SYMPOSIUM U

Science and Applications of Carbon Nanotubes

March 28 - 31, 2005

Chairs

Pulickel M. Ajayan

Dept. of Materials Science & Engineering Rensselaer Polytechnic Institute Troy, NY 12180-3590 518-276-2322

Mauricio Terrones

Advanced Materials Dept IPICyT Camino a la Presa San Jose 2055 Lomas 4a seccion San Luis Potosi, SLP, 78216 Mexico 52-444-834-2039

Meyya Meyyappan

Center for Nanotechnology NASA Ames Research Center MS 229-3, Bldg. 229, Rm. 214 Moffett Field, CA 94035 650-604-2616

Marko Radosavljevic

Components Research Intel Corporation RA3-252 5200 NE Elam Young Pkwy. Hillsboro, OR 97124-6497 503-613-4732

Ralph Krupke

Institut für Nanotechnologie Forschungszentrum Karlsruhe Karlsruhe, 76021 Germany 49-7247-82-6417

Symposium Support

FEK Company Latin America
†JEOL USA, Inc.
†Raith USA, Inc.
Sociedad Mexicana de Nanociencias y Nanotechnologia (SOMENANO)
†2005 Spring Exhibitor

* Invited paper

TUTORIAL

Carbon Nanotube-Based Nanotechnology Monday March 28, 2005 1:30 PM - 5:00 PM Room 2000 (Moscone West)

Carbon nanotubes (CNTs) have been receiving much attention due to their unique electronic properties and extraordinary mechanical properties, thus offering promise for a broad range of applications. This tutorial will provide an introduction to the field for those who are new and offer a status review for those who have some exposure to the field. The tutorial will begin with the structure of CNTs contrasting with other familiar forms of carbon, followed by a discussion of electrical, mechanical, and other properties. Various methods of preparation including arc synthesis, laser ablation, CVD and plasma CVD will be covered. Common approaches to characterize the material will be discussed. The remainder of the tutorial will focus on applications such as electronics, composites, field emitters, sensors, nanoprobes and others.

Instructor:

M. Meyyappan, NASA Ames Research Center

SESSION U1: Structure, Synthesis and Purification Chair: P. M. Ajayan Tuesday Morning, March 29, 2005 Room 3024 (Moscone West)

8:30 AM *U1.1

ACCVD Growth of Vertically Aligned Single-Walled Carbon Nanotubes on a Quartz Substrate. Shigeo Maruyama, Dept. of Mech. Eng., The University of Tokyo, Tokyo, Japan.

Vertically aligned single-walled carbon nanotubes (SWNTs) up to 5 microns thick were produced by an alcohol CVD process [1]. In contrast to the first report of CVD growth of vertically aligned SWNTs [2], hydrogen gas was supplied only during the heating-up stage with the improved background vacuum condition. A time-progressive investigation of the growth process was studied by observing SEM images of SWNT films grown for different CVD times. Measurements of the film thickness by both SEM and optical absorbance show a non-linear growth rate, as well as an eventual decrease in the film thickness after extended reaction times. This is attributed to the presence of oxygen in the reaction chamber, which decreases catalyst activity as well as oxidizes the nanotube film. By using the relation between light absorbance and the thickness determined by SEM, the in situ monitoring of the vertically aligned SWNT film thickness has made possible for the further investigation of the growth mechanism. Polarization dependence of resonant Raman scatterings from vertically aligned SWNT films and polarized optical absorption properties of SWNTs are studied by using these samples. M. Kohno, "Low-Temperature Synthesis of High-Purity Single-Walled Carbon Nanotubes from Alcohol," Chem. Phys. Lett., (2002), vol. 360, no. 3-4, pp. 229-234. [2] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, "Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy," Chem. Phys. Lett., (2004), vol. 385, no. 3-4, pp. 298-303. [3] Y. Murakami, S. Chiashi, E. Einarsson and S. Maruyama, "Polarization dependence of resonant Raman scatterings from vertically aligned SWNT films," submitted to Phys. Rev. B. [4] Y. Murakami, E. Einarsson, T. Edamura and S. Maruyama "Polarized Optical Absorption Properties of Single-Walled Carbon Nanotubes," submitted to Phys. Rev. Lett.

9:00 AM <u>*U1.2</u>

Rings of Functionalized Single Walled Carbon Nanotubes: Characterization and Properties of a Novel Magnetic and Inductive Material. Francesco Stellacci¹, Benjamin H. Wunsch¹, Lisa Vaccari² and Maurizio Prato²; ¹Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²Dipartimento di Scienze Farmaceutiche, Universita' di Trieste, Trieste, Italy.

Carbon nanotubes are a promising material for electronic, optical and biological application due to the large number of novel (i.e. ballistic conductivity) and outstanding (i.e. high current density and thermal conductivity) properties. Unfortunately, they are also very difficult to produce on large scale free of impurities, typically amorphous carbon. They are insoluble and thus difficult to process. Carbon nanotubes covalently functionalized on their side walls with organic ligands represent a possible solution to generate soluble and processable nanotubes. Here we show that under certain conditions bundle of functionalized single walled carbon nanotubes can be induced to form

rings. A thorough analysis of the rings will be presented together with models explaining their formation. Various measurement techniques have shown that currents can flow through these rings when an alternating magnetic field is applied. Thus these rings exhibit magnetic properties in solution or when assembled on a substrate. Indeed it has been observed that these tubes, when suspended in a liquid, are attracted to the edges of magnets. We will show that this magnetic attraction is present only if the tubes are coiled into rings and consequently can be used to separate nanotubes from impurities within a sample, opening up new possibilities for an efficient and cost effective magnetic purification of carbon nanotubes. Also the inductive response of these tubes to an alternating electrical field will be presented.

10:00 AM U1.3

4 Centimetre-Long Carbon Nanotubes by Chemical Vapour Deposition. Lianxi Zheng¹, Michael J. O'Connell¹, Stephen K. Doorn¹, Xiaozhou Liao¹, Yonghao Zhao¹, Mark A. Hoffbauer¹, Quanxi Jia¹, Dean E. Peterson¹, Jie Liu² and Yuntian T. Zhu¹; ¹Los Alamos National Lab, Los Alamos, New Mexico; ²Chemistry Department, Duke University, Durham, North Carolina.

In this talk we report a chemical-vapour-deposition method to grow long carbon nanotubes (4 cm long Single Walled Carbon Nanotube), which were successfully grown on a Si substrate. Atomic force microscopy and Raman spectrum were performed, indicating that resulted carbon nanotubes are single walled with diameter range of 1nm~2.25nm. The evolution of surface morphology according to growth conditions was also studied using scanning electronic microscopy. Growth and termination mechanism will be discussed.

10:15 AM *U1.4

Electrical and Optical Properties of Long Single-Walled Nanotube Strands. Bingqing Wei, ¹Electrical and Computer Engineering, Louisiana State University, Baton Rouge, Louisiana; ²Center for Computation and Technology, Louisiana State University, Baton Rouge, Louisiana.

Future devices consisting of organized structures of various functional materials with new and exciting properties will be built from nanoscale building blocks. These nanoscale building blocks can be produced by a variety of synthesis routes, and novel properties arising from their low dimensionality and electronic structure are known for a wide range of materials. Carbon nanotube is one such material, which promises to have a wide range of applications. Carbon nanotubes have been full of surprises since their discovery and this trend continues. For example, it has been shown that single nanotube devices possess excellent properties. Metallic tubes have conductivity and current density that meet or exceed metals, and semiconducting tubes have mobility and transconductance that meet or exceed semiconductors. Opportunities also exist for integrating nanotube electronics with chemical, mechanical, or biological systems. This talk, therefore, will focus on long single-walled nanotube strands (centimeter long) and exploit new electrical and optical properties of the strands. Specifically, we found a super-small energy gap of $1{\sim}3$ meV, which is an intrinsic property of the "metallic" SWNT bundles in long SWNT strands, by measuring the temperature dependence of the resistance R (T). Electrically induced light emission was demonstrated using the strands as incandescent light bulb filaments. This property was also identified to be an intrinsic property of nanotube strands, which cannot be explained with the concept of blackbody emission.

10:45 AM <u>U1.5</u>

Controlled Synthesis of Hierarchically Branched Carbon Nanotubes via Rationally Designed Porous Templates.

Guowen Meng, Yung Joon Jung, Anyuan Cao, Robert Vajtai and Pulickel M. Ajayan; Department of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Controlled Synthesis of Hierarchically Branched Carbon Nanotubes via Rationally Designed Porous Templates Guowen Meng, Yung Joon Jung, Anyuan Cao, Robert Vajtai & Pulickel M. Ajayan Department of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA The design and controlled synthesis of complex nanowire structures will impact developments in nanotechnology applications. The present synthesis approaches however limit the degree of complexity that can be controllably configured into these structures; for example, there has only been limited success in the controlled fabrication of branched nanotubes with junctions, e.g. the Y-shaped geometry. Here we report a generic synthetic approach, based on the rational design of hierarchically branched nanochannels inside anodic aluminum oxide templates, to design and build a large variety of complex nanotube architectures. Using the nanochannels as templates, we have successfully synthesized a broad set of multiply connected carbon nanotube structures. These include nanotubes having several generations of Y-branches, and a multiplicity (up to sixteen presently obtained) of sub-branches. The

controlled arrangement of these Y shapes and multiple branches produces hierarchically organized complex nanotube units, unforeseen to date. The total number and frequency of branching, and the dimensions of the nanotubes are controlled precisely through pore design and assembly. The technique has been also used to fabricate branched metallic nanowires (e.g. Ni) and can be extended to several other material systems. The synthesis protocol provides the first rational approach to produce nanotubes of greater complexity, and could have far reaching implications in the design of future nanoscale architectures.

11:00 AM <u>U1.6</u>

Energetics, Chirality, and Electronic Structure of Carbon Nanotubes. <u>Susumu Saito</u>, Yoshio Akai and Kenjiro Kanamitsu; Department of Physics, Tokyo Institute of Technology, Tokyo, Japan.

We report the energetics of a wide variety of chiral nanotubes as well as achiral ("zigzag" and "arm-chair") carbon nanotubes as a function of the diameter obtained in the framework of the density-functional theory. In the case of chiral nanotubes we utilize the screw-symmetry operation as well as the rotational-symmetry operation, and deal with the system with the minimal unit cell of only two atoms. In the case of achiral nanotubes we use both "screw-symmetry" method and the translational unit-cell method. Interestingly, the total energy per atom of each nanotube measured from that of a flat graphene sheet is in inverse proportion to the diameter squared, with considerable dependence of its chiral angle, or, the n/m ratio of the chiral index (n,m). The arm-chair nanotubes are found to be energetically more stable than the zigzag nanotubes. Some chiral nanotubes are found to be less stable than the arm-chair nanotubs also. This implies the presence of the selectivity of carbon nanotubes at their production process. In the case of fullerenes, it is known that there is a strong selectivity of the cage topologies. For example, there are as many as 24 possible isomers for C84 but only a few isomers have been extracted from soot so far. We discuss the possible selectivities of carbon nanotubes based on the energetics obtained in this work. In addition to the energetics, we also report the electronic structure of chiral and achiral carbon nanotubes obtained by using the screw-symmetry method. It is found that the electronic structure obtained in the present density-functional study is different from what one can obtain from the parametrized tight-binding methods, especially for "metallic" nanotubes.

11:15 AM U1.7

Magnetism in Corrugated Carbon Nanotori: The Importance of Symmetry, Defects and Negative Curvature.

Julio Alejandro Rodriguez-Manzo, Florentino Lopez-Urias, Mauricio

Terrones and Humberto Terrones; Advanced Materials Department, Instituto Potosino de Investigacion Científica y Tecnologia (IPICYT), San Luis Potosi, San Luis Potosi, Mexico.

We demonstrate that carbon nanotori constructed by either coalescing C60 molecules along the five-fold axis (incorporating pentagons and octagons) or by joining the ends of Haeckelite tubes (containing heptagons, hexagons and pentagons), exhibit large magnetic moments when an external magnetic field is applied. In particular, we have used a π -orbital nearest-neighbor tight-binding Hamiltonian with the London approximation in order to study the influence of uniform external magnetic fields on various types of torous-like carbon nanostructures with negative and positive Gaussian curvature. We have calculated the ring currents and the induced magnetic moments on these structures. The results reveal the presence of an unexpected magnetic response, which is due to the presence of non-hexagonal carbon rings. Our results could also explain the existence of ferromagnetic nanocarbons. We envisage that coalesced peapods may exhibit unusual magnetic properties. Reference: J.A. Rodriguez-Manzo, F. Lopez-Urias, M. Terrones, and H. Terrones, Nanoletters (2004) in press.

11:30 AM <u>U1.8</u>

Atomistic Model for Phonons in Single-Wall Carbon Nanotubes with Defects. Vinod K. Tewary, Materials Reliability, National Institute of Standards & Technology, Boulder, Colorado.

Practical application of single-wall carbon nanotubes in electronics and other devices requires their precise characterization in terms of chirality and other characteristics such as internal strains, discrete atomistic arrangements in the lattice, and presence of lattice defects. Measurement of phonon frequencies through optical spectroscopy has been found to be a very useful tool for characterizing single-wall carbon nanotubes. Calculations of phonon spectra of perfect single-wall carbon nanotubes are available in the literature, but the effect of lattice defects on phonons has not yet been calculated. A real nanotube almost always has lattice defects such as extra atoms attached to a carbon atom, missing or additional atoms, branching etc. I will describe a fully atomistic model for calculating the phonon dispersion relations of a single-wall carbon nanotube containing a

point defect. The model is useful for interpretation of optical spectra and extracting useful information for characterizing the nanotubes. The phonons will be represented in terms of causal Green's function that will be calculated by using the Born-von Karman type model and the force constants derived from a recently calculated interatomic potential between carbon atoms in a nanotube. This model includes off-diagonal force constants in contrast to some previous models in which force constant matrices were assumed to be diagonal. The effect of the defect is represented by a change in the phonon Hamiltonian. The corresponding defect Green's function is calculated by solving the Dyson equation in the defect space. The phonon frequencies are calculated from the poles of the defect Green's function whereas the phonon density of states is obtained from the imaginary part of the defect Green's function. Raman and infrared active modes are separately identified. Numerical results will be presented for lattice defects in single-wall carbon nanotubes with different chiralities.

11:45 AM <u>U1.9</u>

Nucleation of Single-Walled Carbon Nanotubes: Total Energy Calculations. <u>Lan Li</u>, Stephanie Reich and John Robertson; Engineering Department, University of Cambridge, Cambridge, United Kingdom.

To control and optimise the growth of carbon nanotubes we need to understand the nucleation and growth mechanism. Single wall nanotubes only grow in the presence of a metal catalyst. Here, we investigated the nucleation of carbon nanotubes and the role played by the metallic catalyst using first-principles total-energy calculations. Calculations of the energy of finite clusters of carbon atoms compared to an infinite sheet of graphite show that the by far the largest excess energy is due to carbon dangling bonds at the edge of the cluster. This causes carbon clusters in the absence of metals to form closed shapes, the fullerenes. The presence of a transition metal is able to saturate these dangling bonds by forming carbon-metal bonds, removing this excess energy. Curvature of a sheet to help form these C-M bonds costs little extra energy. Thus, we find that on a metal surface a curved carbon configuration, such as caps or capped single-walled carbon nanotubes, are favoured over configurations with dangling bonds, such as a small piece of graphene, as noted by Fan et al [1]. We also find that chirality has an effect on the energies of the dangling bond, the C-C bond and the C-metal bond. The total energy for a capped achiral tube, i.e., armchair (capped 5,5 tube) or zigzag (capped 9,0 tube), is slightly smaller than that for a capped chiral tube (capped 6,4 tube). The driving force for the nucleation of a nanotube in the presence of a metal surface is therefore that curvature minimizes the total energy by replacing carbon dangling bonds by carbon-metal bonds. However, this introduces strain. Incorporation of pentagons releases the strain energy associated with forming the cap. We discuss the consequence of our results in connection with possible nucleation and mechanism for carbon nanotube growth. [1] X. Fan, R. Buczko, A. A. Puretzky, D. B. Geohegan, J. Y. Howe, S. T Pantelides, and S. J. Pennycook, Phys. Rev. Lett. 90, 145501 (2003).

> SESSION U2: Electrical Properties and Applications Chair: Marko Radosavljevic Tuesday Afternoon, March 29, 2005 Room 3024 (Moscone West)

1:30 PM *U2.1

Carbon Nanotubes for Self-Assembling Functional Nanoelectronics. Cengiz Sinan Ozkan, Mechanical Engineering, University of California at Riverside, Riverside, California.

Conventional device fabrication strategies must be augmented by new techniques including self assembly methods in order to truly take advantage of the quantum nature of novel nanoscale electronic devices and systems and permit the use of these properties for real applications in a larger system (> 10 nm and < 1000 nm). I will describe a novel technique for the fabrication of nano-assemblies of carbon nanotubes (CNT) and nano crystals/quantum dots (QD) -formation of CNT-QD conjugates-. Such heterojunctions could become better alternatives for the synthesis of nanoscale devices which would preserve the electronic properties of MWCNTs compared to configurations that depend on the bending or overlapping of CNTs. Such configurations could provide pathways for the bottom-up assembly of nanoscale circuits or as drop-in technologies for the existing device platforms. During processing, CNTs are primarily functionalized with carboxylic end groups by oxidation in concentrated sulfuric acid. Thiol stabilized QDs in aqueous solution with amino end groups were conjugated to carbon nanotubes using the ethylene carbodiimide coupling reaction. Detailed chemical and physical characterization of the heterojunctions have been conducted using Fourier transform infrared spectroscopy, transmission electron microscopy and energy dispersive spectroscopy. Next, I will describe the possibilities of using carbon nanotubes for encapsulation and mass transport applications and present our first experimental observations

in this area. Our current research aims to combine chemically mass-produced nanoscale building blocks with biomimetic structuring schemes employing DNA recognition to encode the desired structure at various levels. The use of self-assembly and highly-integrated materials will allow novel routes to circumvent current challenges of CMOS such as environmental friendliness and capital costs of next generation fabrication facilities.

2:00 PM *U2.2

Self-Assembled Carbon Nanotubes based Electronic Devices. Ron Naaman, Miron Hazani, Dimitry Shvarts, Dana Peled and Victor Sidorov; Chemical Physics, Weizmann Institute, Rehovot, Israel.

Self-assembled carbon-nanotubes-based electronic devices can be produced with high yield using the natural process of DNA hybridization. In principle, the devices made by this method behave like those made using direct metal-carbon nanotubes contacts. The devices are robust and open the possibility of direct interaction between electronic devices and biological systems.

3:00 PM *U2.3

Transport Imaging in 1D Structures – From Nanowires to Nanotubes. Sergei V. Kalinin¹, Junsoo Shin^{1,2}, Arthur P. Baddorf¹, Robert J. Harrison³ and Vincent Meunier³; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge,

Tennessee; ²Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee; ³Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Electronic transport in low dimensional systems including carbon nanotubes and oxide nanowires is determined by a small number of electroactive elements, including contacts, junctions and atomic defects. Incorporation of these materials into functional devices requires an understanding of the origins of field effect and frequency-dependent transport properties on the level of individual defects. We illustrate the use of recently developed Scanning Impedance Microscopy (SIM) and Scanning Frequency Mixing Microscopy (SFMM) to real space imaging of frequency dependent electronic transport in low-dimensional systems and illustrate measurements of the current-voltage curve of individual defect in oxide nanowires and carbon nanotube networks. Local field effect in carbon nanotube circuits is addressed using Scanning Gate Microscopy. We present a new approach to quantitatively interpret SPM which treats the interaction between the probe and the system using a combination of first principles density functional calculations and continuum electrostatics modeling. An approach for experimental measurement of the tip radius of curvature from the electrostatic SPM data is developed. Within this approach, we can quantitatively describe, for the first time, the capacitive tip-surface interactions and predict the magnitude of the tip gate effect in nanoscale systems, such as carbon nanotubes, oxide nanobelts and semiconductor nanowires, permitting quantitative determination of electronic properties of atomic defects in these systems. Research performed as a Eugene P. Wigner Fellow (SVK), under contract DE-AC05-00OR22725 with UT-Battelle, LLC. VM and RJH acknowledge support from the Mathematical, Information and Computational Sciences Division, Office of Advanced Scientific Computing Research of the U.S. Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

3:30 PM <u>*U2.4</u>

Carbon Nanotube Based Nano-Floating Gate Memory. Yuegang Zhang, Intel Research/Nanotube SRP, Intel Corporation, Santa Clara, California.

Floating gate (flash) memories have dominated the non-volatile memory products for about two decades. The further miniaturization and improvement of speed, however, have been hindered by the tunnel oxide leakage as well as the yield and the reliability problems. Using nano-crystals as floating gates for electron storage has attracted much interest in recent years as a potential solution for these problems. A single-electron memory was demonstrated by combining a single floating dot with a thin silicon channel [1]. In this talk, we demonstrate a new type of non-volatile memory device fabricated with a carbon nanotube channel and metallic nanoparticles as floating gates. The memory effect has been measured at both room temperature and low temperature. Single-electron charging effect has been observed at 10 K. [1] Toshiro Futatsugi, Anri Nakajima, Hiroshi Nakao, FUJITSU Sci. Tech. J., 34, No. 2, pp.142-152, 1998.

4:00 PM *U2.5

Performance Evaluation of Carbon Nanotube Interconnects and Transistors. Georg S. Duesberg, Robert V. Seidel, Andrew P. Graham, Maik Liebau, Eugen Unger, Bijoy Rajasekharan, Anita Neumann and Franz Kreupl; Corporate Research, Infineon Technologies AG, Munich, Germany. Carbon nanotubes (CNTs) are widely investigated for beyond-the-roadmap applications in microelectronics. CNT interconnects and transistors outperform conventional materials in many aspects. However, numerous parameters and integration issues remain unresolved and, therefore, further detailed investigations have to be carried out. In this presentation the recent research work at Infineon Technologies AG on CNT-based interconnects and transistors is reviewed. The electrical characteristics of vertical interconnects consisting of individual CNTs are presented. The MWCNTs were grown in lithographically defined positions on metallic underlayers and have diameters of approx. 20 nm. These individual CNTs were contacted by e-beam lithography for electrical characterization. Current densities of up to 5x108 A/cm2 and resistances as low as 7.8 kOhm were measured for these vertical CNT interconnects. Furthermore, a comprehensive study of the transport behaviour depending on the graphitization of the CNTs is presented. The performance and integration of field-effect transistors based on single-walled CNTs (CNT-FETs) is continuously being pushed forward. An important requirement for high integration density is the scalability of CNT transistors to very short channel lengths. We have used a negative tone e-beam resist to fabricate ultra-short CNT-FETs with channel lengths below 20 nm. The ultra-short CNT transistors could carry up to 15 microA and did not show ambipolar behavior, a further important requirement for their integration. In addition, it is shown that low temperature high-k materials can be successfully integrated as gate oxides. The capability to switch high currents makes CNTs especially interesting for power transistor applications. To demonstrate their feasibility a number of CNTs were contacted in parallel with only one lithographic step. With this CNT-Power FET currents higher than 2 mA were switched, sufficient to drive macroscopic devices such as LEDs or motors. The prospects for applications in future microelectronics will be discussed in the light of the outstanding performance of carbon nanotube-based devices and the rapidly developing tools to manufacture CNTs.

4:30 PM <u>U2.6</u>

Wafer Scale Self Assembled Carbon Nanotube Single Electron Memories. Vincent Bouchiat¹, Anne-Marie Bonnot², Aurore Bonhomme¹, Antonio Iaia², Cecile Naud² and Laetitia Marty^{2,1}; ¹Centre de Recherches sur les Tres Basses Temperatures, CNRS, Grenoble, France; ²Laboratoire d'Etudes des Proprietes Electroniques des Solides, CNRS, Grenoble, France.

We demonstrate wafer-scale integration and operation of single electron memories based on carbon nanotube field effect transistors (CNFETs). Our method involves a two step double self assembly process. The first step consists of a CVD growth and in situ electrical connection of single walled carbon nanotubes on a predefined submicron catalytic electrode pattern. We obtain an integration yield of semiconducting carbon nanotubes exhibiting field effect that can exceed 50% for 9000 devices on a 2 inches wafer. The second step is a wet step which consists of local functionalization and controlled attachment of a 30 nm colloidal gold bead on the nanotube. The bead acts as a storage node for the memory while the CNFETs operated in the subthreshold regime are the electrometers. Operation of devices with retention of single charge quantum is successfully demonstrated at liquid helium temperature. Extension of the devices performance at room temperature will be discussed.

$4:45 \text{ PM } \underline{\text{U2.7}}$

Nonvolatile Memory Behavior from Multi Channel CNTFETs. Donghun Kang¹, Junghee Han¹, Jae Woong Hyun¹, EunJu Bae¹, Byoung-Kye Kim², Ju-Jin Kim² and Wanjun Park¹; ¹Device Lab, Samsung Advanced Institute of Technology, Yongin, South Korea; ²Physics Department, Chonbuk National University, Jeonju, South Korea.

Hysteresis behavior of back-gated carbon nanotube field effect transistors (CNTFET) have been studied recently due to their possible application for nonvolatile memory. Previous research demonstrated nonvolatile memory action from individual single wall CNTFETs. For future memory applications, an in-depth study on memory effects of CNTFET is necessary. In this study, a single cell multi-channel CNTFET was chosen for systematic study on charge trapping near the channel region in parallel with hysteresis behavior at different measurement conditions such as air and vacuum. Carbon nanotubes, whose typical diameter is about $2.5\mathrm{nm}$ to $3\mathrm{nm}$, were grown by thermal chemical vapor deposition method with a metal catalyst at 900oC for 10mins. About 10mm long multi-channels were grown between metal electrodes, which were formed by lift-off process on the SiO2 layer. The amount of hysteresis depends on the pressure inside the chamber and the sweeping direction of gate bias. Threshold voltages shift by more than 10V after one cycle of up and down sweeping. Up sweep (from negative to positive gate bias) results in a lower amount of hysteresis than that of down sweep (the opposite direction of up sweep). The amount of hysteresis decreases as the pressure decreases irrespective of the sweeping direction. The turn-on

voltages of p-and n-channel shift in a nonlinear fashion with pressure change. Nonvolatile memory actions were demonstrated with the multi-channel CNT FET. Writing was performed with a down sweep and then read at Vg = -1.8V. After erasing the device with a gate voltage pulses of -15 or 20V for 1 second, a read at Vg= -1.8 V followed. Using the write, read, and erase scheme, it is found that multi-channel CNT FET can be used as a NVM memory device.

SESSION U3: Poster Session: Science and Applications of Carbon Nanotubes I Chair: P. M. Ajayan Tuesday Evening, March 29, 2005 8:00 PM Salons 8-15 (Marriott)

U3.1

High-density Field Emission from Carbon Nanotubes.

Michael J. Bronikowski and Harish Manohara; Jet Propulsion
Laboratory / California Institute of Technology, Pasadena, California.

The field emission behavior of bundles of multiwalled carbon nanotubes (CNT) arranged in a variety of array geometries has been investigated. We have found that such arrays of CNT bundles perform significantly better in field emission than arrays of isolated nanotubes or dense, continuous mats of CNT, and that the field emission performance depends strongly on the bundle diameter and inter-bundle spacing. In particular, arrays of 1- 2 micron diameter CNT bundles spaced 5- 10 microns apart produced the largest emission densities, routinely giving 1.5- 1.8 A/cm2 at electric fields of 4 V/micron, and >6 A/cm2 at 20 V/micron. Studies of the optimization of field emission from such CNT bundle arrays with respect to various array and process parameters will be presented and discussed.

U3.2

Synthesis of One-Dimension Carbon Nanomaterials from Flames Using Liquid Fuels. Chunxu Pan^{1,2}, Feng Cao¹, Xiang Qi¹ and Yueli Liu¹; ¹Dept. of Physics, Wuhan University, Wuhan, Hubei Province, China; ²Center for Nanoscience and Technology, Wuhan University, Wuhan, Hubei Province, China.

Recently carbon nanomaterials have been extensively studied because of their unique mechanical and physical properties related to quantum size effects. Regular methods, such as arc-discharge, laser ablation, chemical vapor deposition (CVD), and solar method, etc. have been successfully used to synthesize CNTs. Diffusion flame synthesis of CNTs is a newly developed method. Flaming synthesis offers several inherent advantages: 1) Flame could provided quite naturally both the elevated temperature and the hydrocarbon reactant for CNTs synthesis at atmospheric pressure similar to flame synthesis of fullerenes; 2) Flame synthesis is proven to be a more economical method for large areas by either flame restering or with multiple flames; 3) It allows a controllable residence time within a desired flame region, etc. However, the diffusion flame generally uses a very complicated burner and other apparatus, and the gaseous fuels need to be safely and carefully maintained. In the present work, flames using fuels ethanol, methanol, acetone and liquefied petroleum gas with very simple burners are successfully used to synthesize two main one-dimension carbon nanomaterials, i.e. highly graphitic hollow-cored carbon nanotubes (CNTs) and disorder solid-cored carbon nanofibers (CNFs). The substrates with variant pre-treatments such as polishing, etching, coating and pulse plating etc. also play a key role in this process. It is found that: 1) When the substrates are pre-treated using the polishing and etching processes, the combustion materials are determined mainly by substrates, that is, the substrate containing element Fe or its compounds intends to produce the solid-cored CNFs on low carbon mild steel substrates, whereas the substrate containing Ni element or its compounds intends to produce hollow-cored CNTs on the Ni-contained substrates. This is because Fe has a strong affinity for carbon and Ni has a weak affinity for carbon. 2) When the substrates are electro-deposited a nanocrystalline Ni layer using a periodic reverse (PR) pulse plating, the dimension of CNTs is relates to the size of Ni nanocrystalline., and then the CNTs growth can be precisely controlled. 3) When the substrates are coated with a Ni(NO3)2 layer as the catalyzing precursor, the synthesizing process becomes easier to be controlled and has higher repeatability and stability when comparing to other pre-treatments. 4) The fuels influence the morphologies of the nanomaterials due to the differences on carbon content and combustion energy. The models of "hollow-cored mechanism" and "solid-cored mechanism" were proposed to explain the present CNTs and CNFs formations, based on the theory that "Fe has a strong affinity for carbon and Ni has a weak affinity for carbon". It is expected that the present flames may provide a much simpler and more economic approach for mass-production of CNTs and CNFs by using large flame or multi-flames.

U3.3

Carbon Nanotube Perpendicular Branching Structure.

<u>Liwei Liu</u>^{1,2} and Li Lu¹; ¹Institute of Physics Chinese Academy of Sciences, Beijing, China; ²Department of Physics, Qiqihar University, Qiqihar, China.

A novel multiple perpendicular branching structure was synthesized by a simple chemical vapor deposition (CVD) method of carbon nanotubes using methane as feeding gas and Fe nanometer particles as catalyst. Transmission electron microscopy (TEM) images revealed that some slender carbon nanotubes (branch) protruded perpendicularly from the larger carbon nanotubes (stem) are branches of L-shape junction in carbon nanotube bundles. The outer diameters of the stem is about 3-10 nm and the branch is single-walled, double-walled or multi-walled carbon nanotube with the branching diameters range from 1 to 7 nm. This like-T type junction structure can be reproducible and controlled by changing catalytic textural and pore structure. The multiple perpendicular branching structures are observed forming two dimensional or three dimensional complex network structures, which are the first step towards building nanotube architectures.

$U_{3.4}$

Spin Transport Characteristics of Carbon Nanotubes Magnetically Assembled on Ferromagnetic Contacts.

Sandip Niyogi, Carlos M. Hangarter, Ramesh Thamankar, Rolan Kawakami, Nosang V. Myung and Robert C. Haddon; Center for Nanoscale Science and Engineering, University of California, Riverside, California.

A facile method for assembling carbon nanotubes (CNT) on ferromagnetic metal contacts will be described. Multiwalled carbon nanotubes (MWNT) with a magnetic cap were fabricated by thermally evaporating nickel on top of a vertical array of MWNTs grown on silicon. Magnetic interaction between the magnets on the nanotubes and lithographically patterned ferromagnetic electrodes caused the relative alignment and directed placement of nanotubes. The lithographically patterned electrodes were further modified using electrochemical deposition to form asymmetric ferromagnetic electrodes as well as improve the electrical and magnetic interactions at the contacts. MWNTs thus assembled were found to show characteristics that have been established for various nanotube device configurations. Spin transport behavior of these devices will be discussed.

U3.5

High Yield Single-Walled Carbon Nanotubes for Microarray Based Protein Chip Substrate. Hye Ryung Byun and Hee Cheul Choi; Department of Chemistry, Pohang University of Science and Technology, Pohang, South Korea.

High yield single walled carbon nanotube (SWNT) film has been demonstrated as an efficient substrate for microarray-fluorescence based protein chip. Using a microarrayer, micro-spots of probe proteins (biotin-BSA and Protein A (SpA)) are reliably formed on CDI-Tween20 functionalized SWNT substrates. Further reactions with fluorescent dye tagged target proteins (Cy5-SA and Cy3-IgG) show high specificity without cross reactivity. In the specific binding of SpA and Cy3-IgG, fluorescence intensity counts show ca 60,000 while it shows only ca. 100 for non-specific binding (biotin-BSA and Cy3-IgG). The role of CDI-Tween20 is critical for the efficient SWNT protein chip application since it allows covalent coupling of probe proteins on SWNT as well as inhibition of non-specific binding on bare SiO₂/Si surface.

U3.6

Sulfonated Carbon Nanotubes as a Strong Protonic Acid Catalyst. Peng Feng, Lv Ping, Wang Hongjuan and Zhang Lei; Department of Chemical Engineering, South China University of Technology, Guangzhou, China.

The discovery of carbon nanotubes and the prospect of developing novel carbon-based nanomaterials have excited worldwide interest among researchers. Following the enthusiastic scientific response, Carbon nanotubes have attracted a great deal of attention due to their unique structure-dependent electronic and mechanical properties. They are thought to have a host of wide-ranging, potential applications, for example, as catalyst supports in heterogeneous catalysis, field emitters, high-strength engineering fibers, sensors, actuators, tips for scanning probe microscopy, gas storage media, and as molecular wires for the next generation of electronics devices. Chemical modification is essential for the deposition of catalysts and other species onto nanotube surfaces for nanocatalytic and sensor applications. Sulfonated carbon nanotubes with a high density of sulfonic acid groups was first prepared by a simple sulfuric acid sulfonation. It is as a novel strong protonic sold acid catalyst as

replacements for such unrecyclable and inefficient separation liquid acid catalysts. Furthermore, the SO3H groups act as proton carriers, which means that the carbon nanotubes with a high density of SO3H groups is also useful as a proton conductor. 1g of multiwall carbon nanotubes (MWNTs) prepared by the catalytic decomposition were heated in concentrated sulfuric acid (> 98%, 50 ml) at 523 K under a flow of N2 (80ml min-1) for 18h, cooled to room temperature and then washed repeatedly by distilled water until impurities such as sulfate ions were no longer detected in the wash water. And finally the precipitates were dried in an air oven at 393K for 12h to prepare sulfonated carbon nanotubes, which was characterized using TEM (Philips CM 300), SEM (LEO1530VP), FT-IR (Brouker 550), EDS (Oxford Inca 300), NH3-TPD and TG-DSC (Netzsch STA449C). The strength and density of the acid sites of the material were demonstrated through ammonia adsorption and the esterification of acetic acid (328 K). The results showed that sulfonated carbon nanotubes kept still nanotubes structures, ammonia adsorption took place onto sulfonic acid groups of carbon nanotubes, and $16~\mathrm{wt}\%$ SO3H was attached to carbon nanotubes. The sulfonated carbon nanotubes has four times higher catalytic activity for acetic acid esterificartion to methyl acetate than those of the nitric acid treated carbon nanotubes and activated carbon.

U3.7

Properties and Structure Characterization of CNT Based Transparent Conductive Coating. Jiazhong Luo, Philip Wallis, Mike Trottier, Paul Glatkowski and David Arthur; Eikos, Inc., Franklin. Massachusetts.

Transparent and electrically conductive coatings and films have a variety of fast-growing applications ranging from window glass to flat panel displays. These mainly include semiconductive metal oxides such as indium tin oxide (ITO), and polymers such as poly(3,4-ethylenedioxythiophene) doped and stabilized with poly(styrenesulfonate) (PEDOT/PSS). In recent years Eikos, Inc. has conceived and developed technologies to deliver novel alternatives using single wall carbon nanotubes (SWNT). As previously reported, these technologies offer products having a broad range of conductivity, excellent transparency, neutral color tone, good adhesion, abrasion resistance and flexibility. Additional benefits include ease of both processing and patterning. This paper reports our recent progress on optoelectronic properties and structure characterization of these materials. Highly transparent and conductive coatings are formed by applying specially formulated, purified SWNT dispersions onto PET or glass substrates. The CNT coating is protected by the addition of polymer binders. The selection of polymer binders is critical for maximizing the opto-electronic performance of the coating in addition to optimizing adhesion, abrasion resistance and flexibility. Typically visible light transmittance value of 90-97% can be obtained corresponding to sheet resistance (Rs) value in the range of 200-500 ohms/square. This is close to that of ITO and much better than that of PEDOT in the same resistivity range. Characterization of the CNT coating thickness and structures presents significant challenges Microscopic methods including AFM, SEM and TEM are used to study the coating structures and morphology. As comparison, ellipsometry analysis and optical profilemetry are also used to measure nominal coating thickness and surface roughness. Ellipsometry also allows the determination of nominal optical constants including the refraction index and the extinction coefficient. In a typical coating of approximately 30 nm for 500 ohm/square, 1-2 nm diameter carbon nanotubes self-assemble into ropes or bundles of 10-30 nm in diameter. These ropes or bundles are interwined with 2-D orientation on the thin film plane to form a relatively dense layer with open interstices. The exploratory results of characterization provide some basic guidance for understanding structure-property relationship and future product design. This new category of transparent conductor has remarkable potential for versatile applications in the areas including (but not limited to) flat panel display, touch screen, flexible display and ESD coating.

<u>U3.8</u>

Carbon Nanotube Based Power Electronic Devices and Equipments. Arindam Chakraborty and Ali Emadi; ECE, Illinois Institute of Technology, Chicago, Illinois.

When the semiconductor industry faces immense changllenges, in the process of miniaturization of power electronic devices, carbon nanotubes are most likely to replace all conventional silicon based device technology, because of its unique physical properties. One big advantage of carbon nanotubes are their dual properties, such as it can behave both as a metal or a semiconductor, by geometrical arrangement of its atoms. With the technological advancement, of field effect transistors, carbon nanotubes will have many contributions as switching elements in nano power electronic circuits. We will discuss in this paper about the structure of carbon nanotube field effect transistors and their performance as a power electronic device. Nano scale devices are fabricated by depositing technique of carbon

nanotubes, with single wall. The structure of such FET devices consists of two electrodes, constituted by gold or platinum, which form the source and drain, and remain connected by the channel made of carbon nanotubes. Certain differences between conventional MOSFETs, and the carbon nanotube FETs, will be discussed based on their device performance. There are many high frequency, GHz scale, applications of carbon nanotubes have been possible so far, and the research is at full swing for utilizing most of the advantages associated with the unique properties of carbon nanotubes to explore a new world of nano power electronics. To utilize the high frequency behavior of carbon nanotubes, it is very important to analyze the ac and dc contact impedances, which include electrostatic and dynamic inductance and device capacitance values. One great development of carbon nanotubes has been possible as nanotriodes, which is done by using carbon nanotube as field emitters; whereby an improved device performance can be achieved. By the use of carbon nanotubes of different heights, a variation in the geometry of the nanotriode can be achieved, with superior device performance. Based on non-uniformly distributed electric field, the analysis of improvised device configuration and current emission rates can be achieved. Carbon nanotubes have wide applications in battery technology, such as Lithium being stored inside carbon nanotubes for the purpose of carrying charges. In fuel cell technologies, which are the future of automobile industries, a very efficient method is to put hydrogen into carbon nanotubes, and is a very advantageous method. The field emission theory of carbon nanotubes, where a small electric field is applied parallel to the axis of nanotubes, have been found to be very useful in flat panel displays, as controlled electron guns. Some development organizations, are utilizing this electron emission principle to develop vacuum tube lamps, which are very useful.

U3.9

Electrochemical Characteristics of Supercapacitors with Manganese Oxide-Carbon Nanotube Nanocomposite Electrodes. Chia Ying Lee¹, Tseung Yuen Tseng¹, Sue Yi Li² and Pang Lin²; ¹Electronics, National Chiao Tung University, Hsinchu, Taiwan; ²Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

The manganese oxide/carbon nanotubes/nickel (MnOx/CNTs/Ni) nanocomposite electrodes were investigated for the supercapacitors. The CNTs were deposited on the Ni substrate by electrophoresis, while the MnOx were synthesized by anodic deposition on substrates. The crystalline structure and surface morphologies of the electrodes were determined by X-ray diffraction, scanning electron microscopy and transmission electron microscopy, respectively. The specific capacitances of MnOx/CNT/Ni nanocomposite electrode were 415 and 388 F/g with scan rates of 5 and 100 mV/s, respectively. After 1000 cycles of operation, this capacitance of the electrode can maintain 79 % of its original capacitance. Therefore, the MnOx/CNT/Ni nanocomposite electrodes with good electrochemical reversibility and high capacitance may be applied to supercapacitors in the future.

U3.10

Nano-Bending of Aligned Carbon Nanotubes.

Joseph Francis AuBuchon 1.2, Li-Han Chen2, Dong-Wook Kim2,

Andrew Gapin1.2, Chiara Daraio1.2 and Sungho Jin1.2; ¹Materials

Science and Engineering Program, University of California, San

Diego, La Jolla, California; ²Mechanical & Aerospace Engineering

Department, University of California, San Diego, La Jolla, California.

Since their discovery over a decade ago, carbon nanotubes (CNTs) have been studied for many different applications because of their exceptional electrical and mechanical properties. Carbon nanotubes have already been shown to be useful for a variety of applications like field emission devices, nano-scale electromechanical actuators, field-effect transistors (FETs), CNT based random access memory (RAM), and atomic force microscope (AFM) probes. Carbon nanotubes are potentially useful as nanoscale current carrying conductors as they can transport very high current densities on the order of 1010 A/cm2. In order to utilize CNTs as nano circuit interconnects and other device components, the ability to control their growth morphology is desired. Although vertical alignment of individual CNTs and CNT arrays during their growth has been demonstrated, there has been very little progress towards more complicated morphologies. In this work, we show the ability to use direct current plasma enhanced chemical vapor deposition to grow CNTs with sharp bends that maintain a constant tube diameter before and after a bend and the ability to grow structures with multiple bends resulting in a zig-zag morphology [1-2]. Additionally, bend angles over 90 degrees and other interesting morphologies have been synthesized. The sharp bends are achieved by strongly manipulating the electric field direction using field concentrating conductor plates. The microstructural characterization and electrical transport properties of nano-bent structures will be discussed. Zigzag structured or signally bent CNTs could be used for many applications, e.g., related to mechanical nano-springs, nano-solenoids,

or complicated circuit nano-interconnections especially where straight nanoconductors have a limited use. [I] J. F. AuBuchon, L. -H. Chen, A. I. Gapin, D. -W. Kim, C. Daraio, and S. Jin, "Multiple Sharp Bendings of Carbon Nanotubes during Growth to Produce Zigzag Morphology", Nano Lett. 4, 1781 (2004). [2] L.-H. Chen, J. F. AuBuchon, A. I. Gapin, C. Daraio, P. Bandaru, S. Jin, D. -W. Kim, I. K. Yoo, and C. M. Wang, "Control of Carbon Nanotube Morphology by Change of Applied Bias Field During Growth", Appl. Phys. Lett. 2004 (in press).

U3.11

Modification of Electronic Properties of Carbon Nanotubes. <u>Vsevolod V. Rostovtsev</u>, R. Scott McLean, Dennis J. Walls and Ajit Krishnan; DuPont Central Research and Development, Wilmington, Delaware

The current interest in applications of single-walled carbon nanotubes for the manufacture of nano-scale electronic devices is due to their unique electronic and structural properties. However, before industrial fabrication of carbon nanotube-based devices is possible, a number of problems associated with synthesis, separation and placement of tubes will need to be resolved. Furthermore, the use of carbon nanotubes in electronic devices will require fine-tuning of electronic properties of the semiconducting carbon nanotubes. We are interested in the effect of chemical functionalization on the electronic properties of CNT-based FETs. In particular, we are exploring the covalent chemistry of CNTs with diazonium salts. We have studied the mechanism of this reaction as it applies to the modification of CNT FETs and carried out detailed physical and electronic measurements of the modified devices. We find that the reaction changes the electronic parameters such as ON/OFF ratio, mobility and trans-conductance of CNT FET devices, although these changes are largely reversible. The results of our studies will be presented at the meeting.

U3.12

Synthesis of Suspended SWNTs and Their Functionalization using DNA and Gold Nanoparticles. Goo-Hwan Jeong¹, Akira Yamazaki², Daisuke Takagi², Satoru Suzuki¹, Yoshihiro Kobayashi¹, Kazuaki Furukawa¹ and Keiichi Torimitsu¹; ¹NTT Basic Research Labs., Kanagawa, Atsugisi, Japan; ²CREST, JST, c/o Dept. of Physics, Tokyo University of Science, Tokyo, Japan.

Among the various materials to functionalize carbon nanotubes, DNA has been investigated very recently both experimentally and theoretically. Their specific assembling property provides the possibility of scaffolding in a nanoscale as well as DNA mediated carbon nanotube electronics. In addition, a number of studies have also been devoted to modify surface property of carbon nanotubes via attaching various nanoparticles. From this background, we have recently performed the experimental approach to create nanotube-based novel hybrid structures using DNA and metal nanoparticles and demonstrate here the results. Ferritin as a nanoscale wet-catalyst is utilized to synthesize single-walled carbon nanotubes (SWNTs). Ferritin is covered with protein shell with a spherical shape and encapsulates iron in its inner space. Here, ferritin spincoated onto SiO2 pillar structure was thermally annealed due to protein shell elimination. Suspended SWNTs synthesized by typical methane CVD were characterized by Raman spectroscopy and scanning and transmission electron microscopy. To modify SWNTs, lambda DNA and Au nanoparticles are selected due to their specific binding ability. At first, we have successfully performed the DNA-combing process on hydrophilic silicon oxide substrate to manipulate DNA more easily. After this, the conjugation of DNA-Au nanoparticles is performed using thiol-modified DNA. In order to attaching Au particles, carboxyl group was introduced to suspended SWNTs via thermal oxidation and acidic treatment using nitric and sulfuric acid. Finally, amine group in aminopropyl-triethoxysilane (APTES) solvent was introduced to combining carboxyl group on the suspended nanotube surface. It is found that Au nanoparticles are attached along the suspended SWNTs which represent the existence of interactions between nanotubes and nanoparticles. These results can be utilized to construct site-selective nanowires or nanosenseors.

U3.13

Carbon-Nanotube and Carbon-Nanofibre Copper-Matrix Composites: Copper Deposition on CNT and CNF by an Electroless Plating Method. <u>Jean-Francois Silvain</u>¹, Philippe Richard¹, Joel Douin³, Alain Peigney², Christophe Laurent², Emmanuel Flahaut² and Jean-Marc Heintz¹; ¹Institut de Chimie de la Matiere Condensee de Bordeaux, ICMCB-CNRS, Pessac, France; ²Centre Inter-universitaire de Recherches et d'Ingenierie des Materiaux, Universite Paul Sabatier, Toulouse, France; ³LEM, ONERA, Chatillon, France.

Carbon nanotubes (CNT) and carbon nonofibres (CNF) are known to present high length diameter ratio, high strength, flexibility and high

thermal conductivity. One of the possible applications in the field of electronic devices is the thermal management, which is one of the key critical aspects of the design of multichip modules to ensure reliability. There is thus a strong need for the developments of novel heat dissipation materials having a low coefficient of thermal expansion combined with high thermal conductivity. Very high thermal conductivity CNT (close to 2000 W/mK) and high thermal conductivity CNF (close to 1000 W/mK) can therefore be used on top of conventional thermal copper heat sink or adaptive composite heat sink (Al/SiC, Cu/W, Cu/C) in order to dissipate the heat in the surface of the heat sinks and therefore avoid hot spots. Such adaptive composite heat sink (thickness ranging from 0.1 mm to 1 mm) using CNT and/or CNF can be obtained using of a) conventional tape casting process or b) conventional powder metallurgy process. This work presents the first stage of this project, namely the study of the use of electroless metal plating as a technique for coating CCVD double-walled CNT and vapor-grown CNF. Since many metals can be deposited on almost any substrate by electroless plating after a previous activation, the encapsulation of CNT and CNF by a thin copper layer has been investigated. However, because the CNT and CNF have low chemical reactivity, the nucleation and coating steps could be enhanced by pre-oxidation and pre-activation of the surface of CNT and CNF. For the pre-oxidation step, dipping time and temperature and acid bath composition have been optimized. X-ray photoelectron spectroscopy (XPS) and transmission (TEM) and scanning (SEM) electron microscopy analysis of both CNT and CNF have been performed before and after each chemical treatment. For the copper deposition step, electroless plating has been used (deposition by autocatalytic reduction of the metal onto the fibers immersed in appropriate chemical baths). Activated substrate surfaces are essential to trigger the autocatalytic reaction. Pd is most widely used as catalyst and, therefore, many methods have been developed for seeding non-active surfaces with Pd nuclei, according to the substrates or applications. The most common procedures use Sn. In this two-step method, the substrate is sensitized by immersion in an acid SnCl2 solution before the activation step with PdCl2 solution. XPS, TEM and SEM analysis have allowed the identification of the different compounds formed along the process, to describe the nucleation growth processes that take place and to optimize the different factors that play the main roles in the deposition processes.

U3.14

Microcantilever with Integrated Carbon Nanotube Strain Sensor. Jakob Kjelstrup-Hansen¹, Soren Dohn¹, Dorte Norgaard Madsen², Kristian Molhave¹ and Peter Boggild¹; ¹Department of Micro and Nanotechnology, Technical University of Denmark, Kgs. Lyngby, Denmark; ²Department of Physics and Technology, The University of Bergen, Bergen, Norway.

In this paper we present a method for integrating a carbon nanotube (CNT) in a microcantilever system. We demonstrate an approach for an integrated strain sensor, which exploits the extraordinary electromechanical properties of CNTs to achieve a conductance change upon deflection of the cantilever. The remarkable electronic and mechanical properties of CNTs have generated a strong focus on possible technological applications. Whereas numerous electronic devices and sensors have been demonstrated, relatively few nano-electromechanical systems using carbon nanotubes have been reported. Tombler et al. [1] showed that the strain ϵ , applied by pushing down on a single-walled carbon nanotube bridge using an AFM tip, can change the resistance by orders of magnitude, corresponding to a gauge factor $\Delta R/\epsilon R$ of around 10³. This is nearly ten times higher than doped silicon, which is used in integrated piezoresistive silicon strain sensors fabricated by conventional photolithography techniques, such as in Ref. [2]. In this work we investigate the possibility of using a multi-walled CNT integrated on a microcantilever as a strain sensor. A high-resolution manipulation setup equipped with microfabricated manipulation tools is used to pick up an individual multi-walled CNT and position it near the clamped end of a silicon oxide cantilever, aligned with the length axis. A nanowire is then positioned across the nanotube, thereby acting as a shadow mask during deposition of metal electrode material onto the structure. Subsequent removal of the nanowire leaves two metal electrodes only connected through the nanotube that spans a 500 nm gap. Hence, the CNT is connected mechanically as well as electrically. A linear deflection of the cantilever's free end is translated into surface stress, which allows for small and precise values of tensile strain to be applied to the nanotube with negligible transverse deformation or bending. From measurements performed while deflecting the cantilever the gauge factor is found to be between 20 and 500. We discuss the possibilities of improving the reproducibility as well as fabricating CNT-based force sensors on a large scale. References [1] T. W. Tombler et al., Nature, 405 (2000), pp. 769-772 [2] J. Thaysen et al., Sensors and Actuators, 83 (2000), pp. 47-53

<u>U3.15</u>

Hybrid Architectures from Aligned Carbon Nanotubes on

SiO₂ Microsphere Assemblies: Fabrication and Alignment Mechanism. Saurabh Agrawal¹, A. Kumar¹, A. A. Farajian², M. J. Frederick¹, Y. Kawazoe² and G. Ramanath¹; ¹Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Institute of Materials Research, Tohoku University, Sendai, Japan.

Growth of aligned carbon nanotubes (CNTs) is essential for their incorporation into micro electromechanical, electronic and optoelectronic devices. Here, we report the growth of novel hybrid structures comprised of aligned CNT bundles on silica micro- and nano-sphere assemblies, and discuss the effects of substrate shape and size on CNT alignment based on tight binding calculations. Aligned CNTs were grown by a substrate-selective chemical vapor deposition technique using a xylene-ferrocene mixture on drop-coated films of silica spheres of 6.8 μ m to 160 nm diameter assembled on Si(001). Dense, aligned CNT bundles grow on $> 4 \mu \text{m}$ -diameter SiO₂ spheres, forming aligned CNT bundles of size limited by the microsphere diameter. No CNT growth is observed on silicon. Novel configurations, namely, pillars, walls, and films of aligned CNTs can be obtained from isolated microspheres, their 1-D chains, or 2-D array assemblies. We also observe coconut shell like morphologies of CNTs curling around the microsphere. The resultant CNT-silica hybrid building blocks are amenable to further chemical manipulation, functionalization, and assembly. Close-packed microsphere assemblies result in vertically aligned CNT bundles due to support from the adjacent bundles. Increasing the separation between microspheres does not have any effect on the alignment of the CNTs grown from a given microsphere, but results in randomly oriented hybrid structures. CNTs grown on < 4 μ m-diameter microspheres are not aligned even within each microsphere, and exhibit a wool-like morphology. Further decreasing the microsphere diameter decreases CNT density, and no CNT growth is observed on < 330-nm-diameter spheres. Based upon our experimental observations, and tight-binding calculations supplemented by van der Waal's potentials, we propose a model to describe the dependence of growth process on the sphere diameter. Flatter surfaces of the larger spheres allow the CNTs, growing in an explosive fashion, to be aligned due to energy decrease obtained by coordinated van der Waal's interactions between adjacent tubes. Imposing spatial constraints, e.g., by increasing sphere curvature, decreases the number of CNTs growing along the same direction. Instead, the CNTs grow radially in a random fashion. At very high curvatures, amorphous carbon deposition is favored over $\tilde{\text{CNT}}$ growth.

U3.16

Monitoring of Multi-walled Carbon Nanotubes Growth by Tapered Element Oscillating Microbalance. <u>Vladimir Svrcek</u>, Jullien Amadou, Thierry Dintzer, Coung Phan-Huu, Benois Louis, Dominiques Begin and Marc J. Ledoux; LMSPC-ECPM, 25, rue Becquerel, F67087 Strasbourg, France.

The carbon nanotubes (CNTs) itself were subjected to increased attention as a unique 1D nano-material in last decade. The reasons are simple, they have characteristics and properties which make them a promising material in several application fields. In particularly, the unique optical properties of carbon nanotubes are due to the one dimensional confinement of electronic states, resulting in so-called van Hove singularities in the nanotube density of states. One of the most promising approach of multiwall CNTs fabrication at industrial scale is by chemical vapor deposition (CVD) at temperatures varied between 600 °C and 800 °C depending on catalyst (Fe, Ni, Co), flowing ratio of gas hydrogen (H2) and ethane (C2H6)). However, to fabricate well defined and good quality CNTs at industrial scale it is necessary to well understand the growing process and most importantly initial stages of growing. To obtain useful and desired measurements, the instrument must simulate a packed bed reactor in which the reactive gas flow through the bed, making ready and equal contact with all the particles of the sample. The technique that can achieve this high degree of contact and permit us to monitor of growing process is Tapered Element Oscillating Microbalance (TEOM) pulse mass analyzer. As show our preliminary results unique capacity of TEOM allow us to record relatively small weight changes and permit us to monitor and we believe better understand growing processes of CNTs. In our experience, available TEOM is able to measure desirable weight changes accurately (less than 1 mg at 700 °C). Even more, the salient features of TEOM are the measurements of the rates of uptake and release is done such way that they depend solely on the intrinsic chemical and physical properties of the material that relate to hydrogen storage. This means, in particular, that they are measured without complication from the effects of mass transfer limitations such as would occur in instruments in which the sample is simply placed in a weighting pan with the reactive gas passing over it which is case of standard CVD. In the present contribution we will report results of growing multiwall CNTs by TEOM and compare to CVD growth. Iron-based catalyst is used to growth multiwall CNTs. We will focus our study on three aspects of growing process. First, we will evaluate the temperature when the first CNTs appears. Second, we will investigate influence of the temperature on the quality and

quantity of obtained CNTs. Third, we will report results of dependence of ratios H2/C2H6 on growing process. Finally, we will compare and discuss in details the influence of structural properties of CNTs on the photoluminescence at room temperature growth at different conditions mentioned above.

U3.17 Abstract Withdrawn

U3.18

Single- and Multi-walled Carbon Nanotube Field Effect Transistors for in-situ Transmission Electron Microscope Analyses. Taekyung $\operatorname{Kim}^{1,2}$, Eric Olson², Ivan Petrov² and Jian-Min Zuo¹.²; ¹Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²The Frederick Seitz Materials Research Laboratory, Urbana, Illinois.

Since the discovery of carbon nanotubes by S. Iijima¹ in 1991, much effort has been exerted to understand the structure and the electronic structure as well as the electrical transport phenomena of the carbon nanotubes (CNTs). Scanning tunneling microscopy (STM) has been predominantly applied to investigate the structures and electronic properties of single-walled nanotubes (SWNTs)² due to the atomic resolution imaging and electronic property analysis capability of STM. However, STM is not suitable for the study on the inner structure of nanotubes because STM can only see the outer shell. Transmission electron microscope (TEM) has atomic resolution imaging capability and is appropriate for the study of multi-walled carbon nanotubes (MWNTs). One drawback is the sample thickness limitation due to the transmission probability of electrons though the specimen. This sample thickness usually limits the application of TEM to in-situelectrical measurements in the TEM. In order to investigate the structure and electronic properties of SWNTs and MWNTs in the TEM, a new type of CNT device is needed. Here, we present in - situtransmission electron microscope study of the electrical transport and the structure of the CNTs. In order to perform the experiments, we have fabricated a bottom-gated structure device³ with a trench ranging $1\sim 2~\mu m$ so as to be able to be used inside the TEM (JEOL 2010F, Peabody, MA). SWNTs and MWNTs were dispersed on top of the electrodes (Ti) and the electrical transport measurements were performed outside the TEM at room temperature to find the appropriate devices for TEM study. Inside the TEM, the structure analyses as well as the electrical measurements were performed by applying high resolution TEM and nanoarea electron diffraction (NED) techniques⁴. By this approach, we have determined the diameters of the tubes accurately while the electrical transport measurements and confirmed the helicities from the diffraction patterns afterwards. References 1. S. Iijima, "Helical microtubules of graphitic carbon", Nature, 354, p56 (1991) 2. Jeröen W. G. Wildoer et. al., "Electronic structure of atomically resolved carbon nanotubes" Nature, **391** p59 (1998) 3. A. Javey et. al., "Carbon nanotube transistor arrays for multistage complementary logic and ring oscillators", NanoLetters, 2 (9), p929 (2002) 4, J. M. Zuo et. al., "Atomic resolution imaging of a carbon nanotube from diffraction intensities", Science, 300, p1419 (2003)

U3.19

Nanoscale DNA Biosensor for Respiratory Syncytial Virus (RSV) Diagnosis. Arun Kumar¹, Souheil Zekri², Ashok Kumar^{1,2} and Shree R. Singh³; ¹Nanomaterial and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; ²Department of Mechanical Engineering, University of South Florida, Tampa, Florida; ³Department of Mathematics and Science, Alabama State University, Montgomery, Alabama.

Respiratory syncytial virus (RSV) is a major cause of respiratory illness in young children. RSV infection produces a variety of signs and symptoms involving different areas of the respiratory tract, from the nose to the lungs. A novel electrochemical DNA sensor was deviced using single walled functionalized carbon nanotubes to detect the RSV infection. The single walled carbon nanotubes are functionalized with a carboxyl group (SWCNT-COOH) and covalently linked with specific single strand DNA (ssDNA) of Respiratory Syncytial Virus (RSV) using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). The hybridization with the complimentary DNA (cDNA) probe was carried out by exposing the ssDNA to a solution containing the cDNA in the presence of a redox intercalator daunomycin. Cyclic voltametry and differential pulse voltametry techniques was explored to detect the DNA hybridization The excellent surface area to volume ratio of single walled carbon nanotube along with its outstanding charge transport characteristics are the main factor in improving the binding sites for hybridization process. Increase in binding sites further contributed to enhance the sensitivity of the electrode. Glassy carbon electrode modified with single walled carbon nanotubes (SWCNT) attached with ssDNA used as a working electrode (probe). Where as platinum wire and Ag/AgCl are used as a counter electrode and reference electrode respectively.

Three electrodes cell configuration were used to measure the current and voltage of the non-functionalized SWCNT, functionalized SWCNT, non-hybridized and hybridized probes. The modified carbon naotubes are characterized with SEM, TEM and FTIR. Further experiments are in progress in our laboratory.

U3.20

Fluorescent Labeling of Single-Walled Carbon Nanotubes by Quantum-Dots. Sumit Chaudhary¹, Joong Hyun Kim², Krishna Veer Singh² and Mihrimah Ozkan^{1,2}; ¹Electrical Engineering, UC Riverside, Riverside, California; ²Chemical and Environmental Engineering, UC Riverside, Riverside, California.

The research towards carbon nanotube based bio, opto, chemical and electronic devices can be tremendously benefitted by their visualization and manipulation under simple optical microscopes. We demonstrate the fluorescent microscopy visualization of single-walled carbon nanotubes (SWNTs) using CdSe-ZnS core-shell nanocrystals (Quantum-Dots (QDs)). Stable surfactant dispersions of SWNTs were employed for this study. QDs were functionalized with linear hydrophilic mercaptoacetic acid ligands and then homogenized with SWNT dispersions. By virtue of the electrostatic interaction between the shell of QDs and the surfactant chains present of nanotube surface, the QDs fluorescently label the sidewalls of these SWNTs. Using this technique, we have identified different cluster sizes of SWNTs and their ropes using simple fluorescent microscopes. Transmitted brightfield microscopy and Scanning/Transmission Electron microscopy further reinforce our observations.

U3.21

Dynamic Observation of Field Emissions from a Single Multi-Walled Carbon Nanotube by Transmission Electron Microscopy. Tadashi Fujieda¹, Kishio Hidaka¹, Mituo Hayashibara¹, Hiroaki Matsumoto², Takeo Kamino², Mitsuo Sato³, Hidekazu Abe⁴, Testuo Shimizu⁴ and Hiroshi Tokumoto^{4,5}; ¹Materials Research Laboratory, Hitachi, Ltd., Hitachi, Japan; ²Hitachi Science Systems, Ltd., Hitachinaka, Japan; ³Hitachi High-Technologies, Ltd., Hitachinaka, Japan; ⁴National Institute of Advanced Science and Technology, Tsukuba, Japan; ⁵Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan.

The stability of the emission current is important for applying carbon nanotube (CNT) electron emitters to electron beam instruments. Structural change at the tip of the CNT in terms of the stability of the emission current is an important subject in understanding the mechanism of the current fluctuation. Though it is expected that the emission sites are closely related to the tip form of the CNT, this relation is not clear. Here in this study, we used a Lorenz microscopy method in transmission electron microscopy (TEM) operational modes to observe emission sites near the tip-end of a single multi-walled carbon nanotube (MWNT) while measuring the field emission currents. The emission site was observed as a bright spot near the tip-end of a MWNT. The bright spot appeared above electric fields of 0.68V/um as electrons were emitted. The bright spot is assumed to be related to the emission site on the MWNT. A drastic fluctuation was observed in the emission current above a few tens of uA, which was closely related to structural changes at the tip of a MWNT. The layers of the MWNT were peeled off during field emission and they worked as the second emission site by the concentration of the electric field. We will also present the behavior of an iron catalyst at the tip-end of a MWNT during field emission.

U3.22

Thermal Conductivity of Single-Walled Carbon Nanotubes with Carbon 13 Isotopes and with Junctions. <u>Junichiro Shiomi</u>, Yuki Taniguchi and Shigeo Maruyama; Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan.

The theoretically high thermal conductivity (k) of single walled carbon nanotubes (SWNTs) plays a key role in the many of the prospective industrial applications. In the actual applications, SWNTs may have defects, impurities and junctions, which may limit the values of k. These nano-scale defective structures, having scales of the order of the phonon mean free path, are expected to have strong influence on thermal properties of the bulk material. The decrease of k is considered to result from the scattering of phonons at structure interfaces, when the operated temperature is below the Debye temperature. In the current study, molecular dynamics simulations were performed to investigate the nano-scale axial heat conduction of (5,5)-SWNT by visualizing the spatio-temporal behavior of phonons. The carbon interactions in an SWNT were expressed by the Brenner potential. The defective nano-structures were represented by mixing C13 isotopes to a C12-SWNT either at random or in order. When the system is at equilibrium, k can be well computed through the Fourier's law. Non-Fourier aspects of the heat transfer in the non-equilibrium SWNTs are also examined in the latter part of the

present study. The random mixing of C13 isotopes to C12-SWNTs results in the decrease of k. The results show not only that k decreases against the fraction of mixed C13, but also that the value of k is dependent on the structure of C13 clusters, seemingly on their sizes. However, the random nature of the study leaves us with uncertainties of the size dependence. In order to highlight the influence of axial scales of the defects, another set of simulations were performed by mixing C13 in order. In this case, SWNTs consist of C12 and C13 periodically connected with certain interval thickness. By shortening the interval length from about 10 nm, k was observed to decrease with the interval thickness. Consistently to the experiment reported by Huxtable for Si/SiGe super-lattices, the phonon scattering increased with the number of intervals per unit length. The simulation allowed us to decrease the interval thickness further which resulted in finding the critical interval thickness (2 nm) below which k begins to increase. The spectral analysis reveals that, below the critical interval thickness, the system behaves not as connections of cells with individual dispersion relations, but rather as a diatomic crystal with continuous spectra in axial direction. When nano timescale heat transport phenomena in SWNT system take place, since the timescale becomes comparable to the relaxation time of the heat flow, Fourier's assumption should not hold any more. The non-Fourier aspect of the heat transfer in SWNTs was examined by applying a local heat pulse with duration ranging from 40 fs to 4 ps. The results of the simulations exhibit the heat waves of selected phonons traveling from the heated end of the SWNT to the other. The characteristic properties of the heat flow will be discussed.

U3.23

Selective Adhesion and Alignment of Osteoblasts on Aligned Carbon Nanotubes/Nanofibers. Dongwoo Khang¹, Minbaek Lee³, Sun Namkung³, Seunghun Hong³ and Thomas J. Webster²;

¹Department of Physics, Purdue University, West Lafayette, Indiana;

²School of Biomedical Engineering, Purdue University, West Lafayette, Indiana;

³School of Physics and NANO Systems Institute, Seoul National University, Seoul, South Korea.

There has been an increasing interest for self-assembled, functionalized, hybrid carbon nanotube based materials for controlling specific cell interactions pertinent for tissue engineering applications. This is because they are light weight and strong, have high conductivity, and can mimic the dimensions of proteins (such as collagen in our tissues). One of the most promising applications of carbon nanotubes/nanofibers is for regeneration of the human skeleton system. In this work, we describe the first successful selective adhesion and alignment of osteoblasts (bone-forming cells) on hydrophobically aligned carbon nanofiber/nanotube arrays on both a polymer matrix and a SiO2 substrate. To align carbon nanofibers (CNFs) on polymers, we developed a novel imprinting method. In addition, we used surface-templated assembly to aligned single wall carbon nanotube (swCNT) arrays on a SiO2 substrate. On both substrates, results demonstrated for the first time that hydrophobically aligned carbon nanofiber/nanotube arrays can be used to direct osteoblast morphology important for the development of a novel biocompatible substrate with strong potential for regenerative bone applications. These results also illustrated the high interactions osteoblasts have with surfaces containing aligned carbon nanotubes/nanofibers. Due to their ability to mimic the dimensions of collagen and hydroxyapatite as well as their alignment in bone. aligned carbon nanotubes/nanofibers in a polymer or Sio2 matrix may be promising bone tissue engineering materials.

$\frac{\text{U3.24}}{\text{Abstract Withdrawn}}$

U3.25

Effects of UVO Treatment and Functionalization of MWNTs on Mechanical Performance and Residual Stresses in Polymer Composites. Man-Lung Sham and Jang-Kyo Kim; Department of Mechanical Engineering, HK Univ Sci & Technol, Kowloon, Hong Kong.

Carbon nanotubes (CNTs) possess exceptional structural and transport properties, such as superior strength, modulus, electrical and thermal conductivities along with low density. There have been significant efforts toward exploiting these unique properties by incorporating them into a polymer matrix material. These composites hold the promise of delivering superior mechanical properties and multi-functional characteristics. The potentials of employing CNTs as reinforcements has been severely limited, however, because of the difficulties associated with dispersion of entangled CNTs during processing and the poor interfacial interactions between the CNTs and polymer. The residual stresses generated due to thermal mismatches between the composite constituents are detrimental to mechanical and functional performance of composites in many critical applications. The main objectives of this paper are twofold: the first is to functionalize the multi-walled carbon nanotubes (MWNTs) by

applying ultra-violet/ozone (UVO) treatment on the MWNTs, followed by mixing in a triethylenetetramine (TETA) solution to attach amino function groups; and the second is to study the mechanical/functional properties and the evolution of residual stresses in MWNT reinforced epoxy composites. The UVO treatment is considered to be moderate compared to many oxidative processes using strong acids such as HNO3, H2SO4 or a mixture of them, which may provide linkage between the CNTs and organic molecules in the polymer. However, the acid treatments often create defects on the side wall and end caps of CNTs in otherwise perfect structures, which were shown to be detrimental to mechanical performance of nanocomposites. Fourier transform infrared spectroscopic analysis of the functionalized MWNTs shows the changes in chemical functional groups, in particular the hydroxyl and carboxyl groups, on the surface with the use of UVO and TETA treatment. To achieve uniform dispersion of MWNTs within epoxy resin, acetone was used as dispersant and a high speed shear mixer and an ultrasonicator were used at various stages during the fabrication process. The effects of UVO treatment and functinalization of CNTs on mechanical properties of composites were measured. The changes in composite strength and modulus were attributed to the modification of the CNT-epoxy interfacial adhesion, which was in turn influenced by the UVO treatment. The bi-material strip bending (BMSB) experiment was performed in a dynamic mechanical analyzer (DMA) chamber to in-situ monitor the curvature changes in the nanocomposite-glass strip specimen. Based on the constitutive relation between the residual stress and the elastic modulus change with temperature, the coefficients of thermal expansion of the composites were estimated and compared with those measured from the thermo-mechanical analysis. The implications of the residual stress evolution in practical applications of CNT reinforced polymer composites are discussed.

U3.26

Electrochemical Gating of Aligned Single-Walled Carbon Nanotube Network Field-Effect Transistors. Seung-Beck Lee¹, Bong-Hyun Park¹, Chae-Hyun Lim¹, Sung-Min Kang¹, Il-Shik Nam¹, Jong-Wan Park^{2,1} and Cheol-Jin Lee¹; ¹Nanotechnology, Hanyang University, Seoul, South Korea; ²Material Science and Engineering, Hanyang University, Seoul, South Korea.

Electrochemical gating of individual multiwalled and single-walled carbon nanotubes (SWNT) has recently gained much attention due to its high gating efficiency and its potential application as ionic sensors. However, nanotube networks, which have demonstrated effective gas sensing operation, could have higher application possibilities due to their relative ease of fabrication. Here, we report on electrochemical gating of aligned SWNT network field-effect transistors. The SWNTs were prepared by chemical vapor deposition and dispersed in iso-propanol. Interdigitated Cr/Au electrodes were fabricated on highly doped Si substrates with 100 nm thermal oxide. A drop of SWNT solution was placed on the electrodes and 10 Vpp, 5 MHz ac bias was applied between the source and drain electrodes for 10 min to align the SWNTs between the contacts. This produced aligned SWNT network with 3 $\mu \text{m--}2$ density. Using the substrate-backgate, p-type field-effect transistor operation was demonstrated with minimal leakage currents. We used 10 mM NaCl as the electrochemical gating solution and the electrolyte potential was modified using Ag electrodes. At positive gate voltages the current transport through the device was suppressed. As the applied electrolyte gate voltage increased in the negative direction the current through the device was also increased. When -0.9 V was applied to the electrolyte gate, the source-drain current at -0.8 V bias voltage increased from -0.4 μA to -50 μA giving an on-off current ratio greater than 100. The threshold voltage shifted from -0.85 V to -0.1 V as the source-drain voltage increased from 0.2 V to 0.8 V. This may be due to the ions in the electrolyte actively regulating hole conduction by donating or removing charge from the SWNTs. Also since transport between interconnected nanotubes within the device takes place by means of tunneling, the ions may act to change the potential height of the tunnel barrier between SWNTs by changing the population of ions along the interface between adjacent SWNTs. We will present electrochemical gating of aligned SWNT networks with differing SWNT density and electrolyte concentrations.

U3.27

Mechanical Properties of Functionalized Carbon Nanotubes based Polymer Nanocomposites. Luqi Liu and Daniel Hanoch Wagner; Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

Carbon nanotubes are potentially ideal reinforcement for high performance polymer nanocomposites due to their low density, larger aspect ratio, high strength, stiffness and flexibility. Both theory and experiment indicate that the interfacial properties between nanotubes and polymer matrix are key issues in this respect. In this work, nanocomposites were prepared using functionalized carbon nanotubes incorporated into semi-crystalline thermoplastic poly(vinyl alcohol)

(PVA) and epoxy resin (Epon 828/D2000 and Epon 828/T-403) matrices, respectively, through a simple mixing process, where H-bonds and covalent bonds are created as a bridge at the nanotube-polymer interface. In-situ Micro-Raman tensile tests demonstrate that, in comparison with pristine carbon nanotubes, efficient load transfer is realized using functionalized carbon nanotube as reinforcement. Further mechanical measurements show that (1) using PVA as the matrix, a 78% tensile modulus improvement is obtained after addition of less than 1 wt % carbon nanotubes; (2) using epoxy resin as the matrix, a 28% improvement of the tensile modulus is obtained using 1 wt% nanotubes; (3) impact resistance (thus, toughness) is improved by 50% using 1 wt% nanotubes. These results imply that functionalized carbon nanotubes can be used as an effective reinforcing phase in future high performance polymer nanocomposites.

U3.28

Synthesis and Microstructure of Single-Walled Boron Nitride Nanotubes. Wei-Qiang Han, Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

Since the discovery of fullerene and carbon nanotubes, similar structures have been theoretically predicted for boron nitride (BN) and then experimentally prepared. Electron structure of BN nanotubes is very different from that of carbon nanotubes because of the wide gap of BN sheets as opposed to the zero-gap in graphite sheet. In contrast to carbon nanotubes, which have electronic properties depending on their structure, the band gaps of BN nanotubes are predicted theoretically to be nearly independent of their radius and chirality. The predicted structural independence of the electronic properties and thermal stability of BN nanotubes open promising opportunities for application in nanoelectronic and nanophotonic devices. Mutil-walled BN nanotubes have been made by arc-discharge, laser ablation, CVD, carbon nanotubes substitution-reaction and ball-milled methods. Single-walled BN nanotubes have been synthesized by laser ablation, arc-discharge and carbon nanotubes substitution-reaction, but either the purity is quite low or single-wall nanotubes mixed with multi-walled nanotubes. Here I describe a simple method which involving a gas-solid reaction to efficiently produce single-wall BN nanotubes. High-resolution TEM, electron diffraction patterns and electron energy loss spectrometer are used to characterize the microstructure and composition of the product. Acknowledgment: W. H. acknowledges support of this work by the U. S. DOE under contract DE-AC02-98CH10886.

U3.29

Complex Crystalline Patterns Induced by Single-Walled Carbon Nanotubes (SWNTs). Caroline Woelfle¹ and Richard O. Claus²; ¹Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia; ²Electrical and Computer Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Formation of complex patterns resulting from the crystallization of proteins or from the self-assembly of nanoparticles on a uniform surface is a fascinating phenomenon. Both types of patterns can be induced by the drying of a droplet of protein or colloidal solution on a substrate. In the case of proteins, it is an essential step for the determination of their structure. For nanoparticles, it leads to the creation of new material properties and behavior, for example, the topology of nanoparticles network may be responsible for different electrical or magnetic properties. The emergence of these morphologies is strongly dependent on critical parameters like concentration of the solution, precipitant, pH, ionic strength, temperature, and surface properties. We report on the formation of complex crystalline patterns induced by the presence of SWNTs in a solution of poly (amidoamine) (PAMAM) dendrimer. PAMAM dendrimers are highly branched globular macromolecules possessing a large amount of amino groups that enable the solubilization of SWNTs. The influence of dendrimer and SWNTs concentrations, as well as physical parameters like pH and ionic strength are investigated. The similarity of the shape and size of the PAMAM dendrimer molecule with globular proteins leads us to believe that SWNTs could represent a new type of additive for obtaining protein crystallization. Acknowledgement: This material is based upon work supported by, or in part by, the U.S. Army Research Laboratory and the U.S. Army Research Office under grant number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI.

U3.30

Transmission Electron Microscopy of Interfaces between Carbon Nanofibers and Metal Thin Films. Hans Yoong¹, Yusuke Ominami¹, Nobuhiko Kobayashi¹, Kevin McIlwrath³, Quoc Ngo¹, Alan M. Cassell², Jun Li² and Cary Y. Yang¹; ¹Center for Nanostructures, Santa Clara Univ, Santa Clara, California; ²Center for Nanotechnology, NASA Ames Research Center, Moffett Field, California; ³Hitachi High Technologies America, Pleasanton,

California.

We report detailed structural and chemical analyses of the interfaces between carbon nanofibers (CNFs) and metal thin films using scanning transmission electron microscopy (STEM). CNFs with potential applications as interconnects in integrated circuits were fabricated on e-beam-evaporated metal films on silicon (100) substrates. In particular, the CNFs were vertically grown on chromium thin films by plasma-enhanced chemical vapor deposition using ethylene and ammonia with nickel catalysts. Sample preparation was accomplished utilizing a 40kV Focused Ion Beam system with a variable accelerating voltage. To maintain the integrity of the forest-like arrays of CNFs for STEM analysis, during the final thinning stages a 10kV (FIB) post ion beam polish was used to reduce amorphous damage to the cross-section surface so that imaging and energy dispersive X-ray (EDX) analysis would be optimized. Unlike conventional thinning techniques, such as ion milling, FIB can prepare materials with a wide Z difference at a desired location with a positional accuracy of <50nm. The STEM images and X-ray microanalysis reveal a thin amorphous layer of metal alloy between the Cr film and vertically-aligned CNFs. Current-voltage measurements show that the formation of such an interfacial structure during the growth process has a significant impact on electrical conduction through the CNFs.

U3.31

Encapsulated Vertically Grown Carbon Nano-Tubes for Submicron and Nano-Lithography. Yaser Abdi, Javad Koohsorkhi, Pouya Hashemi, Shamseddin Mohajerzadeh, Hadi Hosseinzadegan and Leila Rezaei; ECE Dept., Thin Film Lab, University of Tehran, Tehran, Iran.

We report a novel technique for nanolithography using vertically grown nickel seeded carbon nano-tubes (CNT) on silicon substrates. The field emission characteristic of carbon nano-tubes is utilized to create nano-scale features. The narrow electron beam, emitted from encapsulated CNT's, is the basis of this lithography process. The structure used here consists of vertical CNT's encapsulated with titanium-dioxide and chromium (or silver) bi-layers. While CNT is responsible for electron emission, the surrounding metal (separated from inner CNT by a dielectric layer) acts as a self-defined gate to control the level of electron emission as well as an integrated electrostatic lens for beam shaping. Fabrication process starts with e-beam evaporation of a 5nm layer of nickel on (100) silicon substrates. The deposition is performed at a base pressure of 10-6torr, a deposition rate of 0.4Å/sec and at a temperature of 300°C. Ni-coated samples are then patterned using standard photo-lithography and are placed in a DC-PECVD chamber to perform CNT growth. The pre-growth treatment is done at a pressure of 1.6torr in the presence of H2 and at a temperature of 650°C. After 15mins of H2 blow, plasma turns on with a current of 30mA to form nano-islands with a typical size of 10-50nm. Immediately after this step, acetylene (C2H2) is introduced into the chamber to initiate the growth at a pressure of 1.8torr. After unloading the samples, they are coated with a 200nm of titanium oxide using an atmospheric pressure CVD reactor at a temperature of 220°C. The gate electrode is composed of a $0.1\mu m$ -thick layer of Cr (or Ag) deposited by e-beam evaporation at temperature of 350°C. Final fabrication requires one step of chemical mechanical polishing followed by plasma ashing to open the nano-tubes and to form partially hollow nano-pipes. This step is crucial in obtaining beam-shape emission of electrons from nano-tubes and it is achieved by plasma ashing of exposed carbon in plasma. SEM and TEM were used to study the grown nano-structures. By applying proper voltage between carbon tip (cathode) and a photoresist-coated substrate (anode) electrons are emitted from negative side and nano-size features are developed on the resist-coated substrate. Using this technique we have drawn lines with a width of 120nm and a length of 5-10 μ m. Also round dots with sizes smaller than $0.4\mu m$ were realized. SEM analysis confirms the evolution of such nano-metric features in a reproducible fashion. Straight lines with a thickness less than 100nm have also been achieved, although thinner features are expected by more proper control on the gate electrode and distance between CNT emitter and resist-coated substrates. Width of the features depends mostly on the diameter of grown CNT's. Preparing rectangular features with controlled spacing, suitable as the gate of deep-submicron MOSFET's is being pursued.

U3.32

Controlled Growth and Post-growth Processing of Carbon Nanotube Arrays. Aijun Yin, Karl Hanson, Hope Chik and Jimmy Xu; Engineering, Brown University, Providence, Rhode Island.

Carbon nanotubes (CNTs) have become one of the most fascinating and attractive nanostructures for a variety of potential applications [1]. Future advances will require a fabrication method capable of producing uniform CNTs controllably with well-defined and reproducibility of their properties. A nanopore-template based growth

approach [2] has proven to be effective in providing us with nanotubes of uniform diameter, length and periodicity. These together with the desired parallel alignment, and the spatial and electrical isolations offer us a promising material base for many applications such as mechanical resonators, field emission displays and bio-sensors etc. However, to build up from a good base material into a good base technology, it is imperative to gain more control over the growth process and the post-growth processing in order to be able to alter selectively and controllably the geometric and physical characteristics of the individual tubes without losing the uniformity and ordering. The post-growth processing steps could be as important as the growth itself. For example, nanotubes could bundle together to form haystack like structures or remain separate and stand straight up, depending on how they are processed post-growth. Here, we present approaches for controllable growth of 1-D and 2-D CNT arrays with varied CNT diameters, lengths and periodicities, as well as a new post-growth treatment process that has resulted in well-aligned and spatially separated free-standing nanotube arrays. A distinctive advantage of the template-based growth process is in that a good degree of control can be gained from controlled variation of the template. For 1-D array fabrication, we insert a thin layer of pure Al film between a silicon substrate and a SiO2 protection layer, while for 2-D array, a pure Al foil was used. A by now standard two-step anodization method is used to form the nanopore array in alumina. Two approaches can then be deployed to vary the key parameters - diameters and interpore distances: (i) by applying different anodization voltages with different electrolytes; (ii) by widening the pore via wet-etch. With these two appraoches, we can controllably vary the pore diameter and the periodicity between 10~250 nm and 20-500nm, respectively. With a well-defined growth template, one can proceed to grow the CNTs by a standard CVD [2]. Post-growth processing normally begin with a dry-etching process (via RIE or ion milling) followed by a chemical wet-etching process to expose the nanotubes out of the template by a certain length. To counter the natural tendency of bundling of the exposed CNTs, we developed a new etching recipe with an added dispersant, resulting in well exposed CNT arrays [3]. Reference 1. A. Huczko, Appl. Phys. A74, 617, 2002 2. J. Li, C. Papadopoulos, J. M. Xu, and M. Moskovits, Appl. Phys. Lett., 75, 367, 1999. 3. A. Yin, H. Chik, and J. M. Xu, IEEE Trans. Nanotechnol. 3, 147, 2004

U3.33

Topological Forms of Carbon and Carbon-Metal Superstructures: From Nanotubes to Toroids and Nanodiscs. Vladimir V. Kislov and Igor V. Taranov; Institute of Radioengineering & Electronics, Russian Academy of Sciences, Moscow, Russian Federation.

A continual model of topologically closed carbon and carbon-metal nanostructures is presented. This model considers mechanical properties of chemical bonds and external pressure of gas phase. A sequence of transitions for various topological forms of possible superstructures is described for continuous growth of external pressure (from vacuum to atmospheric): from sphere to slightly pressed shape, then via growing negative curvature of "anti-caps" to toroidal structures and then via flattening and thinning of toroids and growth of their diameter to nanorings ("crop-circle" structures [1]). Some of these structures have been predicted and discovered earlier [2, 3], some, like topologically closed nanocapsules (carbon nanodiscs), with specific chain of geometrical transformation of shape, has been observed by us recently [4, 5]. Incorporation of metal atoms into carbon structures seems to soften mechanical properties of superstructures with some optimal ratio for producing complex topologies at atmospheric pressure. The results of calculations fit well with our experimental observations, including nanotoroids and nanocapsules (size from 10 to 40 nanometers) for both carbon and carbon-metal superstructures at atmospheric pressure and room temperature [4, 5]. Literature: [1]. J. Liu, H. Dai, J. H. Hafner, D. T. Colbert, R. E. Smalley, S. J. Tans, C. Dekker, Fullerene "crop circles", Nature, 1997, 385, 780. [2]. M. Terrones, W.K. Hse, J.P. Hare, H.W. Kroto, H. Terrones, D.R.M. Walton, Graphitic structures: from planar to spheres, toroids and helices, Phil. Trans. R. Soc. Lond. A, 354, 2025 (1996). [3]. V. Kislov, Rings of the strings - topologically closed superstructures of nanoclusters, Nano-8, 8-th International Conference on Nanometer-Scale Science and Technology, June 28 July 2, 2004, Venice, Italy [4]. V. Kislov, B. Medvedev, Experimental observation of carbon and carbon-metal nanotoroids, 2005 MRS Spring Meeting, March 28- April 1, San Francisco, CA, USA. [5]. V. Kislov, Carbon and metal superstructures at nanoscale: from nanotubes to helices, toroids and nanodiscs, 2005 MRS Spring Meeting, March 28- April 1, San Francisco, CA, USA.

<u>U3.34</u>

Magnetic Susceptibility of Carbon Nanotubes and Peapods. Younghyun Kim and David E. Luzzi; Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Various purification methods have been developed to remove impurities such as amorphous carbon and ferromagnetic catalyst particles from carbon nanotubes. Still, purified samples do not have sufficient quality for various analyses, especially magnetic-related analyses such as Nuclear Magnetic Resonance or magnetic susceptibility measurement, due to the presence of residual ferromagnetic catalyst particles. Here, we report a new purification method, which combines conventional air oxidation-hydrochloric acid treatment with magnetic filtration. By this method, we reduce ferromagnetic catalyst content from 2.30 wt. % in as-received material to 0.022 wt. % in purified material as measured from 9 Tesla magnetic hysteresis curves. This small residual ferromagnetic particle content in magnetically purified buckypaper allows the recovery of the inherent diamagnetic property in magnetic fields over 0.04 Tesla. The purification method provides the additional benefit of a substantial improvement in SWNT content (166%) compared to as-received material. With a mean diameter of 1.4 nm, the magnetically purified sample was found to be a good material for filling with C60, where filling efficiency was measured to be over 70 %. Using this novel diamagnetic and ready-to-fill SWNT buckypaper, we report magnetic susceptibility measurement on SWNTs and C60 filled peapods as a function of temperature.

U3.35

Bulk Synthesis of Large Diameter Single-Walled Carbon Nanotubes at Atmospheric Pressure in the Absence of Sulphur. Fabio Lupo¹, Julio Alejandro Rodriguez Manzo², Adalberto Zamudio², Ana Laura Elias², Yoong Ahm Kim³, Takuya Hayashi³, Hiroyuki Muramatsu³, Humberto Terrones², Morinobu Endo³, Manfred Ruhle¹ and Mauricio Terrones²; ¹Max-Planck-Institut fuer Metallforschung, Stuttgart, Germany; ²Advanced Materials Department, IPICyT, San Luis Potosi, San Luis Potosi, Mexico; ³Faculty of Engineering, Shinshu University, Nagano, Japan.

We describe the synthesis of ropes consisting of single-walled carbon nanotubes (SWCNTs) of large diameters (2-3 nm OD) in high yields. The method involves the thermolisis of ferrocene (FeCp₂) - alcohol solutions under an Ar-H₂ atmosphere at 750 - 950 °C. The samples have been characterized by Raman spectroscopy, scanning electron microscopy (SEM)and high-resolution transmission electron microscopy (HRTEM). Interestingly, the method results in uniform ropes of SWCNTs of large diameters. We noted that the best material was produced at 950 °C. This method is simpler and more efficient than other that have been reported in the literature because it does not require vacuum, sulphur agents, relatively large temperatures or large amounts of H₂. We envisage this method could be used to produce uniform SWCNTs of desired diameters if conditions are accurately tuned up.

U3.36

Self-Adhesion and Collapse of Carbon Nanotubes. Tian Tang¹, Anand Jagota² and Chung Yuen Hui¹; ¹Theoretical and Applied Mechanics, Cornell University, Ithaca, New York; ²Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania.

Self-adhesion and potential internal collapse of carbon nanotubes are two important features of their mechanical behavior, relevant both for their processing and final use. By representing single-walled nanotubes (SWNTs) by a simple analytical model for flexible shells, we can model such deformations accurately. Molecular Dynamics (MD) simulations are carried out to study the self adhesion of two identical SWNTs and the collapse of a SWNT due to van der Waals interaction. Our model allows us to compute the deformed equilibrium shape and the elastic strain energy of the nanotube. We predict that there exist a critical tube radius below which no contact or collapse can occur. This critical radius scales with square root of D/W, where D is the effective bending stiffness of the nanotube, and W is the work needed to separate two parallel graphite flat sheets of unit area. We demonstrated good agreements between the prediction of the continuum analysis and the molecular dynamics simulations.

U3.37

Magnetic Processing of Carbon Nanotube-Polyethylene Composites: Molecular Dynamics Simulation.

Marwan S. Al-Haik and M. Yousuff Hussaini; School of Computational Science and Information Technology, Florida State University, Tallahassee, Florida.

Molecular dynamics simulations at constant temperature and pressure are carried out to study the reorientation of a zigzag and armchair single-wall-carbon nanotubes in polyethylene matrices under the influence of a 25 Tesla magnetic field. Simulations reveal that the reorganization of the polyethylene chain facilitates the reorientation of the nanotube parallel to the direction of the applied magnetic field. The trajectory evolution after 10 picoseconds shows more noticeable deformation in the zigzag nanotube system compared to the armchair system. A comparison of the simulation results with the related

experimental observations shows qualitative agreement.

U3.38

Carbon Nanofibers Control Protein Interactions for Aligned Neurite Extension from Neurons. Janice McKenzie¹, Rachel Price¹, Riyi Shi^{2,1} and Thomas Webster^{1,3}; ¹School of Biomedical Engineering, Purdue University, West Lafayette, Indiana; ²Basic Medical Sciences and Center for Paralysis Research, Purdue University, West Lafayette, Indiana; ³School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Neural materials have experienced reduced effectiveness when implanted for long time points due to poor interactions between the biomaterial surface and local neuronal cell populations. The reduced efficacy of these implants is largely due to glial scar tissue formation mediated by astrocytes. It is desirable to design implants that retain functionality, but mimic the properties of native tissue in order to reduce chronic implant difficulties such as glial scar tissue around implant surfaces and thus improve the interface between the biomaterial and neurons. Carbon nanofibers mimic the nanoscale dimensions of macromolecules in the brain (such as proteins) and have unique material properties including high conductivity and high strength to weight ratios. These properties make them attractive candidates for neural biomaterial applications, but cytocompatibility properties of carbon nanofibers remain largely unexplored. Recent results indicate reduced astrocyte functions and increased neuronal functions on carbon nanofiber materials. Since initial protein adsorption to biomaterials dictates subsequent cellular responses, protein adsorption to carbon nanofibers was investigated in this study. Specifically, vitronectin and fibronectin adsorption were separately investigated on carbon fibers with diameters of 200, 125, 100 and 60 nm. Vitronectin adsorbed significantly more to the 100 nm than to all of the other fibers. Fibronectin adsorbed significantly more to the 125, 100, and 60 nm fibers than to the 200 nm fiber. These results indicate that proteins adsorb differently on carbon nanofibers based solely on dimension. Lastly, the present study aligned 60 nm carbon fibers in a polycarbonate urethane matrix using an applied voltage to form a homogenous electrical field. This alignment was able to direct neurite growth from neurons parallel to carbon nanofiber orientation in the polymer in vitro. Collectively, the results suggest the possibility of using these carbon nanofiber materials to control protein adsorption and subsequent cellular functions including prescribed orientation to improve various neural applications such as probes and bridging materials.

U3.39

Novel In-situ Grown Carbon Nanotube-Iron Composites: Synthesis and Properties. Amit Goyal and Zafar Iqbal²; ¹Otto York Department of Chemical Engineering, New Jersey Institute of Technology, Newark, New Jersey; ²Department of Chemistry and Environmental Sciences, New Jersey Institute of Technology, Newark, New Jersey.

A novel in-situ technique for the growth of carbon nanotube-iron composites using chemical vapor deposition will be discussed. A pelletized matrix of micron size pure iron particles with and without catalyst is infiltrated with single and multiwall carbon nanotubes using carbon monoxide and acetylene, respectively, as the precursor gas. Catalyst precursors used were nitrates of cobalt and molybdenum and acetates of iron, cobalt, and molybdenum. The novel nanocomposites produced using various synthesis parameters were characterized by a combination of x-ray diffraction, Raman scattering and scanning electron microscopy. The spectroscopic and diffraction data indicated the absence of iron carbide formation. Sizable increases in micro-hardness and the Youngs modulus of the composites were measured after infiltration with 2-4 weight percent of nanotubes. The effect of the porosity of the starting matrix, and the vapor deposition time and temperature, will also be discussed.

U3.40

Mechanical Properties of Hybrid Carbon Nanotube Systems: The Effects of Structural Modifications by Filling and Intertube Cross-Linking. Papot Jaroenapibal¹, David E. Luzzi¹ and Stephane Evoy²; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Nanoscale cantilevered resonators offer great potential as sensing devices due to their high sensitivity to added masses or external forces. Highly-sensitive resonators can be produced using long, thin, stiff, low density, and high quality cantilevers. The intrinsic structure of carbon nanotubes (CNTs) offers a platform upon which functional nanoscale resonating systems can be designed. The unique mechanical properties of CNTs make them suitable for the development of high frequency nanoscale resonators that could allow the analysis of extremely small displacements and forces at the molecular scale.

Hybrid nanotube systems in which fullerenes or other molecules are encapsulated within single-walled carbon nanotubes (SWNTs) represent a new class of tunable nanoscale materials that could provide both high quality resonance and sensing specificity for such devices. We have studied the mechanical properties of empty and C_{60} -filled SWNT bundles through the observation of their mechanical resonances in a transmission electron microscope (TEM). The specimen holder was custom built to allow the application of electrical signals between the sample and a counter electrode. Electron diffraction was used to confirm the filling of each bundle prior to the measurement of individual mechanical resonance frequencies. The Euler-Bernoulli analysis of a cantilevered beam was employed to calculate the bending modulus of each bundle. An average ratio of $(E_b/\rho)^{1/2} = 10030 \pm 400$ Hz-m was observed for the C₆₀-filled bundles, compared to a ratio of $(E_b/\rho)^{1/2}=7630\pm540$ Hz-m for unfilled bundles. Such values indicate an increase of the average bending modulus by as much as 136% in C₆₀-filled bundles. The observed dependence of this ratio on the diameter shows an increasing importance of inter-tube slipping in bundles of large diameter. The change in mechanical properties of SWNT bundles when sliding between neighboring tubes is prevented by the formation of cross-links between the individual nanotubes of the bundle using electron-beam irradiation inside a TEM will be presented.

U3.41

Patterning and Assembly of Nano-Devices using Chemical Markers. Alex Neal Meece and Ingrid St.Omer; Electrical and Computer Engineering, University of Kentucky, Lexington, Kentucky.

In the quest to develop viable electronics alternatives, researchers are exploring the use of carbon nanotubes for device applications. To fabricate device structures it is imperative to develop a controllable placement methodology. This work expands on a patterning technique developed by Rao et. al. at Florida State University. Guided assembly of commercially available Multi-Walled Carbon Nanotubes (MWCNT/s) is accomplished using e-beam lithography, and surface functionalization. Using this technique the tubes have been successfully placed onto contacts for characterization and testing. We have studied the I-V characteristics, resistance and conductance using aluminum, platinum, and gold contacts. The average diameter and length of the MWCNT/s have been estimated using AFM measurements.

U3.42

High Temperature Oxidation of Boron Nitride Nanotubes. Ying Chen, Research School of Physical Science, Australian National University, Canberra, Australian Capital Territory, Australia.

Carbon nanotubes have many properties that are superior to those of graphite. An exception is the weak resistance to oxidation, mainly due to their large surface area and defects (pentagons) at tips. Carbon nanotubes readily oxidize in air (400 oC) and burn completely at 700 oC when sufficient oxygen is supplied, which limits applications under high temperature environment. Boron nitride (BN) nanotubes have the same nanostructure as carbon nanotubes, but are found to exhibit significant resistance to oxidation at high temperatures. Our study has revealed that BN nanotubes are stable at 700 oC in air and some thin nanotubes (diameter less than 20 nm) with perfect multi-walled cylindrical structure can survive up to 900 oC. Thermogravimetric analysis revealed an onset temperature for oxidation of BN nanotubes at 800 oC compared with only 400 oC for carbon nanotubes under the same analysis conditions. This stronger resistance to oxidation of BN nanotubes is inherited from the hexagonal BN and also depends on the nanotube structure. The boron oxide layers formed over nanotubes might stop further oxidation. This high level of resistance to oxidation allows promising BN nanotube applications at high temperatures.

U3.43

Ultrafast Electron Dynamics of Single-walled Carbon Nanotubes. Libai Huang and Todd D. Krauss; Department of Chemistry, University of Rochester, Rochester, New York.

The electronic properties of single-walled carbon nanotubes (SWNTs) are of significant fundamental and technological interest. Despite abundant efforts devoted to this field, there are still many crucial parameters of electronic structure, such as radiative lifetime and nonradiative lifetime of the first excited state, to be determined. These lifetimes fundamentally determine the photoluminescence quantum efficiency and also the relative strength of resonant linear and nonlinear optical processes. Thus, these parameters are important not only for a complete fundamental understanding of SWNTs, but also for potential optoelectronic applications. We will present the study of the electronic structure of isolated SWNTs using the complementary technique of ultrafast two-color pump-probe spectroscopy. The excitation wavelengths were tuned to 975 nm, 1170 nm, 1250 nm and 1323 nm to resonantly excite (6,5), (8,6), (10,5) and (9,7) nanotubes respectively. Excitation intensity ranged from 0.01

 $\rm GW/cm^2$ - $5~\rm GW/cm^2$ and a white-light continuum served as the probe. We found that photoexcited electrons in SWNTs isolated in surfactant micelles decay through many channels, exhibiting a range of decay times ($\sim\!200$ fs to $\sim\!>\!100$ ps). The magnitude of the longest-lived component in the ultrafast signal specifically depends on resonant excitation, thus suggesting that this lifetime corresponds to the band-edge relaxation time. For a probe with a higher energy than the pump, we observed both induced absorption and saturation of absorption, with the dynamics strongly dependent on the excitation intensity. The implications of these results regarding the magnitude and nature of electron-hole interactions in SWNTs will be discussed.

U3.44

High-Bias Transport in Semiconducting Carbon Nanotubes. Yung-Fu Chen and M. S. Fuhrer; Department of Physics and Center for Superconductivity Research, University of Maryland, College Park, Maryland.

Charge transport in individual semiconducting single-walled nanotubes (SWNTs) with Schottky barrier contacts has been studied at high bias voltages. We observe nearly symmetric ambipolar transport, and find that both electron and hole currents may significantly exceed 25 μA , thought to be the limiting current in metallic SWNTs due to optical phonon emission. The current for a ballistic ambipolar nanotube field-effect transistor has been calculated carefully, treating the potential and the charge of the nanotube self-consistently, and including electron-hole recombination. The result is directly compared with the experimental transport data, and it is found that the current may be as high as one-quarter that expected for a ballistic nanotube field-effect transistor, even for nanotubes with lengths of tens of microns. The high-bias behavior in semiconducting nanotubes is better explained by velocity saturation, rather than current saturation. We propose a charge-controlled current model of transistor operation, with maximum saturation velocity v_s of 2 imes 10 $\,\mathrm{cm/s},$ which explains the magnitude of both the differential conductance under symmetric bias and the transconductance.

U3.45

Carbon Nanotube / Silicon Heterostructures: A Pathway to Integration for Electronics and Sensing Applications.

Marian Tzolov, Tend-Fang Kuo, Daniel Straus, Aijun Yin and Jimmy Xu; Division of Engineering, Brown University, Providence, Rhode Island.

The intensive research that has followed the discovery of carbon nanotubes has revealed the many attractive properties of this new form of carbon material. Ultrahigh strength, light weight, high thermal conductivity, high charge carrier mobility and current carrying capacity, widely variable electrical and optical properties, chemical functionalization, and bio-functionalization are few of the remarkable attributes that readily render themselves for applications in electronics and sensing. Our results demonstrate that highly ordered arrays of carbon nanotubes of uniform diameter, length, and alignment can be made on both stand-alone flexible thin (e.g., aluminum) films and crystalline semiconductor substrates such as silicon. In the latter case, the integration of the carbon nanotubes on semiconductors can be not only physical but also electronically functional, forming a heterojunction with a rectifying ratio as high as five orders of magnitude. As such, this new form of heterojunction merges the benefits of this new material with the well-established advantages of a dominant electronic technology. This is a fundamental advance for both technologies which holds great promise for enabling new applications such as radiation detection and electro-chemical sensing, thanks to the unique properties of carbon nanotubes: their inherent and ultra broad spectral coverage, tunable over an even broader range through varying the tube diameter, their scalability and conformability to large and curved surface areas; and their high resistance to mechanical, electrical, chemical, and radiation loading. Most recently, we have further developed the technology of carbon nanotube / silicon heterostructures to include n-type silicon substrates, a technologically non-trivial feat because the anodization process is drastically different, though it turns out to be functionally superior. The results confirm that the rectification direction correlates with the doping type of the substrate. The polarity of the detected photocurrent response, which was limited to the silicon spectral range in the p-type case, is also consistent with the rectification direction. Impedance and photocurrent measurements provide insights into the details of the heterojunction, and they reveal the presence of a depletion region that scales with the applied voltage. The temperature dependence also unveils a complex picture for the defect states. The photocurrent measurements reveal the existence of a transient component more dominating than the static component, indicating the existence of a barrier layer. This hypothesis was confirmed by SEM studies. The device preparation was improved by introducing better control in the template preparation and in using different source gas for nanotube growth, resulting in a better interface between the nanotubes and silicon, thus suppressing the AC

SESSION U4: Processing and Composites Chair: Meyya Meyyappan Wednesday Morning, March 30, 2005 Room 3024 (Moscone West)

8:30 AM *U4.1

Polymer-Nanotube Composite Materials: From Interactions to Applications. <u>Jonathan Nesbit Coleman</u>¹, Martin Cadek¹, Kevin Ryan¹, Valeria Nicolosi¹, Rob Murphy¹, Mauro Ferreira¹, Dragan Mihailovic², Rowan Blake³, Ian O'Connor³, Yurii Gounko³ and Werner Blau¹; ¹Physics, Trinity College Dublin, Dublin, Ireland; ²Jozef Stefan Institute, Ljubljana, Slovenia; ³Chemistry, Trinity College Dublin, Dublin, Ireland.

In recent years, carbon nanotubes have been shown to possess exciting electronic, thermal and mechanical properties. However accessing these properties as proven problematic due to difficulties processing nanotube material. One solution to this problem involves the formation of polymer-nanotube composites. By dispersing nanotubes in a polymer matrix we expect to retain the processing advantages of the polymer while accessing the desirable properties of the nanotubes. In this work we have studied the interaction of a range of polymers with carbon nanotubes. Microcopy and calorimetry measurements show that a number of polymers interact with nanotubes in an ordered fashion to form crystalline polymer coatings. While these coatings are probably formed in the solution phase, they persist during drying resulting in solid state composite materials with significant nanotube-nucleated crystallinity. This crystallinity in turn strongly affects the composite physical properties. As a result it is possible, among other things, to produce composite plastics as strong as steel. In addition, composite fibres, significantly tougher than Kevlar have been produced. Finally some new one-dimensional materials with significant advantages over carbon nanotubes will be introduced.

9:00 AM *U4.2

Polymer and Aligned Carbon Nanotube Nanocomposites and Nanodevices. Liming Dai, Lingchuan Li and Kyungmin Lee; Chemical and Materials Engineering, University of Dayton, Dayton, Ohio.

We have previously developed a simple pyrolytic method for large-scale production of aligned carbon nanotube arrays perpendicular to the substrate. These aligned carbon nanotube arrays can be transferred onto various substrates of particular interest in either a patterned or non-patterned fashion. The well-aligned structure provides additional advantages for not only an efficient device construction but also surface functionalization (both the inner and outer surface). The surface functionalization of aligned carbon nanotubes is particularly attractive, as it allows surface characteristics of the aligned carbon nanotubes to be tuned to meet specific requirements for particular applications while their alignment structure can be largely retained. These aligned carbon nanotubes with tunable surface characteristics are of great significance to various practical applications, including nanotube sensors and optoelectronics. For instance, we have previously immobilized glucose oxidase (GOX) onto the aligned multi-wall carbon nanotube arrays by electropolymerization of pyrrole in the presence of GOX. The resultant GOX-containing polypyrrole-carbon nanotube coaxial nanowires were shown to be promising new sensing active materials for making advanced glucose sensors with a high sensitivity. Also, single-strand DNA chains have recently been chemically grafted onto aligned carbon nanotube electrodes, leading to novel aligned carbon nanotube-DNA sensors of a high sensitivity and selectivity for probing complementary DNA and target DNA chains of specific sequences. More recently, we have also developed a rational approach to fill conducting polymers (e.g. polyaniline) into the aligned carbon nanotubes with each of the nanotube cores acting as a tiny reactor. In this talk, we present our recent work on the preparation of polymer and aligned carbon nanotube nanocomposites and nanodevices.

10:00 AM *U4.3

The Direct Spinning of Carbon Nanotube Fibres. <u>Ian Kinloch</u>, Ya-Li Li, Marcelo Motta, Martin Pick, Venugopalan Premnath and Alan Windle; Dept. of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambs, United Kingdom.

Many routes have been developed for the synthesis of carbon nanotubes, but their assembly into continuous fibres has so far been achieved only through post-processing methods. In this work, carbon nanotube fibres were obtained by directly spinning an aerogel of carbon nanotubes formed during chemical vapour deposition synthesis (1). Typically a mixture of ethanol, ferrocene and thiophene is injected into a hot hydrogen atmosphere (1150 °C) and these

compounds rapidly react to form the carbon nanotubes. The carbon nanotubes then interact to form a continuous sock-like aerogel that travels down the reaction zone without sticking on the furnace walls. The sock is then spun into a fibre using a variety of different spindle orientations. Overall, this process can be split broadly into three stages; the initial chemical vapour deposition reaction, the formation of sock and the drawing and properties of the fibre. Each of these processes will be addressed in the talk. Different hydrocarbons have been used for the reaction, with the yield and products being found to vary greatly with the feedstock used. These products were characterised using Raman spectroscopy and electron microscopy. The presence of small amounts of oxygen was found to be enhance sock formation and hence spinning of the fibre. Also, the process parameters were found to have a strong effect on whether multi-walled or single-walled nanotubes are produced. Physical properties of the fibres were also assessed, with special emphasis on tensile strength and electrical conductivity. Tensile strengths are greatly dependant on process conditions and therefore, the different microstructures observed. On average, values lie in the range of 0.7 0.2± GPa, with the current maximum tensile strength reaching 1.5 GPa. The electrical conductivity of the carbon nanotube fibre is consistently higher than for carbon fibres, ranging from 2.5 to 8.3 per Ohms per metre. All experimental evidence points out to the fact that very significant improvements in properties can be accomplished by better controlling the synthesis process. 1. Li et al., Science, 304, 276, 2004

10:30 AM *U4.4

Damping Properties of Carbon Nanotube Composites.

Nikhil Koratkar, Mechanical, Aerospace and Nuclear Engineering
Dept, Rensselaer Polytechnic Institute, Troy, New York.

The paper explores the fundamental mechanisms for interfacial friction damping in carbon nanotube filled polymer composites. Two distinct mechanisms for energy dissipation are identified: (1) interfacial sliding at the tube-tube interface and (2) interfacial slip at the tube-polymer interface. Both of these mechanisms exploit the enormous interfacial contact area associated with carbon nanotube fillers to achieve high damping with minimal weight penalty. In polymer thin films (with dense packing of nanotube fillers) where tube-tube slip is the dominant mechanism, our tests indicate upto 1400% increase in the loss factor (damping ratio) compared to the baseline. In bulk polymer systems, where tube-polymer slip may be the dominant mechanism, our tests indicate between 500 to 700% increase in mechanical damping by the use of nanotube fillers. These results demonstrate that nanotube filled polymer systems show great promise as novel high performance damping materials.

11:00 AM <u>U4.5</u>

Carbon Nanotube- Polyvinylalcohol Nanocomposite Film Devices: Application for Femtosecond Fiber Laser Mode-Locker. Aleksey G. Rozhin¹, <u>Youichi Sakakibara</u>¹, Madoka Tokumoto¹, Yohji Achiba² and Hiromichi Kataura¹; ¹AIST, Tsukuba, Japan; ²Tokyo Metropolitan Univ., Hachioji, Japan.

We fabricated a single wall carbon nanotube (SWNT)/polyvinylalcohol (PVA) nanocomposite self-standing film for a saturable absorption device usable in mode-locked Erbium fiber short pulse laser. We integrated a 30-um-thick SWNT/PVA film into a conventional FC/PC fiber connection adaptor with the film sandwiched by a pair of fiber ferrules. A ring fiber laser inserted with the SWNT/PVA saturable absorber operated very easily in mode-locked short pulse mode with a best pulse width of about 200 fs, which is to our knowledge the world shortest in this class of lasers using carbon nanotube saturable absorbers. This result demonstrates that the SWNT/PVA film is very promising as a passive mode-locker for femtosecond Er-doped fiber lasers. The easy controllability of film thickness and SWNT concentration enables fine material tuning, being profitable in the future laser improvement. The easy device fabrication using conventional fiber connection techniques with reproducible device performance will extremely make the laser construction easy and reliable.

11:15 AM $\underline{\text{U4.6}}$

Processing and Characterization of Conductive
Thermoplastic/Carbon Nanotube Films. Giang Pham and
Young-Bin Park; Industrial and Manufacturing Engineering, Florida

A & M University and Florida State University, Tallahassee, Florida.

Carbon nanotube(CNT)-filled polymer composite films have a number of applications due to the multi-functionalities of CNTs, including exceptional mechanical, electrical, thermal, and optical properties. We report our study on conductive thermoplastic/CNT composite films. The films were fabricated via melt processing of CNTs and thermoplastics of different elastic properties. The electrical conductivities of the films were measured at varying combinations of matrix material, CNT concentrations, and loading conditions, including uniaxial/biaxial stretching and bending. The dependence of

electrical conductivity on the loading conditions indicates that the in-plane deformation of the films has significant influence on the conductive path network formed by CNTs. The measured results provide insights to potential applications of CNT-based films, such as, strain sensing, electronic circuits, aerospace electrostatic charge mitigation, and thermally bondable coating.

11:30 AM <u>U4.7</u>

Polyurethane Multi-walled Carbon Nanotube Composite Fibers. Wei Chen, Xiaoming Tao and Pu Xue; Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Multi-walled carbon nanotubes (MWNTs) reinforced thermoplastic polyurethane (TPU) composite fibers have been fabricated via a twin-screw extrusion system. Significant improvement in tensile modulus and tensile strength were achieved by incorporating MWNTs up to 9.3 wt% while without sacrificing TPU elastomer's high elongation at break and hysteresis resistance. SEM, TEM and Raman techniques were used to evaluate the MWNTs/PU composite system. Results indicated that the homogeneous dispersion of MWNTs throughout PU matrix and strong interfacial adhesion between chemically functionalized MWNTs and the matrix are responsible for the significant enhancement of mechanical properties of the composite fibers.

11:45 AM <u>U4.8</u>

Production and Characterization of Surfactant Suspensions of Single-Wall Carbon Nanotubes. <u>Richard M. Russo</u>¹, Igor Rubtsov², Pravas Deria², Michael J. Therien² and David E. Luzzi¹; ¹Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania.

One of the major limiting factors to the use of single-walled carbon nanotubes (SWNTs) has been the difficulty in producing a dispersed form suitable for chemical processing. Due to their large size and often intractable rope structure, SWNTs are insoluble in most solvents. Recent work has shown that individual SWNTs have been successfully wrapped in a surfactant micelle and suspended in water, albeit at low concentration. The suspension process involves a combination of mixing, sonication, and centrifugation. Initial data, consisting of absorption and emission spectra, has confirmed that nanotubes and nanotube bundles can stably exist in suspension for extended time periods. Steady-state emission measurements show that the suspensions contain some individual, surfactant-coated SWNTs. In the present work, we investigate the evolution of SWNTs from a tangle of bundled rope structures to individual micelles. A wide range of experimental parameters are used for the centrifugation and sonication process steps. In addition, some variations in the identity and concentration of surfactant are explored. The suspensions are characterized using optical UV-VIS-NIR absorption spectroscopy, steady-state fluorescence emission and excitation spectroscopies, and full spectrum 100fs-resolution transient absorption spectroscopy. A maximum of four distinct excited state lifetimes, which vary with processing condition and surfactant system, are observed. These lifetimes can be as long as 1 nanosecond for certain surfactant systems. Results suggest, despite the most comprehensive processing conditions, that surfactant suspensions of SWNTs are a mixture of bundles and single tubes. Optimization of these conditions, as well as the choice of the surfactant systems, results in the maximization of single tube content. These studies demonstrate the importance of using multiple optical spectroscopy techniques to elucidate the true nature of nanotube suspensions, and the quality and completion of dispersion.

> SESSION U5: Optical and Electro-Optical Properties Chair: Ralph Krupke Wednesday Afternoon, March 30, 2005 Room 3024 (Moscone West)

1:30 PM <u>*U5.1</u>

The Luminescent Properties of SWNTs. Jacques Lefebvre¹, Paul Finnie¹ and Yoshikazu Homma²; ¹Institute for Microstructural Sciences, National Research Council, Ottawa, Ontario, Canada; ²NTT Basic Research Laboratories, Nippon Telegraph and Telephone Corporation, Atsugi, Kanagawa, Japan.

Semiconducting single walled carbon nanotubes (SWNTs) have direct bandgaps in the near- to mid-infrared. This property suggests that SWNTs should be good light emitters, but it is only recently that photoluminescence (PL) from SWNTs has been detected. Control of the nanotube environment is key. For example, individual SWNTs can be grown directly on a patterned substrate with pillars and ridges. High quality, micrometer long sections of SWNTs are then freely

suspended in air, with minimum interaction with the underlying substrate. The PL from such SWNTs is observed without post-growth processing, and many spectral properties reveal the one-dimensional nature of SWNTs. The PL from suspended nanotubes differs in many ways from those in solution, including being blueshifted and narrower in linewidth. The importance of environment is also manifest in temperature-dependent measurements for which different gas ambients produce dramatic spectral changes, and even PL quenching. In helium ambient, SWNT PL is remarkably robust with only modest changes in emission energy, linewidth and intensity over a wide range of temperatures.

2:00 PM *U5.2

Probing Charge-Transferred Doping and Electroluminescence in Carbon Nanotube Transistors. Jia Chen, Marcus Freitag, Christian Klinke, Ali Afzali, James C. Tsang and Phaedon Avouris; T. J. Watson Research Center, IBM Corp., Yorktown Heights, New York.

Significant progress has been made recently on carbon nanotube based field effect transistors(CNTFET), in terms of understanding both their scaling and performance limits. However, the Schottky barriers(SB) formed between the CNT and the source/drain metal contacts lead to contacts dominated switching, low drive current, undesirable subthreshold characteristics, and strong ambipolar conduction when the transistor is scaled down vertically, all unacceptable in logic gate applications. Here we report on chemical doping schemes utilizing molecules and a charge transfer mechanism to obtain self-aligned, air-stable and unipolar CNTFETs to meet the performance challenges. We demonstrate an ability to change carrier injection properties; and to improve device performance in both ONand OFF-states. In particular, oxidizing and redox-active molecules are introduced to modify the workfunction of the source and drain electrodes of CNTFETs and, correspondingly, of their SBs. We demonstrate successful ambipolar-to-unipolar conversion and p-to-n polarity switching of CNTFETs. Although ambipolar character is undesirable in logic applications, it is particularly valuable in optoelectronic applications. Using ambipolar CNTFETs with appropriate biasing we can inject electrons and holes simultaneously from the source and drain of the nanotube, and observe radiative e-h recombination from individual CNTs. CNTFETs provide a novel form of molecular light source that requires neither external doping nor well defined space charge region as in conventional LEDs. CNFETs being three-terminal devices allow the tuning of not only the intensity of electroluminescence, but also the position along the length of the CNT from which the emission originates. Thus the recombination region can be translated over large distances (tens of microns) in long CNTs by varying the gate potential. Such experiments provide new insights into the transport processes in carbon nanotubes. They allow us to follow the fronts of the electron and hole currents under varying bias conditions, determine the recombination lengths and recombination times, observe defects, etc.

3:00 PM <u>*U5.3</u>

Carbon Nanotube Electron Sources for Electron Microscopes. Niels de Jonge¹, Maya Doytcheva¹, Monja Kaiser¹ and Erwin Heeres^{1,2}; ¹Philips Research, Eindhoven, Netherlands; ²Leiden Institute of Physics, Leiden University, Leiden, Netherlands.

Carbon nanotube electron sources were made by mounting individual carbon nanotubes (multi-walled type) on tungsten tips in a scanning electron microscope (SEM) equipped with a nano-manipulator. In exploring suitable mounting procedures it was discovered that thin carbon nanotubes exhibit a cap closing mechanism. The behavior of the structure of the carbon nanotubes while emitting electrons was investigated in-situ in a transmission electron microscope. The emission properties of individual carbon nanotubes with closed caps were investigated aimed at developing a new type of electron source for electron microscopes to improve their resolution. It was found that the sources have an extraordinary large stability of the emitted current and a long lifetime. It followed that the Fowler-Nordheim model describes the emission mechanism, without the need of corrections. This allowed the numerical calculation of the emission behavior from the geometry of the emitter and work function only. These sources provide an extremely high brightness: 3x109 A/(Sr*m2*V); this is an order of magnitude larger than that of state-of-the-art commercial sources, i.e. Schottky emitters and cold-field-emission guns. The energy spread is more than two times smaller than that of Schottky emitters and is the same as that of cold field emission guns. Based on the experiments, a model was developed describing the brightness as function of the energy spread.

3:30 PM *U5.4

Magneto-Optics in Carbon Nanotubes. <u>Junichiro Kono</u>, Dept. of Electrical & Computer Engineeering, Rice University, Houston, Texas.

This talk will describe our recent magneto-optical studies of micelle-suspended single-walled carbon nanotubes in aqueous solutions. Using magneto-absorption, magneto-photoluminescence, and magneto-photoluminescence-excitation spectroscopies in ultrahigh magnetic fields, we have detected optical signatures of the Aharonov-Bohm effect [1] (predicted more than 10 years ago by Ajiki and Ando [2]) and determined the magnetic susceptibility anisotropy of semiconducting nanotubes [3]. 1. S. Zaric et al., Science 304, 1129 (2004). 2. H. Ajiki and T. Ando, J. Phys. Soc. Jpn. 62, 1255 (1993). 3. S. Zaric et al., Nano Lett. 4, 2219 (2004).

4:00 PM *U5.5

Raman Spectroscopy and Optically Induced Resistance Changes in Individual Carbon Nanotubes. <u>Alf Mews</u>¹, Matteo Scolari¹, Kannan Balasubramanian², Tilman Assmus² and Marko Burghard²; ¹Physical Chemistry, University of Siegen, Siegen, Germany; ²Solid State Research, Max Planck Institute, Stuttgart, Germany.

While optical spectroscopy and transport measurements of individual carbon nanotubes (CNTs) are well established methods by now, much less is known about the opto-electronic behavior of individual CNTs. Here we present a method where the transport measurements of individual CNTs are performed under local in-situ illumination with sub-micron resolution using a scanning optical microscope (SCOM). The CNTs were independently identified as being metallic or semiconducting by means of electrical measurements and Raman spectroscopy on the same CNTs. The charge transport studies under local in-situ illumination revealed that the photoconductivity in semiconducting CNTs is highest close to the contacts, consistent with the formation of Shottky-barriers at the metal/CNT interface. Furthermore, local electronic structure effects along the CNT could be monitored by determining the variations of photo response as a function of illumination position. In addition the metallic tubes exhibited reversible resistance changes upon illumination, which are likely originating from optically induced desorption and adsorption of molecular species from the gas phase.

4:30 PM *U5.6

Carbon Nanotubes under Electron Irradiation.

Florian Banhart, Institut fur Physikalische Chemie, Johannes Gutenberg-Universitat Mainz, Mainz, Germany.

The structure and morphology of carbon nanotubes can be modified by irradiation with energetic electrons. This is achieved in the focused beam of a transmission electron microscope (TEM). Modern TEMs with field emission guns allow the irradiation of nanotubes or other objects with electron beams of less than 1 nm in diameter and, hence, to modify structures on an atomic scale. To avoid the agglomeration of radiation defects and gradual destruction of nanotubes, interstitial atoms should be highly mobile; therefore irradiation and imaging have to be carried out at high specimen temperatures. Knock-on displacements of carbon atoms lead to the formation of interstitials, vacancies, and dangling bonds. The controlled formation of these point defects is the key to 'nanoengineering' of tubes or related carbon particles. Several alterations of the structure and morphology of nanotubes have been achieved. Examples for single-wall tubes are the merging of parallel or crossing tubes and the formation of molecular junctions between tubes. Multi-wall tubes can be tailored under the electron beam by removing graphene layers locally, bending the tubes by a pre-defined angle, local transformation of the tubes into spherical 'onions', or the controlled collapse of tubes. Bundles of single-wall tubes can be transformed into multi-wall tubes and, conversely, multi-wall tubes into single-wall tubes under electron irradiation. Furthermore, the injection of carbon atoms into the inner hollows of tubes can be achieved by applying an electron beam. Thus, it can be shown that tubes act as pipes for the effective diffusion of free carbon atoms.

> SESSION U6: Poster Session: Optical and Electro-Optical Properties II Chair: P. M. Ajayan Wednesday Evening, March 30, 2005 8:00 PM Salons 8-15 (Marriott)

U6.1

Ultrafast Transient Absorption Studies of Semiconducting and Metallic Single-Wall Carbon Nanotubes.
Randy J. Ellingson, Engtrakul Chaiwat, Marcus Jones, Garry Rumbles, Arthur J. Nozik and Michael J. Heben; Center for Basic Sciences, National Renewable Energy Laboratory, Golden, Colorado.

We compare the ultrafast photoresponse of metallic and semiconducting species within a polydisperse aqueous sample of single-wall carbon nanotubes (SWNTs) using sub-picosecond transient absorption (TA). Our measurements employ excitation wavelengths in

the range of 430-1700 nm, and a broadband white light probe covering the range of 440-1050 nm. Tuning the excitation energy above and below the bandgap of a specific semiconducting nanotube produces significant variation in the photoinduced absorption change measured at the bandgap (lowest exciton transition). Specifically, our TA spectra demonstrate the transparency of semiconducting SWNT species photoexcited below their first exciton absorption energy. On the other hand, the photoresponse at the lowest exciton transition of metallic SWNTs shows little variation with excitation above and below the lowest exciton. We compare the recovery times of the photoinduced absorption change for metallic and semiconducting SWNTs when exciting above and below the lowest interband transition. Photogenerated excitons in metallic SWNTs show no long-lived state for the lowest exciton, due to the absence of a true energy gap. In contrast, we observe substantially longer lifetimes for excitons within semiconducting species. Preliminary results show a long-lived absorption bleach for the (6,5) SWNT of 1.7 ns, indicating a lifetime component approximately 10 times that of the longest previously reported SWNT lifetime.

U6.2

Electrochemical Application of Carbon Nanotube for Counter Electrode of Dye-Sensitized Solar Cell. Dong-Yoon Lee, Won-Jae Lee, Jae-Sung Song, Hyun-Ju Kim and Bo-Kun Koo; Electric and Magnetic Devices Group, Korea Electrotechnology Research Institute, Changwon, Kyeongnam, South Korea.

Carbon nanotube (CNT) films were prepared for the counter electrode of a dye-sensitized solar cell (DSSC) and their electrochemical properties were measured in this study. DSSC is a sort of electrochemical solar cell composed of transparent conducting oxide on glass plates, TiO2 nano-porous electrode, photo sensitized dye, electrolyte, and counter electrode. The counter electrode of DSSC should have high electrical conductivity and good catalytic effects on redox reaction of iodides in electrolyte. Pt thin films, deposited by electro-deposition or sputtering, are most prevalent materials for the counter electrode. Carbon materials like active carbon or graphite are sometimes used for the same purpose, instead of Pt, because of their low price, although their catalytic ability is less than Pt. Recently, it is expected that CNT can be used as an effective electrode material in DSSC because it has high electrical conductivity as similar to metals and good catalytic effects like graphite. However, the electrochemical properties and catalytic effect of CNT are not enough studied until this time. In addition to, CNT has not been employed as the counter electrode of DSSC. In this study the electrochemical properties of CNT for DSSC were studied using cyclic voltammeter and AC impedance analyzer in association with the redox reaction of iodine ions on the interface between the CNT film and electrolyte. The I-V characteristics of DSSC having the CNT counter electrode were measured under the illumination of monochromator and solar simulator. As results, it was shown that CNT electrodes had higher catalytic performance for the redox reaction of iodine ions than Pt electrode, and then DSSC having CNT electrode had higher opto-electric conversion efficiency than that of Pt counter electrode.

U6.3

Enhanced Solar Energy Conversion Efficiency of Dye-Sensitized Solar Cell by Combination of Carbon Nanotube and Thermoelectric Generator. Jae-Sung Song, Dong-Yoon Lee and Won-Jae Lee; Electric and Magnetic Devices Group, Korea Electrotechnology Research Institute, Changwon, Kyeongnam, South Korea.

The new type solar cell composed from a dye-sensitized solar cell (DSSC) and a thermoelectric generator (TEG) was designed and tested in this study. The purpose of the new solar cell design is to use the full range of solar wavelength for electric generation and enhance solar cell efficiency. In general, DSSC use the wavelength range of 400 \sim 800nm and has the maximum efficiency of below 10%. If it is possible to utilize most of solar energy in the wavelength range of 350 $\sim 2500 \mathrm{nm}$ for electric generation, it can be expected to obtain higher solar energy conversion efficiency exceeding the known limit of maximum efficiency. As a solution of this purpose we suggest the composite solar device constructed with two parts. The upper part is composed of DSSC and the lower part is a thermoelectric generator attached beneath DSSC. DSSC of the upper part is a sort of transparent electrochemical solar cell, composed of transparent conducting oxide on glass plates, TiO2 nano-porous electrode, photo sensitized dye, electrolyte, and counter electrode. The DSSC of this study is characterized by using a carbon nanotube film as counter electrode, instead of Pt widely adopted in DSSC. To use the carbon nanotube counter electrode has several merits compared to Pt electrodes; first, carbon nantube films absorb all solar energy transmitted through DSSC; second, absorbed solar energy can be effectively transformed to heat energy; third, increasing the catalytic redox reaction rate of iodine ions on the surface of the electrode, due to its high surface area; forth, effectively transporting electrons

through counter electrode because of its high electric conductivity. The TEG beneath DSSC generates electric power by heat flux flowing from high temperature carbon nanotube of DSSC to the cold bottom of TEG. The power generated in TEG depends on temperature difference between upper and lower surface of TEG. Using this new design solar cell, we could obtain solar energy conversion efficiency of maximum 15%.

U6.4

Ballistic and Diffusive Transports in Carbon Nanotubes. Ji-Yong Park¹, Sami Rosenblatt², Xinjian Zhou², Yuval Yaish², Vera Sazonova², Hande Ustunel², Stephan Braig², Shaoming Huang³, T. A. Arias², Piet W. Brouwer², Jie Liu³ and Paul L. McEuen², ¹Division of Natural Sciences, Ajou University, Suwon, South Korea; ²Laboratory of Atomic and Solid-State Physics, Cornell University, Ithaca, New York; ³Chemistry, Duke University, Durham, North Carolina.

In this talk, the electrical transport properties of metallic and semiconducting single-walled carbon nanotubes will be discussed. The electron-phonon scattering rates in metallic single-walled carbon nanotubes are studied using an atomic force microscope as an electrical probe. From scaling of the resistance of the same nanotube with length in the low and high bias regimes, the mean free paths for both regimes are inferred. The observed scattering rates are compared with calculations for various phonon scattering processes in carbon nanotubes. The intrinsic transport properties of semiconducting nanotubes are studied with the good ohmic contacts and growth of long carbon nanotubes in their diffusive transport regime. Conductance and mobility of semiconducting nanotubes are determined both at low and high temperature. The effects of defects and comparison with semiclassical transport theory will also be discussed.

U6.5

Self-Defined PECVED-grown Carbon Field-Emission Transistors with Applications in Electron Diffraction. Javad Koohsorkhi¹, Yaser Abdi¹, Shamseddin Mohajerzadeh¹, Jaber Derakhshandeh¹, Leila Rezaee¹ and M. D. Robertson²; ¹ECE Department, Thin Film Lab, University of Tehran, Tehran, Iran; ²Department of Physics, University of Acadia, Wolfville, Nova Scotia, Canada.

We report a novel technique for the fabrication of carbon-based field-emission transistors using a self-defined process. The growth of carbon nano-tubes is achieved on (100) silicon substrates using a DC-PECVD system using a combination of C2H2 and H2 at a pressure of 1.8torr and at 650°C. Nickel is used as the seed of growth where its thickness on silicon substrates is set to be 5nm. Before starting the growth of carbon nano-structures, the Ni-coated Si sample is treated in hydrogen for 15min at the growth conditions with the DC-plasma on. After this hydrogenation step, nano-scale islands of nickel seeds are formed on silicon substrate, which are suitable for the vertical growth of CNT's. vertically aligned CNT's are then coated using titanium-dioxide and silver metallic layers with typical thicknesses of 0.1 and $0.3\mu m$, respectively. The quality and purity of carbon nano-structures have been examined using SEM and TEM analyses. The field-emission transistors, proposed in this paper, consist of an inner carbon-based nano-structure surrounded by a concentric bi-layer of TiO2 and silver. The growth condition of CNT/s $\,$ is adjusted so that sparsely distributed nano-structures are formed on the surface of silicon substrate. TiO2 is being deposited using atmospheric pressure CVD whereas metal is deposited using thermal evaporation. After depositing the last metallic layer, the sample is treated using a chemical-mechanical-polishing step to polish off the top dielectric/metal bi-layer and to expose the buried carbon tip. A step of plasma-ashing (oxygen-argon RF-plasma) is also needed to burn the exposed carbon to a desired depth and to form partially filled pipes. This structure acts as a field-emission transistor where by applying a proper voltage between the nano-scale carbon tip (cathode here) and another flat substrate (anode), an electric current is measured. The amount of current depends on the negative voltage applied on the surrounding metal layer which acts as an integrated gate.electrical characteristic of the devices has been measured using a Keithley K96 probe-station. By applying 7.5 volts on the gate the current in the anode side drops by more than one order of magnitude, indicating a controllable tunneling behavior. The fabrication procedure can be implemented on an already-patterned Si substrate where $2x2\mu m^2$ islands are realized using standard photo-lithography. Each island consists of a cluster of nano-structures and can be individually addressed. Due to special physical shape of these self-defined nano-structures, the emitted electrons can be in the form of an electron beam and its application for low energy electron diffraction has been investigated. We used $0.1\mu m$ thin layers of Ge and Si crystals (deposited on salt and washed off) for electron diffraction. The evolution of diffraction patterns has been observed using optical and electron microscopy and further verification of such patterns is being examined using SEM microscopy.

U6.0

Assembly of Single-Walled Carbon Nanotubes using an Electric Field for Gas Sensor. Heewon Seo and Chang-Soo Han; Dep.Intelligence and Precision Machine, Korea Institute of Machinery & Materials, Daejeon, South Korea.

This study is about the single-walled carbon nanotube (SWCNT) device for the gas detection sensor such as the NO2 or SO2. The SWCNT is very useful for the gas detector due to their high adsorption property. But, it is difficult to making for the device using a general micro manipulator because they are too small. Dielectrophoresis is a very useful technique for controlled assembly of the nanotubes on microstructures that has the possibility to be scaled to nano level manufacturing. We control the number and the position of SWCNT between Au electrodes under electric fields by means of simple and cheap method using dielectrophoresis. It is the control factor of the electric field that is applied voltage and electrical type. And we also discussed the electric field effect between electrodes using a computer simulation program. The morphology of the electrode and the number of the SWCNTs were examined by scanning electron microscopy. This fabricated device is useful to make the gas sensor in a commercial product.

U6.7

Long and Oriented Single-Walled Carbon Nanotubes Grown by Ethanol CVD. Limin Huang^{1,3}, Xiaodong Cui^{2,3}, Brian White^{2,3} and Stephen O'Brien^{1,3}; ¹Department of Applied Physics & Applied Mathematics, Columbia University, New York, New York; ²Department of Chemistry, Columbia University, New York, New York; ³the Columbia Nanocenter (NSEC), Columbia University, New York, New York, New York, New York.

Single-walled carbon nanotubes (SWNTs) have been regarded as attractive building blocks for future nanoscale electronic devices. Most of the applications will require the ability to grow or assemble SWNTs with control over diameter, orientation and length. A general chemical vapor deposition (CVD) growth without any external guidance normally yields short (up to tens of micrometers) and randomly oriented SWNTs. Recently, control over the orientation of SWNTs was achieved by introducing an external electric field or by a fast heating technique which involves mechanically sliding the catalyst coated substrate through the furnace. We report a more simple CVD process that can achieve the similar controlled growth in orientation, length and diameter, while neither the specific fast heating technique nor the guidance of external electric field is required. Ethanol and bimetallic CoMo-doped mesoporous silica were used as a carbon feedstock and a catalyst, respectively. Ultralong (millimeters) and horizontally aligned SWNTs can be grown directly on flat substrates or across slits (up to 0.3 mm apart), and the orientation of the nanotubes is always parallel to gas flow direction. The control of the growth direction and length also enables us to fabricate parallel nanotube arrays or two-dimensional networks on flat surfaces. The growth of the carbon nanotubes is relatively fast, due to the high reactivity of ethanol and high activity of the CoMo/silica catalyst, and no doubt contributes to increased length and orientation control. Moreover, the as-grown SWNTs have a relatively narrow size distribution of 0.8-2 nm, a result of the narrow size distribution of the CoMo nanoparticles embedded in the mesoporous silica. This simple CVD process represents an advance towards the controlled growth for large-scale fabrication of nanotube-based devices. Optical and electrical measurement on SWNTs growing across slits will also be demonstrated.

$\underline{\text{U6.8}}$

Carbon Nanotube/Polyaniline pH Sensor. Martti Kaempgen and Siegmar Roth; von Klitzing, Max-Planck-Institute for Solid State Research, Stuttgart, Germany.

Conductivity and high aspect ratio are the basic properties of Carbon Nanotubes (CNTs) in composites. They can be used in order to get conductive composites at a very low percolation threshold and with a minimum amount of material. For conductive transparent electrodes CNTs, are simply sprayed on glass or plastic. Additionally when the CNTs are coated with a sensitive layer one can get a sensor, e.g., for potentiometric applications. We used polyaniline (Pani) coatings on CNTs in order to get a pH sensor. Such composites combine optical and potentiometric pH sensors in a simple way. The coatings can be prepared on nearly any surface. We measured the response over the complete pH range and characterized our sensor in terms of AFM, SEM, potentiometry and UV/VIS spectra

U6.9

Synthesis and Characterization of Carbon-SiOx Nanocomposites. Adela Morales¹, Moises Hinojosa¹, David

Meneses², Emilio Munoz-Sandoval² and Mauricio Terrones²; ¹Div. de Ingenieria Mecanica, FIME-UANL, San Nicolas de los Garza, Nuevo Leon, Mexico; ²Advanced Materials Department, IPICYT, San Luis

Potosi, San Luis Potosi, Mexico.

A route for processing novel nanocomposites consisting of SiOx matrices together with multi-walled carbon nanotubes (MWNTs) or N-doped multi-walled carbono nanotubes (N-MWNTs) is described. The nanotube materials were produced by pyrolizing solutions of ferrocene-touluene and ferrocene-benzylamine in inert atmospheres at 700 °C. Subsequently, the tubes were treated in various ways and embedded in an amorphous SiOx matrix using a room temperature sol-gel method. In particular, tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) were used as SiOx precursors. The materials were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and DTA. We believe these novel composites may be used in the fabrication of reinforced glasses with enhanced mechanical strength and novel optical properties.

U6.10

Label-Free Electronic DNA Sensors Using the Carbon Nanotube Films. Dae-Hwan Jung and Hee-Tae Jung; Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

Recent years have witnessed significant interest in biological applications of novel nanomaterials such as nanotubes with the motivation to create new types of analytical tools for life science and biotechnology. Single-walled carbon nanotubes (SWNTs) are interesting molecular wires with unique electronic properties that have been spotlighted for future solid-state nanoelectronics. Because semiconducting SWNTs could perform as nanoscale Schottky-type field-effect transistors, only semiconducting nanotubes exhibit a large conductance change. For the realization of nanotubebased electronic biosensors, it is necessary to manipulate metallic and semiconducting SWNTs separately. Unfortunately, the conventional synthesis approaches provide SWNT with mixed chiralities, which are not separable on a large scale with current technology. This has open been a bottleneck in the application of SWNT to biosensors that require ready-made semiconducting nanotubes. We have created label-free electronic DNA sensors via large-scale assembly of mixed carbon nanotubes without the need for separating. The electronic structure of metallic SWNTs can be modified by the coupling of π -electrons between a nanotube and aromatic molecules, and that SWNT-based sensors can be use for detecting biological molecules readily without the need for labeling. Sensing for label-free DNA detection was carried out by monitoring electrical current through the SWNT devices dominated by metallic property to each step of the π -stacking of pyrenly group, the immobilization of probe DNA, and the hybridization of target DNA. We observed that the conductance of SWNT film can be substantially decreased by π -stacking of pyrenly group, and regularly increased by probe DNA linkage and target DNA hybridization.

U6.11

WO3 Films Doped with Oxygen Functionalized Carbon Nanotubes: NH3, NO2 and CO Sensing at Room Temperature. Carla Bittencourt¹, Alexandre Felten¹, E. H. Ionescu², R. Ionescu², E. Llobet² and J. J. Pireaux¹; ¹LISE/FUNDP, University of Namur, Namur, Belgium; ²ETSE - DEEA, Universitat Rovira i Virgili, Tarragona, Spain.

Since gas-sensing properties were found in WO3 films, much effort has been made for their improvement, among them the addition of noble metals to the WO3 matrix has proved to improve the selectivity and sensibility of the active layer and to decrease the operation temperature. However, the important goal of working at room temperature was not achieved for this material. On the contrary, carbon nanotubes (CNTs) based gas-sensors work well at this temperature which reduces the power consumption of the device and enables the safe detection of flammable gases. Nevertheless they show a very slow response, what can prevent their use in several situations. Moreover, the agglomeration of CNT into bundles during their synthesis appears as a technological difficulty for forming a well dispersed active layer. To overcome these difficulties, modification of the chemical composition of the carbon nanotubes surface was proved to be efficient. This work shows the feasibility of using a WO3 film doped with CNTs functionalized by oxygen RF-plasma as active layer of gas sensor operating at room temperature. The gas sensing properties were investigated for NO2, NH3 and CO. The influence of the concentration of nanotubes added to the WO3 matrix and their surface chemical composition on the sensing properties were investigated. Films were prepared by mixing tungsten oxide nano-powders and oxygen-functionalized nanotubes in glycerol; the solution was then dropped (using a micro-injector) onto the electrode area of a micro-hotplate transducer and subsequently annealed at 400oC. Different types of active layer were prepared: CNTs with 20 %oxygen at the surface, CNTs with 20 % oxygen +Co +Fe + Al at the

surface, WO3 and WO3 + CNTs. The formation of a well-adhered thick film and dispersed mesh of CNTs was observed by SEM analyses. XPS analyses allowed to evaluate the chemical change at the CNT surface due to the plasma treatment applied before the sensor fabrication as well as the changes induced by adding CNTs to the WO3 matrix. By analyzing the W 4f core level spectra recorded on the WO3 based films it was found that their main structure were properly reproduced by three doublets and the Shirley background. Two doublets were associated to photoelectrons emitted from tungsten atoms with oxidation state +6 and +5. The third doublet was associated with surface defects; this component was found to increase with increasing CNTs concentration in the WO3 matrix. The sensing test showed that the sensors fabricated with pure WO3 were not able to sensing NO2, NH3 or CO when working at room temperature (RT). On the other hand, when working at RT the CNTs sensors showed response to NO2 at 500 ppb, for NH3 at 200 ppm and for CO at 100 ppm. However the best performance was found for sensor fabricated with films WO3:CNTs, response to NO2 at 500 ppb, to NH3 at 1ppm and to CO at 10 ppm.

U6.12

CF4 Plasma Functionalization of Carbon Nanotubes.

Alexandre Felten¹, G. Van Lier², C. P. Ewels³, H. Okuno², J. C.

Charlier^{2,4} and J. J. Pireaux¹; ¹LISE, University of Namur, Namur,
Belgium; ²Unite de Physico-Chimie et de Physique des Materiaux
(PCPM), UCL, Louvain-la-Neuve, Belgium; ³Laboratoire de Physique
des Solides, Universite Paris Sud, Orsay, France; ⁴Research Center in
Micro and Nanoscopic Materials and Electronic Devices (CERMIN),
UCL, Louvain-la-Neuve, Belgium.

Due to their unique electrical, mechanical, thermal and structural characteristics, carbon nanotubes are expected to give rise to a large range of new applications. They are promising in domains such as composites, field emission, electronic devices and gas sensors. But for most of these applications, their exceptional characteristics are tempered by the non-reactive nature of their surface. In order to increase this reactivity, it is necessary to functionalize the surface of carbon nanotubes. Several methods can be used: chemical and electrochemical treatments, polymer wrapping, fluorination, plasma treatments [1]. In this work, the functionalization of carbon nanotubes by a CF4 inductive RF-plasma (13.56 MHz) is presented. The advantages of this method are the fast reaction and processing time, low temperature conditions and the possibility of scaling up to large quantities, possibly via a continuous process. MWNTs have been used, produced both by CVD and by arc discharge. These nanotubes differ by the amount of amorphous or graphitic carbon present at their surface and in the powder. In order to perform a uniform functionalization, the nanotubes were placed inside a glass vessel and a magnet, externally controlled from the plasma chamber, was used to stir the nanotube powder during this treatment. This technique allows us to treat large amounts of nanotubes. The obtained CNT powder was analyzed by X-Ray photoelectron spectroscopy (XPS), confirming that fluorine atoms were successfully grafted onto the CNTs [2]. XPS furthermore showed that the concentration of the grafted groups can be varied up to surface saturation by controlling certain plasma parameters (pressure, power, time treatment, position inside the chamber). F1s spectra show that semi-ionic and covalent C-F bonds are present with varying ratio depending on the plasma parameters. This ratio also depends on the type of carbon nanotubes used. Contact angle measurements were also performed and show that after a CF4 plasma treatment, the surface of the CNTs is very hydrophobic due to the fluorine atoms. Finally HRTEM images were taken to see the structural changes induced by the plasma treatment, showing that the CNTs were not destroyed by the plasma treatment. These results are compared to theoretical Ab Initio calculations, showing the different addition patterns and the expansion of fluorinated domains on the nanotube surface [3]. The difference between semi-ionic and covalent addition, and transitions in addition behaviour are discussed. Acknowledgment: This work is supported by a grant from Region wallone, RW-ENABLE 1 N. O. V. Plank L. Jiang, and R. Cheung, Appl. Phys. Lett., 83 (2003) 2426-2428. 2 A. Felten, C. Bittencourt, G. Van Lier, J.-C. Charlier and J.J. Pireaux, Appl. Phys. Lett., (2004) Submitted for publication. 3 G. Van Lier, C.P. Ewels, F. Zuliani, A. De Vita, J.-C. Charlier, J. Phys. Chem. B, (2004) Submitted for publication.

$\underline{\text{U6.13}}$

Long, Suspended Individual Carbon Nanotube Devices: Growth, Fabrication and Transport. Todd Brintlinger^{1,2} and Michael S. Fuhrer^{1,2}; ¹Dept. of Physics, Univ. of Maryland, College Park, College Park, Maryland; ²Center for Superconductivity Research, Univ. of Maryland, College Park, College Park, Maryland.

We have fabricated devices consisting of individual suspended carbon nanotubes (CNTs) spanning trenches over $70\mu\mathrm{m}$ long and $500\mu\mathrm{m}$ deep. The carbon nanotubes are grown via chemical vapor deposition over existing gold or platinum electrodes, forming complete

electronically addressable devices without exposure of the CNTs to resists or etchants. These CNT devices allow study of the intrinsic transport properties of the nanotubes without disorder induced by the substrate or chemical residues from conventional lithography. Our technique also allows for comparisons between suspended and substrate-bound sections of the same CNT. We present the growth and fabrication procedures along with transport measurements on long, suspended CNTs.

U6.14

Synthesis and Structural Characterisation of Dense Zirconium Oxide-Carbon Nanotube Composites. Fabio Lupo¹,

Neng Yun Jin-Phillip¹, Manfred Ruehle¹ and Radha Kamalakaran¹; ¹Metallforschung, Max Planck Institut, Stuttgart, Germany; ²Advanced Materials Department, IPICyT, San Luis Potosi, Mexico.

Inclusion of carbon nanotube in dense zirconium oxide (ZrO2) was obtained by precipitation of zirconium hydroxide [(Zr(OH)4 nH2O] in the presence of carbon nanotubes and calcinations at 800°C. Dense tetragonal zirconia-carbon nanotubes composite was obtained. Traditional and cross sectional high resolution transmission electron microscopy were performed using different electron microscopy techniques. The carbon-ceramic interfaces were studied in detail by EELS analysis.

U6.15

Multiwalled Carbon Nanotubes (MWNT) Arrays as Dry Adhesive Interface Materials with Enhanced Thermal Contact Conductance. Yang Zhao¹, Tao Tong², Lance Delzeit³, Meyya Meyyappan³, Ali Kashani¹ and Arun Majumdar^{2,4}; ¹Atlas Scientific, Inc., San Jose, California; ²Mechanical Engineering, UC Berkeley, Berkeley, California; ³Center of Nanotechnology, NASA Ames Research Center, Moffett Field, California; ⁴Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

When two surfaces are brought into contact with each other, the actual contact area may be much less than the apparent area of the surfaces depending on the surface roughness, elastic and plastic properties of the surface, as well as the applied load at the interface. Traditionally, thermally conducting epoxies and grease [1] are frequently used to improve interface thermal conductance, but have limited improvement compared to chemically-bonded solid interfaces between two materials [2]. Furthermore, epoxies and grease are often incompatible with high vacuum and cryogenic environment. With extraordinary electrical, thermal, mechanical properties and compatibility with ultra high vacuum (UHV) environment, multiwalled carbon nanotube (MWNT) towers are studied in this work as an interface bridging material to improve the thermal contact properties. Shi et al. [3] have demonstrated that individual MWNTs have thermal conductivity around 3 kW/m-K at room temperature. However, their effectiveness as an interface material has not been studied. In this paper, we will report results both adhesion properties and contact thermal conductance between two surfaces bridged by a MWNT tower. The ultra-fine structure of CNT tower enables effective filling of the cavities at the interface to greatly enhance the thermal conductance. In addition, based on van der Waals attraction, the vertically aligned MWNT towers can be used as re-attachable dry adhesive to bond two surfaces. Adhesion strengths on the order of 10 N/cm2 has been measured. It is conjectured that such MWNT-based thermal conducting dry adhesive will have many applications, especially those involved in space and microelectronics technologies. In the present work, vertically aligned MWNT towers grown on silicon substrates are engaged onto various mating surfaces. Experimental measurement of the interface thermal conductance along with the interface adhesion force will be presented and discussed. References [1] J.P. Gwinn and R.L. Webb, 'Performance and Testing of Thermal Interface Materials,' Microelectronics Journal, 34, 215-222, 2003. [2] R.J. Stoner and H.J. Maris, 'Kapitza Conductance and Heat-Flow Between Solids at Temperatures From 50 to 300 K,' Physical Review B, 48, 16373-16387, 1993. [3] P. Kim, L. Shi, A. Majumdar, P. L. McEuen, 'Thermal Transport Measurements of Individual Multiwalled Carbon Nanotubes,' Physics Review Letters, 87, 215502:1-4, 2001.

U6.16

Physical Properties of Direct-Spun Carbon Nanotube Fibres.

Marcelo Senna Motta, Ian A. Kinloch, Yali Li and Alan H. Windle;

Materials Science and Metallurgy, University of Cambridge,

Cambridge, United Kingdom.

The current accepted wisdom is that carbon nanotubes are the strongest materials known up to date. In theory, individual single-walled nanotubes may have a resistance to elastic deformation as high as 5 TPa[1]. The mechanical properties of carbon nanotube strands, ropes and fibres have also been extensively studied, however the values obtained are only fraction of those obtained for individual nanotubes. In the present work, the tensile strength and electrical

conductivities of carbon nanotube fibres directly spun from chemical vapour deposition are assessed. A detailed description of the fibres preparation method can be found on our previous work[2]. Raman spectroscopy and electron microscopy with associated digital image processing techniques were applied to determine the relationship between the microstructures obtained and the resulting properties of the fibres. Initial results show that a typical microstructure of the direct-spun fibres may consist of a mixture of small single-walled nanotubes and relatively thick multi-walled ones. Despite the structural non-uniformity, the electrical conductivity of the fibres produced under specific conditions can be even higher than that for graphite fibres. Mechanical tests indicated that the fibre properties are strongly dependant on process conditions. The average tensile strength observed was 0.7 ± 0.2 GPa, however, in all cases the mechanical properties could be improved by re-testing shorter lengths. The high values obtained for the mechanical properties of an individual carbon nanotube[1] set the challenge for improving properties of current fibres. Realisation of such a challenge will only be achieved by better understanding and controlling the gas-phase chemical reactions, and the consequent obtainment of a more uniform internal structure in the fibres. [1] V. Popov. Mater. Sci. and Eng. R, 43, 61-102, 2004. [2] Y. Li, I. Kinloch and A.H. Windle. Science, 304

U6.17

Experimental Observation of Carbon and Carbon-metal Nanotoroids. Vladimir V. Kislov and Boris K. Medvedev; Institute of Radioengineering & Electronics, Russian Academy of Sciences, Moscow, Russian Federation.

We report experimental observation (by AFM, STM and HRTEM methods) of nanotoroids for both carbon and carbon-metal superstructures produced by methods of arc discharge and laser ablation. Size of superstructures is \sim 10 nm for carbon and \sim 30 nm for carbon-metal (outer diameter), with inner diameter $\sim 1/3$ of the total. Initial observation of toroids were made for pure carbon, but gradual increase of metal to some optimal concentration dramatically increased the yield of toroidal structures. The influence of pressure, humidity and temperature was also investigated. Also effects of reversible transition of topology (sphere - toroid) on the same sample were observed depending on external parameters. The possibility of such structures was discussed earlier [1, 2], but we also discovered carbon-metal nanocapsules among toroids, with shapes like nanodiscs, reminiscent of human erithrocites. Changing concentrations and metals (Mo, Cr, etc.) leads to differences in shapes and sizes of superstructures. Therefore, new types of topologically closed carbon and carbon-metal nanostructures are discovered, with the theoretical model presented elsewhere [3]. We also discuss some technological aspects of the growth of such toroidal nanostructures. Literature [1]. M. Terrones, W.K. Hse, J.P. Hare, H.W. Kroto, H. Terrones, D.R.M. Walton, Graphitic structures: from planar to spheres, toroids and helices, Phil. Trans. R. Soc. Lond. A, 354, 2025 (1996). [2]. V. Kislov, Rings of the strings - topologically closed superstructures of nanoclusters, Nano-8, 8-th International Conference on Nanometer-Scale Science and Technology, June 28 - July 2, 2004, Venice, Italy [3]. Kislov, I. Taranov, Topological Forms of Carbon and Carbon-Metal Superstructures: from Nanotubes to Toroids and Nanodiscs, 2005 MRS Spring Meeting, March 28- April 1, San Francisco, CA, USA

U6.18

Tensile Loading Experiments and Microstructure Characterization of Macroscopic Neat Single-Wall Carbon Nanotube Fiber. Yeonwoong Jung¹, Hua Fan², Wen-Fang Hwang², Richard E. Smalley² and David E. Luzzi¹; ¹Department of Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Center for Nanoscale Science and Technology, Rice University, Houston, Texas.

We present the first extensive study of the mechanical properties of pure carbon nanotube fibers. The mechanical behavior of macroscopic neat single-wall carbon nanotube (SWNT) fiber extruded from super acid suspensions is studied through monotonic, cyclic and load relaxation experiments in tension. The effect of processing conditions on the properties is investigated. We find that vacuum annealing decreases elongation ratio and increases Young's modulus by over three times. The cyclic application and release of a tensile load induces irreversible hysterisis in fiber strain while increasing tensile strength. The first cycle produces 55% of the total property change produced through cyclic loading. Strain aging of SWNT fibers produces a pronounced load drop of greater than 50% at long times; this effect is greatly reduced by annealing. Cyclic tensile loading tests produce a similar hardening effect as vacuum annealing. We interpret the observed mechanical behaviors based on the interaction mechanisms of individual SWNTs and acid resides between the SWNTs. The microstructure of fibers is characterized using Focused Ion Beam (FIB) processing combined with Scanning Electron

Microscopy (SEM). Cross sections of fibers prepared by step-wise FIB milling reveal that the macroscopic fiber is composed of fibrils of SWNT ropes aligned in the direction of the fiber axis. The structure of fiber sections selectively cut with different orientations is investigated and will be discussed using the FIB lift-out technique and Transmission Electron Microscopy (TEM).

U6.19

Magnetic Properties of O2 or NO Assembly Confined in SWNTs Bundles. Hironori Ogata¹, Masato Mukaiyachi¹, Hiroko Kamemura¹, Hitoshi Kino¹ and Yahachi Saito²; ¹Dept. of Materials Chemistry, Hosei University, Tokyo, Japan; ²Quantum Engineering, Nagoya University, Nagoya, Japan.

It is well known that single-walled carbon nanotube (SWNT) bundles have consideably uniform and one-dimensional micropore, in which various kinds of molecules could be adsorbed. Oxygen (O2) or nitrogen monoxide (NO) has the spin S=1 or 1/2. The magnetic properties of O2 or NO molecules confined in the micropore of SWNT bundles have been investigated by dc-magnetic susceptibility measurements. Adsorption of O2 or NO molecules at various pressure were performed in the SQUID magnetometer in-situ. Adsorption isotherm of O2 or NO was also measured to determine the value of micropore (interstitial site of SWNT bundles shows Curie-Weiss behavior and no clear magnetic transition down to 1.9 K. We can also conclude that NO molecules adsorbed in the interstitial site form a dimer structure even at 301 K due to the micropore effect.

U6.20

An Investigation into Carbon Nanotube based Shear Force Sensing through Capacitive and Optical Polarization Measurements. Chi-Nung Ni, Christian Deck, Prabhakar Bandaru and Kenneth S. Vecchio; Mechanical & Aerospace Engineering, University of California, San Diego, La Jolla, California.

Carbon Nanotubes (CNT) have high mechanical stiffness and strength as well as tunable electrical properties. These properties have been exploited for the use of individual nanotubes or ensembles of nanotubes as scanning probes, electron emitters through field emission, and for actuators and force sensing application in NEMS. While the majority of the applications to date use either their superior mechanical or electrical characteristics, we report on the possibility of a CNT based mechano-electrical transduction device where minute tactile and shear forces can be sensed through capacitance/optical polarization measurements. Electron-beam lithography was used to pattern a Ni catalyst particle at the tips of two gold electrodes with nanometer spacing. Metallic carbon nanotube bundles are then grown on the Ni surfaces through thermal Chemical Vapor Deposition (CVD) in a mixed gas environment of acetylene and ammonia, with argon as a carrier gas. In response to shear forces/breeze, the nanotubes bend and the corresponding change in capacitance between the nanotubes is measured, with great sensitivity, through an external electrical circuit. We will also report on using optical polarization measurements to estimate the amount of nanotube bending and perform diagnostics, e.g., the polarization signal would saturate when the nanotubes are lying sideways. The effect of carbon nanotube height, diameter and spacing on the shear force sensing capability will be analyzed. Other potential applications of the above device, viz., the monitoring of boundary layer fluid flows, security sensors for intruder detection, and molecular sensors where the capacitance change through molecules attaching to functionalized vertical CNTs is monitored, will be presented.

$\underline{\text{U6.21}}$

Electronic Properties of Boron Carbonitride Nanotubes.

Fabrice Piazza², Jose Eneider Nocua² and Gerardo Morell^{1,2};

Physical Sciences, University of Puerto Rico, San Juan, Puerto Rico;

Physics, University of Puerto Rico, San Juan, Puerto Rico;

Chemistry, University of Puerto Rico, San Juan, Puerto Rico;

Biology, University of Puerto Rico, San Juan, Puerto Rico.

Boron carbonitride nanotubes (BCNNTs) are extremely interesting materials due to the many properties they share with carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs), and some unique differences that represent advantages when it comes to technological applications. One crucial difference is the relative simplicity in controlling the electronic properties of BCNNTs because they are primarily determined by the atomic composition, whereas for CNTs they are determined by their helicity, which remains elusive to control. Particularly important is the possibility of nanostructures with tunable band-gap between that of BNNTs and CNTs. Therefore, BCNNTs are promising candidates for nanoscale electronic and optical devices. We have synthetized BCNNTs with a high yield without catalyst particles or pre-grown template nanostructures by producing an arc discharge in the presence of elemental boron, elemental carbon and molecular nitrogen. Combined transmission

electron microscopy, electron energy loss spectroscopy and Raman spectroscopy analyses indicate that CNTs and BCNNTs wrapped around CNTs are formed during the process. The detailed analysis of the findings suggest the early formation of CNTs followed by the template growth of BCNNTs through the concerted substitution of boron and nitrogen for carbon in the in situ grown carbon nanotubes without causing topological changes. Interdigitated device structures on Si substrates were used to study the electronic properties of the BCN nanotubes. A solution of BCNNTs was dispersed over the device structures, out of which some fell appropriately across digits and enabling their electronic characterization. Their intermediate properties between those of CNTs and BN nanotubes is discussed.

U6.22

Structure-Based Carbon Nanotube Separations by Ion-Exchange Chromatography of DNA/CNT Hybrids. Steve Lustig¹, Anand Jagota², Constantine Khripin² and Ming Zheng¹; ¹DuPont, Wilmington, Delaware; ²Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania.

The realization of nanotube-based electronics in many widespread applications is critically dependent on the ability to install a nanotube with the required properties in the required circuit location. Since current SWNT synthesis methods grow ensembles of different chiralities, it remains necessary to disperse the grown bundles and isolate SWNTs according to electronic character. Single-stranded DNA wraps helically around individual single walled carbon nanotubes to form a DNA/CNT hybrid, which is both stable and dispersible in aqueous solution. Subjected to ion-exchange chromatography, a hybrid elutes at an ionic strength that depends on the electronic character and diameter of the core nanotube, thus providing a mechanism for separating nanotubes by chirality. We present a theoretical model for this separation process that explains all the salient features observed experimentally to date, and provides accurate predictions for critical elution salt concentration. The competition between adsorption on the stationary phase and counterion condensation in the mobile phase is characterized by estimating the difference in free energy between the two states of the hybrid. Parametric study of the DNA wrapping geometry, SWNT dielectric properties, hybrid length and diameter indicates that the elution is most sensitive to the hybrid's effective charge density, primarily governed by the DNA helical pitch. The model correctly predicts hybrids with metallic nanotubes are weaker binding than hybrids with semiconducting nanotubes and larger diameter nanotubes are eluted at later times.

$\underline{\mathbf{U6.23}}$

20 nm Nanoimprint Lithography Stamps RIE-etchhed in Silicon using Carbon Nanotubes as Etch Masks. Michael Stenbaek Schmidt, Theodor Nielsen, Tommy Schurmann, Dorte Norgaard Madsen, Anders Kristensen and Peter Boggild; MIC - Department of Micro and Nanotechnology, Technical University of Denmark, Kgs. Lyngby, Denmark.

We have developed a method for etching silicon anisotropically using individual multiwalled nanotubes as etch masks and demonstrated down to 20 nm wide, 150 nm tall ridges with the undamaged nanotube still lying on top. Preliminary studies show that these sharp protrusions could be used both for nanoimprinting in PMMA, a thermoplast, and elastomer moulding with PDMS. Channels with diameters less than 50 nm and with extreme smoothness are crucial for examining individual DNA molecules: wider channels cause the DNA to curl up, and rough channels disturb the liquid flow and the passage of the biomolecules [1]. Carbon nanotubes are chemically inert, which make them highly etch resistant. This has been used by several research groups [2,3] to underetch supporting silicon to form a suspended nanotube device as well as for purification, where the etching primarily attacks other forms of carbon than nanotubes, as well as catalytic particle residues from the growth process. In Reactive Ion Etching (RIE) a combination of physical and chemical etching makes anisotropic etching of silicon possible. The etch process was optimized to obtain nearly vertical etching profiles of silicon with no measurable damage to the carbon nanotubes, by carefully balancing of the pressure, oxygen contents and power of the RIE process. We have investigated the parameter space of the etching process and have arrived at a highly reproducible approach towards line-shaped protrusions defined by the diameter of the multiwalled nanotube. A simple setup was used to imprint such samples into PMMA. At this stage, the feasibility of imprinting has been demonstrated, however not yet with the intended resolution. A method of increasing the adhesion of the CNTs to the silicon substrate is demonstrated, hence the CNT is not lost as a result of the pattern transferring process, and the stamp can be used multiple times. We discuss the prospects of transferring the extreme molecular smoothness of the MWNT to the nanochannels, and how the method can be adapted to large-scale production. References [1] J. O. Tegenfeldt, C. Prinz, H. Cao, R. L. Huang, R. H. Austin, S. Y. Chou,

E. C. Cox, J. C. Sturm, Anal Bioanal. Chem., 378, 1678-1692, 2004.
[2] P.A. Williams, S. J. Papadakis, M. R. Falvo, S. Washburn, and R. Superfine, Physical Review Letters, 89, 255502-1, 2002.
[3] J. Nygaard, D. H. Cobden, Appl. Phys. Lett., 79, 4216-4218, 2001.

U6.24

Resonant Raman Spectroscopy of Single-Walled Carbon Nanotubes. Angela Hight-Walker¹, Guangjun Cheng¹ and Danilo Romero²; ¹Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ²Laboratory for Physical Sciences, University of Maryland, College Park, Maryland.

We investigate the effects of electron-hole correlations on the optical properties of single-walled carbon nanotubes (SWCNT) by means of resonant Raman spectroscopy. The measurements are carried out with the newly built confocal Raman microscope at the NIST-Optical Technology Division. The microscope is capable of working over a wide range of temperatures (T=4.2-300K) and magnetic fields (H=0-8T). Resonance enhnacement of the Raman scattering intensity of the radial breathing modes in SWCNTs is probed with tunable laser excitation sources. Excitonic effects are explored by comparison of the resonant Raman spectra of bulk and individual carbon nanotubes.

U6.25

Raman Characterization of Functionalized Carbon Nanofiber.

Brandon Black, Max Alexander, Rajiv Berry and Heather Dowty; Air
Force Research Lab, WPAFB, Ohio.

There has been great interest in functionalized carbon nanofibers for their use in creating polymer nanocomposite systems, that can be used for highly conductive nanocomposites. Here we report on the raman characterization of carbon nanofibers containing various functionalities in order to investigate the surface chemistry of the nanofiber. Raman spectra will be presented and tentatively correlated with the electrical and mechanical characterization of nanofiber/polymer resin system.

U6.26

Carbon Nanotubes: Research and Learning for Undergraduate Students. T. Randy Dillingham, Tim Porter, Cynthia Hartzell, Tim Vail and Marilee Sellers; Northern Arizona University, Flagstaff, Arizona.

Providing research and learning opportunities in nanoscience and nanotechnology for undergraduate science and engineering students will become increasingly important as these important areas continue to rapidly expand. Faculty at Northern Arizona University (which is a predominantly undergraduate institution) have joined forces to develop a cross-disciplinary course with an overarching theme centered around carbon nanotubes. Research laboratories with various analytical capabilities are utilized from the Departments of Physics, Chemistry, Biology, and Electrical Engineering. The techniques that are used include x-ray photoelectron spectroscopy, nuclear magnetic resonance, scanning electron microscopy, and micro-sensor technology. The course content, the student activities, and the initial experience in developing and team-teaching the course are described. *Supported by the National Science Foundation under grant number 0304667

U6.27

Nanotube Transistors under Electrolyte: Intrinsic and Extrinsic Responses. <u>Ju Hee Back</u>, Taner Ozel and Moonsub Shim; Materials Science and Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois.

Electrochemically gated carbon nanotube transistors are promising in sensor applications due to their high sensitivity and performance in an electrolyte environment. Understanding how nanotube transistors respond to changes in the surrounding medium is essential in incorporating them into chemical and biological applications. Carbon nanotube transistors integrated with microfluidic channels are utilized to study effects of pH, electrolyte concentration, composition, etc. on transport characteristics. Influences arising from variations at the nanotube-metal contacts, the substrates, and the sidewalls of nanotubes are examined.

U6.28

Production and Characterization of Single-Crystal FeCo Nanowires inside Carbon Nanotubes. Ana Laura Elias¹, Julio Alejandro Rodriguez Manzo¹, Molly R. McCartney², Dmitri Golberg⁴, Adalberto Zamudio¹, Samuel Eliazar Baltazar¹, Florentino Lopez Urias¹, Emilio Munoz Sandoval¹, Chengchun Tang³.⁴, Yoshio Bando³.⁴, David J. Smith², Humberto Terrones¹ and Mauricio Terrones¹.⁴; ¹Advanced Materials Department, IPICyT, San Luis Potosi, San Luis Potosi, Mexico; ²Department of Physics and Astronomy and Center for Solid State Science, Arizona State University, Tempe, Arizona; ³Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan;

 $^4{\rm International}$ Center for Young Scientists (ICYS), National Institute for Materials Science, Tsukuba, Japan.

Periodic arrays of ferromagnetic nanostructures could be used in the fabrication of high density magnetic storage devices [1]. In the past, it has been demonstrated that Fe-filled carbon nanotubes exhibit large magnetic coercivities at room temperature (e.g. 430 Oe) [2], greater than those associated with Ni and Co nanowires [3]. However, FeCo alloy nanowires offer an alternative to magnetic data storage because they could exhibit even larger coercive fields at room temperature [4]. Due to its robustness, FeCo alloys are also used in high temperature magnetic applications (e.g. high temperature space power systems, wiring materials for audio and radio frequency transformers, magnetic bearings, magnetomechanical actuators, etc.). For data storage devices, it is believed that nanowire arrays may have significant potential in magnetic data storage devices (Quantized Magnetic Disks) due to their size and anisotropic behavior, which permits the use of a smaller bit size (one per nanowire), thus increasing the attainable recording density [5]. We describe the production and characterization of aligned multi-walled carbon nanotubes (MWNTs) filled with monocrystalline FeCo nanoalloys. The method involves the aerosol thermolysis of toluene-ferrocene (FeCp₂)-cobaltocene (CoCp₂) solutions at temperatures ranging from 600 - 800 °C in an inert atmosphere. The materials were carefully characterized using state-of-the-art high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, X-ray powder diffraction (XRD) and SQUID magnetometry. Interestingly, these FeCo materials exhibit large magnetic coercivities (e.g. 1200 Oe) at room temperature. Elemental mapping studies reveled homogenous concentrations of Fe and Co within the nanowires. To the best of our knowledge, the production of monocrystalline FeCo nanowires has never been reported hitherto. 1. S.Y. Chou, M.S. Wei, P.R. Krauss and P.B. Fischer, J. Appl. Phys. 1994, 76, 6673. 2. N Grobert, WK Hsu, YQ Zhu, JP Hare, HW Kroto, DRM Walton, M Terrones, H Terrones, P Redlich, M Ruhle, R Escudero, F Morales, Appl. Phys. Lett. 1999, 75, 3363. 3. T.M. Whitney, J.S. Jiang, P.C. Searson, C.L. Chien, Science 1993, 261, 1316. 4. M.E. McHenry, M.A. Willard, D.E. Laughlin, Progress in Materials Science 1999, 44, 291. 5. S. Y. Chou, Proc. IEEE 1997, 85, 652.

U6.29

Floating Catalyst Carbon Nanotube Production in a Vertical Furnace. Christine Larson^{2.1}, Bruce M. Clemens² and Brett Cruden¹; ¹Center for Nanotechnology, NASA Ames Research Center, Moffett Field, California; ²Materials Science and Engineering, Stanford University, Stanford, California.

Because of their remarkable electronic properties, carbon nanotubes have proven valuable to many applications, such as for novel semiconductor devices. Carbon nanotubes also have remarkable mechanical properties that are valuable for thermal protection and high strength materials applications, among others. These applications require large quantities of nanotubes unlike the electronics applications, and the development of these products is limited by the current small-scale production of nanotubes. In order to produce commercially viable products, a large-scale production system for nanotubes must be created. Current production is done in laboratory small-scale systems and produces a few grams of nanotubes per day. The cost can be as much as \$500 per gram. The floating catalyst method of carbon nanotube production in a vertical furnace can produce grams of nanotubes in an hour with a much lower cost. In the floating catalyst method, catalyst and carbon containing gas are continuously supplied to the reaction chamber, preventing the spoiling of catalyst, typically seen in supported catalyst methods. Nanoparticles of catalyst are suspended in the carbon gas flow allowing nanotubes to form. The vertical furnace system is composed of a three-zone 3-inch tube furnace with methane as the carbon source and ferrocene as the iron catalyst. Methane gas will carry ferrocene vapors into the lower end of the reaction tube. Nanotubes formed in the tube will be carried out the exhaust and captured. This poster will present a parametric study of the carbon nanotubes produced in this reactor for varying gas flow rates, catalyst concentration, and growth temperatures. The products are characterized by TEM, TGA and Raman spectroscopy.

U6.30 Abstract Withdrawn

U6.31

Toward a Dense, Monolithic, Carbon Nanotube Material.

Glenn Paul Sklar and Jeff C. LaCombe; Materials Science, University of Nevada, Reno, Reno, Nevada.

Dense arrays of multi-walled carbon nanotubes were grown by chemical vapor deposition. Anodic aluminum oxide templates were used from which to grow these MWCNT's (1). Our work improves

upon this template approach by employing pulse-reverse electrodeposition to deposit cobalt catalyst to the bottom of the 50 nm diameter aluminum oxide pores (2). This electrodeposition method produced an active catalyst in the template pores for MWCNT growth. There was no need to reduce the catalyst deposit for hours under carbon monoxide or hydrogen gas in a tube furnace. The result, after chemical vapor deposition, being MWCNT's growing out of the template pores to lengths of tens of microns in 10 minutes in greater than 90 % of the pores. While others employing the templated MWCNT technique are interested in MWCNT arrays for microelectronics and high surface area electrodes, our focus is in making the initial steps toward realizing the production of an actual MWCNT, dense, monolithic, macroscopic material. We are investigating how the anodized aluminum template morphology, pulse-reverse electrodeposition, and the chemical vapor deposition conditions can be manipulated to casuse MWCNT's to grow side by side in tightly packed arrays and even fuse together along their lengths, as they grow, to give the desired material. We have obtained a number of FE-SEM micrographs that support this type of MWCNT growth. (1) S. Jeong, et al., Chemistry of Materials 14, 1859 (2002). (2) K. Nielsch, et al., Advanced Materials 12, No. 8, 582 (2000).

U6.32

Electrical Properties of 0.4 cm Long Single-Walled Carbon Nanotubes. Zhen Yu, Chris Rutherglen, Shengdong Li and Peter Burke; EECS, UC Irvine, Irvine, California.

Centimeter scale aligned carbon nanotube arrays are grown from nanoparticle/metal catalyst pads. We find the nanotubes grow both with and against the wind. A metal underlayer provides in-situ electrical contact to these long nanotubes with no post growth processing needed. Using the electrically contacted nanotubes, we study electrical transport of 0.4 cm long nanotubes. The source drain I-V curves are quantitatively described by a classical, diffusive model. Our measurements show that the outstanding transport properties of nanotubes can be extended to the cm scale and open the door to large scale integrated nanotube circuits with macroscopic dimensions.

U6.33

Effect of Heat Treatment on Structure of Multi-walled Carbon Nanotubes. <u>Kris Behler</u> and Yury Gogotsi; Material Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

The effects of oxidation in air and high-temperature vacuum annealing on the structure of small-diameter multi-walled carbon nanotubes has been investigated using Raman spectroscopy and transmission electron microscopy (TEM). Heat treatments of tubes at 1800°C, and above, in vacuum leads to improved wall graphitization. Annealing, at temperatures of 2000°C, is conducive to polygonalization, mass transfer and overgrowth shown by TEM studies. Raman spectroscopy confirms the TEM studies through the observation of peak separation between the G and D' bands, a decrease in the R-value (ID/IG ratio) and an increase in intensity of the second order peaks. Since the D-band position of carbon and the second order peak intensity are dependent on the excitation wavelength, investigation of the D-band shift and enhancement of the second order peaks over the range of 1.59 eV to 5.08 eV yields results that facilitate characterization of the multi-walled nanotubes. Oxidation at and below 600°C in air results in removal of small amounts of amorphous or disordered carbon, but does not have a significant effect on Raman spectra of the nanotubes.

U6.34

Directional Growth of Single-Walled Carbon Nanotubes on Insulator for Integrated Nanoelectronic Applications.

Song Han, Xiaolei Liu and Chongwu Zhou; EE-Electrophysics,
University of Southern California, Los Angeles, California.

In the past decade, single-walled carbon nanotubes (SWNTs) have attracted enormous attention as model systems for nano-science and nanotechnology. Many applications have been proposed and demonstrated such as nanotube electronic devices and sensors. To develop integrated nanoelectronic systems based on nanotubes, ordered SWNT architectures are of special interest for both fundamental research and industrial applications. Great effort has been devoted to carbon nanotube synthesis using chemical vapor deposition methods; however, the product usually consists of entangled mats of carbon nanotubes. To address this problem, we have developed a novel high-throughput method to grow highly aligned and evenly spaced carbon nanotube arrays on crystalline insulating substrates for the first time. The nanotube orientation was found to favor certain crystalline directions of the substrate, regardless of the gas flow direction. This is in sharp contrast to the randomly oriented growth of nanotubes on Si/SiO2 substrates. These nanotubes are commonly tens of micrometers long, and the inter-tube spacing is typically around 200 nm. In addition, a second layer of nanotubes can be grown along the gas flow direction atop the first layer by carrying out a second round of CVD synthesis. This

observation, as a side proof, supports the hypothesis that the substrate-nanotube interaction plays an important role. Our synthesis of dense arrays of well aligned and evenly spaced carbon nanotubes paves the way toward large-scale assembling of nanotube-on-insulator (NOI) devices and circuits, in analogy to the silicon-on-insulator (SOI) approach adopted by the semiconductor industry.

U6.35

Biological Self Assembly of Carbon Nanotubes for Nanoelectronics. Cengiz Sinan Ozkan¹ and Xu Wang²; ¹Mechanical Engineering, University of California at Riverside, Riverside, California; ²Chemical and Environmental Engineering, University of California at Riverside, Riverside, California.

We describe self assembly processing of functional carbon nanotubes using single strand deoxyribonucleic acid (DNA) and peptide nucleic acid (PNA) fragments. Previous research has shown the self assembly of carbon nanotubes to quantum dots via a simple peptide bonding. Here, we make use of the DNA and PNA for self assembly of nanoscale components because of its spatial encoding capabilities which will be eventually useful for the integration of devices. During self assembly, first multiwalled carbon nanotubes have been functionalized via oxidation to introduce COOH groups at the nanotube ends. Amine functionalized ss-DNA and PNA fragments were attached to the COOH groups via the (1-ethyl-3-dimethylaminopropyl) carbodiimide HCl (EDC) coupling reaction. The resulting heterostructures have been characterized using Fourier transform infrared spectroscopy, Raman spectroscopy, scanning and transmission electron microscopy and energy dispersive spectroscopy. We have also conducted platinum metallization of DNA and PNA fragments to study the properties conductive biological linkages to inorganic components. The metallized nanotube-DNA and nanotube-PNA complexes have potential applications in future applications including nanoelectronics and sensors.

06.30

Virus Based Self Assembly of Carbon Nanotubes and Quantum Dots. Cengiz Sinan Ozkan¹ and Chunglin Tsai²;

¹Mechanical Engineering, University of California at Riverside, Riverside, California; ²Electrical Engineering, University of California at Riverside, Riverside, California.

Application of biomolecules in self-assembly has an advantage to produce functional building-block for bottom-up approach in nanofabrication. Well known unenveloped viruses such as poliovirus (PV) and tobacco mosaic virus (TMV) were used in our self-assembled nanostructure. Icosahedral PV and cylindrical TMV particles provides different geometric options for heterostructure assembly along with their well characterized surface properties and nanoscale dimensions. 1-Ethyl-3-(3-dimethyl aminopropyl)-carbodiimide (EDC) coupling was applied for covalent conjugation between organic virus capsid and functionalized inorganic nanoparticles such as single-walled carbon nanotubes (SWCNT) or quantum dots (QD). We have demonstrated several building blocks using EDC coupling such as SWCNT with PV particles and carboxylated QDs with TMV particles to form heterojunctions in nanoscale self-assembly. By taking advantage of the receptor recognition to its virus counterpart, we have also shown that antibody functionalized nanoparticles (SWCNTs, QDs, and Pt particles) attached only to where the virus counterpart was. In this case, directed and selective hybridization of hetero-nanostructures can be implemented. While using viruses as linkers, we can selectively make conductive interconnects by metallizing virions with metal particle functionalized antibodies which open an avenue to bio-nanoelectronics.

U6.37

Novel Electrical Properties of Carbon Nanotube Based Y-Junctions. <u>Prabhakar Bandaru</u>, Pengyuan Yu, Chiara Daraio and Sungho Jin; Materials Science Program, UC, San Diego, La Jolla, California.

In recent years, Carbon Nanotubes (CNT) have emerged as one of the foremost contenders for a nanoelectronics based technology. We report on the electrical properties of CNT based Y-junctions, with the ultimate aim of implementing a nanotube based circuit topology and electronics. The Y-junction morphologies have a natural asymmetry at the junction region due to the presence of non-hexagonal defects which are required for energy minimization. The carrier delocalization and the inevitable presence of catalyst particles, introduced during growth, at the bend induce a net charge and scattering which can be exploited in constructing electronic devices. Our preliminary electrical measurements on these CNT Y-junctions reveal the possibilities of using these for switching and transistor related applications. The CNT Y-junctions are synthesized through thermal Chemical Vapor Deposition (CVD) using a carbon feedstock mixture of ferrocene $(C_{10}H_{10}Fe)$ and xylene $(C_{10}H_{10})$ together with a Ti containing precursor gas-C₁₀H₁₀N₄Ti. Argon and hydrogen are used as carrier

gases. We have assembled and electrically characterized the DC resistance and the AC impedance of several Y-junctions. The observation of inverting/switching in a three-terminal Y-junction, up to 42 kHz, alerts us to the vast potentialities of the Y-junction devices in the development of nanoelectronic components including inverters, logic gates, and frequency mixers. An electrical impedance model of a MWNT Y-junction will be presented which will help gain an understanding of the current transport mechanisms in these structures. 1. N. Gothard, et al. Controlled growth of Y-junction nanotubes using Ti-doped vapor catalyst, Nanoletters 4, 213-217 (2004).

U6.38

Intercalation and Exfoliation of Nanosize Graphitic Cones and Polyhedral Crystals. Svetlana Dimovski¹, Haihui Ye¹, Yury Gogotsi¹, Maritza Gallego² and Igor Barsukov²; ¹Drexel University, Philadelphia, Pennsylvania; ²Superior Graphite Co., Chicago, Illinois.

Polyhedral axial nanostructures in the shapes of faceted needles, rods, barrels, and double-tipped pyramids that we named graphite polyhedral crystals (GPCs) [Y. Gogotsi et al., Science, 290, pp. 317-320 (2000)], and graphite conical crystals (GCCs) [Gogotsi et al., Carbon, 40, pp. 2263-2267 (2002)] were intercalated and exfoliated, and structure of the produced material was studied by SEM, TEM, XRD and Raman Spectroscopy. Carbonaceous material containing GPCs and GCCs was intercalated in concentrated 50:50 H2SO4/HNO3 for 1 hour. An acid mixture was decanted and the sample was washed with DI water and dried on a filter paper for about 24 hours. This material has been expanded in accordance with AIMS standard procedure. Upon cooling, the graphite worms formed were transferred to a graduated cylinder where their volume and weight were determined. Graphite polyhedral crystals (GPCs) can be considered as giant radially extended carbon nanotubes having polygonal cross-section. TEM studies of these materials confirm their graphitic nature, and our exfoliation experiments indicate that tube walls consist of closed coaxial graphene shells (Russian-doll model). GPCs survived very severe intercalation and exfoliation conditions, most of them retaining their original shape of faceted axial whiskers, although the damage in the form of cracks along the axis and striations on the conical surfaces was observed on most of the crystals.

U6.39

Anodic Aluminum Oxide as a Template for Carbon Nanotube Field Emitters in the Triode Structure. Fu-Ming Pan¹,

Chen-Chun Lin¹, Bo-Lin Chen¹, Cheng-Tzu Kuo¹, Mai Liu² and Chi-Neng Mo²; ¹Dept. Materials Science and Engineering, National Chiao-Tung University, Hsinchu, Taiwan; ²Chunghwa Picture Tubes, Ltd., Taoyuan, Taiwan.

We have used anodic aluminum oxide (AAO) as the template to grow carbon nanotubes (CNT) as the field emitter of the triode structure by electron cyclotron resonance chemical vapor deposition (ECR-CVD). The density and the length of the carbon nanotubes grown from AAO pore channels can be controlled by the CNT growth time and the CH₄ concentration of the precursor gas mixture. A too high CH₄ concentration leads to the CNT growth of a small tube length and density on the AAO surface. A relatively small CH₄ concentration, on the other hand, results in a high CNT density, and thus a deteriorated field emission property due to a larger screen field effect. The triode structure is fabricated on silicon wafers. The triode structure is first fabricated on the wafer by conventional integrated circuit processes with a polysilicon layer as the gate electrode and silicon oxide as the dielectric layer. Al film is then sputter-deposited on the wafer, followed by annealing and chemical-mechanical polishing (CMP). The AAO template is formed using oxalic acid as the electrolyte solution at temperatures < 20°C. Cobalt is used as the catalyst to grown CNT in the AAO pore channel. We have studied the dependence of the AAO growth on the pattern window size of the triode structure. The field-emission characteristics of the AAO-CNT triodes are studied and to be presented in the meeting.

> SESSION U7: Chemistry and Manipulation Chair: Florian Banhart Thursday Morning, March 31, 2005 Room 3024 (Moscone West)

8:30 AM *U7.1

Manipulating Carbon Nanotubes with Nucleic Acids.

Ming Zheng, Bruce A. Diner, Robert S. Mclean and Xueying Huang;

DuPont Central Research & Development, Wilmington, Delaware.

Single-stranded DNA (ssDNA) forms stable complex with CNT and effectively disperses CNT into aqueous solution. We found that a particular ssDNA sequence ($d(\mathrm{GT})n,\,n=10$ to 45) self-assembles into an ordered supramolecular structure around individual CNT, in

such a way that the electrostatic properties of the DNA-CNT hybrid depend on tube type, enabling CNT separation by anion-exchange chromatography. In this talk, I will show the purification of single (n, m) type carbon nanotubes, solution redox chemistry of purified and separated DNA-CNTs, and alignment of DNA-CNTs on solid substrates for device applications. This work comes from the Molecular Electronics group at DuPont CR&D.

9:00 AM *U7.2

Double Resonance Theory and the Evolution of Defects in Multiwalled Nanotubes following Carboxylation.

Seamus Anthony Curran¹ and David L. Carroll¹; ¹Physics

Department, New Mexico State University, Las Cruces, New Mexico; ²Physics Department, Wake Forrest, Winston-Salem, North Carolina.

The nature of defects in nanotube cause significant changes in the electronic response using different laser lines after substantial defect introduction caused by carboxylation. The most dramatic effect can be seen in the D_I line whose position and intensity is dependent on significant resonance response. This is caused by the presence of Stones-Wales defects which change the density of states. We also see strong resonant behavior in the Ln+D_I (n = 1,2) modes and D_{II} phonon modes. All the dispersive modes such as the D_I, D_{II}, L1 and L2 can be explained by an intervalley and intravalley transitions which are strongly resonant dependent.

10:00 AM *U7.3

Tuning the Electronic Properties of Single Wall Carbon Nanotubes by Controlled Functionalization. Thomas Pichler, IFW-Dresden e.V., Dresden, Germany.

The electronic properties of single wall carbon nanotubes (SWCNT) are determined by the local one-dimensional arrangement of their sp2 hybridised carbon atoms, such that their character can be insulating, semiconducting or metallic, the latter exhibit a Luttinger liquid ground state. Examples of our recent work on how one can analyse these electronic properties using high energy spectroscopy as a probe and how to functionalise them in a controlled manner will be given. The latter aspect will be discussed in detail and will include typical examples of the three alternative doping routes, namely, substitution, intercalation and endohedral doping. For metallic SWCNT and those filled with C60 doping induced changes will be discussed in the framework of a dimensionality crossover which causes a transition from a Luttinger liquid to a Fermi liquid. The detailed understanding of these fundamental electronic properties of functionalized SWCNT is key to their future success as basic elements for nanoelectronic devices.

10:30 AM <u>U7.4</u> Abstract Withdrawn

10:45 AM *U7.5

Solution Phase, Near-Infrared Optical Sensors based on Single Walled Carbon Nanotubes. Paul W. Barone¹, Seunghyun Baik¹, Daniel A. Heller² and <u>Michael S. Strano¹</u>; ¹Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Molecular detection using near infrared (n-IR) light between 0.9 and 1.3 eV has important biomedical applications because of greater tissue penetration and reduced auto-fluorescent background in thick tissue or whole blood media. Carbon nanotubes have a tunable n-IR emission that responds to changes in the local dielectric function but remains stable to permanent photobleaching. In this work, we report the synthesis and successful testing of solution phase, near-infrared sensors, with β -D-glucose sensing as a model system, using single walled carbon nanotubes that modulate their emission in response to the adsorption of specific biomolecules. New types of non-covalent functionalization using electron withdrawing molecules are shown to provide sites for transferring electrons in and out of the nanotube. We also show two distinct mechanisms of signal transduction fluorescence quenching and charge transfer. The results demonstrate new opportunities for nanoparticle optical sensors that operate in strongly absorbing media of relevance to medicine or biology. Note: Drs. Barone and Baik contributed equally to this work.

11:15 AM U7.6

Site-Selective Functionalization of Carbon Nanotubes.
Raghuveer S Makala, A. Kumar, P. G. Ganesan, G. P. Louie and G. Ramanath; Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Functionalizing carbon nanotubes (CNTs) is of widespread interest for separating CNTs of different chiralities, assembling and interconnecting CNTs, and tailoring the matrix-CNT interactions in nanocomposites. Derivatizing CNTs with nanostructures is also

attractive for new CNT-based hybrid nano- and bio-device concepts that harness the unique properties of the constituent nanostructures. However, conventional wet-chemical functionalization routes (e.g. aggressive acid treatments) do not allow control over the functionalization location. Here, we demonstrate a novel, flexible and scalable approach of using focused ion-irradiation combined with mild chemical exposures to derivatize preselected nanoscale segments of CNTs with desired moieties, optically and electrical functional nanoparticles, an amino-acid and an electro-active protein via covalent and electrostatic interactions. This strategy opens up possibilities for creating electrically and optically addressable hybrid nanodevices and chips for a variety of applications. Transmission electron microscopy of ion-irradiated CNTs reveals vacancy cluster formation, which ultimately leads to the amorphization and destruction of the tube with increased ion dosage. High momentum transfer cross-sections (e.g., $\sim 5~\mathrm{x~10^{-6}~nm^2}$ for 30 keV Ga⁺ ions) and high energy density ($\sim 420 \; \mathrm{eV/nm}$) transferred onto the CNTs allows energetic recoils to create dangling bonds, bridge adjacent tubes during irradiation and increase chemical reactivity. Air-exposure of CNTs rastered with focused ion beams results in the creation of carboxyl, carbonyl and allyl moieties in the modified segments with a lateral spatial resolution that can be as small as 5 nm. We utilize these moieties to site-selectively anchor Au nanoparticles, fluorescent nanospheres, lysine-an amino acid, and azurin-a charge-transfer metalloprotein, by means of electrostatic or covalent interactions. Ion doses in the range of $\sim 10^{15}$ - 10^{17} ions cm⁻² –depending on the CNT diameter-are the most conducive for defect creation and selective attachment. No observable anchoring is noted at lower doses ($\leq 10^{13}$ ions ${\rm cm}^{-2}$), compared to unirradiated locations, while higher doses sputter away the CNTs. The chemical nature of anchoring and the immobilization-induced-transformation of the protein structure are revealed by IR spectroscopy, X-ray photoelectron spectroscopy and spatially resolved Raman spectroscopy. Finally, we show the feasibility of extending our approach to modify CNT films and CNT segments using a novel photochemical strategy.

11:30 AM U7.7

Study of the Non-Covalent Functionalization of Carbon Nanotubes by DNA. Germarie Sanchez-Pomales, Yarinel Morales-Negron and Carlos Raul Cabrera; Chemistry Department, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico.

The study of biological applications of inorganic nanostructures has grown exponentially in the past few years. Chemical functionalization of carbon nanotubes (CNTs) with biological molecules is a particularly attractive goal, as it can improve the solubility of the nanotubes and transform them into powerful manageable reagents. Additionally, it allows us to combine the unique properties of CNTs with those of other biomaterials. Progress in the chemical functionalization of CNTs has included studies in both molecular and supramolecular chemistry. Non-covalent supramolecular approaches to the functionalization of CNTs preserve the unique properties of the tubes, while improving their solubility and manageability features. Compared to other polymers that have been used to functionalize CNTs, DNA offers the advantages of defined length and sequence, and well-developed chemistries for further functionalization (M. Zheng, et al., Nature Mater. 2003, 2, 338). We present a study of the supramolecular complex formed by the non-covalent functionalization of carbon nanotubes by DNA. The optimal conditions for the formation of these hybrids in aqueous solutions will be determined. These hybrids will be characterized by microscopic and spectroscopic techniques. In addition, self-assembled monolayers of thiol-modified-DNA-CNTs hybrids will be formed on gold substrates and the efficiency of this immobilization process will be determined by microscopic, electrochemical, and spectroscopic techniques. These studies will enhance our understanding of the characteristics and behavior of DNA-CNT hybrids under different conditions, which might ultimately lead us to the design and fabrication of a new generation of more efficient bionanomaterials.

11:45 AM U7.8

Using Aqueous and Non-Aqueous Solvents as a Delivery System for the Encapsulation of Molecules within Single-Wall Carbon Nanotubes. Jinwoo Hwang, Younghyun Kim and David E. Luzzi; Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

We present a systematic study of the encapsulation of molecules inside single-wall carbon nanotubes (SWNTs) using aqueous and non-aqueous solvents as a delivery system. This method of filling is studied using various solvent media, such as ethanol, hexane, toluene, dichlorobenzene, and water, which exhibit a wide range of C60 solvent solubility. Various molecules, including fullerenes, fullerene adducts, and planar molecules such as pyrene, have been encapsulated within AP-SWNT and P2-SWNT from Carbon Solutions Inc. and Elicarb SWNTs from Thomas Swan & Co. Both of these SWNT materials

have diameters in a range suitable for filling. The analysis of this work is separated into two components, which are the effects of organic solvents on the interior and exterior surface of SWNTs, and the quantification of the filling ratio of the encapsulated molecules within SWNTs. The former was investigated by transmission electron microscopy (TEM), and X-ray diffraction (XRD). TEM confirms that there are remanent solvent molecules on both the interior and exterior surfaces of the SWNTs. In addition, the reduction of the 10 X-ray rope reflection suggests that solvent molecules have intercalated within the space between SWNTs in nanotube ropes. The filling ratio was quantified using XRD, which accounts for the effects of solvent molecules on the 10 rope reflection. Using these methods, we have encapsulated two fluorescent species, a fullerene-azothiophene dyad an optically active dye molecule within SWNTs. Absorption and fluorescence spectroscopy have been used to study the resulting optical properties of molecules confined to a one-dimensional geometry, and the associated charge transfer effects on the fluorescence of SWNTs.

> SESSION U8: Miscellaneous Applications Chair: Mauricio Terrones Thursday Afternoon, March 31, 2005 Room 3024 (Moscone West)

1:30 PM *U8.1

Growth of Aligned Carbon Nanotube for Nanoelectronics. Huang Jun, Vedala Harindra, Young-Chul Choi and WonBong Choi; Mechanical and Materials Engineering, Florida Int University, Miami,

The miniaturization of electronic devices into nanometer scale is indispensable for next-generation semiconductor technology. Carbon nanotubes (CNTs) have already been shown to be useful in a variety of functional devices such as nano-electromechanical system (NEMS), field-effect transistors (FETs), interconnects, atomic force microscope (AFM) probes, etc. The Y-junction Singlewall CNTs have attracted much attention due to their potential to be used as future nano electronics, where the third terminal is used for controlling the switching, power gain, or other transisting purposes. Our recent work demonstrated the successful growth of Y-SWNTs by controlling catalyst type. The Y-SWNTs were catalytically synthesized by thermal CVD using a doped Fe particle as catalysts. Most of the synthesized SWNTs have branches, forming Y-junctions. Transmission electron microscopy (TEM) images confirmed that a Y-SWNT consists of three isolated SWNTs with different diameters. Raman spectra showed that our sample has both semiconducting and metallic SWNTs. The results of TEM and Raman measurements are indicative of the possible formation of Y-SWNTs with different electrical properties. Most recently, we have also found that the Y-SWNTs grown at different temperature have demonstrated different electrical characteristic. The Surface modification of the carbon nanotubes plays an important role for their utilization in various applications. The surface of grown nanotubes was modified and the wettability on nanotubes was investigated. This functionalisation tends to change the surface of nanotubes into hydrophilic thus increasing its sensitivity. The electrical characterization of these modified nanotubes was performed since it is expected that by adapting analysts onto the modified nanotubes, the electric transport property of CNT may be changed. In this presentation we will discuss the central issues to be addressed for realizing carbon nanotube (CNT) future electronic devices. We focus on the controlling CNT growth, electron energy bandgap engineering and device integration.

2:00 PM *U8.2

Growth and Applications of Carbon Nanotubes.

Manish Chhowalla, Ceramic and Materials Engineering Dept, Rutgers University, Piscataway, New Jersey.

We will present the results of our efforts to produce high quality single wall carbon nanotubes (SWNTs). Our chemical vapor deposition method has been optimized to eliminate deposition of impurities such as amorphous carbon so that SWNTs can be grown on pre-fabricated electrodes for self-assembled devices. Adjusting the growth parameters slightly, we can also make larger multi-wall nanotubes (MWNTs) which can be aligned vertically or laterally. Because of the catalytic nature of the growth process, pre-patterning of the catalyst allows us to control the precise location an orientation of the nanotubes. Based on this process, we show that it is possible to fabricate complex triode devices for field emission displays and gas sensors. In addition to the electronic applications of SWNTs, we will also describe how as fabricated and functionalized SWNTs can be used to probe proteins. Specifically, we will describe our results on blocking of ion channels using as fabricated and functionalized SWNTs.

3:00 PM <u>U8.3</u>

Multifunctional Carbon Nanotube Based Brushes.

Anyuan Cao¹, Vinod Veedu², Xuesong Li¹, Mehrdad Ghasemi-Nejhad² and Pulickel Ajayan¹; ¹Materials Science & Engineering Department, Rensselaer Polytechnic Institute, Troy, New York; ²Mechanical Engineering Department, University of Hawaii at Manoa, Honolulu, Hawaii.

We report the fabrication of multifunctional carbon nanotube based brushes by directly growing nanotubes on thin silicon carbide fibers (SiC: diameter 16 μ m). We combined conventional chemical vapor deposition and selective substrate area growth to graft aligned multi-walled nanotubes exclusively on the fiber ends as the brush head with the fiber as the handle in various designs. The span of brush head can be controlled from 1 to 600 μm with nanotube length up to 100 μm . The closely arranged nanotube tips serve as numerous nano-bristles, and the brush can be easily physically manipulated, either manually or with the aid of motors. The high aspect ratio and small dimension, mechanical stability and flexibility, surface chemical and adhesive characteristics and high electrical conductivity provide a wide range of functionalities and uniqueness to the nanotube brush. Here, we demonstrate the multifunctionality of these brushes by applying these in the manipulation and removal of nanoparticles on planar as well as microstructured surfaces (e.g. terrains with microscale trenches and elevations), selective surface cleaning via chemical/physical adsorption, painting and coating in normally inaccessible spaces such as inside micro-capillaries, and as movable brush-contacts which could act also as electro-mechanical switches that can work swiftly in both air and liquid environments. With surface modification and functionalization, the nanotube brushes could become a versatile micro-tool in many chemical and biological applications and in the creation of novel electro-mechanical devices with excellent thermo-mechanical stability and endurance.

3:15 PM <u>U8.4</u>

Frictional Anisotropy and Electrical Contact Resistance of Oriented Carbon Nanotube Surfaces. Pamela Dickrell¹, S. B. Sinnott², D. W. Hahn¹, N. R. Raravikar³, L. S. Schadler³, P. M. Ajayan³ and W. G. Sawyer^{1,2}; ¹Mechanical and Aerospace Engineering, University of Florida, Gainesville, Florida; ²Materials Science and Engineering, University of Florida, Gainesville, Florida; ³Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

This presentation examines the tribological properties and contact resistance of oriented nanotube films. Highly anisotropic tribological behavior of multiwalled nanotube films oriented in mutually orthogonal directions is observed. The average values of coefficient of friction varied from extremely high values (0.795) for vertically aligned nanotubes grown on rigid substrates to very low values (0.090) for nanotubes dispersed flat on the same substrates. The results were insensitive to humidity, in contrast to graphite materials, and indicate that nanotubes could be utilized as both low and high frictional surfaces. Additionally, multiwalled nanotube layers realized a monotonic decrease in friction coefficient with an increase in sample temperature, regardless of orientation. Furthermore, the contact resistance of nanotube films is investigated as a function of applied static load and during reciprocating contact. These investigations into the tribological properties of nanotube films may show how patterning on surfaces could achieve inert electrical contacts with frictional properties tailored by deposition-controlled nanotube orientation.

3:30 PM <u>U8.5</u>

Short Channel Effects In Ballistic Carbon Nanotube Transistors With Ohmic Contacts. <u>Francois Leonard</u> and Derek Stewart²; ¹Sandia National Laboratories, Livermore, California; ²Cornell Nanoscale Facility, Ithaca, New York.

We present self-consistent, non-equilibrium calculations of the characteristics of short channel carbon nanotube transistors. By focusing on the ultimate regime of ballistic transport with ohmic contacts, we present a benchmark for evaluating the performance of experimental devices. The properties of these devices differ markedly from those of traditional transistors. In particular, tunneling leads to short channel effects, and the ON state conductance shows a temperature dependence even in the absence of phonon scattering and Schottky barriers.

3:45 PM <u>U8.6</u>

The Aharonov-Bohm Interference and Beating in Single-Walled Carbon Nanotube Interferometers. <u>Jien Cao</u>, Qian Wang, Marco Rolandi and Hongjie Dai; Department of Chemistry, Stanford University, Stanford, California.

A hallmark of the Aharonov-Bohm (AB) effect is conductance oscillations of metallic rings or cylinders as a function of enclosed magnetic flux with a period on the order of the flux quantum F0=h/e due to quantum interference. Carbon nanotubes are chemically derived cylinders with atomically well-defined structures. Multi-walled

nanotubes (MWNT) have radius $r \sim 10$ nm and in magnetic fields parallel to the tube axis, conductance modulations with a period of B0=F0 /p r 2 \sim 10T in magnetic field have been seen. Single-walled nanotubes (SWNT) are ultra-small with r ~ 1 nm and the magnetic field needed to approach 1F0 flux through the nanotube cross section is B0 \sim 1000T, far beyond reach by experiments. We show here that in the Fabry-Perot interference regime, beating in the AB-interference between two modes of spiraling electrons with non-degenerate wave-vectors causes conductance modulations under fields much smaller than that needed to reach 1F0. Relatively low magnetic fields applied parallel to the axis of a chiral single-walled carbon nanotube are found causing large modulations to the p-channel or valence band conductance of the nanotube in the Fabry-Perot interference regime. Beating in the Aharonov-Bohm type of interference between two field-induced non-degenerate subbands of spiraling electrons is responsible for the observed modulation with a pseudo period much smaller than that needed to reach the flux quantum F0 = h/e through the nanotube cross-section. We show that single-walled nanotubes represent the smallest cylinders exhibiting the Aharonov-Bohm effect with rich interference and beating phenomena arising from well-defined molecular orbitals reflective of the nanotube chirality. The observation of quantum beats for the Aharonov-Bohm effect is to our knowledge unprecedented in mesoscopic systems and is a result of well-defined molecular orbitals of nanotubes in magnetic fields. Large band-gap semiconductor SWNTs with low Schottky-barrier p-channels in the Fabry-Perot regime could exhibit much more rapid beats than the small band-gap SWNTs. Clearly, many future opportunities exist for elucidating quantum interference and beating between well-defined molecular orbitals.

4:00 PM <u>U8.7</u>

Phase-Imaging with a Sharpened Multi-Walled Carbon Nanotube AFM Tip: Investigation of Low-k Dielectric Polymer Hybrids. Cattien V. Nguyen¹, Ramsey M. Stevens¹, Meyya Meyyappan², Willi Volksen³ and Robert D. Miller³; ¹Center for Nanotechnology, ELORET/NASA Ames Research Center, Moffett Field, California; ²Center for Nanotechnology, NASA Ames Research Center, Moffett Field, California; ³IBM Almaden Research Center, San Jose, California.

Phase shift tapping mode scanning force microscopy (TMSFM) has evolved into a very powerful technique for the nanoscale surface characterization of compositional variations in heterogeneous samples. Phase shift signal measures the difference between the phase angle of the excitation signal and the phase angle of the cantilever response. The signal correlates to the tip-sample inelastic interactions, identifying the different chemical and/or physical property of surfaces. In general, the resolution and quality of scanning probe microscopic images are highly dependent on the size of the scanning probe tip. In improving AFM tip technology, we recently developed a technique for sharpening the tip of a multi-walled carbon nanotube (CNT) AFM tip, reducing the radius of curvature of the CNT tip to less than 5 nm $\,$ while still maintaining the inherent stability of multi-walled CNT tips¹. Herein we report the use of sharpened (CNT) AFM tips for phase-imaging of polymer hybrids, a precursor for generating nanoporous low-k dielectrics for on-chip interconnect applications. Using sharpened CNT tips, we obtained phase-contrast images having domains less than 10 nm. In contrast, conventional Si tips and unsharpened CNT tips (radius > 15 nm) were not able to resolve the nanoscale domains in the polymer hybrid films. Clearly the size of the CNT tip contributes significantly to the resolution of phase-contrast imaging. In addition, a study on the nonlinear tapping dynamics of the multi-walled CNT tip indicates that the multi-walled CNT tip is immune to conventional imaging instabilities related to the coexistence of attractive and repulsive tapping regimes². This factor may also contribute to the phase-contrast image quality of multi-walled CNT AFM tips. This presentation will also offer data in support of the stability of the CNT tip for phase shift TMSFM. Cattien V. Nguyen, Chris So, Ramsey M. Stevens, You Li, Lance Delziet, Philippe Sarrazin, and M. Meyyappan, J. Phys. Chem. B, 108, 2816, (2004) ² S I Lee, S W Howell, A Raman, R Reifenberger, C V Nguyen and M Meyyappan, Nanotechnology 15, 416, (2004)

4:15 PM <u>U8.8</u>

Carbon Nanotube Coatings for Space Applications. Keith Rebello¹, Jennifer Sample², Bruk Berhane¹ and Robert Osiander¹; ¹Research Technology Development Center, The Johns Hopkins University Applied Physics Lab, Laurel, Maryland; ²Technical Services Department, The Johns Hopkins University Applied Physics Lab, Laurel, Maryland.

Carbon Nanotube materials, with their high thermal conductivity and the high aspect ratios, provide innovative materials for thermal control applications such as improved thermal interfaces, which allow developing thermal switches with low power and weight. We investigate the feasibility of carbon nanotube based systems for use in spacecraft thermal control applications e.g. as a contact layer between

two thermally connected materials. A carbon nanotube surface extending vertically from the surface, in different length, would touch another structure at much more positions than two not very flat surfaces would touch each other. Measurements have shown that by using self assembly for patterned deposition of catalyst particles, multi-wall carbon nanotube (MWCNT) arrays grown as a contact layer on silicon and copper surfaces will improve thermal transport in vacuum. We have measured the heat flow between rough surfaces, as well as compared the effects of differing densities, lengths, and diameters on thermal transport. An important application is the thermal switch, where the contact between the two surfaces is not static and conducting epoxies cannot be used. When used as part of a switch we have shown that the CNT coatings are durable.

4:30 PM U8.9

Polymer Electrolyte Gating and Doping of Individual and Networks of Carbon Nanotubes. Moonsub Shim, Materials Science & Engineering, Univ of Illinois, Urbana, Illinois.

Due to large electric double layer capacitance, application of electrochemical potential provides a simple method of efficiently modulating conductance in carbon nanotube transistors. Ideal gate efficiencies are achieved with single nanotube transistors without the complications of hysteresis observed in back-gating. In high density networks of nanotubes screening of gate electric field from, for example, metal catalyst nanoparticles and other nanotubes leads to poor gate efficiencies making it difficult to examine electrical characteristics. Due to short Debye lengths, such effects can be avoided and significant current modulation is observed with polymer electrolytes. Furthermore, versatility of polymer electrolyte gating is demonstrated by changing mode of operation simply by variations in host polymer chemical groups.

4:45 PM <u>U8.10</u>

Dynamic Friction Force in a Novel Ultra-High Frequency Oscillator. <u>Haibin Su</u> and William A. Goddard III; Caltech, Pasadena, California.

Very recently, it has been reported by Zettle group that frictional forces is very small, c.a. in the magnitude of 10^{-14} N per \mathring{A}^2 , during the controlled and reversible telescopic extension of multiwalled carbon nanotubes. Moreover, a new type of nano-oscillator operating completely different from conventional quartz oscillator has been proposed based upon this interesting observation. Since then, designing this type of nano-oscillator has been carried out actively. Legoas and collaborators first simulated a 38 GHz nano-oscillator consisting of a (9,0) carbon nanotube(CN) inside of (18,0) CN. However, no successful experimental tests have been reported so far. This is probably due to the difficulty of preparing the bi-tube type oscillator unit from multiwalled carbon nanotubes with high quality, and the considerable amount of energy dissipation. We propose a new generation of fullerene nano-oscillator: a (10,10) single wall carbon nanotube with one buckyball inside. The molecular dynamics studies predict the operating frequency is ultra-high, c.a. 50 GHz. The energy dissipation from simulation shows significant effects of temperature, and impulse velocity on dynamic friction force. In particular, it has been shown that edge effects are the main cause of dynamic friction force.