and experimental demonstration of the enhanced photoluminescence and its blueshift of CdTe nanoparticles(NP) and nanowires(NW) that are polymerically and biologically conjugated with different sizes of metallic nanoparticles such as Au and Ag in aqueous state. This results from the exciton-plasmon resonance interaction collectively like surface enhanced Raman scattering(SERS) effects. With this superstructure, several applications are addressed such as dynamic nano/microfluidic sensing devices for nanothermometer, energy transfer devices for solar cell, and biological applications.

Ra22.55/Rb22.55

Preparation of large area nanoparticle thin film: Characterization and mechanistic study. Bratindranath Mukherjee, Shwetha A. Shetty and Ravishankar Narayanan; Materials Research Centre, Indian Institute of Science, Bangalore, India.

Nanoparticle thin films have a wide range of applications such as nanoelectronics, magnetic storage devices, SERS substrate fabrication, optical grating and antireflective coating. Present work describes a method to prepare large area nanoparticle thinfilm of the order of few cm2. XRD, VSM, TEM, SEM, AFM, SERS study has been done to characterize the films produced on wide range of conducting as well as nonconducting substrates such as carbon coated copper grid, silicon, m-plane of alumina, glass, NaCl single crystal. Critical experiment has been done to understand the process of deposition of the colloidal nanoparticle thin film and a mechanism has been proposed.

Ra22.56/Rb22.56

Confinement of conducting polymer in the nanospace of mesoporous silica and organosilica. Hiroshi Itahara, Shinji Inagaki and Ryoji Asahi; TOYOTA Central R&D Laboratories. Inc., Aichi, Japan.

Conducting polymers with unidirectionally aligned polymer chain, such as polymers confined in one-dimensional channels of mesoporous materials, are expected to lead the novel applications for electroconductive and optoelectronic devices. Although many approaches have been proposed for the confinement of polymers into the pores of mesoporous materials, only insufficient amount of polymers was confined to realize the above applications. In order to increase the amount of confined polymers, we investigated the adsorption behavior of the poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylen vinylene] (MEH-PPV) to various mesoporous materials, such as mesoporous silica (FSM-16) and mesoporous organosilica, both of which were organically surface modified. The surface of the pores was modified with various terminal organic groups (e.g., SH, SO3H and C6H5) through grafting the organosilane coupling agents. Adsorption of MHE-PPV was conducted by immersing the mesoporous silica to a chlorobenzene solution of MHE-PPV. The mesoporous silica absorbed MHE-PPV was characterized by XRD, N2 adsorption and TG-DTA measurements. It was found that the grafted organic groups significantly influence the adsorption amount of MHE-PPV. We also examined optical property of the confined MHE-PPV by using UV-vis spectroscopy. The optical absorption edge of confined MHE-PPV was clearly blue-shifted when compared to that of a free MHE-PPV. On the other hand, the grafted organic groups showed small influence on the optical absorption edge of the confined MHE-PPV.

SESSION Ra23: Nano/Molecular Electronics
Chair: Massimiliano Cavallini
Friday Morning, December 2, 2005
Room 207 (Hynes)

8:30 AM Ra23.1
Fabrication and Electrical Characterization of Nanoscale Crossed-Wire Molecular Junctions. Heayoung Yoon, Lintao Cai, Marco Cabassi and Theresa S. Mayer; Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Considerable attention has been devoted to developing molecular-scale devices that function as nonlinear circuit elements and nanowires that interconnect these circuit elements. In this talk, we will discuss the fabrication and characterization of a new nanoscale crossed-wire molecular junction device structure comprised of lithographically-defined bottom metal contacts and self-assembled metal nanowire top contacts. This structure serves as an excellent testbed for studying the electrical properties of nanoscale molecular junctions because the flexibility of the fabrication process permits rapid integration of junctions with different molecules and metal contacts. The integrity of the integration process was validated by isolating individual crossed-wire molecular junctions and connecting them to large-area metal probe pads for electrical characterization. Temperature dependent current-voltage (I-V(T)) characteristics and inelastic electron tunneling (IET) spectra were collected on a series of junctions containing alkanethiol self assembled monolayers (SAMs) of Decane (C10), Dodecane(C12), Tetradecane (C14), Hexadecane (C16), and Octadecane (C18). In these junctions, the bottom contact was formed by self assembling the alkanethiol molecules directly onto the thermally evaporated Au wires, while the top contact was formed by physically contacting the SAM with a single Au nanowire of diameter less than 200 nm. All of the alkanethiol junctions exhibited temperature independent I-V properties (10 - 300 K), which confirms that the dominant transport mechanism is coherent tunneling. The junction conductance increased with decreasing alkane chain length giving rise to a bias-independent decay coefficient of $\beta \sim 1$. This is in agreement with previously published data collected using other molecular junction testbeds including conducting probe atomic force microscopy, which has a similar configuration of top and bottom contacts. IET spectra exhibited peaks that are consistent with the vibrational modes expected for these alkanethiol junctions. Additional data that investigates the properties of junctions formed using dithiolated alkane molecules as well as conjugated molecules such as oligo(phenylene-ethynylene) will also be presented.

8:45 AM Ra23.2
Combining self-assembly with new lithographic methods for the fabrication of reliable nanometer-scale device structures. Charan Srinivasan[1], Mary Elizabeth Anderson[2], Mark W. Horn[1] and Paul S. Weiss[2]; [1]Chemistry and Physics, Pennsylvania State University, State College, Pennsylvania; [2]Engineering Science and Mechanics, Pennsylvania State University, State College, Pennsylvania.

We create metal electrode structures with precise proximal placement in the 10-40 nm regime by combining the superior qualities of traditional top-down and bottom-up lithography. Selective self-assembly of ωmercaptoalkanoic acids on patterned gold structures is utilized to grow films of metal-organic coordinated multilayers, whose thickness is controlled with nanometer scale resolution tailored by the number of molecular layers and their lengths. These films are employed as lift-off resists to create tailored gaps between lithographically patterned metal electrodes.$^{1-3}$ The evaluation of our process has included a variety of electrode dimensions and tailored nanogaps resulting in an initial yield of ~90% (for electrode lengths less than or equal to 5 μm). ^{4} To improve the electrical fidelity of our device structures, a new negative-tone lithographic process, which is more compatible with self-assembly techniques, has been developed. Electrode dimensions have been scaled down to the sub-100 nm regime using e-beam lithography. Methods are also underway to diversify the materials compatible with our technique and to tailor the heights of initial and secondary structures to be identical. We will report on the improved electrical fidelity of electrodes fabricated using these new processes. The optimization of lithographic processes compatible with self-assembly has opened a novel avenue to create nanoscale architectures for reliable device fabrication. We continue to push this technology toward mainstream industrial manufacturing and these techniques will be discussed. 1 A. Hatzor and P.S. Weiss, Science 291, 1019 (2001). 2 M. E. Anderson et. al., Journal of Vacuum Science and Technology B 20, 2739 (2002). 3 M. E. Anderson et. al., Journal of Vacuum Science and Technology B 21, 3116 (2003). 4 M. E. Anderson et. al., MicroElectronic Engineering, 78-79, 248 (2005)

9:00 AM Ra23.3
Electrical Measurements of Parallel, Linear Arrays of 1.5 nm Au-Nanoparticles Assembled on SiO$_2$ Using DNA Scaffold Directed Assembly. Gregory J. Kearns and James E. Hutchison; Chemistry, University of Oregon, Eugene, Oregon.

Nanoparticles are of great interest as components in new materials and devices due to their size dependent optical and electronic properties. Two significant challenges in developing nanoparticle-based devices are assembling nanoparticles in a useful way and bridging nanoscale assemblies to microscale electronics. We have developed methods to form arrays of 1.5 nm particles that can be easily integrated with the microscale in order to exploit the properties of the nanoscale components while allowing access to the devices through microscale contacts. Metal nanoparticles with core diameters of less than 2 nm exhibit Coulomb blockade at room temperature, which can be exploited to develop new electronic devices such as single electron transistors (SET). These devices offer several advantages over semiconductor-based transistors–(i) they are 1-2 orders of magnitude smaller than current state-of-the-art transistors, (ii) SETs are not hindered by electron tunneling that can lead to device heating and/or failure in semiconductor based transistors, and (iii) it is possible to use a greener, bottom-up assembly approach to develop complex structures. We have developed a convenient synthetic route to monodisperse 1.5 nm gold nanoparticles that can be functionalized with a wide range of ligand shells. Using these particles, we have shown that, in solution, nanoparticles can be organized into linear arrays using electrostatic interactions between the negatively charged backbone of DNA and the positively charged ligand shell of functionalized nanoparticles. These interactions result in extended linear chains of close-packed nanoparticles. Close-packing of the nanoparticles on the DNA scaffold allows precise control over interparticle spacing by the appropriate choice of ligand shell. In order to make useful devices of these arrays, we have been working to align DNA on surfaces prior to coating with nanoparticles in order to obtain parallel, linear arrays of nanoparticles. Using specially fabricated TEM grids composed of a silicon grid with thermally grown, electron transparent SiO$_2$ windows, we have shown that we can make long-range (tens of microns) parallel arrays of nanoparticles on thermal SiO$_2$ in a three step assembly process involving (i) silanization of the SiO$_2$ surface, which promotes molecular combing of DNA and limits nonspecific adsorption of positively charged nanoparticles, (ii) molecular combing of DNA on the silanized surface, and (iii) nanoparticle assembly on the linear arrays of DNA. TEM analysis of these arrays shows that the arrays are parallel over the entire substrate and that high purity nanoparticles maintain their core size and spacing as determined by the thickness of the ligand shell. With these arrays we are able to develop electronic test structures for measuring Coulomb blockade at room temperature. This is the first step toward developing arrays of single electron transistors that operate at room temperature.

9:15 AM Ra23.4
Exciton Energy Transfer in Supramolecular Systems of Semiconductor Nanoparticles and Free-Base Porphyrins. Thomas Blaudeck[1], Edvard Zenkevich[3], Alexander Shulga[3], Frank Cichos[1] and Christian von Borczyskowski[2]; [1]Photonics and Optical Materials, TU Chemnitz, Chemnitz, Germany; [2]Optical Spectroscopy and Molecular Physics, TU Chemnitz, Chemnitz, Germany; [3]Institute of Molecular and Atomic Physics, Belorussian Academy of Sciences, Minsk, Belarus.

One of the core challenges of modern technology is the merging of its oppositional approaches towards the nanometer scale. Whereas the top-down approaches driven mainly by the physical engineering are facing their limits, bottom-up techniques emerging from chemistry are seen as an intriguing subject in both material and fundamental science. Within the latter, molecular electronics is a field of growing interest, with distinct applications in mind characterized by custom-tailored properties and a low-cost fabrication. Referring to the bottom-up concept, our scientific interest is laid on the elementary interaction processes between inorganic and organic entities in nanoassemblies. During the past decade, we have developed concepts on self-assembly of porphyrin arrays that are tunable with respect to their chemical and optical properties [1]. Recently, we could prove the self-assembly of pyridyl-substituted porphyrin on semiconductor nanoparticles (NPs) [2]. Due to their atomic-like electron structure and tunable emission properties the latter are important building blocks in nanoelectronics. In this presentation, we report on an efficient exciton energy transfer process directed from the NP to the porphyrin molecules in the assemblies. We present data from both steady-state spectroscopy and time-resolved photoluminescence dispersed in toluene. The various experimental approaches are discussed with respect to the transfer efficiency. We elucidate the roles of complexation and ensemble heterogeneity of the NPs and how these influence the photophysical properties, i. e. fluorescence quantum yield and decay rates. The results are extended by estimations on the general validity of the approach in assemblies designed from NPs and other molecules, with the latter either suitable for array formation such as perylenbisimide dyes or known in biophysical applications such as surfactants with thiol and amino end-groups. References 1 E. Zenkevich, C. von Borczyskowski: ″Multiporphyrin Self-Assembled Arrays in Solutions and Films: Thermodynamics, Spectroscopy, and Photochemistry″, in S. K. Tripathy, J. Kumar, H. Nalwa (Eds.): ″Handbook of Polyelectrolytes and Their Applications″, Vol. 2, Chapter 11, Stephenson Ranch: Am. Scientific Publishers (2002). 2 E. Zenkevich, F. Cichos, A. Shulga, E. Petrov, T. Blaudeck, and C. von Borczyskowski: ″Nanoassemblies Designed from Semiconductor Quantum Dots and Molecular Arrays″, J. Phys. Chem. B 109, 8679 (2005).

9:30 AM Ra23.5

Manipulating the Electronic Properties of Artificial Atom Solids Based on Ligand Stabilized Metal Nanocrystals.
Gareth Redmond, Nanotechnology Group, Tyndall National Institute, Cork, Cork, Ireland.

Metal nanocrystals can behave as artificial atoms due to their diameter-dependent single electron charging energies. Organically passivated nanocrystals with narrow size distributions can self-assemble into ordered arrays, offering the possibility of artificial atom solids with unique collective electronic properties, derived from both the size-dependent electronic properties of the individual nanocrystal cores and the inter-nanocrystal electronic coupling mechanisms. The electronic properties of artificial atom solids based on arrays of metal nanocrystals depend on of the relative magnitudes of the classical electrostatic array charging energy, the inter-site quantum mechanical exchange energy, and the site energy dispersion, which arises from the non-zero size and geometric disorder in nanocrystal arrays. Control of these energy terms is a prerequisite for manipulating the properties of artificial atom solids. We present our progress on probing the electronic properties of artificial atom solids via variable temperature charge transport measurements on arrays of ligand stabilized CoPt3 metal nanocrystals self-assembled between lateral contact electrodes, together with development of combined synthesis and processing routes to manipulate these properties. The electronic properties of these arrays, measured following mild thermal annealing, are found to be characteristic of weakly-coupled artificial atom solids. In fact, we show that control of the array charging energy can be achieved by varying the nanocrystal core diameter under conditions of controlled inter-nanocrystal separation. Also, mild thermal annealing is used to tune the electronic properties of nanocrystal arrays progressively from insulating through to metallic regimes. This behavior is shown to be consistent with a Mott-Hubbard model for artificial atom solids. Finally, we demonstrate a new route for growth of 1D nanocrystal structures based on the use of an external magnetic field to direct the destabilization and anisotropic aggregation of CoPt3 nanocrystal dispersions. The wires comprise disordered assemblies of discrete nanocrystals, separated from each other by protective organic ligand shells. Magnetic fields can also be employed for directed assembly of the wires across electrodes. Electrical data indicates that the activated charge transport properties of the wires are determined by the nanocrystal charging energy, governed by the size and capacitance of the individual nanocrystals. Together, these results highlight just some of the possibilities for development of hybrid top-down and bottom-up assembly methodologies for fabrication of future nanoelectronic devices.

9:45 AM Ra23.6

Low-Temperature Synthesis and Thermoelectric Properties of Molecularly Capped Bismuth Telluride Nanoparticles from Microemulsions. Arup Purkayastha, [1]Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]Department of Mechanical Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We report a new room temperature synthesis method to create bismuth-telluride nanoparticles from microemulsions. By virtue of the unique thermoelectric properties of bismuth telluride, this material has been exploited for cooling and power generation applications[1]. Nanostructuring allows possibilities for further dramatic improvements in thermoelectric efficiency due to phonon and electron confinement effects[2]. Previous works have reported the synthesis of bismuth telluride nanoparticles by co-precipitation[3] solvothermal synthesis[4] or using microemulsions. The microemulsion method is very promising in terms of producing very small nanoparticles with control over size and size distribution. In our synthesis, hydrazine monohydrate was added to the microemulsion formed from an aqueous solution of bismuth and tellurium salts, thioglycolic acid, isooctane, and an ionic surfactant AOT at room temperature. Upon nanoparticle formation, the surfactant was removed by washing and centrifuging repeatedly with toluene to get the final black solid. The bismuth telluride nanoparticles are found in the regime of 1-5 nm. The particle size and shape (spherical to rod shaped) could be controlled by tailoring the water to surfactant ratio.Thermoelectric transport measurements in bismuth telluride nanoparticles films and pressed nanoparticle bulk pellets will be reported. References: 1. Goldsmid, H. J.; Douglas, R. W. Br. J. Appl. Phys. 1954, 5, 458 2. Chen, G.; Dresselhaus, M. S.; Dresselhauss, G.; Fleurial, J. P.; and Caillat, T.; International Materials Reviews, (2003), 48, 45. 3. Ritter, J. J. Inorg. Chem. 1994, 33, 6419 4. Deng, Y.; Zhou, X-S.; Wei, G-D.; Liu, J.; Nan, C-W.; Zhao, S-J. J. Phys. Chem. Solids 2002, 63, 2119

SESSION Rb23: Nanoparticles III
Chair: Joydeep Dutta
Friday Morning, December 2, 2005
Room 208 (Hynes)

8:30 AM *Rb23.1

1-D Assemblies of Gold Nanoparticles with Tunable Interparticle Distances. Muriel K. Corbierre[1,2], Jean Beerens[2], Jacques Beauvais[2] and Bruce R. Lennox[1]; [1]Chemistry, McGill University, Montreal, Quebec, Canada; [2]Electrical and Computer Engineering, Sherbrooke University, Sherbrooke, Quebec, Canada.

We report the preparation and controlled assembly of gold nanoparticles in 1-dimension. Ours is a straightforward approach, where an electron beam is used to write patterns from thin films of gold(I) compounds on various substrates. The negative patterns are then developed in suitable organic solvents, leaving on the substrate only the e-beam-exposed parts. After development, lines of organogold compound with linewidths as small as 15 nm are obtained. Subsequent pyrolysis of the organogold compound removes the organic material from the patterns and leads to the growth of small gold nanoparticles (diameters of 2 to 20 nm depending on the conditions, verified by TEM and SEM). Lines of single particles (1-D arrays) are obtained (Figure 1). Variations in the e-beam exposure conditions allow us to precisely tailor the interparticle distances within the 1-D lines, while variations in the initial organogold film thickness or organogold compound nature allow for controlling the gold nanoparticle diameters. By varying the electron beam dose, we are also able to control nanoparticle densities in 2-D arrays. This method is extremely versatile and can be used to prepare 1-D and 2-D assemblies with desired shapes on large scales and on a wide variety of surfaces.

9:00 AM Rb23.2

Self-Assembly of Polymer-Tethered Nanorods.
Mark A. Horsch[1], Zhenli Zhang[1] and Sharon C. Glotzer[1,2]; [1]Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Nanoparticles functionalized by polymer tethers constitute a class of shape amphiphiles that share important attributes with block copolymers, surfactants and liquid crystals[1]. Through these attributes, the tethers may be used to assemble nanoparticles into useful and unusual structures. Here we present new results of molecular simulations that predict the phases formed by the self-assembly of rod-like particles functionalized by a polymer tether. For end-tethered rods[2], we predict that microphase separation of the immiscible tethers and rods coupled with the liquid crystal ordering of the rods induces the formation of a smectic C phase, a tetragonally perforated lamellar phase and a honeycomb phase; the latter two have been observed experimentally for rod-coil block copolymers but have not been predicted previously via theory or simulation. We also predict a new phase - a racemic mixture of hexagonally-ordered chiral cylinders that self-assemble from these achiral building blocks. We compare the assemblies formed from end-tethered nanorods with those formed from side-tethered nanorods, and present new results that show how the tethered building block topology affects their local and mesoscopic packing. In particular, we predict several new phases for side-tethered nanorods that have no analog in typical block copolymer, surfactant or liquid crystal systems and which have potential use as functional nanoscale materials. [1] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, Nano Letters, 3, 1341 (2003). [2] M.A. Horsch, Z.L. Zhang and S.C. Glotzer, Physical Review Letters, in press.

9:15 AM Rb23.3
Kinetics of Place-Exchange Reactions of Alkyl Thiols on Gold NPs. Adil Kassam, Glen Bremner and R. Bruce Lennox; Chemistry, McGill, Montreal, Quebec, Canada.

After the initial report of a relatively facile method to synthesize gold nanoparticles(Au-NPs) by Brust et al.[1], the research into these systems has exploded. In order for these Au-NPs to be used in biological and materials applications, their surface ligand composition must be known and readily manipulated. The place-exchange reaction of the surface-bound thiol is one reaction that enables the functionalization of particles for these applications.[2] By developing a methodology to study place exchange reactions of alkyl thiols of different chain length using gas chromatography, we have been able to study the entire course of the place exchange reaction with great accuracy and precision. The kinetics of the place exchange reactions have been fitted via diffusion controlled Langmuir kinetics. In addition, the observed reactions proceed to a thermodynamic equilibrium governed by the ratio of the incoming thiol concentration to the amount of thiol on the starting Au-NPs. These results should enable researchers in the field to be able to make Au-NPs with known composition. Other aspects of the reaction including temperature and chain length dependence of the reaction will be discussed. (1) Brust et al. J. Chem. Soc Chem. Commun.1994 801-802. (2) Hostetler, M., Templeton, A., Murray, R.W.. Langmuir 1999, 15, 3782-3789

9:30 AM Rb23.4
Size-Controlled Monodisperse Gold Nanoparticles as Building Blocks for Thin Film Assembly. Mark J. Schadt, Hyein Koh, William Cheung, Mathew M. Maye, Kaylie Young and Chuan-Jian Zhong; Chemistry, State University of New York at Binghamton, Binghamton, New York.

The ability to control the size and monodispersity of metal nanoparticle building blocks for use in sensing materials is a challenge of increasing interest. While previous work has shown the viability of obtaining select particle sizes by manipulating the feed ratios of metal precursors, very little work has focused on the controlled modification of core size and shape using pre-synthesized nanoparticles. The main obstacle precluding this work has been an incomplete understanding of the synthetic parameters affecting the particle growth environment. Here we describe an improved isothermal and isotemporal synthetic route for the controlled evolution of core size and shape from pre-fabricated nanoparticles. This improved synthesis eliminates many subjective processing variables, and has allowed us to obtain monolayer protected gold nanoparticles reproducibly with monodisperse core diameters between 3 and 10 nm. These nanoparticles have then been used as size-selectable building blocks for the construction of thin film assemblies in our nanoparticle sensor-array devices, and have allowed us to further investigate and refine sensor-array performance.

9:45 AM Rb23.5
Self Assembly and Nano-Ordering of Zirconia during Sol-Gel Synthesis. Gerald Spijksma[1,2], Margareta Sundberg[3], Henny J. M. Bouwmeester[1], Vadim G. Kessler[2] and Dave H. A. Blank[1]; [1]Inorganic material science, University of Twente, Enschede, Netherlands; [2]Department of Chemistry, SLU, Uppsala, Sweden; [3]Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, Stockholm, Sweden.

Zirconia is an important material widely used in ceramics, gas sensors, catalysts and opto-electrics. In the recent years the general focus of materials research has been on the preparation of nano-structured thin films, powders and nano-tubes. With the trend of further of miniaturization there has been an increasing interest in zirconia. This high-k material is an attractive candidate for very large scale integrated circuits and as gate dielectric in metal oxide-semiconductors (MOS) devices. The latter application requires low dimension ordered materials, e.g., wires or rods. The latter can either be produced through preparation of metal wires with subsequent oxidation or via sol-gel process where a template is filled with the desired oxide, which is then crystallized upon heating. This last method has allowed the preparation of wires with a diameter around 80 nm. Further scaling down in dimension is restricted by the required template. Here we report the direct formation of highly ordered zirconia central cores during sol preparation from highly anisotropic molecular precursor. The obtained material contained wire shaped material with a length up to ~400 nm and a diameter of ~8 nm, the latter dimension is an order of magnitude smaller than the state of the art zirconia nanowires. The self assembly mechanism presented in this work opened the door to formation of wires and other nano-scale ordered materials. Besides the formation of nano-rods we will show the preparation and characterization of hollow spheres with a diameter around 250 nm and a shell thickness of 5 nm. The formation mechanism of these type structures allows in-situ encapsulation of medicine what makes this method an attractive new tool for drug delivery applications.

SESSION Ra24: Nanostructured Oxides
Chair: Lionel Vayssieres
Friday Morning, December 2, 2005
Room 207 (Hynes)

10:30 AM *Ra24.1
Metal-Semiconductor Core-Shell Nanodiskettes and Nanotubes. Puxian Gao, Zhong Lin Wang, Changshi Lao and Yong Ding; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Zinc oxide is an important functional material with semiconductivity, piezoelectricity and pyroelectricity [1]. To design and rationally control the synthesis of functional nanostructures with different morphological configurations are the cornerstone for further ultilizing the nanoscale building blocks for multifunctional nanodevice systems. As the partner of ZnO, metal Zn also has the hexagonal structure. Together with a low melting point of Zn and the high melting point of ZnO, this has given us a great advantage for designing and fabricating various metal-semiconductor core-shell nanostructures [2-4]. An important fact is that ZnO tends to grow epitaxially on the surface of Zn via an oxidation process, forming Zn-ZnO metal-semiconductor core-shell structures [2, 3]. In this work, by using a solid-vapor synthesis approach and taking the advantage of selective oxidation on the surfaces of the as-formed Zn nanostructures, we present the synthesis, structure and growth process of Zn-ZnO core-shell nanostructures, from single crystal nanodisks, polycrystalline nanodisks, mesoporous nanodisks to a variety of ZnO nanotubes. The results suggest that, by controlling the kinetics in the Zn and ZnO system, the lower energy facets, and the oxidation rates of different surfaces, we have controlled fabricated Zn-ZnO core-shell single-crystal-, polycrystalline- and mesoporous-nanodiskettes, as well as a variety of nanotubes of ZnO. The oxidation of the Zn nano-object leads to the formation of Zn-ZnO core-shell nanodiskettes. A lower temperature oxidation results in formation of single-crystal-like Zn-ZnO core-shell structure, while higher oxidation temperature leads to the formation of textured and even polycrystalline nanostructures. A re-sublimation process of Zn in the core leaves a ZnO shell structure. This study offers a detailed description about the kinetics controlling procedures, the nanostructures received, their morphological and crystal structures and their formation mechanisms. The newly synthesized nanostructures made of textured and aligned nanocrystallites of ZnO could be the fundamental building blocks for fabricating piezoelectric resonator and sensors. 1) "Semiconducting and piezoelectric oxide nanostructures induced by polar surfaces", Z.L. Wang, X.Y. Kong, Y. Ding, P.X Gao, W.L. Hughes, R.S. Yang, and Y. Zhang, Adv. Funct. Mater. 14 (2004), 944. 2) "Mesoporous polyhedral cages and shells formed by textured self-assembly of ZnO nanocrystals ", P. X. Gao and Z. L. Wang, J. Am. Chem. Soc., 125 (2003) 11299-11305. 3) "Metal-semiconductor Zn-ZnO core-shell nanobelts and nanotubes", X. Y. Kong, Y. Ding and Z. L. Wang, J. Phys. Chem. B 108 (2004), 570-574. 4) "Interface and defect structures of Zn-ZnO core-shell hetero-nanobelts", Y. Ding, X. Y. Kong and Z. L. Wang, J. Appl. Phys. 2004, 95, 306. 5) Research sponsored by NASA, NSF and DARPA. 6) Details can be found at: www.nanoscience.gatech.edu/zlwang *email: zhong.wang@mse.gatech.edu

11:00 AM Ra24.2
Photochemical Metal Organic Deposition of Patterned Nanostructured Oxide Films. Xin Zhang and Ross H. Hill; Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada.

Photochemical metal organic deposition is a method for depositing patterned metal or metal oxide layers that has potential for making microelectronics, optical devices and sensors. This photoresist-free patterning method, operating under ambient conditions, uses photosensitive metal complexes as precursors to deposit patterned layers on substrates. In this paper, recent advances in the deposition of patterned nanostructured metal oxide films by photochemical metal organic deposition will be presented. Different strategies are used to control the nanostructure within the films. The first strategy is to choose metal complexes where the decomposition rate of the two metal complexes can be individually controlled. For example, by allowing decomposition of one metal complex to proceed in the absence of radiation, nanostructuring of the material occurs when the resulted metal oxide and the second metal complex tend to form separate phases. Then the second metal complex is photochemically decomposed, resulting in the formation of the nanostructured material. The photochemical step provides the opportunity for lithography. This will be demonstrated by preparing nanostructured tantalum-manganese oxide films from tantalum (V) tetraethoxide acetylacetonate and manganese (II) 2-ethylhexanoate. In this case, decomposition of the tantalum complex is induced by hydrolysis during a ripening period. The formation of a nanostructured tantalum-manganese oxide film is completed by photochemical decomposition of the manganese complex. By changing the precursor composition or altering the ripening time, tantalum-manganese oxide films with different refractive indices were obtained. Patterned nanostructured tantalum-manganese oxide films with a feature size smaller than 1 micron were obtained by photolithography. A second strategy involves using two photosensitive metal complexes that form nano-sized immiscible phases in the precursor films to result in regions of one metal complex separated from the other metal complex. These precursor films can be photochemically converted to form nanostructured metal oxides. This will be illustrated by the lithographic deposition of nanostructured zirconium-yttrium oxide films from zirconium (IV) 2-ethylhexanoate and yttrium nitrate.

11:15 AM Ra24.3

Self-Assembled Complex Oxide Nanostructures using 3-D Heteroepitaxy. Haimei Zheng, F. Zavaliche, L. W. Martin, L. Mohaddes-Ardabili, Q. Zhan, S. P. Crane and R. Ramesh; Physics and Materials Science and Engineering, University of California, Berkeley, Berkeley, California.

We report on the unique growth of the BiFeO3-CoFe2O4 nanostructures by self-assembly during a pulsed laser deposition process. In a few nanometer thick film, CoFe2O4 forms nanodots embedded in a BiFeO3 matrix on a single crystal SrTiO3 substrate. The size, shape and distribution of the CoFe2O4 nanodots are strongly dependent on the growth temperature, growth rate, substrate and film thickness. The magnetic behaviors of the BiFeO3-CoFe2O4 nanostructures studied using magnetic force microscopy and VSM are also reported. This project is funded by an ONR MURI program under contract No. E-21-6RU-G4. The authors acknowledge the support of the staff and facilities at the National Center for Electron Microscopy in Lawrence Berkeley Laboratories.

11:30 AM Ra24.4

Pulsed Laser Deposition of Cluster-assembled Thin Films with Controlled Nanostructure. Andrea Li Bassi, Carlo Spartaco Casari, Fabio Di Fonzo, Alessandro Bailini, Paolo Maria Ossi, Valeria Russo, Andrea Baserga, Diego Cattaneo and Carlo Enrico Bottani; Nuclear Engineering, NEMAS (Center for NanoEngineered MAterials and Surfaces) - INFM - Politecnico di Milano, Milano, Italy.

Amorphous or nanocrystalline metal and metal oxide thin films synthesized by assembling nanosized building units present interesting and unusual chemical and physical properties, associated to a high specific surface. These systems are appealing for different functional applications, especially in the fields of sensing and catalysis (e.g. thin films of transition or noble metals, and their corresponding oxides). At the same time clusters with selected size and structure supported on crystal surfaces are interesting both for nanocatalysis applications and for fundamental research. By means of nanosecond pulsed laser deposition (PLD) in a background atmosphere (either inert or reactive) we can induce cluster aggregation in the ablation plume and control the deposition kinetic energy of the clusters. These phenomena strongly depend on the plume expansion dynamics and their influence on the properties of the deposited films has been investigated as a function of the background gas mass and pressure, of the substrate-to-target distance, and of the laser energy density. The control of these parameters permits to vary the surface morphology of the deposited films, ranging from a compact structure with a very smooth surface, to a film with a controlled roughness at the nanoscale, to an open, low density meso- and nanostructure characterized by a high fraction of voids and by a large specific area. Thin films of WO_3, TiO_2, Pd/PdO, and Ag were deposited in order to test their catalytic or gas sensing activity and characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) and Raman spectroscopy. Post-deposition annealing permits to control the crystallinity (and sometimes the crystal phase) of the films, which in the case of WO_3 and TiO_2 is found to depend on the original nanostructure, while a different degree of oxidation can be induced by controlling the amount of oxygen in the deposition chamber. In-situ scanning tunneling microscopy (STM) was employed to study the first stages of growth of W and WO_3 films on different substrates (e.g. Si, HOPG), and to characterize the size distribution of the clusters in the ablation plume. This opens the possibility to tailor the material properties through the control of the building nano-units.

11:45 AM Ra24.5

Ordered and Parallel Packed Niobium Oxide Nano-Tubes Fabricated using Atomic Layer Deposition in Anodic Alumina Templates. Marten Rooth, Anders Johansson, Mats Boman and Anders Harsta; Dep. of Materials Chemistry, Uppsala University, Uppsala, Sweden.

Amorphous niobium oxide (Nb2O5) nano-tubes were fabricated using atomic layer deposition in a template. The nanoporous templates were in-house fabricated anodic alumina membranes having an inter-pore distance of about 100 nm and a pores length of 2 μm. The pores were parallel and well ordered in a hexagonal pattern. Atomic layer deposition was performed using gas pulses from niobium iodide and oxygen with purging pulses of argon in between. By employing long gas pulse lengths (30 s) it was possible to get homogeneous Nb2O5 films conformally covering the pore-walls of the alumina template. The outer diameter of the nano-tubes was tailored between 30 and 70 nm by using alumina templates with different pore sizes. The wall thickness, and hence the inner diameter of the tubes, could be controlled between a few Angstroms to several nanometers by variation of the number of deposition cycles. By using template membranes with pores not opened in the bottom, nanotubes with one side closed (as a test tube) could be fabricated. Free-standing, and still parallel, nanotubes could be obtained by selectively etching away the alumina template using phosphoric acid (5 wt-%). From the above mentioned procedure it was possible to fabricate unsurpassed parallel niobium oxide nano-tubes of equal length and equal wall-thickness ordered in a perfect hexagonal pattern. The samples were analysed using X-ray diffraction, high resolution scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy.

SESSION Rb24: Carbon Nanotubes IV
Chair: Zhong Liu
Friday Morning, December 2, 2005
Room 208 (Hynes)

10:30 AM *Rb24.1

Carbon nanotubes and nanostructures grown at below 400C. Guan Yow Chen, Patrick C. H. Poa, Simon J. Henley, Vlad Stolojan and S. R. P. Silva; Nano-Electronic Centre, Advanced Technology Institute, University of Surrey, Guildford, Surrey, United Kingdom.

In this paper, we report clear evidence for the growth of carbon nanotubes and nanostructures at low substrate temperatures, using direct-current plasma-enhanced chemical vapour deposition. The catalyst particles are mounted on a titanium layer which acts as a thermal barrier, and allows for a larger temperature gradient between the Ni catalyst surface and the substrate. A simple thermodynamic simulation shows that the amount by which the substrate temperature can be lowered is determined by the thickness of the titanium layer. This facilitates the growth of nanotubes, as opposed to nanofibres with herring-bone or amorphous structures. The growth properties are discussed as a function of the bias voltage and hydrocarbon concentration. The heating during growth provided solely by the plasma is below 400C and is dependent on the process conditions and the dimensions of the electrodes. These conditions need to be taken into account when comparing processes across different growth methods and instruments. The novel approach based on the use of using a thermal barriers ensures the synthesis of carbon nanotubes at room temperature substrate conditions, which can be attained with a suitable cooling scheme.

11:00 AM *Rb24.2

Fabrication of Carbon Nanotube Devices with Known Chirality. Xue Ming Henry Huang[1], Robert Caldwell[2], Mingyuan Huang[1], Matthew Sfeir[3], Feng Wang[4], Limin Huang[2], Stephen O'Brien[2], Tony Heinz[4], Louis Brus[3] and James Hone[1]; [1]Department of Mechanical Engineering, Nanoscale Science and Engineering Center, Columbia University, New York, New York; [2]Department of Applied Physics, Nanoscale Science and Engineering Center, Columbia University, New York, New York; [3]Department of Chemistry, Nanoscale Science and Engineering Center, Columbia University, New York, New York; [4]Department of Physics, Nanoscale Science and Engineering Center, Columbia University, New York, New York.

Carbon nanotubes hold great promise for a number of applications due to their outstanding electrical, thermal, and mechanical properties. However, nanomanufacturing issues constitute a major area of challenge for successful implementation of nanotubes. In particular, because subtle changes in physical structure (chirality) can cause the electronic structure to vary from metallic to semiconducting, the goal of fully controlled nanotube device fabrication has proven elusive. Using a mechanical transfer technique in parallel with efforts to combine optical scattering and structural characterization, we have achieved the goal of placing 'the nanotube we want, where we want it.' Long nanotubes are grown by CVD across a slit etched through a Si wafer, and then examined by optical spectroscopy techniques, in particular Rayleigh scattering. Rayleigh scattering can readily distinguish different nanotube species, and by combining this technique with structural characterization by electron diffraction, we are able to map each spectrum to a unique (n,m) structure. After structural characterization, a chosen nanotube can be transferred to a substrate in the desired location, and devices fabricated using standard e-beam lithography techniques.

11:30 AM Rb24.3

Carbon Nanotube Growth by CH_4 Plasma-Enhanced Chemical Vapor Deposition and Estimation of Carbon Amount.

Yoshiyuki Suda[1], Atsushi Okita[1], Akinori Oda[2], Junji Nakamura[3], Atsushi Ozeki[1], Hirotake Sugawara[1] and Yosuke Sakai[1]; [1]Graduate School of Information Science and Technology, Hokkaido University, Sapporo, Japan; [2]Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Japan; [3]Graduate School of Pure and Applied Sciences, Tsukuba University, Tsukuba, Japan.

Carbon nanotubes (CNTs) are attracting great interest in their excellent physical and electronic properties for LSI. Plasma-enhanced chemical vapor deposition (PECVD) is an advantageous technique because this can yield CNTs by low temperature operation, which is essential for its application. However, it is still unclear how plasmas contribute to the CNT growth [1,2]. We investigate the effect of plasmas by experiment and plasma simulation for understanding of the CNT growth [3]. We performed a CNT growth experiment by CH_4 rf PECVD at pressures 1-10 Torr. We used three-layered catalyst film ($Al_2O_3/Fe/Al_2O_3$, 3 nm/3 nm/3 nm) for catalyst on SiO_2/Si substrate. The CNTs length, diameter, and number density were characterized by scanning electron microscopy. We investigated the contributions of radicals and ions to CNT by one-dimensional fluid modeling. This model assumed the sticking probability of radicals on substrate: CH, 0.025; CH_2, 0.025; CH_3, 0.01; C_2H_5, 0.01; H, 0.01, respectively [4]. The effect of CH_4 plasma on the CNT growth is discussed from the viewpoint of estimation of carbon amount. As the experimental results, the CNTs at 1 Torr continued to grow up to 60 min, while their height leveled off by 20 min at 4 Torr. CNTs hardly grew at 10 Torr and amorphous carbon was deposited instead. Simulation result shows that carbon was supplied to the substrate via the flux of radicals and ions such as CH_3, C_2H_5, and $C_2H_5^+$. We estimated the number of C atoms per unit substrate area and compared it to the number of C atoms in the grown CNTs. The deposited carbon amount from the experimental result is less than the carbon supply estimated from the simulation results. This would be related to the loss by the production of amorphous carbon and its coverage on the catalyst particles. [1] L. Delzeit, et al., J. Appl. Phys. 91, 6027 (2002) [2] M. Meyyappan, et al., Plasma Sources Sci. Technol. 12, 205 (2003) [3] A. Okita, et al., submitted [4] I. B. Denysenko, et al., J. Appl. Phys. 95, 2713 (2004)

11:45 AM Rb24.4

Strain-induced quantum interference effects on the resonant Raman cross section of carbon nanotubes.

Antonio Gomes Souza[1], N. Kobayashi[2], Jie Jiang[2], Alexander Gruneis[2], Riichiro Saito[2], Setephen Cronin[3], Josue Mendes[1], Georgii G. Samsonidze[5], Gene Dresselhaus[4] and Mildred S. Dresselhaus[4,5]; [1]Fisica, Universidade Federal do Ceara, Fortaleza, Ceara, Brazil; [2]Physics, Tohoku University, Young-In, South Korea; [3]Physics, Harvard, Cambridge, Massachusetts; [4]Physics, MIT, Cambridge, Massachusetts; [5]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts.

In this paper we report the effects of strain on the electronic properties of single wall carbon nanotubes and its consequence on the resonant Raman cross section. A quantum interference effect has been predicted for the radial breathing mode spectra for metallic tubes. For metallic tubes, the lower and upper components of E_{ii} resulting from the trigonal warping effect are affected differently and for low chiral angle they cross for some strain value. Near (at) the crossing point, the resonant Raman spectra profile exhibits a maximum (minimum) value due to a quantum interference in the Raman cross section. This Raman cross section interference effect was observed in Raman experiments carried out on isolated SWNTs. The Raman experiment performed on an isolated strained metallic SWNT supports our modelling predictions.