SYMPOSIUM Q

"Smart" Surfaces and Interfaces

March 29 - 30, 2005

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* Invited paper

SESSION Q1: Macromolecules, Brushes, and Soft Matter

Chair: Russell Composto
Tuesday Morning, March 29, 2005
Room 3000 (Moscone West)

8:00 AM *Q1.1

Responsive Polymer Brushes Through Main Chain Self-Assembly. Stephen L. Craig, Chemistry, Duke University, Durham, North Carolina.

Polymer brushes on surfaces modulate an array of properties such as colloidal stabilization and ordering, adhesion, wettability, and friction. Of particular current interest are polymer brush layers whose structure and concomitant materials properties change in response to external stimuli. Linear polymers that are defined by reversible interactions along their main chains potentially combine the conventional polymeric physics that are central to brush properties with ease of fabrication and new forms of chemical responsiveness through the defining, reversible interaction, particularly in soft, wet environments. Using both synthetic and bioconjugate systems, we have investigated the dynamic and mechanical properties of self-assembled polymer brushes. Surface properties are found to be extremely sensitive to the molecular details of the system, providing a mechanism for rational control of responsive brush properties.

8:30 AM Q1.2

Charged Polymer Brushes: Really Soft Matter? Tamer Farhan, Omar Azzaroni and Wilhelm T. S. Huck; Department of Chemistry, University of Cambridge, Cambridge, United Kingdom.

The behaviour of polymers adsorbed or anchored to surfaces has been the subject of many studies ranging from fundamental to applied aspects. In particular, polyelectrolyte brushes (surface-confined polyelectrolytes) have recently attracted a great deal of attention because of their tendency to collapse or expand depending on solvent conditions. These properties could be exploited in the development of "smart" surfaces and nanoactuators. It would allow the incorporation of moving parts in devices that consist of organic or "soft" material. One key feature related to the nanoscale properties of these charged systems that has been scarcely explored concerns the stiffness of polymer brushes in different environments. In this work we will show our recent results on the mechanical behaviour of polymer brushes in different solvents and electrolytes based on tapping-mode atomic force microscopy (TM-AFM) studies under liquids. TM-AFM studies of PMETAC brushes in water (a good solvent) show that these charged polymer brushes in an extended conformation can be easily deformed or indented by the AFM tip. Specifically, AFM analysis of 4x2 μm patterned PMETAC brushes under water are shown to have $\sim$ 45 nm high features at an amplitude setpoint of 8.5 V. However, at a higher load (i.e. an amplitude setpoint of 5 V) measurements give rise to decreased feature heights of $\sim$ 12 nm. In addition, similar stiff behaviour is observed when the same experiments are performed on the polymer brushes in a collapsed conformation, using methanol/water as the liquid environment. Conversely, this "soft" behaviour is dramatically different in presence of electrolytes. Our initial studies in electrolyte solutions at different concentrations show that these brushes become so rigid that they cannot be at all indented or deformed by the AFM tip, even at high loads, unlike that in pure water or methanol/water.

8:45 AM Q1.3

Fluorine End-capped Polyethylene Glycol Materials as Water/Oil Fluid Responsive Surfaces. Jeffrey Youngblood and John Howarter; School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Due to the need for permi-selective and chemo-selective membranes, stimuli-responsive materials are of great interest. Within this context we investigate brushes of polyethylene glycol (PEG) with perflourinated end-caps to create stimuli-responsive surfaces selective to polar and non-polar liquid environments. Optimization of the surface modification was done by varying size of constituent chain segments, grafting mechanism and reaction time. Results were characterized by water and hexadecane dynamic contact angle and X-ray photoelectron spectroscopy. Contact angle on optimized surfaces showed PEG-like response in aqueous environment, while exposure to hexadecane results in a high energy surface similar to a fluorinated surface. Constituent chain length affected the surface behavior, with variations in perfluoro-chain length having greater effect. There was no apparent hysteresis in the responsiveness due to switching environments with an immediate response relative to measurement time. Results were applied to create cross-linked materials containing these fluorinated PEGs for stimuli-responsive coatings.

9:00 AM Q1.4

Self-Recognising Fluid Monolayers of DNA-Based Surfactants: Properties and Applications. Vesselin N. Paunov, Chun Xu, Pietro Taylor and Paul D. I. Fletcher; Department of Chemistry, University of Hull, Hull, North Humberside, United Kingdom.

We have designed novel DNA-surfactants prepared by covalent attachment of a hydrophobic anchoring group to the (3'- or 5'-) end of short DNA oligonucleotides. This anchoring group turns these DNA-strands into amphiphilic molecules. Such DNA-surfactants can adsorb at air-water and oil-water surfaces which orients them with respect to the liquid surface and can promote programmable interaction based on Watson-Crick pairing. We show that these materials are surface-active at various fluid surfaces, including air-water and oil-water interfaces, as well as lipid bilayers. We demonstrate that once adsorbed the DNA-surfactants used remain on the liquid surface upon hybridisation with a complementary DNA chain. Complementary DNA-surfactants are used to functionalise fluid surfaces and to program the interactions between them based on Watson-Crick pairing. By selecting the appropriate DNA base sequences the interaction between the fluid surfaces functionalised with DNA-surfactants can be programmed with the level of specificity as the enzyme-substrate interaction. We studied the adsorption of DNA surfactants at the oil-water interface by Drop Shape Analysis and demonstrated that the interfacial tension isotherm at the oil-water interface depends strongly on the number of bases as well as the base sequence in the DNA surfactant. DNA hybridization at the oil/water interface was studied by measuring the interfacial tension of DNA surfactant during temperature jump across the melting point of complementary DNA-surfactants. Complementary sequences and non complementary sequence of DNA surfactant show clear difference during the temperature jump process. We also found that DNA surfactants can be immobilised on hydrophobic solid surfaces by hydrophobic interactions which allowed us to design a novel method for fabrication of DNA arrays based on microcontact printing of aqueous 'inks' containing DNA surfactants on solid substrates. Novel type of aqueous inks based on DNA-functionalised small liposomes for micropatterning of solid surfaces with DNA by a microcontact printing technique has been used. We illustrate the capabilities of this technique by specific deposition of complementary DNA-functionalised liposomes onto DNA-micropatterned solid surfaces. Special attention is paid to the wetting properties of the ink with respect to the stamp and the solid substrates. The method allows for efficient attachment of DNA strands to solid surfaces and hybridisation with complementary fluorescently-tagged oligonucleotides. This new technology could be utilised for rapid preparation of DNA-assays and genetic biochips.

9:15 AM Q1.5

Selective, Controllable, and Reversible Aggregation of Polystyrene Latex Microspheres via DNA Hybridization. Phillip Henry Rogers[1], Peter V. Schwartz[1], Carl Bauer[1], Daniel Hansen[1], Stephen Vanderet[1], Antoine Calvez[1], Jackson Crews[1], Alistair Wood[1], James K. O. Lau[2], Brad Roberts[2], Eric Michel[3] and David Pine[3]; [1]Physics, California Polytechnic State Univ., San Luis Obispo, San Luis Obispo, California; [2]Materials Engineering, California Polytechnic State Univ., San Luis Obispo, San Luis Obispo, California; [3]Materials and Chemical Engineering, Univ. of California Santa Barbara, Santa Barbara, California.

The directed three dimensional self-assembly of microstructures and nanostructures through the selective hybridization of DNA is the focus of great interest toward the fabrication of new materials. Single stranded DNA is covalently attached to polystyrene latex microspheres. Single stranded DNA can function as a smart Velcro® by only bonding to another strand of DNA that has a complementary sequence. The attachment of the DNA increases the charge stabilization of the microspheres and allows controllable aggregation of microspheres by hybridization of complementary DNA sequences. In a mixture of microspheres covered with different sequences of DNA, microspheres with complementary DNA form aggregates, while microspheres with non-complementary sequences remain suspended. The process is reversible by heating, with a characteristic "aggregate dissociation temperature" that is dependent on salt concentration, and the evolution of aggregate dissociation with temperature is observed with optical microscopy.

10:00 AM *Q1.6

New Monolayers: Molecular Recognition, Catalysis, and Electronics. Colin Nuckolls, [1]Chemistry, Columbia University, New York, New York; [2]Nanoscience Center, Columbia University, New York, New York.

This presentation will explore several new classes of molecules, their assembly on metals and metal oxides, and their properties in nanoscale test structures. The goal is to develop a fundamental understanding of how a particular molecular substructure encodes assembly and how in turn the superstructure influences properties at short length scales. One strategy that is explored here is the use of hydrogen bonding and pi stacking to work synergistically. There are three significant findings from studies on these systems. First, the dipole moments of the subunits provide a stack that has a macroscopic dipole moment. Second, because the association in the stacking direction is stronger than in typical pi stacks, it is possible to create isolated strands of molecules that can be visualized with scanning probe microscopy. Third, it is possible to create the shortest of pi stacks, dimers, on metallic surfaces that are held together through noncovalent forces. Another area of exploration is in developing molecular semiconductors that can assemble on the surface of high k dielectrics. We have found new chemistry to afford linear acenes that have their short ends functionalized with endgroups that react with surface oxides. Incorporating this assembly motif into electronic devices allows field effect transistors to be constructed that are one molecule high with approximately a 100 molecules separating the source and drain electrodes.

10:30 AM *Q1.7

Modifying Interfacial Interactions. Thomas P. Russell[1], Duyeol Ryu[1], Eric Drockenmuller[2] and Craig J. Hawker[3]; [1]Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; [2]IBM Almaden Research Center, San Jose, California; [3]Materials Research Laboratory, University of California, Santa Barbara, California.

The chemical dissimilarity of the constituent blocks in a copolymer will, in general, lead to the preferential segregation of one of the blocks to an interface. Since the blocks of the copolymer are covalently linked, the microphase separated morphology will orient parallel to the interface. In thin films, this produces an orientation of the microdomain morphology parallel to the films surface. While external fields can be used to overcome these interactions, manipulation of the interfacial interactions can be use to the same end. While for any surface, specific chemistries can be developed to alter the chemical nature of a surface, designing a generalized approach has been a major impediment. Here, using a crosslinked thin film of a random copolymer where the chemical composition of the copolymer can be varied, an approach has been developed where interfacial interactions can be controlled on virtually any surface. Using this approach surfaces of many materials, including passivated silicon, silicon oxide, aluminum, gold and an aromatic polyimide, have been controlled. Asymmetric diblock copolymers of polystyrene and polymethylmethacrylate having a cylindrical microdomain morphology are used to demonstrate the effectiveness of this approach.

11:00 AM Q1.8

Towards Tunable Interaction between Conjugated Molecules and Metal Surfaces in Self-Assembled-Monolayers: A Theoretical View. Georg Heimel[1], Egbert Zojer[1,2] and Jean-Luc Bredas[1]; [1]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; [2]Institute of Solid State Physics, Graz University of Technology, Graz, Austria.

Highly ordered self-assembled monolayers (SAMs) of molecules on (noble) metal surfaces are currently the focus of intense, multidisciplinary research. Potential applications of such SAMs include molecular electronics, chemical sensors, the tuning of macroscopic surface properties like wetting or corrosion stability, the improvement of electrode interfaces in organic light-emitting devices and photovoltaics, and many more. In order to endow these self-assembled systems with functionality suitable for use in either macroscopic or nanoscale (opto-)electronic devices, the use of π-conjugated systems has been proposed. The goal of our work is to gain a basic understanding of the interfacial processes occurring in conjugated-SAM/metal systems and how they can subsequently be fine-tuned to work as building blocks in molecular electronics and/or macroscopic organic electronic devices. In our present theoretical study, we focus on a simple model system for a functionalized, π-conjugated molecule self-assembled on a metal substrate: substituted benzene-thiols on Au(111). DFT band structure methods are employed in order to give a full theoretical characterization of the 2D-periodic infinite system, including adsorption energies, geometries, band alignment, charge transfer, interface dipoles, core-level shifts, grazing-incidence infrared absorption spectra, and STM images. Particular emphasis is put onto the effect of donor and acceptor substitutions on the alignment of the frontier molecular orbitals with the Fermi energy of the substrate, the resulting charge transfer, and changes in the metal work function. Furthermore, we investigate the influence of quantum-confinement effects and dimensionality of the metal substrate (represented by gold quantum-wells and gold nano-clusters, respectively) on the degree and nature of electronic coupling between the SAM and the supporting metal substrate.

11:15 AM Q1.9

Phospholipid Morphologies on Photochemically Patterned Silane Monolayers. Micheal C. Howland[1], Annapoorna R. Sapuri-Butti[1], Sanhita S. Dixit[1], Andrew M. Dattelbaum[2], Andrew P. Shreve[2] and Atul N. Parikh[1]; [1]Applied Science, University of California, Davis, Davis, California; [2]Bioscience Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have studied the spreading of phospholipid vesicles on photochemically patterned n-octadecylsiloxane monolayers using epifluorescence and imaging ellipsometry measurements. Self-assembled monolayers of n-octadecylsiloxanes were patterned using short-wavelength ultraviolet radiation and a photomask to produce periodic arrays of patterned hydrophilic domains separated from hydrophobic surroundings. Exposing these patterned surfaces to a solution of small unilamellar vesicles of phospholipids and their mixtures resulted in a complex lipid layer morphology epitaxially reflecting the underlying pattern of hydrophilicity. The hydrophilic square regions of the photopatterned OTS monolayer reflected lipid bilayer formation and the hydrophobic OTS residues supported lipid monolayers. We further observed the existence of a boundary region composed of a non-fluid lipid phase and a lipid-free moat at the interface between the lipid monolayer and bilayer morphologies spontaneously coralling the fluid bilayers. The outer-edge of the boundary region was found accessible for subsequent adsorption by proteins (e.g., streptavidin and BSA), but the inner edge closer to the bilayer remained resistant to adsorption by protein or vesicles. Mechanistic implications of our results in terms of the effects of substrate topochemical character are discussed. Furthermore, our results provide a basis for the construction of complex biomembrane models, which exhibit fluidity barriers and differentiate membrane properties based on correspondence between lipid leaflets. We also envisage the use of this construct where two-dimensionally fluid, low-defect lipid layers serve as sacrificial resists for the deposition of protein and other material patterns.

11:30 AM Q1.10

Structural and Mechanical Properties of Dendrimer-mediated Thin Films. Fengting Xu and John A. Barnard; Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Dendrimers are three-dimensional, globular, highly-branched macromolecules made up of a central core surrounded by repetitive units all enclosed by a terminal group shell. They can be synthesized with highly controllable sizes (they are monodisperse) determined by the core type, extent of branching, and nature of the end groups, in the range from a few to several tens of nm in diameter. Dendrimers also assemble into monolayers on technologically interesting substrates using simple cleaning, dipping, and rinsing procedures. In this condensed monolayer phase dendrimers can act as surfactants mediating the growth of ultra-flat films, and create novel nanomechanical, adhesive, frictional, and tribological behavior. We have recently reported on the dramatically enhanced quality (superior flatness and adhesion) of metal films deposited on dendrimer monolayers. Different tribological responses are also observed in dendrimer-mediated metal thin films. The physical intermixing between dendrimer and metal was proposed to explain the distinct physical, mechanical, and chemical properties of the resulting dendrimer-based nanocomposites. To better understand substrate/dendrimer monolayer/adlayer interactions, we designed an experiment to better understand the intermixing between metals (in this case Au) and dendrimer monolayers as a function of deposited metal film thicknesses.

SESSION Q2: Tunable and Bio-Active Surfaces and their Applications

Chair: Tom Krupenkin
Tuesday Afternoon, March 29, 2005
Room 3000 (Moscone West)

1:30 PM *Q2.1

Switchable Interfaces for Integrated Bio-Systems. Bruce C. Bunker, Biomolecular Materials and Interfaces, Sandia National Laboratories, Albuquerque, New Mexico.

Integrated microfluidic systems are under development in which functionality is provided by programmable monolayers in channel walls rather than by complex architectures. Research is underway to develop monolayers that undergo reversible conformation changes in response to external stimuli, including heat, light, and electric fields. The primary consequence of switching is to mediate interaction potentials between the surface and solution species ranging from water to ions to proteins. Interactions of interest include hydration forces, electrical double layer forces, and hydrophobic-hydrophilic interactions. Such interactions have been monitored using the interfacial force microscope (IFM), which provides force-distance profiles between functionalized substrates and scanning probe tips. The behavior and applications of three types of films that can be switched in a reversible fashion will be reviewed: 1) poly(n-isopropylacrylamide) monolayers for the adsorption and release of proteins based on tuning of repulsive hydration forces, 2) spiropyran monolayers for the optical switching of electrical double layer forces, and 3) monolayers in which host-guest interactions can be mediated via electrochemistry for the localized capture and release of specific functional groups.

2:00 PM *Q2.2

Super-hydrophobic Surfaces: From Natural to Artificial. Lei Jiang, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

The wettability of solid surfaces is a very important property, and is governed by both the chemical composition and geometrical microstructure of the surface. Currently, super-hydrophobic surfaces with water CA higher than 150° are arousing much interest because they will bring great convenience in daily life as well as in many industrial processes. Various phenomena, such as snow sticking, contamination or oxidation, and current conduction, are expected to be inhibited on such a surface. Conventionally, super-hydrophobic surfaces have been produced mainly in two ways. One is to create a rough structure on a hydrophobic surface, and the other is to modify a rough surface by materials with low surface free energy. While the water CA has commonly been used as a criterion for the evaluation of hydrophobicity of a solid surface, this alone is insufficient to assess the sliding properties of water droplets on the surface. A fully super-hydrophobic surface should exhibit both high CA and low sliding angle. Our recent studies on lotus and rice leaves reveal that a super-hydrophobic surface with both a large CA and small sliding angle needs the cooperation of micro- and nanostructures, and the arrangement of the microstructures on this surface can influence the way a water droplet tends to move. These results from the natural world provide a guide for constructing artificial super-hydrophobic surfaces and designing surfaces with controllable wettability. Accordingly, super-hydrophobic surfaces of aligned carbon nanotube films, aligned polymer nanofibers and differently patterned aligned carbon nanotube films have been fabricated. The large scale fabrications of super-hydrophobic polymer surfaces have been developed by modification of the traditional template method, the adoption of one-step coatings and electrohydrodynamics, respectively. The super-hydrophobic surface is also realized in all pH range, which extends its applications not only to pure water, but to acid and base solution as well. By combining the two factors of super-hydrophobic and super-oleoliphilic, the water-oil separation mesh has been built successfully. Considering the arrangement of the micro- and nanostructures, the surface structures of the water-strider's legs were studied in detail, indicating the relationships between super-hydrophobicity and orientation of the micro- and nano-scale composite structures, which will guide us to fabricate micro-fluid devices artificially in the near future. In further, the cooperation between surface micro- and nanostructures and surface modification of poly (N-isopropylacrylamide) gave reversible switching between superhydrophilicity and superhydrophobicity in a narrow temperature range of about 10°C. The transition can be enhanced by depositing the polymer onto patterned silicon substrates. Additionally, UV light stimulated switcher of superhydrophobic and superhydrophilic transition by aligned ZnO film are successfully obtained.

2:30 PM *Q2.3

Manipulating Liquids using Nanostructured Surfaces. Ashley Taylor, Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

Surfaces with appropriately engineered nano-scale topography provide a powerful mechanism to modify liquid-solid interfacial behavior. A number of basic interface properties such as advancing and receding contact angles, contact line mobility, and viscous drag can be dynamically modified using this approach. This potentially opens new ways of manipulating liquids at both micro and macro scales. This talk will concentrate on the properties of the recently demonstrated electrically tunable nanostructured superhydrophobic surfaces. The dependence of the superhydrophobic - wetting transition on the liquid surface tension, surface coatings, and geometry of the nanostructured layer will be discussed. Possible ways to achieve reversibility of the wetting transition will be addressed. Several emerging applications of these surfaces including microfluidics, chemical microreactors, and skin drag reduction will be discussed as well.

3:00 PM *Q2.4

Dynamically Reconfigurable Surfaces For Microfluidic Applications. Richard B. Fair, ECE, Duke University, Durham, North Carolina.

Microfluidic systems based upon manipulation of discrete microdroplets within open structures are a promising alternative to conventional continuous flow systems. A number of methods for manipulating microdroplets based on direct electrical control of transport surfaces have been proposed, including dielectrophoresis, structured surfaces, and thermocapillary, electrostatic, electrochemical and photochemical effects. Electrowetting is a method of transporting and manipulating microdroplets based upon direct electrical control of surface tension. We have demonstrated high speed transport of picoliter to microliter volumes of droplets across two-dimensional arrays of electrodes buried beneath a hydrophobic insulator. The metal-insulator-solution transport (MIST) device is based on charge-control manipulation at the solution/insulator interface of discrete droplets by applying voltage to a control electrode. The MIST is the MOSFET equivalent for microfluidics, and it has been shown to be a versatile component for dispensing, transport, splitting, merging and mixing of aqueous droplets. We have also shown that it is possible to transport biological liquids by electrowetting, including protein solutions of concentration up to 10mg/ml. A silicone oil transport medium surrounds the droplet and forms an interface between the droplet and the hydrophobic transport surface. We find that the oil interface prevents non-specific protein adsorption on the hydrophobic transport surface. However, as the applied electrowetting voltage is increased, the oil is squeezed out from beneath the droplet. This effect has been verified using dynamic capacitance measurements. As a result, proteins in a droplet solution can be selectively stamped onto a receiving surface. This effect has been demonstrated in an oil-based electrowetting system for stamping proteins on MALDI plates. Besides selective deposition of proteins, we have also shown that it is possible to collect adsorbed inorganic particles from an impacted hydrophobic surface by a scanning droplet method. The sample collection is performed by impacting airborne particles directly onto the surface of the chip. After the collection phase, the surface of the chip is washed with a micro-droplet of solvent that is clad with a thin film of silicone oil. The droplet is digitally directed across the impaction surface in air, dissolving sample constituents. The oil-film cladding is formed by transporting the droplet through an oil/air interface. Because of the very small droplet volume used for extraction of the sample from a wide collection area, the resulting solution is relatively concentrated and the collected analytes can be detected after a very short sampling time (1 min) due to such pre-concentration.

3:30 PM *Q2.5

Strategies for Assembly of Live Cells into Biocomposite Coatings and Membranes. Orlin D. Velev, Shalini Gupta, Lindsey B. Jerrim, Rossitza G. Alargova and Peter K. Kilpatrick; Dept. of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina.

The self-assembly of colloidal micro- and nanoparticles is a powerful tool for making new materials with advanced functionality. We have developed a range of techniques for nanoparticle assembly into materials with well defined 2D and 3D structure. Live cells can be used as "particles" in similar types of assembly, yielding new classes of "smart" biomaterials with potentially rich areas of application. A powerful and versatile method for manipulation and assembly of particles is dielectrophoresis, interactions and mobility in alternating electric fields. We demonstrate how on-chip dielectrophoresis can be used to co-assemble yeast cells and synthetic micro- and nanoparticles. Depending on the frequency of the field and relative polarizability of the cells and particles, one and two dimensional arrays can be obtained. These arrays can be bound into permanent biocomposites by using molecular recognition. Lectin molecules are used to bind selectively to polysaccharides on the yeast cell surfaces to obtain cell-nanoparticle chains and membranes, which can form the basis of sensors, microscopic bioreactors and artificial tissue. We also present the principles for assembling and immobilizing large-scale coatings from yeast cells. The coating method is based on convective assembly and deposition in a moving meniscus to make dense two-dimensional arrays. On the basis of this method, we designed a robust technique for rapid deposition of monolayer cell coatings. The wetting, adhesive and structural properties of these biocomposite coatings will be discussed.

4:00 PM Q2.6

Biological Detection based upon Nanoaggregation. Philip Joseph Costanzo[1], Enzhu Liang[2], Timothy Patten[1] and Rosemary Smith[3]; [1]Chemistry, University of California at Davis, Davis, California; [2]Electrical Engineering, University of California at Davis, Davis, California; [3]Electrical and Computer Engineering, University of Maine, Orono, Maine.

Novel micro- and nano-scale aggregates were prepared from inorganic building blocks using biological crosslinkers. Difunctional, asymmetric poly(ethylene glycol) (PEG) linkers were synthesized and utilized to prepared water-soluble, biologically active nanoparticles. Aqueous dispersions of these particles were prepared and upon addition of the appropriate analyte, aggregation was observed. Aggregation was induced by small molecules, proteins, and antibodies, which demonstrated the versatility of the system. The kinetic growth mechanism for nanoparticle aggregation was characterized by dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Particle functionality and analyte concentration were varied and their effect on the aggregation rate was measured. Different microchannels with various electrode arrays were employed to detect the aggregation process optically by using fluorescent microscopy or electrically by measuring the change in conductivity.

4:15 PM Q2.7

DePEGylative Triggering of DOPE Liposomes with Tunable Acid-Sensitivity. David H. Thompson, Junhwa Shin, Jong-Mok Kim, Jeroen Van den Bossche and Pochi Shum; Department of Chemistry, Purdue University, West Lafayette, Indiana.

More than 90% of new drug leads currently fail due to ADMET problems. Almost half of these failures can be attributed to problems with delivery. Several targeted carrier systems (e.g., liposomes, polymer micelles, erodible polymeric particles, and dendrimers) are under development to address this problem. Nearly all of these targeted carrier systems presently suffer from low drug bioavailability due to inefficient drug release once the carrier has accumulated at the target site. First generation plasmenylcholine [Adv. Drug Del. Rev. 1999 38, 317] and diplasmenylcholine [J. Am. Chem. Soc. 1998 120, 11213; Pharm. Res. 2002 19, 1289] liposome systems that release their contents upon exposure to low pH (less than 6.5) or oxidative environments have been developed in our laboratory to obviate these limitations. We have recently focused on the development of plasma-stable DOPE liposomes, containing low molar percentages of acid- or photooxidatively-labile PEG lipids, as fusogenic vehicles for the cytoplasmic delivery of liposomal contents. These systems utilize 0.5-5 mol% of 1,2-di-O-(1,9-octadienyl)-sn-glyceryl-3-omega-methoxy-poly(ethylene[112]glycol)ate (BVEP) [Biophys. Chem. 2003 104, 361] or 3-beta-cholesteryl-(1-O-butenyl-4-omega-methoxypoly(ethylene[112]glycol)ate (CVEP) to stabilize the lameller phase of DOPE. CTEM and HPLC evidence indicates that cleavage of the vinyl ether linkages of these PEG-lipid derivatives results in bilayer dePEGylation and liposome collapse to a state that is consistent with the HII phase of DOPE. Contents release and lipid mixing assays, however, suggest that the liposome leakage and membrane fusion processes occur on different kinetic timescales. Cell culture experiments indicate that receptor-mediated uptake of folate-targeted DOPE:CVEP liposomes can efficiently deliver water soluble molecules to the cytoplasm of KB cells upon endosomal acidification. Experiments with variable electron-demand vinyl ether PEG lipids show that liposomal contents release rates can be rationally controlled over a range of rates that vary by eleven orders of magnitude. This capability clearly shows that the reactivity of the vinyl ether module can be tuned in accordance with a quantitative structure-property relationship. We are now extending this reactive module to the construction of amphiphilic diblock copolymers and crosslinked hydrogels with variable pH-sensitivity. These results demonstrate that it is possible to molecularly engineer a specific drug delivery rate through appropriate design of the carrier system functionality.

4:30 PM Q2.8

Microfluidic Detection and Analysis by Integration of Evanescent Wave Sensing with Thermocapillary Actuation. Joseph Patrick Valentino[1], Sandra M. Troian[2] and Sigurd Wagner[1]; [1]Electrical Engineering, Princeton University, Princeton, New Jersey; [2]Chemical Engineering, Princeton University, Princeton, New Jersey.

Recent development of various microfluidic devices based on modulation of the liquid surface tension through electric or thermal fields requires the development and integration of innovative methods for in-situ droplet detection and analysis. Given that portability is a major design goal for such devices, the requisite sensors should be directly incorporated into the chip to minimize size requirements without compromising measurement sensitivity. Ideally, the sensing mechanisms should be based on non-intrusive techniques, which don't alter the liquid sample properties. Sensor integration can also provide additional benefits such as reduction in fabrication and packaging costs. We present here an integrated system capable of microfluidic actuation, detection and analysis that combines evanescent wave sensing with thermocapillary manipulation. Liquid droplets transported across the beam path of a planar thin film waveguide cause attenuation of the propagating waveguide modes. In this study, the attenuated signal is used to monitor droplet location, dye concentration in solution and reaction kinetics for enzymatic hydrolysis of the sugar X-galactose (X-gal) by beta-galactosidase (β-gal). The chip is a multi-layer structure composed of microheaters, an insulating layer, a planar optical waveguide and a chemically patterned surface, which laterally confines droplets to prescribed surface pathways. Droplets are transported on the surface of a chip via thermal stress gradients generated by the embedded heater arrays. Helium neon laser light is prism-coupled into and out of the waveguide and its output intensity is recorded by a photodiode. As a liquid sample is moved on the chip's surface over the propagating beam, the light in the waveguide is attenuated, providing a basic indicator of sample presence. The guided wave may also be attenuated by absorption due to analytes in solution. We show that the attenuation signal correlates well with an increase in the concentration of FD&C blue 1 dye in 400 nl aqueous droplets. This same attenuation property is used to measure the rate of an enzyme-catalyzed reaction induced on the chip surface. Two droplets, one phosphate buffer solution containing the enzyme β-gal, and a second dimethylsulfoxide droplet, containing X-gal, were merged by thermocapillary actuation over the optical beam path. The enzyme catalyzed the conversion of X-gal into a blue precipitate leading to signal attenuation from which the reaction rate could be estimated. The microheaters used for droplet transportation can also increase the temperature of spatially confined droplets. The measured increase in the rate of the β-gal/X-gal reaction upon local heating is used to extract information about the thermal dependence of the reaction rate. The integration process described here is expected to work equally well with open format microfluidic devices based on electrowetting on dielectric layers and dielectrophoretic systems.

4:45 PM Q2.9

Abstract Withdrawn

SESSION Q3: Poster Session
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

Q3.1

Physical and Electrical Characteristics of p-GaN after Cl_2/Ar Dry Etching. Hsueh Kuang-Po[1], Huang Shou-Chian[1], Sheu Jinn-Kong[2] and Hsin Yue-Ming[1]; [1]Department of Electrical Engineering, National Central University, Chung-Li, Taiwan; [2]Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan, Taiwan.

Although GaN based devices have been developed comprehensively for wireless and optical communications. GaN based HBTs are still under developing due to the difficulties of obtaining high doping p-GaN base and good base ohmic contacts. The major reason is that the roughness and the contamination resulted from the dry etching process of p-GaN surface will increase Schottky barrier height (SBH) at the metal/semiconductor interface. However, the dry etching process is required for GaN based npn or pnp HBTs, it is the key research to obtain the good ohmic contact on p-GaN after dry etching. This paper presents both the etched surface root mean square (RMS) roughness and the depth display monitor (the Bearing analysis) of the doped p-GaN after Cl_2/Ar reactive ions etching (RIE) as well as the study of Ni(20nm)/Au(20nm) metallization. All GaN materials were grown by MOCVD on sapphire substrates. An undoped GaN layer with thickness of 2 μm was grown first, followed by the growth of 1 μm thick p-GaN doped with Mg. The activation annealing was carried out at 750°C for 20 min in the furnace. Dry etching effect of 500 nm p-GaN using RIE has been investigated by systematically varying RF plasma power and Cl_2/Ar mixture gas composition. There is no significant increase in etching rate by only increasing Cl_2 flow rate while keeping the power and chamber pressure constant. SBH calculations showed that the SBH is 0.47 eV for the Ni/Au contact without dry etching. The SBHs after Cl_2/Ar etching are increased to around 0.6 eV and summarized in Table I. In addition to vary Cl_2/Ar composition, different RF plasma power demonstrated the significant effect on etched p-GaN surface. The observed Bearing ratio of the nanorods on etched surface decreased significantly with decreasing the RF power and reached almost 0% at RIE power of 50 W. As a function of RF power, calculations show that the SBHs are 0.50 eV, 0.52 eV and 0.60 eV for RF power of 50 W, 100 W and 200 W, respectively. From experimental results, the surface roughness RMS is not directly related to the I-V characteristics of Ni/Au contacts, but Bearing ratio is. We concluded the I-V characteristics (and thus Schottky barrier height) is more consisted with the Bearing analysis of existing nanorods than that with surface roughness in the Cl_2/Ar etch.

Q3.2

Versatile Helical Polymer Films: Chiroptical Switching and Memory with Re-Writable (RW) and Write-Once Read-Many-Times (WORM) Modes. Akihiro Ohira[1], Michiya Fujiki[1], Masanobu Naito[1], Kento Okoshi[1], Takahiro Hagihara[1] and Masashi Kunitake[2]; [1]Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara, Japan; [2]Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Kumamoto, Japan.

Solid-state chiroptical switching and memorizing property of molecules would be crucial for molecular based devices such as optical switch and data storage applications. By carefully designing chiral molecules and chiral polymers, several chiroptical switching and memorizing systems have been achieved in solution. Among the polymers, several chromophoric helical polymers exhibit excellen chiroptical amplification and chiroptical inversion due to high cooperativities. However, a more versatile solid film system exhibiting chiroptical inversion "-1 and 1" or on-off "0 and 1" switching and/or chiroptical memories with write-once read-many-times (WORM) and re-writable (RW) modes based on molecular and/or polymeric materials still remains rare. Here we demonstrate an easy, versatile approach for chiroptical inversion switching and chiroptical memory with RW and WORM modes in solid films by using certain polysilanes that can undergo helix-helix transition at -20 degree Celsius in isooctane by controlling both their molecular weight and thermal modulation. In the case of low molecular weight fraction (Mw: 1.3x10$\hat{4}$, Mw/Mn: 1.16), the solid film exhibits the chiroptical inversion switching based on reversible change of circular dichroism (CD) signal in heating and slow-cooling cycle. The transition temperature was 47 degree Celsius estimated from the temperature dependence of Kuhn's dissymmetry ratio (gsolid = DeltaOD/OD). The transition in the solid state was also observed in differential scanning calorimetry (DSC) thermogram. A chiroptical memory state, furthermore, occurred during rapid quenching from above the transition temperature. This memory effect is resettable by heating to above transition temperature. These results reveal that a chiroptical inversion switch and chiroptical memory with RW modes are feasible by controlling the cooling conditions in a solid film and the molecular weight of the polysilane sample. At the middle molecular weight fraction (Mw, 6.9 x 10$\hat{4}$; Mw/Mn: 1.25), another memory state can be achieved by controlling the molecular weight only. In this case, management of cooling conditions is not required. The transition is observed only on heating, and the state above transition temperature remains unchanged during the cooling phase. This irreversible change in the CD signal indicates the non-erasable memory as the WORM mode. Concerning the high molecular weight fraction (Mw: 3.9 x 10$\hat{5}$, Mw/Mn: 3.02), the transition in the CD signal is no longer observed. These different behaviors as to molecular weight might be ascribed to entanglement of polymer chains in the solid films.

Q3.3

Nucleation of Pd Nanoparticles on a Smart Molecular Surface of Fibrous Hydrogen-Bonded Molecular Assemblages.

Daisuke Ishii[1], Masaru Nakagawa[1], Tomokazu Iyoda[1], Taichi Nagashima[2], Shinichi Kawasaki[2] and Mitsuaki Yamada[2]; [1]Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [2]Osaka Gas Co., Ltd., Osaka, Japan.

Pyridinecarboxylic acids bearing both hydrogen acceptor and donor groups form fibrous molecular assemblages having a submicron diameter in aqueous solutions.[1] We have recently reported that the fibrous molecular assemblages are available for a template-directed synthesis of hollow nickel-phosphorus (Ni-P) microfibers through electroless plating.[2−3] The hollow Ni-P microfibers could be obtained by immersing the template fibers in an acidic aqueous solution containing palladium chloride ($PdCl_2$) as a catalyst precursor and in a Ni-P electroless plating bath containing phosphinate ions as a reductant, followed by removal of the organic template with an aqueous alkaline solution. The hollow microfibers were composed of amorphous Ni-P nanoparticles having a diameter of about 30 nm, which formed a uniform 50 nm Ni-P layer without deposition defect. In general, Ni-P electroless deposition on organic substrate surfaces involves a surface-etching process using a strong acid before the $PdCl_2$ treatment. The fibrous molecular assemblages required no etching process to form the Ni-P layer on the surfaces. We wondered why the defect-free electroless deposition proceeded on the organic molecular surface of the fibrous template. In this report, we describe the nucleation of Pd nanoparticles as plating catalysts on the organic molecular surface of the template fiber. The Pd nucleation and the subsequent formation of Ni-P particles were studied by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The amphoteric compound of 6-(2-propyl-4-(4-pyridylazo)phenoxy)hexanoic acid was used as a pyridinecarboxylic acid. To comprehend the formation mechanisms of Pd and Ni-P nanoparticles in the electroless plating, we prepared four kinds of fibrous molecular assemblages in respective steps after template formation, $PdCl_2$-treatment, reductant-treatment and plating-treatment. It was revealed that $PdCl_4{}^{2-}$ species in the $PdCl_2$ solution was adsorbed as $PdCl_x$ through coordination bonds with the pyridyl groups. The reductant phosphinate ions included in the plating bath reduced the surface-adsorbed $PdCl_x$ species to Pd nanoparticles having a diameter of about 5 nm. The defect-free Ni-P deposition was due to dense adsorption of the $PdCl_x$ species on the surface pyridyl groups existing periodically at a molecular level. [1] Aoki, K.; Nakagawa, M.; Ichimura, K. *J.Am.Chem.Soc.* **2000**, 122, 10997. [2] Ishii, D.; Aoki, K.; Nakagawa, M.; Seki, T. *Trans.Mater.Res.Soc.Jpn.* **2002**, 27, 517. [3] Nakagawa, M.; Ishii, D.; Aoki, K.; Seki, T.; Iyoda, T. *Adv.Mater.* in press.

Q3.4

Hydrophilic Effect of Indium Tin Oxide (ITO) and Leadframe by Atmospheric Pressure RF Glow Discharge Plasma.

Won-Youl Choi[1], Jung-Hee Cho[2], Bang-Kwon Kang[2] and Sae-Hoon Kim[1]; [1]Kangnung National University, Kangnung, South Korea; [2]Changjo Engineering Co., Ltd., Hwaseong, South Korea.

We report on a novel method for the surface modification of indium tin oxide (ITO) in LCD glass and metal leadframe (alloy 42) by direct exposure to a dielectric barrier discharge (DBD) at atmospheric pressure and room temperature. To make the oxide and metal surfaces hydrophilic, the atmospheric pressure RF glow discharge plasma was used. Argon (Ar) and oxygen (O_2) were used as the ignition gas and cleaning gas, respectively. The addition of O_2 gas to Ar decreased the contact angle of water and increased the surface cleaning rate due to the increase of oxygen radicals in the plasma. The ITO contact angle of 64° before the plasma treatment was decreased to 7° in the processing condition with oxygen flow rate of 50 sccm, treatment speed of 100 mm/sec, and input power of 300 W. And the leadframe contact angle of 82° before the plasma treatment was decreased to 5° by the same process. The morphologies of the ITO and leadframe surfaces were analyzed with atomic force microscope (AFM). The chemical characteristics of the surfaces after the plama treatment were investigated using X-ray photoelectron spectroscopy (XPS), and new carboxyl group bond at binding energy E_b=288.5 eV was produced. The carboxyl group bonds (O-C=O) offered a better wettability and adhesion. These hydrophilic effects will be very useful in the manufacturing process of LCD glass and electroplating process.

Q3.5

Stable Charge Storage in Granular Thin Films.

Fengting Xu[1], Sean M. Thaler[1], Alejandro Butera[2], James L. Weston[3] and John A. Barnard[1]; [1]Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]Centro Atomico Bariloche, Rio Negro, Argentina; [3]Center for Materials for Information Technology (MINT), The University of Alabama, Tuscaloosa, Alabama.

Unique opportunities exist for utilizing thin film electrets (dielectrics which exhibit quasi-permanent charge or alignment of dipoles) and nanoscale charge patterning for electrostatically directed assembly of complex functional nanostructures from discrete charged/polarized nanoparticles and macromolecules. Realization of such nanostructures depends on developing a thorough understanding of the basic mechanisms and dynamics of charge storage and dissipation combined with high resolution quantitative characterization of electrostatic interactions in these systems. Highly stable local charge storage by SPM methods has been observed for the first time in Fe-SiO2 (and Co-SiO2) granular thin films (5 nm metal granules embedded in SiO2) with decay times as much as two orders of magnitude longer than previously reported for heterogeneous films. Charge dissipation is well described as occurring in two regimes, a comparatively fast regime at short times (decay times of thousands of seconds) and a much slower regime at longer times (decay times of tens of thousands of seconds). Negative charging occurs more readily in these systems but positive charges are significantly more stable. Granular thin films thus appear to have great potential as a new class of stable, tunable electrets suitable for charge patterning and electrostatically directed assembly of nanostructures.

Q3.6

Wettability Changes Depending on Wavelengths of UV-Light in an Organosilane Monolayer Bearing a 4-(2-Naphthylmethylsulfonyl)phenyl Moiety.

Motohiro Tagaya, Masaru Nakagawa and Tomokazu Iyoda; Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

It is essential in surface science to comprehend interfacial phenomena such as wettability, adhesion, friction and so forth at a molecular level. From this viewpoint, photoreactive self-assembled monolayers and adsorbed monolayers are interesting materials. We and our coworkers have demonstrated that the photoreactive monolayers are applicable to liquid crystal photoalignment,[1] light-driven liquid motion,[2] mesoporous silica alignment,[3] particle assembly[4] and selective metallization.[5] To achieve photoselective polymer grafting, we previously synthesized a new type of UV-sensitive silane coupling reagent of 2-(4-(benzylsulfonyl)phenyl) ethyl-1-chloro-1,1-dimethylsilane (BPSS).[6] By exposure to 254-nm UV-light, the BPSS monolayer was transformed to a monolayer having chemically active benzenesulfinic acid due to photoremoval of the benzyl group. However, the BPSS monolayer had a problem that the photogenerated sulfinic acid groups were decomposed by a subsequent photochemical reaction. To avoid the subsequent reaction, we designed a UV-sensitive silane coupling reagent of 2-(4-(2-naphthylmethylsulfonyl)phenyl)-ethyl-1-chloro-1,1-dimethylsilane (NPSS) responding to a UV-light wavelength more than 280 nm. In this report, we describe the synthesis of NPSS and the characterization of a NPSS monolayer. Photoinduced wettability changes of the NPSS monolayer were investigated using three kinds of UV-light wavelengths at 172 nm, 254 nm and 280 nm. Contact angle and UV weak absorption spectral measurements indicated that only benzenesulfinic acid moieties were formed without subsequent photoreaction in the case of 280 nm light. The hydrophobic outermost surface of naphthylmethysulfonyl groups was transformed to a hydrophilic sulfinic acid surface and further to a hydrophobic phenyl surface in the case of 254 nm light. A bare silica substrate surface was formed by exposure to 172 nm light. It was found in the NPSS monolayer that photogenerated surfaces depended on irradiation wavelengths of UV-light. [1] Ichimura, K. Chem. Rev. 2000, 100, 1847. [2] Ichimura, K. et al. Science 2000, 288, 1624. [3] Kawashima, Y. et al. Chem. Mater. 2002, 14, 2842. [4] Nakagawa, M. et al. Langmuir, 2003, 19, 8769. [5] Nakagawa, M. et al. Langmuir, 2004, 20, 9844. [6] Nakagawa, M. et al. JP2003-301059(A2).

Q3.7

Interface Engineering for Improved Growth and Microstructural Control of Dense/Porous Multilayer Devices.

Aram Amassian, Richard Vernhes, Jolanta Ewa Klemberg-Sapieha, Patrick Desjardins and Ludvik Martinu; Regroupement Quebecois sur les Materiaux de Pointe (RQMP) and Department of Engineering Physics, Ecole Polytechnique de Montreal, Montreal, Quebec, Canada.

We investigate the growth of dense/porous $SiN_{1.3}$ multilayers by dual-mode radiofrequency/microwave plasma-enhanced chemical vapor deposition using in situ real-time spectroscopic ellipsometry (RTSE) and post-deposition atomic force microscopy. Dense $SiN_{1.3}$ films grown under medium-energy (0.1 to 0.4 keV) ion bombardment on flat c-Si (001) substrates are very smooth (root mean square roughness $R = 0.5$ nm) and exhibit bulk-like optical properties ($n = 1.93$ at 550 nm). In contrast, porous $SiN_{1.3}$ films deposited at low ion energies (1-10 eV) are porous and columnar, with $n \sim 1.6$ and $R \sim 2$ nm. When $SiN_{1.3}$ layers are grown under high ion-energy bombardment conditions on porous films, RTSE analyses reveal a rapid, but incomplete filling of surface porosity, at a rate depending on the incident precursor flux, before the total film thickness starts to increase. Films prepared under these conditions exhibit a lower average n ($\sim$1.8), an ascending index depth profile, and a higher roughness ($R > 3$ nm) than the layers deposited under identical conditions on initially flat surfaces. We also demonstrate that the use of Ar ion bombardment, under RF plasma conditions, is an effective method for decreasing the roughness of porous films. $SiN_{1.3}$ layers deposited under RF-plasma conditions on such surface-engineered substrates are dense with high and homogeneous n values. Such an approach has been successfully used to grow dense/porous multilayer optical interference filters. It efficiently stops roughness propagation through the multilayer stack and allows fabrication of filters with enhanced environmental stability and optical characteristics essentially identical to those predicted from the design.

Q3.8

Porous Germanium.

Cheng Fang, Sergiu Langa, Le Jiang, Juergen Carstensen and Helmut Foell; Chair for General Materials Science, Faculty of Engineering, Christian-Albrechts-University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany.

Porous semiconductors are of growing interest for a range of reasons stretching from fundamental studies concerning their formation and properties to hard-core applications. A bewildering variety of pore geometries and morphologies has been found, first in Si, but by now also in III-V compound semiconductors, SiC and even CdSe. Porous semiconductors, in particular nanoporous materials, exhibit many novel properties, which are the object of intensive studies. However, until recently, little was known about porous Ge, and this was partially due to the difficulties encountered in rendering Ge porous by anodic dissolution in ways similar to those used for its semiconducting cousins. In this paper we report substantial progress in producing porous Ge. The original difficulties in producing pores at all have vanished, and the spectrum of different pore types by now rivals that of Si. While there are some similarities to pore formation in Si and the III-Vs, there are also remarkable differences, which will be discussed. The major results can be summarized as follows. 1. n-type Ge in aqueous solution: Nucleation and pore growth in n-type Ge with different doping concentrations and orientations were investigated for various Ge single crystal specimens with {100}, {110} and {111} orientations, and doping concentrations of (10^{14}-10^{18}) cm^{-3}. Various types of illumination conditions (front side, backside or none), and pre-treatments for optimizing nucleation were used. Several different kinds of pores could be obtained, mostly for the first time. Pore geometries, morphologies and growth peculiarities were found to be quite different from other semiconductors. Nucleation is generally difficult, the preferred growth direction is ⟨100⟩, stop planes are of {110} type, and most remarkably, there is always a strong electropolishing component compromising pore geometry and stability. 2. n-type Ge in organic solution: In DMSO solution, results are quite different from that in aqueous solution. The growth direction is not ⟨100⟩ but ⟨111⟩, while the stopping plane is still {110}. ⟨111⟩ growth directions are unexpected; they have never been observed in Si. Nucleation seems to be very difficult, and new domain-forming phenomena are observed. 3. p-type Ge in organic solution: For the first time, pores in p-type Ge have been obtained. This is quite surprising, because no pores have been found in other p-type semiconductors so far, with the exception of Si. The growth direction is not ⟨100⟩ but ⟨111⟩ once again and the stopping planes are still {110}. Smooth or rough pore walls can be obtained, dependent on the experimental conditions. Porous Ge may find specific applications, e.g. because its surfaces state can be switched from hydrophobic to hydrophilic by simply changing the potential. Results obtained with a porous Ge membrane fabricated by using the insights provided by the experiments mentioned above will be given, proving the viability of the concept.

Q3.9

Modeling of Break-Junction Experiments.

Lorenz Romaner[2,1], Egbert Zojer[2,1] and Jean-Luc Bredas[1]; [1]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; [2]Institute of Solid State Physics, Graz University of Technology, Graz, Austria.

We present theoretical studies investigating the conductance properties of a single molecule device under systematic variation of the geometric arrangement of the electrodes. This includes variation of the gap size between the two electrodes and lateral displacement of the electrodes. These calculations give a contribution to the understanding of break-junction experiments. We intend to clarify what calculations based on density functional theory and non-equilibrium Green's functions predict for the electron transport in these experiments. We focus on systems consisting of dithiol conjugated molecules sandwiched between two infinitely extended gold electrodes. We analyze what geometry is favorable for the molecules and the first electrode layers for the different electrode arrangements and explore the hybridization of the molecular orbitals with the metallic states. This is done by analyzing transmission spectra, density of states, projected density of states, and the eigenstates of the molecular-projected self-consistent hamiltonian for the system in equilibrium and when the system is driven out of equilibrium by applying a finite bias at the electrodes. These results are compared for different degrees of surface coverage. All calculations are performed with the SIESTA and TRANSIESTA-C codes.

Q3.10

Micropatterning of Block Copolymer Micelles by Solvent Capillary Contact Printing.

Cheolmin Park, Jiyoung Hwang and Wonseok Hwang; Materials Science and Engineering, Yonsei University, Seoul, South Korea.

Amphiphilic block copolymer molecules, similar to low molecular weight surfactants, aggregate to form micelles in selective solvents above critical micelle concentration. Block copolymer micelles have been of great interest because they can be used in various potential applications including drug delivery, metal or semiconductor nanoparticle synthesis and nanolithography. For further utilization of the block copolymer micelles it is crucial to develop a micropatterning method with which micelles are selectively positioned and subsequently, for instance, arrays of nanoparticles are controlled on a substrate. A new and facile method, solvent capillary contact printing (SCCP), which is the combination of micro contact printing and micro transfer molding was presented. The method includes the following procedure: 1) spin coated monolayer of block copolymer micelles, 2) conformal contact of flexible poly(dimethylsiloxane) mold on the monolayer film, 3) injection of a preferential solvent in the microchannels, 4) control of solvent adsorption, 5) fabrication of either selectively modified micelle pattern or selectively deposited metal nanoparticles. We systematically investigated the kinetics of selective solvent absorption on monolayered micelles as a function of solvent contact time. Using atomic force microscope and transmission electron microscope, the surface and inner morphology of the micelle film was investigated. Rim-like open core micelles, not observed in solution state, were formed on the regions that the solvent had contacted. Furthermore, our SCCP method successfully produced a micropattern in which metal nanoparicles were selectively deposited on the solvent contact regions.

Q3.11

New Applications of Nano-Structured-Metal/Semiconductor and -Metal/Liquid Interface.

Koichi Okamoto and Axel Scherer; Electrical Engineering, California Institute of Technology, Pasadena,

California.

We demonstrate new applications of nano-structured-metal/semiconductor and -metal/liquid interface. By using nano-structured-metal, we could enhance dramatically the emission efficiency of sold-state light emitting materials [1]. Now the most important requirement for a solid-state lighting is the development of new methods to increase its quantum efficiency of emission. We found a significant enhancement of light emission from InGaN/GaN quantum wells (QWs) with metal layers deposited 10nm above the QWs. This emission enhancement is attributed to strong interaction between QWs and surface plasmons (SPs). Electron-hole pairs excited within the QW couple to electron vibrations at the metal/semiconductor interface when the energies of electron-hole pairs in InGaN and of the metal SP are similar. Then, electron-hole recombination may produce SPs instead of photons, and this new recombination path increases the spontaneous recombination rate. If the metal/semiconductor surface were perfectly flat, it would be difficult to later extract light from the SP, a non-propagating evanescent wave. However, roughness and imperfections in evaporated metal coatings can scatter SPs as light. SPs offer the unique ability to localize, extract and enhance electromagnetic fields, and we can control them by the nanostructure of the metal. We believe that this QW-SP coupling technique provides a foundation for the rapid development of highly efficient and high-speed solid-state light emitters. By using nano-structured-metal/liquid interface, we highly improved the transient grating (TG) technique [2]. The TG technique has been applied to material, chemical, and biological research, but experimental setups were mostly complicated. We demonstrate a convenient new technique; mask pattern transfer (MPT)-TG technique. This method has the same advantages of existing optical heterodyne detected TG techniques but the setting is much simpler. The fabricated thin film grating is placed in the front side of a quartz cell containing the sample solution. An UV pump beam casts a shadow from the grating to the sample solution such that a dark/bright pattern is formed in the solution liquid called transient grating. Such spatial modulation can be detected by the diffraction of a probe beam. By analyzing the probe beam diffraction, we can obtain the intensity and dynamics of the modulated parameters named above. This technique has many advantages compared with existing TG techniques; such as: (1) simple setting, easy alignment, (2) high signal stability, (3) easy control of phase shift, and (4) quick interchange of grating periods. We shall demonstrate this technique from several materials and discuss about the potential benefit of this new technique. [1] K. Okamoto, I. Niki, A. Shvartser, et al., Nature Materials, 3, 601 (2004). [2] K. Okamoto, Z. Zhang, D. T. Wei, and A. Scherer, Appl. Phys. Lett., 85, (2004) in press.

Q3.12

Facile Assembly of Functional Materials Using Confined Dewetting Lithography. Emily Elizabeth Barton[1], Hugo Celio[2,1] and Keith J. Stevenson[1]; [1]Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas; [2]Sematech International, Austin, Texas.

Control of the assembly of colloidal particles with spatial selectivity across large-scale areas is of interest in emerging applications such as chemical sensors and photonic devices. Current lithographic techniques such as electron beam lithography are commonly employed to prepare nanofeatures and microstructures for such devices. This technology continues to advance, but proves to be very expensive and time consuming for practical applications. It is also suited for patterning only a small list of materials. Recently, we have developed a new nontraditional lithographic technique, termed confined dewetting lithography (CDL) that shows promise for patterning a variety of nano-sized components (spheres, particles, rods) on a multitude of surfaces. This approach is particularly attractive in that the lithographic template is low-cost and reusable. Furthermore, the patterning occurs within seconds to minutes without need for use of expensive lithographic agents or instruments. Using polystyrene (PS) microspheres as a model colloid we elucidated the optimal conditions where CDL has a high efficiency. In this presentation we describe our success in fabricating patterned structures of many sizes and shapes. One key aspect in optimization of CDL is to minimize attractive PS-substrate interactions. We show that CDL is a relatively simple and fast method to assemble virtually any geometric colloidal pattern by choosing the suitable conditions and materials and can lead to uniform structures of micro-dimensions for a variety of functions.

Q3.13

Adsorption and Decomposition of Organic Hydroxyl-Carbon Acids on Al (111) Surface: Density Functional Analyses. Jun Zhong[1] and James B. Adams[2]; [1]SEM Program, Arizona State University, Tempe, Arizona; [2]Chemical and Materials Engineering, Arizona State University, Tempe, Arizona.

Density functional theory (DFT-LDA, GGA) is used to investigate the optimal adsorption geometry and binding energy of vinyl phosphorous and ethanoic acids on Al (111) surface. Tri-bridged, bi-bridged and uni-dentate geometries are examined by calculation of binding energy to determine their optimal binding sites. The vibrational frequencies of these molecules are calculated to corroborate their optimal geometries, and the results are compared with experimental observations. For these molecules, the favorable decomposition pathway leads to fragments of hydro-carboxylic chains bound to the Al (111) surface via carbon atoms. The final geometry, bonding, and reaction enthalpies are analyzed. In addition, ab-inito molecular dynamics simulations are conducted to examine the crushing of lubricant molecules between two metal surfaces. The adherency of molecular debris on two different metal surfaces is discussed.

Q3.14

Functional Arrays of Photonic Lattices through Solvent Selective Deposition. Adrian M. Brozell, Michelle A. Muha, David N. Woolf and Atul N. Parikh; Applied Science, UC Davis, Davis, California.

Driven self-assembly of colloidal particles from their dilute solutions onto planar substrates is proving to be a powerful route to designing broad classses of photonic crystals. Many approaches, including electrostatics, solvent evaporation accompanied by physical confinement, and application of mechanical shear, have proved successful in this regard. Here, we show that the slow evaporation of the solvent under physical confinement in conjunction with chemically structured substrates result in the spontaneous arraying of ordered colloidal crystals upon the disassembly of the sample sandwich . The sub-micrometer colloids were characterized using SEM and optical spectroscopies while the larger colloids were visualized using optical microscopy. Chemically structed substrates were imaged with imaging ellipsometery. Colloidal arrays reflect the underlying patterns of hydrophilicity or surface energies and appear to form because of the defect planes that form at the hydrophilic/hydrophobic interface. Since the surface chemistry is not important in the crystal-clevage, colloidal particles of arbitrary sizes and types can be used. Functionalization of the colloidal arrays using (bio) chemically derivatized colloids as well as the secondary functionalization of the pre-formed colloidal crystal arrays and their effects on photonic properties is being currently investigated in our laboratories.

SESSION Q4: Organic and Inorganic Nanostructures I
Chair: Michael Steigerwald
Wednesday Morning, March 30, 2005
Room 3000 (Moscone West)

8:30 AM *Q4.1

Micro, Nano, Macro: Off Road on the Silicon Road Map. Ralph G. Nuzzo[1,2] and John A. Rogers[2,1]; [1]Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; [2]Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois.

The emergence of new forms and applications of electronics presents both opportunities and challenges for developing new approaches to materials patterning. This talk will explore these issues in the context of recent advances made in Soft-Lithography and materials assembly methods that allow the removal of design rule constraints for devices that are intrinsic to patterning protocols based on photolithography. New forms of materials for applications in electronics, processes for integrating them in complex functional arrays, and the development of a new model for fabrication based on both bottom-up and top-down approaches to large area patterning will be discussed.

9:00 AM Q4.2

Nanoscale Tailored and Highly Ordered Self-Assemblies for Molecular Electronics and Photonics. Hong Ma, Mun-Sik Kang, Qing-min Xu, Seok-Ho Kang, Kyoung-Soo Kim, Hinlap Yip and Alex K.-Y. Jen; Materials Science & Engineering, University of Washington, Seattle, Washington.

Self-assembled monolayers (SAMs) of aromatic thiols have been recently studied for electronic and photonic applications due to its pi-conjugated character. It is ideal to obtain highly-ordered and stable SAMs with nanoscale features for exploring the charge injection/transport mechanisms in molecular electronics and opto-electronics. By balancing energetic (pi-pi stacking, hydrogen bonding, dipole-dipole interaction) and geometrical factors, nanoscale tailored and highly ordered self-assemblies of anthracene- and pyrene-based molecules have been realized to provide ideal templates for functional materials. These ordered self-assemblies derived from the electroactive C60 and anthraquinone have shown desirable electrical and optoelectronic properties, such as the nonlinear transporting effect for molecular electronics, and the efficient photocurrent generation for mimicking photosynthesis in nature.

9:15 AM Q4.3

Defect Control on Alkane Thiol-Covered Gold Surfaces. Antti Johannes Makinen, James P. Long, Neil J. Watkins and Zakya H. Kafafi; Naval Research Laboratory, Washington, District of Columbia.

As electronic devices shrink ever smaller, they are starting to approach a moletronic limit, where the device functionality is provided by a single molecule or its contact with a substrate. Subsequently, understanding possible limitations and advantages imposed on contact formation by shrinking the effective "contact pad" size close to molecular dimensions (1 - 5 nm) will be of utmost importance for moletronic architecture design. To explore the effects of nanoscale structure in contacts, we have fabricated and characterized self-assembled monolayers (SAMs) of alkane thiols ($C_nH_{2n+1}S$, n=9-12) on stepped Au(111) vicinal surfaces, which exhibit terraces 3-6 nm wide. These Au(111) vicinals provide naturally patterned surfaces, where terraces can be oriented along one of the principal crystal axis by choice of the small miscut angle (2 - 4 °). The combination of *insitu* scanning tunneling microscopy (STM) and photoemission spectroscopy (PES) reveals high-coverage (>90%) alkane thiol SAMs which were solution-deposited onto a previously sputtered and vacuum-annealed Au(111) substrate. Most notably, the STM images reveal important differences in the organization of the SAMs on vicinal surfaces compared with non-vicinal (flat) surfaces. While both surfaces show a SAM in an ordered, hexagonal stand-up phase, the *flat* surface exhibits randomly-distributed, well-known, vacancy islands in the Au substrate, underlying the SAM that are mostly absent for the SAM fabricated on the terraces of the *vicinal* surface. We explain the absence of the vacancies in the latter case by pinning of the Au vacancy defects by the step edges of a Au vicinal surface. These results point to a potentially important tool for controlling the location and the concentration of defects on patterned metal surfaces, used for alkane thiol SAM fabrication. This capability will be demonstrated for determining defect-related attachment sites for electroactive dithiol molecules.

9:30 AM Q4.4

Exploiting Physically and Chemically Patterned Surfaces to Create Well-Controlled Microemulsions. Rolf Verberg[1], Christopher M. Pooley[1], Julia M. Yeomans[2] and Anna C. Balazs[1]; [1]Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]The Rudolf Peierls Centre for Theoretical Physics, Oxford University, Oxford, United Kingdom.

Using a mesoscale model for hydrodynamics, we simulate driven flow of AB binary fluids past surfaces that contain well-defined roughness or asperities. The geometry and wetting properties of the asperities are found to have a dramatic effect on the flow patterns. We isolate conditions where the A fluid forms vertical bands that bridge the asperities and an imposed shear (or pressure gradient) drives the system to form monodisperse droplets of A within the B fluid. The size of the droplets can be tailored by varying the morphology of the asperities. The surfaces needed to create this rich dynamical behavior are used as the "stamps" in micro-contact printing; thus, the parameter space can readily be accessed experimentally and the predictions suggest an efficient method for forming emulsions with well-controlled morphologies.

10:15 AM Q4.5

Smart Thin Films. Weihong Zhang, Richard Nelson and John Larue; The Henry Samueli School of Engineering, University of California, Irvine, Irvine, California.

We have found that two types of photosensitive polymers exhibit different anisotropic characteristics when they are deposited on substrates through spinning process: In one case, the aromatic layers are perpendicular to the film surface; while in another case, the aromatic layers are parallel to the film surface. This difference in aromatic layer arrangement leads to many differences of the thin films after pyrolysis at 900 degC in their mechanical, electrical, chemical, and electrochemical properties. Besides, the unique orientation of aromatic layers for each material brings about two interesting phenomena after mixing carbon fibers with the photoresist and pyrolyzing: Carbon fibers could grow through the films in the two cases. The carbon fibers sprouted out from top surface in one case while they sprouted from edge in the other case. It seems that carbon fiber grow through the gaps between aromatic molecule groups. The anisotropy characteristics may have potential applications in nanomanipulation and nanostructure fabrication which will be reported as well.

10:30 AM Q4.6

Vapor-Phase Deposition of Crosslinked Poly(2-hydroxyethyl methacrylate) as a Thin-Film Hydrogel. Kelvin Chan and Karen K. Gleason; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

An all-dry, vapor-phase technique was developed for the deposition of crosslinked poly(2-hydroxyethyl methacrylate) thin films. This technique is a one-step process and requires no post-treatment to crosslink the polymer, and the crosslink density is tunable by adjusting reaction conditions. Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy confirm the structure of the polymer. Films with crosslink densities ranging from 18.2 to 2.3 hydroxyl groups per crosslink were obtained, and these densities correlate well with the reaction conditions used. With a broader array of reaction conditions, the range of crosslink densities can be made wider. Sessile water droplet contact angle measurements show pronounced hysteresis of contact angle, which is typical for hydrogels, and the contact angle increases with increasing crosslink density. The smallest receding contact angle of the least crosslinked film is 17°. Variable-angle spectroscopic ellipsometry (VASE) shows that the degree of swelling increases with decreasing crosslink density. Interferometry for thermal stability shows that the onset of thermal decomposition increases with increasing crosslink density, ranging from 272 to 302 °C. High-temperature annealing (400+ °C) of the films leads to near-complete decomposition, providing a method to remove the material. VASE measurements show thickness loss of over 99.4% for the most crosslinked film after annealing.

10:45 AM Q4.7

Conduction in Patterned Noble Metal Nanocolloidal Thin Films. Agnes Mewe, Stefan Kooij, Herbert Wormeester and Bene Poelsema; MESA+ Institute for Nanotechnology, Univ Twente, Enschede, Netherlands.

Deposition of citrate-stabilized metal nanoparticles on silicon oxide by self-assembly is only feasible after a suitable preparation of the substrate surface. Homogeneous surface functionalization is obtained by immersion of the substrate into a solution of amino-silane molecules. Alternatively, local functionalization is achieved by microcontact printing of the amino-silane molecules onto the silicon/silicon oxide substrates. In the latter case, upon immersion in a nanocolloidal gold or silver suspension, the colloids only adsorb on the functionalized part of the surface. The contrast in colloid deposition is found to strongly depend on the specific amino molecule used for patterning (which we attribute to the difference in vapor pressure). In a final step electrical conductivity is achieved by electroless deposition of a noble metal onto the isolated nanocrystals. The seeded growth of various noble metals as well as the percolation threshold in the transition from isolated nanocrystal layers to continuous metal films is investigated. Spectroscopic ellipsometry and Fourier transformed infrared spectroscopy are used to optically characterize the thin film structures in the visible and (near) infrared range. The optical results are complemented by conductivity measurements to characterize the electrical properties.

11:00 AM Q4.8

Metal-Oxide Interface Structure in Growth of Nanowires and Nanobelts. Yong Ding, Puxian Gao and Zhonglin Wang; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Vapor-liquid-solid (VLS) process has been an important approach in growth of quasi-one-dimensional (1D) nanowires and nanotubes (referred to as 1D nanostructures). In the VLS process, the metal liquid droplet serves as a preferential site for absorption of gas phase reactant. Nanowire growth begins after the liquid becomes supersaturated in reactant materials and continues as long as the catalyst alloy remains in a liquid state and the reactant is available. During the growth, the catalyst droplet directs the growth direction and defines the diameter of the nanowire. Ultimately, the growth terminates when the temperature is below the eutectic temperature of the catalyst alloy or the reactant is no longer available. As a result, the nanowires obtained from the VLS process typically have a solid catalyst nanoparticle at the ends with sizes comparable to diameters of the connected nanowires. It is generally believed that the metal particle is a liquid droplet during the growth and its crystal structure in solid may have no influence on the structure of the nanowires/nanobelts to be grown. In this work, using electron diffraction and high-resolution electron microscopy, we studied the interface relationship between catalyst Sn particles and their guided ZnO 1D nanostructures. Tin catalyst not only can guide [0001] growth nanowires, but also can guide [01-10] and [2-1-10] growth nanobelts. The orientation relationship between the [0001] growth ZnO nanowire and the single crystal βphase Sn particle is: (020)Sn —— (0001)ZnO, [-101]Sn —— [2-1-10]ZnO. For nanobelts growing along [01-10] and [2-1-10], the orientation relationships are (200)Sn —— (01-10)ZnO,

[020]Sn —— [0001]ZnO and (200)Sn —— (2-1-10)ZnO, [020]Sn —— [0001]ZnO, respectively. One tin particle can initiate the growth of two 1D nanostructures; the tin particle is single crystal post the growth and it preserves epitaxial relationships with the grown nanostructures. Our results provide new insights in revealing the process involved in VLS growth. Using Sn/ZnO as a model system, we showed that the interfacial region of the tin particle with the ZnO nanowire/nanobelt could be crystalline or atomically ordered during the VLS growth, although the local growth temperature is much higher than the melting point of tin, and it may play a key role in initiating 1D nanostructure. The interface prefers to take the least lattice mismatch, thus, the crystalline orientation of the tin particle may determine the growth direction and the side surfaces of the nanowires/nanobelts. Reference: [1] R.S. Wagner, W.C. Ellis, Appl. Phys. Lett., 4, 89 (1964). [2] Y. Ding, P.X. Gao and Z.L. Wang, J. Am. Chem. Soc., 126, 2066(2004). [3] Research supported by NSF and NASA. [4] For details please visit www.nanoscience.gatech.edu/zlwang

11:15 AM Q4.9

Surface Enhanced Raman Scattering for Plated Silver Dendrites. Masahiro Yanagisawa[1], Mikiko Saito[2], Keiji Nakayama[3], Keisi Ohashi[1] and Yasuo Wada[2]; [1]Fundamental Res.Labs., NEC Corporation, Tsukuba, Japan; [2]Nanotechnology Labs., Waseda University, Tokyo, Japan; [3]Nanotechnlogy Res.Inst., AIST, Tsukuba, Japan.

Surface plasmon excitation and surface-enhanced Raman scattering (SERS) have been investigated for a variety of nano-structured surfaces, particularly for aggregated metal particles [1]. According to the calculation of light scattering from fractal metal surfaces, the strong excitation of electromagnetic near fields was predicted [2]. However, there is no report on SERS for electrochemically deposited dendrite structures. We find the ultrahigh Raman enhancement for carbon films on the silver dendrite structures. Raman spectra were recorded with a confocal Raman microscope at a wavelength of 532 nm in backscattering geometry. Samples with silver dendrites were prepared by an electroplating on Si wafer in Ag(CN) water solution, coated with SiO2. The silver dendrites were grown between gold electrodes. A Raman active carbon film 10 nm thick was then sputter-coated on it. Raman scattering intensity images of the sputtered carbon film on silver dendrites were measured, where many bright points were observed. In order to estimate Raman enhancement on some topographic features, some samples were examined for carbon films on (a) flat substrate without silver film, (b) flat substrate with silver film of 300 nm in thickness, (c) silver projection of 50nm in the tip diameter, and (d) silver dendrites. Raman intensity of G-band for the case (d) is 80,000 times or more in magnitude larger than that on the flat glass substrate. The relative enhancement is 5 times for (b) and 400 times for (c). Every strong Raman scattering point, so called hot spots for (d), seem to be generated from the smaller region than that of 100 nm (space resolution) in dendrite structures, where the electric field intensity can be enhanced by surface plasmon polariton (SPP) resonances Although the plating silver dendrites exhibit the fractal dimension of 1.1 in the 50 um range, the region around hot spots seems to have larger fractal dimensions. Acknowledgement This work was supported by Grant-in-Aid through Ministry of Education, Culture, Sports, Science, and Technology. References [1] M.Moskovits, Surface-enhanced Spectroscopy, Rev.Mod.Phys., 57,3 (1985) pp.783-828. [2] J.A.Sanchez-Gil and J.V.Garcia-Ramos, Strong Surface Field Enhancements in the Scattering of p-polarized Light from Fractal Metal Surfaces, Opt.Comm., 134 (1997) pp.11-15.

11:30 AM Q4.10

Reversible Adsorption of Metallic Nanomaterials at Liquid/Liquid Interface. Jean-Pierre Abid[1], Pierre Francois Brevet[2] and Hubert Girault[1]; [1]Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Federale de Lausanne, Lausanne, Vaud, Switzerland; [2]Laboratoire de Spectrometrie Ionique et Moleculaire, Universite Claude Bernard, Lyon, France.

Over the last decade, nanostructured metallic materials are rapidly gaining attention for possible applications in a wide range of technologies due in part to their size-dependent electronic and optical properties [1]. Noble metal nanoparticles such as gold and silver exhibit a strong surface plasmon absorption in the visible region. Such resonance occurs when the incident photon frequencies match with the collective oscillations of the conduction electrons of the metallic nanoparticles. These properties also strongly depend on the particle environment and surface adsorbed species. Among the plethora of techniques used for a better understanding of the nanoparticles properties, new sensitive methods emerge such as Second Harmonic Generation. In the present work, gold, silver and gold coated with silver are chemically prepared and probed by the nonlinear optical techniques Hyper-Rayleigh Scattering (HRS) and Second Harmonic Generation (SHG) in bulk solution and at the Liquid-Liquid interface respectively. As second order nonlinear optical techniques, signal generation in media with inversion symmetry is forbidden under the dielectric dipole approximation. However, HRS measurements of gold and silver nanoparticles display a strong signal due to a quadripolar contribution. This method has been used for the estimation of the efficiency of conversion of two photons of frequency to called hyperpolarisability [2]. The study has shown a strong dependence of the hyperpolarisability with the size of the metallic nanoparticles. For size of silver nanoparticles ranging from 20 to 40 nm, the hyperpolarisablity increase of a factor of 2, the same effect has been previously observed on gold nanoparticles [3]. HRS can also be used as a calibration method for the estimation of nanoparticles size. In a complementary approach, the technique of SHG has been used for monitoring the reversible adsorption of metallic nanoparticles at liquid/liquid interface. In this case, the inversion symmetry is necessarily broken and for this reason the SHG process is surface specific. For all the samples studied, the measured SHG spectra predictably followed the linear Mie resonance modes for gold and silver particles. Interestingly, the study of AgCladAu nanoparticles showed that SHG signal was significantly enhanced with the increase in thickness of the silver clad layer around the gold core. References [1] U. Kreibig, M. Vollmer, Optical Properties of Metal Clusters (1995), Springer, Berlin. [2] Y.R. Shen, The Principles of NonLinear Optics (1984), New-York. [3] P. Galletto, P.F. Brevet, H.H. Girault, R. Antoine, M. Broyer, Chem. Comm(1999),581

11:45 AM Q4.11

A Bipyridine Molecular Contact between two Au Surfaces - Ab Initio DFT Calculations of Forces and Conductances. Robert Stadler, Kristian Sommer Thygesen and Karsten Wedel Jacobsen; Department of Physics, Technical University of Denmark, Lyngby, Denmark.

In recent experiments[1] the conductance of bipyridine contacts between gold leads has been measured simultaneously to the force required to break single bonds between the molecule and the metal. The statistical data derived from ~1000 independent measurements shows both the conductance and the rapture force to be quantized, thereby indicating that the molecular contacts are formed by single molecules. The surface structure of the gold leads and the atomic configuration of their bonding to the molecule, however, could not be characterized in these measurements, which were carried out in a toluene solution. We present density functional theory (DFT) calculations, which were carried out in order to obtain an atomistic understanding of the processes, which define the bonding and conductance in the experimental setup. By using the plane wave pseudopotential software DACAPO[2] we investigate the energetics of bipyridine molecules positioned between two gold surfaces. The contact between these surfaces and the molecule is modeled by a variety of different structures based on the (111) orientation of the Au fcc-lattice. By varying the substrate/adsorbent distance rigidly we define total energy curves, from which rapture forces can be derived. A recently developed scheme for coherent electron transport[3] allows us to calculate the conductance through the molecule in each atomic configuration within the same rigid theoretical framework as employed for the DACAPO total energy calculations. This is achieved by using a highly localized and efficiently minimal basis set of Wannier functions, which still preserves the numerical accuracy of the plane wave description of the electronic structure of the junction. By comparing our results for the conductance and forces obtained from different structures, we find the best match with the experiments in Ref. [1] for systems with stepped gold surfaces. From varying the step structure of the surface systematically trends can be found for the adsorption energies of the molecules, where the most open structures are bonded to the surface most strongly, and for the conductance, where the molecular LUMO level shifts gradually into alignment with the Fermi level of the system. Both effects can be quantitatively described and qualitatively explained from our electronic structure analysis. For molecular electronics it is essential that the position of molecular levels with respect to the Fermi level of metal electrodes can be tuned. Our results suggest that this could be achieved by controlling the surface morphology of the electrodes on the nanoscale. [1] B. Xu, N. J. Tao, Science 301, 1221 (2003); B. Xu, X. Xiao, N. J. Tao, J. Am. Chem. Soc. 125, 16164 (2003) [2] http://www.fysik.dtu.dk/campos; B. Hammer, L. B. Hansen, J. K. Norskov, Phys. Rev. B 59, 7413 (1999) [3] Y. Meir and N. S. Wingreen, Phys. Rev. Lett. 68, 2512 (1992); K. S. Thygesen, M. V. Bollinger, K. W. Jacobsen, Phys. Rev. B 67, 115404 (2003)

SESSION Q5: Organic and Inorganic Nanostructures II

Chair: Ashley Taylor
Wednesday Afternoon, March 30, 2005
Room 3000 (Moscone West)

1:30 PM *Q5.1

Surface-Assisted Selective Metallization Using Photopatterned Single-Layer Adsorption Films of Cationic

Polymers. Masaru Nakagawa, Yuji Suzuki, Nozomi Nawa and Tomokazu Iyoda; Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Photolithography of an organic photoresist layer usually having a thickness of several tens of micrometers has been widely adopted to manufacture printed-wiring circuit boards with wiring widths from 10 microns to 1 mm in house electric appliances. The thick photoresist layer ends up as industrial wastes in the manufacturing process. A novel method for manufacturing the circuit boards has been highly required to reduce the harmful organic industrial wastes from a standpoint in green sustainable chemistry. There are two categories of subtractive and additive methods in electroless plating for preparing conductive metallic wires. Selective formation of palladium plating catalysts on a substrate surface is a successful key to prepare such metal wires in the additive methods. In this report, we describe two novel methods for preparing Cu- and Ni/P-patterned wires on SiO2, SiO2/Si, polymer PET and PI substrates by using photopatterned single-layer adsorption films. We designed and synthesized two types of cationic polymer adsorbates for the purpose of this study. One is poly(1-dodecyl-4-vinylpyridinium bromide).[1] The single-layer adsorption films remaining on 172nm-VUV-light-unexposed substrate surfaces promoted the surface adsorption of negatively charged SDS-SnO2 colloidal catalyst precursors, by which metallic Pd species were formed from [PdCl4]2- through the redox reaction. Another is poly(4-vinylpyridine-co-1-dodecyl-4-vinylpyridinium bromide).[2] The pyridyl groups worked as ligands for coordinating PdClx species, from which Pd nanoparticles as plating catalysts were formed by reduction. Cu and Ni/P electroless deposition took place selectively on the cationic single-layer adsorption films in accord with the photopatterned shape. It was found that the behaviors of the selective metallization significantly depended on the thickness of the single-layer adsorption films at a nanometer level. We demonstrated that the photopatterned single-layer adsorption films on various kinds of substrates were available for an excellent template in electroless plating to prepare flexible printed-wiring circuit boards. [1] Nakagawa, M.; Nawa, N.; Iyoda, T. Langmuir 2004, 20, 9844. [2] Nakagawa, M.; Suzuki, Y.; Nawa, N.; Iyoda, T. Japanese Patent Appl. No. 2004-079954.

2:00 PM Q5.2

Surface Design Using Initiated Chemical Vapor Deposition. Kenneth K.S. Lau and Karen K. Gleason; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Initiated chemical vapor deposition (iCVD) represents a new technology to design and impart targeted chemical functionality to surfaces. The iCVD process enables in situ formation of polymeric materials on surfaces, ranging from planar silicon wafers to three-dimensional particulates. By making use of vapor to solid phase transitions and reactions, the use of wet chemistry is eliminated, reducing the impact on environment, health and safety to society. The lack of liquid surface tension forces also makes this process ideal in encapsulating fine particulates without agglomeration. The iCVD process involves a thermal initiation of active species in the vapor phase, surface adsorption of these species and subsequent polymerization on a temperature-controlled surface. The decoupling of the temperatures for activation and for surface reaction enables temperature sensitive substrates e.g., organic and biological materials, to be surface functionalized. We will demonstrate the use of the iCVD process to produce polymers, such as poly(tetrafluoroethylene), acrylic polymers and copolymers, which are spectroscopically identical to commercial polymers. These polymers have been deposited on both silicon substrates and particulates of sizes ranging from nanometers to microns in dimension. By designing the surface chemistry and making use of the inherent surface morphology, we can impart properties, such as superhydrophobicity, tuning of hydrophobicity, pH sensitivity, and reactive sites for grafting. We will show results from a variety of characterization tools, among them Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, scanning and transmission electron microscopies, gel permeation chromatography, contact angle goniometry, and quartz crystal microbalance monitor. We will show that the iCVD process follows classical polymerization kinetics, yielding well-defined fundamentals necessary for surface design. We will also discuss the evolution of the iCVD process from coating planar substrates to coating of fine particles down to the nanometer dimension.

2:15 PM Q5.3

A Challenge for Textile Science: Can Clothes Chow Down Grime with Nanotechnology? Roger R. H. Wang[1], J. H. Xin[1], X. M. Tao[1] and G. K. H. Pang[2]; [1]Nanotechnology Center, Institute of Textiles and Clothing, Kowloon, Hong Kong; [2]Department of Applied Physics, Kowloon, Hong Kong.

Substantial effort has been made on developing semiconducting ceramic crystallites acting as photocatalysts on cotton fabrics to produce self-cleaning clothes that help to break down organic materials, grime and bacteria, requiring only light sources that contain ultraviolet (UV) radiation to trigger the reaction [1]. Clothes launder own fabrics appears to be possible with nanotechnology, as anatase titania (TiO2) crystallites can be grown on cotton fabrics at low temperatures [2]. The clothes that never get dirty with the aid of a photocatalytic process energized by the UV radiation, and the catalysts-based self-cleaning fabrics. The photocatalytic process slowly breaks down and loosens organic dirt attached to the self-cleaning fabrics. In fact, UV light is abundant on cloudy days, in shaded areas, or even indoor environment lit with artificial light sources, and thus the photocatalytic process works nonstop throughout the day. The fact that textiles need to provide effective protection against skin damages such as sunburn, premature skin aging, allergies, and even skin cancer [3-5] caused by the elevated exposure to UV radiation of sunlight actually assists the self-cleaning process. Although anatase titanium dioxide finished fabric has substantial UV-blocking ability in the range of UVB (280-315 nm) [6], the effect on UVA (315-400 nm) blocking is less significant and this remains to be a strong challenge. Hence designing and modifying fabrics in such a way that they offer greater absorption in UV range is of significance for multifunctional protective nano-finishing of textile materials, including self-cleaning, sun-blocking, and anti-bacterial. Zinc oxide (ZnO) is an important alternative wide-bandgap semiconducting ceramic material and its properties were considered to be dependent closely on the microstructures of the materials, aspect ratio and even crystalline density [9]. One-dimensional oriented ZnO nanowires were suggested to be synthesized using low temperature, environmentally benign, solution-based approaches [7] with many useful properties, including catalytic degradation of refractory chemicals [7], ultraviolet nanolasing action [8], light-emitting diodes [9], waveguides [10], and water-repellent [11], and were desirable for fabricating multi-functional and intelligent textile fabrics. Further scientific and technological advances should be achievable if one-dimensional colloidal quantum system could be hierarchically grown onto the fabrics in an industrially viable way. In this paper we present a hierarchical growth approach to fabricate functionalities with nanotechnology: one-dimensional zinc oxide nanocrystallites hierarchically grown on cotton fabrics at low temperature. The fabrics allow investigation of potential applications in self-cleaning clothes ranging from medical, military uniforms to environmental catalysis systems.

3:00 PM Q5.4

Growth of a 2-D Multi-component Crystal Exhibiting a Homogeneous Nano-mesh on a Solid Surface. Feng Tao and Steven L. Bernasek; Chemistry Department, Princeton University, Princeton, New Jersey.

The growth of homogeneous 2-D multi-component crystalline thin films is attracting surprising interest because they may offer the multi-functionality of organic materials and the flexibility of fine-tuning the chemical, physical and mechanical properties for desirable needs in wide spectrum of technological areas. Molecular self-assembly on solid surface is a promising route to the design of these films. Coadsorbed monolayers of 5-octadecyloxyisophthalic acid (5OIA) and octanoic acid and of 5OIA and terephthalic acid were fabricated on high-ordered pyrolytic graphite (HOPG). The morphology of these self-assembled monolayers was investigated using scanning tunneling microscopy (STM). 5OIA coadsorbs with terephthalic acid via hydrogen-bonding network, forming ordered domain made of alternating 5OIA and terephthalic acid lamellae. In the coadsorption of 5OIA with octanoic acid, 5OIA and octanoic acid alternately pack at the molecular level in each lamella, forming a homogeneous two-component crystal. Due to the different chain-lengths of the two components, a nano-hole with a size of 1.35 nm x 0.85 nm x 0.18 nm is formed in each lattice unit, producing homogeneous nano-meshes. It is suggested that changing the length of alkyl chain of one component can possibly modulate the size of nano-hole in the lattice. This coadsorbed molecule by molecule self-assembly is the first demonstration of an approach to fabricating multi-component 2-D crystalline thin films at the molecular level. It suggests a new strategy to precisely and controllably grow homogeneous nano-structured composite materials.

3:15 PM Q5.5

Hololithographic Nano-Patterning of Sapphire. Jeffrey M. Biser[1], Sreya Dutta[1], Hyoung-Joon Park[1], Helen M. Chan[1], Bijoy K. Das[2], Volkmar Dierolf[2] and Richard P. Vinci[1]; [1]Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania; [2]Department of Physics, Lehigh University, Bethlehem, Pennsylvania.

The industrial community would benefit greatly from a cost-efficient and environmentally friendly way to pattern sapphire substrates. Patterned sapphire can be used as a substrate for low-strain gallium nitride films via nanoheteroepitaxy. Other applications include waveguides and optical components. Lithographic patterning of sapphire by conventional processes is difficult due to the inherent chemical resistance of the material. The recently developed AGOG process for generating pristine sapphire surfaces has made it easier to produce patterned sapphire. Starting with a planar sapphire surface, we begin by depositing an Aluminum thin film, anneal to Grow a polycrystalline Oxide layer, and follow this with subsequent Grain growth at high temperature, resulting in solid-state conversion into single crystal sapphire with a fresh surface (hence the name, AGOG). An exciting side benefit of the AGOG process is that any desired pattern can easily be introduced into the Aluminum metal layer before conversion. The pattern is introduced to the metal film by conventional lithography, which is then converted to sapphire. We have had success in producing patterned sapphire via e-beam lithography, but unfortunately this technique limits us to the size of the pattern we can produce efficiently (on the order of 1mm^2). To overcome this obstacle, we have applied holographic lithography. This technique relies on the use of a Lloyd setup, in which a photoresist-coated sample is aligned at a right angle to a flat mirror, and a laser (with the appropriate wavelength) is aimed at approximately 45 degrees to each surface. Regularly spaced fringes result from interference between light hitting the sample directly, and light reaching the sample from the adjoining mirror. The fringe spacing can be tuned according to the relationship $= \lambda \,/\, 2 \sin \theta$, where λ is the spacing, λ is the wavelength of the laser, and θ is the angle between the laser and the sample. These periodic fringes expose uniform parallel lines in the photoresist. By exposing the sample once to produce a set of parallel lines, then rotating the sample through 90 degrees and exposing again, a regular periodic structure is created in the photoresist layer. This is then transferred to the metal layer through conventional techniques to produce a large-scale grid of mesas and alleys. Using this setup, the upper limit of the exposure size is determined solely by the power of the laser and the size of the sample holder. The patterned metal film is subsequently put through the AGOG conversion, resulting in a sapphire surface with a periodic array of mesa-like structures. These structures are on the order of 100 nm in size, and have been characterized by electron microscopy and AFM (atomic force microscopy). The effectiveness of conversion from aluminum to sapphire is evaluated using cross-sectional TEM (transmission electron microscopy) and EBKD (electron backscattered Kikuchi diffraction).

3:30 PM Q5.6

In-situ Grazing Incidence Small Angle X-ray Scattering Study of Tunable Nanoripples on Ion-etched Sapphire Surface. Hua Zhou[1], Lan Zhou[1], Randall Headrick[1], Ahmet Ozcan[2], Yiyi Wang[2], Gozde Ozaydin[2] and Karl Ludwig[2]; [1]Physics, University of Vermont, Burlington, Vermont; [2]Physics, Boston University, Boston, Massachusetts.

The interaction between energetic particles and surfaces of materials form features of interests such as ripples directly through a surface instability induced self-organization. In this work, we report an in-situ synchrotron grazing incidence small angle x-ray scattering (GISAXS) study of tunable nano-ripples formed on room temperature sapphire substrate by ion etching. The results provide insights on the mechanism of surface morphology evolution during ion irradiation. Single crystal sapphire surfaces were found to be amorphous after ion etching. Strong dependence of surface morphology on ion incidence angle under normal and off-normal conditions, as predicted by Bradley Harper theory, was confirmed by in-situ GISAXS patterns and ex-situ AFM imaging. A systematic study found that the corrugated ripple wavelength has a power law dependence on the ion energy. Transverse and vertical scans mapping out the scattering patterns in qx-qz plane display characteristic satellite features corresponding well with an asymmetric saw-tooth surface profile. Discussion on the dynamics and mechanism of the ripples formation will be presented.

3:45 PM Q5.7

Structural Characterization and Terahertz Emission of Fe(001) Thin Films. Gregory Lawrence Fisher[1], David J. Hilton[2], Chad A. Meserole[3], Richard D. Averitt[2], David J. Funk[3], Antoinette J. Taylor[2] and Joe D. Thompson[2]; [1]NMT-16, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]MST-10, Los Alamos National Laboratory, Los Alamos, New Mexico; [3]DX-2, Los Alamos National Laboratory, Los Alamos, New Mexico.

Terahertz (THz) emission by optical rectification of an ultrashort laser pulse in noncentrosymmetric materials with a bulk second order nonlinearity, $\chi^{(2)}$, has been reported for numerous systems.[1] We have previously reported our observation of THz emission from 12nm thick Fe(001) excited by 800nm, femtosecond laser pulses at a 1kHz repetition rate.[2] The generated waveform amplitude scales linearly with the pump fluence, consistent with THz generation from a second order nonlinearity. Moreover, the angular data are characteristic of both surface, $\chi_S{}^{(2)}$, and magnetic, $\chi^{(2)}(\text{M})$, contributions to the THz emission. However, second order nonlinearities alone do not account for the narrow THz bandwidth. We propose a mechanism of ultrafast demagnetization[3] to explain the experimentally observed THz bandwidth from Fe(001). The samples probed in these experiments consist of 12nm thin films of Fe(001)/MgO(001). The iron thin films are grown by MBE in an UHV system with a base pressure of $\sim 6\text{x}10^{-10}$ Torr. Growth of the iron thin films is monitored in situ by QCM, AES, and LEED; the films are shown to be continuous, monocrystalline Fe(001). Ex situ analysis of the iron thin films includes SEM and XRD. Additionally, SQUID magnetometry of the iron thin film samples indicates a remanence (M_0) of $0.95\mu_B$/atom. References: (1) Sensing with Terahertz Radiation, D. Mittleman, Ed., Springer, Berlin (2003). (2) D.J. Hilton, et al, Optics Lett. 29 (2004) 1805. (3) E. Beaurepaire, et al, Appl. Phys. Lett. 84 (2004) 3465.

4:00 PM Q5.8

Hydrogen Termination of the Si(110) Surface by Wet Cleaning Revealed by Atomically Resolved Scanning Tunneling Microscopy. Kenta Arima[1], Jun Katoh[2] and Katsuyoshi Endo[2]; [1]Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan; [2]Research Center for Ultra-Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan.

The purpose of this study is to clarify the atomic structure of hydrogen-terminated Si(110) surfaces after wet cleaning such as dilute HF cleaning and subsequent rinsing with ultrapure water. After wet cleaning, atomic images are clearly observed by scanning tunneling microscopy (STM) and their atomic arrangements are determined. A guideline to obtain an atomically flat hydrogen-terminated Si(110) surface is presented. It has been predicted that a Si(110) wafer is a promising substrate for semiconductor devices in the next generation, because the hole mobility of Si(110) with a radical oxidation method has already been achieved to be 2.4 times higher than that of Si(001). One of the most important issue to be solved for Si(110) is to develop a wet cleaning procedure to obtain an atomically flat Si(110) surface terminated with H atoms before the formation of gate insulators. After sacrificed oxides were formed, each n-type Si(110) sample was dipped into a solution of HF(50 wt%): H_2O_2 (30 wt%): H_2O= 1: 1: 98 (by volume) for 3 min in order to remove the sacrificed oxide and terminate the surface with H atoms (Sample A). Some samples were subsequently rinsed with ultrapure water for 10 min (Sample B) or 60 min (Sample C). H-terminated Si(110) surfaces after wet cleaning were observed on the atomic scale with STM. When Si(110) wafers are dipped into HF-containing solution (Sample A), the surface is constructed by piling small terraces and steps running along various directions. Inside each small terrace, neighboring atomic-scale dots form zigzag chains along the [-110] direction. This indicates that an ideal Si(110)1x1 structure with coupled monohydrides is formed. HF-containing solution removed monohydrides not only at the both ends of the chain but also inside the chain. As a result, small terraces with step edges along various directions are formed. When the Si(110) sample after cleaning in dilute HF-containing solution was subsequent rinsed with ultrapure water for short period(Sample B), wide terraces spread along the [-110] direction. Characteristic features such as a zigzag chain inside a terrace, a single row at step edges and an isolated zigzag chain on a terrace are clearly resolved, and their atomic arrangements are determined. It is demonstrated that moderate rinsing with ultrapure water forms a homogeneous Si(110) surface of which the microroughness is improved. However, STM images after rinsing with water for 60 min (Sample C) show the ridge-shaped structure of nanometer height. Excessive rinsing roughens the Si(110) surface, which is induced by anisotropic etching by OH- ions in water. These results reveal that the rinse duration of the Si(110) wafer after cleaning with HF-containing solution should be controlled to obtain atomically flat H-terminated Si(110) surfaces.

4:15 PM Q5.9

Formation of InGaN Low Dimensional Structures over a-Plane GaN ELOG Template. Mikhail E. Gaevski, Changqing Chen, Edmundas Kuokstis, Jiawei Li, Maxim Shatalov, Zheng Gong, Adivarahan Vinod, Ajay Sattu, Irina Mokina, Jinwei Yang and M.Asif Khan; Electrical Engineering, University of South Carolina, Columbia, South Carolina.

We report on growth of InGaN quantum dots (QD) and quantum wires (QW) on non-polar a-plane GaN templates deposited over r-plane sapphire substrates using ELOG approach. InGaN QDs were successfully formed in the overgrowth areas using both self assembly and selective area growth. It was shown that at growth temperatures below 700°C InGaN grown a-plane GaN forms arrays of self assembled islands with typical lateral dimensions of about 10 nm. Comparison of c- and a-plane InGaN photoluminescence (PL) under He-Cd or N2 laser excitation revealed sufficient difference in spectra. Structures with InGaN QDs which were formed over a-plane GaN ELOG templates besides GaN edge emission (around 364 nm) and its yellow band (around 560 nm) showed specific QD PL line at 380 nm. Its spectral position was insensitive to excitation power density in contrast to InGaN over c-plane templates. It was also found that at temperatures above 700 °C InGaN grown on different facets of ELOG templates has strongly different InN mole fraction. Optical properties and composition of InGaN material were studied by means of energy dispersive X-ray spectroscopy and cathodoluminescence (CL). Maximum InN fraction of 18% was measured for InGaN grown over c-oriented facet of ELOG templates. It was also found that In concentration was almost two times lower in layer grown over (1,-1,0,1) facet of ELOG template, and even less indium was found on (0,0,0,-1), (1,-1,0,0), (1,1-2,1) facets. No InGaN growth over a-plane GaN was observed at all. Such strong difference in InGaN growth makes possible formation of QDs and wires using selective area growth. As an example of nano-scale selective area growth we studied InGaN growth on side walls of threading dislocation pits and linear features from basal plane stacking faults formed on the surface of a-plane GaN template. Preliminary TEM studies showed the concentration of these defects far from seeding of ELOG structure to be less than $10\hat{8}$cm$\hat{-}$2 and $10\hat{4}$cm$\hat{-}$1, respectively. As grown these defects formed by (000-1) and (1,-1,0,1) planes have dimensions of 10-100 nm . After growth of InGaN layer these defects exhibited strong blue emission as revealed by high resolution monochromatic CL imaging, whereas no blue emission was observed from flat a-plane surface. These results confirm the formation of QDs by selective area growth on sidewalls of surface defects.