

**SYMPOSIUM HH**  
**Functional Carbon Nanotubes**

November 29 - December 3, 2004

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\* Invited paper

**8:30 AM \*HH1.1**

**Abstract Not Available. P. Bernier**

**9:00 AM HH1.2**

**Diamond Nanowires Grown Inside Carbon Nanotubes Upon Chemical Vapor Deposition: Thermodynamic and Kinetic Approach at the Nanoscale.** Cheng-Xin Wang, Qiu-Xiang Liu, Yu-Hua Yang and Guo-Wei Yang; State key laboratory of optoelectronic materials and technologies, School of Physics Science & Engineering, Zhongshan University, Guangzhou 510275, P. R. China, Guangzhou, China.

One-dimensional nanostructures such as wires, rods, belts, and tubes have become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices. Due to several unique properties including extreme high hardness, very high thermal conductivity, large band gap, and chemical inertness, etc., diamonds are expected to be an important semiconductor material for high-temperature and high-power microelectronics device, and UV-light emitting optoelectronics. Very recently, one-dimensional nanostructures of diamond have received increasing interest in theoretical. For example, due to stronger than fullerene nanotubes, diamond nanorods are expected to be an important and viable target structure for synthesis. The energy band gap of diamond nanowires (DNWs) is significantly reduced by Barnar study, due to the contributions from occupied and unoccupied surface states. However, up to date, any successful syntheses of diamond nanowires have not been found in the literature yet, to our best knowledge. On the other hand, carbon nanotubes (CNTs) have many potential applications as molecular sieves, membranes, and nanotubes for precise delivery of gases or liquid. Furthermore, some studies focused their attentions on transport, adsorbed, and condensed phases of gases inside CNTs. Especially, the transport rates of CH<sub>4</sub> and H<sub>2</sub> gases in CNTs were suggested to be exceptionally high. Interestingly, CH<sub>4</sub> and H<sub>2</sub> gases are just two typical reactive gases that are employed to deposit diamond films upon chemical vapor deposition (CVD). These studies mentioned above naturally imply that CNTs could be expected to be a possible path to fabricate DNWs by CVD. In this study, we propose a nano-scaled thermodynamic nucleation and growth kinetic approach in theoretical, with respect to the effect of nanosize-induced surface tension, for the formation of DNWs inside CNTs upon CVD. Thermodynamic analyses show that the diamond nucleation inside a CNT would be preferable to that on the flat surface of silicon substrate due to the effect of surface tension induced by the nanosize curvature of CNTs. Meanwhile, the capillary effect of the nanosize curvature of diamond nuclei could drive the metastable phase region of diamond nucleation into a new stable phase region in the carbon thermodynamic equilibrium phase diagram. Kinetic analyses indicate that the growing rate of DNWs would go to much high once nuclei formed inside CNTs, due to the same nanosize-induced effect. Eventually, we predict that CNTs could be an effective route to grow DNWs by CVD.

**9:15 AM HH1.3**

**Single Wall Carbon Nanotube by Microwave Plasma CVD.** Roy Gat<sup>1</sup>, Matt Maschmann<sup>2</sup>, A. Goyal<sup>3</sup>, Zafar Iqbal<sup>3</sup> and Tim S. Fisher<sup>2</sup>; <sup>1</sup>Sekitechnotron USA, Somerville, Massachusetts; <sup>2</sup>Mechanical Eng, Purdue University, West Lafayette, Indiana; <sup>3</sup>Chemistry, New Jersey Institute of Technology, Newark, New Jersey.

Microwave plasma enhanced CVD has reproducibly yielded Single wall Carbon Nanotube (SWCNT) deposition. The tubes deposited in bundles containing 5-10 individual tubes each tube was either 1.3nm or 0.9 in diamter. The reactor used was an ASTeX/Seki 1.5KW microwave system commonly used for diamond deposition. The reactor is equipped with RF induction heater and computer programmable operation. This result has provided access to new regions of parameter space for SWCNT deposition and an opportunity for better control over nanotube properties. Deposition temperature was 800oC. Gas mixture was methane and hydrogen. The catalysts was bimetallic Mo/Co supported on MgO and dispersed on a silicon wafer. Raman, AFM and TEM were used to characterize the tubes results will be reported.

**9:30 AM HH1.4**

**Controllable Growth of Single Wall CNTs on Nanotemplates Prepared from Amphiphilic Diblock Copolymers.** Jennifer Lu<sup>1</sup>, Nick Moll<sup>1</sup>, Daniel Roitman<sup>1</sup>, Qiang Fe<sup>2</sup>, Jie Liu<sup>2</sup>, David Riter<sup>3</sup>, Ian Manners<sup>3</sup> and Mitch Winnik<sup>3</sup>; <sup>1</sup>Nanoscale Processing and Nanodevices, Agilent Technologies, Palo Alto, California; <sup>2</sup>Chemistry Department, Duke University, Durham, North Carolina; <sup>3</sup>Chemistry Department, Lash Miller Chemical Labs, University of Toronto, Toronto, Ontario, Canada.

Carbon nanotubes are unique nanostructures with superior electronic and mechanical properties that also exhibit novel physicochemical phenomena. The major obstacle impeding the commercialization of CNT-based devices is the lack of CNT growth control in terms of location, size, orientation and chirality. Moreover, most of the existing methods for CNT growth are very difficult to integrate into conventional device fabrication schemes. In this paper, well-ordered nanocatalysts have been produced by spin coating amphiphilic diblock copolymers. Several amphiphilic diblock polymers consisting of a non-metal containing segment and a metal containing segment have been explored as nanotemplates for generating well-ordered arrays of nanocatalysts. The examples include polystyrene-block-Fe complexed poly(vinylpyridine) and polystyrene-block-poly(ferrocenyl ethyl methyl silane). Nanocatalyst arrays consisting of 2-3nm metal oxide particles with density of 600 particles/um<sup>2</sup> and uniform particle spacing were fabricated. The self-assembled catalyst arrays display a hexagonal close packed arrangement, consistent with the morphology theoretically expected from the diblock polymer formulations. High density and high quality SWNTs with uniform surface coverage were grown from these catalysts. In some cases, highly ordered SWNT arrays were observed. The effect of various surface treatments and annealing conditions on diblock film formation and nanocatalyst size and distribution will be discussed. The quality of carbon nanotubes and their size and distribution based on various amphiphilic diblock polymers will be presented. Physical, chemical and electronic properties of CNTs were measured by various analytical techniques. High density, regular nanotube arrays can enable a multitude of biological and electronic device applications.

**9:45 AM HH1.5**

**Parametric Study of Single Walled Carbon Nanotubes using Alcohol Catalytic Chemical Vapor Deposition.** Husnu Emrah Unalan and Manish Chhowalla; Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

The unique structural, mechanical, and electrical properties of single-wall carbon nanotubes (SWNTs) have rendered these structures highly appealing for investigators. Different methods have been employed for the synthesis of SWNTs, including alcohol catalytic chemical vapor deposition (ACCVD) <sup>1</sup>. However, no detailed parametric study of this method has been undertaken. In this report, we present a detailed analysis of the growth properties of SWNTs as functions of growth time, deposition temperature, flow rate, type of alcohol (i.e. ethanol versus methanol) and catalyst concentration (Fe:Co:Mo acetate ratio). We have analyzed the as-grown SWNTs with high resolution transmission electron microscope (HRTEM), field-emission scanning electron microscope (FE-SEM), Raman spectroscopy and atomic force microscopy (AFM). Nucleation and growth of SWNTs occurs within seconds after introduction of the alcohol vapor. The results show that although multi-walled nanotubes can be grown at 450°C, high quality SWNTs with a narrow diameter distribution without amorphous carbon can be grown using Co acetate catalyst doped with Mo acetate above 700°C. The HRTEM analysis revealed defective nanotubes at low and high temperatures with the optimum temperature being 850°C. The concentration and quality of SWNTs (determined by Raman and TEM) are also improved when methanol vapor was used. In brief, our work is a step towards optimizing SWNTs growth conditions using ACCVD. [1] S. Maruyama, R.Kojima, Y.Miyauchi, S. Chiashi, M. Kohno, Chemical Physics Letters 360 (2002) 229

**10:30 AM HH1.6**

**In situ Optical Monitoring of Vertically-Aligned Multiwall Carbon Nanotube Array Growth During Chemical Vapor Deposition.** Alex A. Puretzky<sup>2,1</sup>, David B. Geohegan<sup>1</sup>, Stephen Jesse<sup>2,1</sup>, Hongtao Cui<sup>1</sup>, Kalayu G. Belay<sup>3</sup>, Jeremy Jackson<sup>3</sup>, Iliia Ivanov<sup>2,1</sup> and Gyula Eres<sup>1</sup>; <sup>1</sup>Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Materials Science and Engineering, University of Tennessee, Oak Ridge, Tennessee; <sup>3</sup>Department of Physics, Florida A&M University, Tallahassee, Florida.

Vertically aligned arrays of multiwall carbon nanotubes (VAA-MWNT) can be synthesized using chemical vapor deposition (CVD) method, but little is known about: the growth mechanism, identity of the precursor species, growth rates and kinetics, the mechanism of growth termination, etc. which hampers their applications. A detailed experimental study of vertically aligned arrays of multi-wall carbon nanotubes (VAA-MWNT) growth by chemical vapor deposition (CVD) based on time-resolved reflectivity (TRR) throughout the first 10 microns of growth and direct remote microscope imaging at longer VAA-MWNT length (up to a few mm) as a diagnostic to measure and control the length of VAA-MWNTs in situ was performed. Attenuation of a reflected HeNe laser beam and Fabry-Perot fringes were used to measure the length of VAA-MWNT arrays throughout the first 10 microns of growth, providing in situ

growth rates and permitting the kinetics and termination of the growth to be studied. The VAA-MWNT growth was investigated between 530 °C and 900 °C on Si substrates with evaporated different multiplayer catalysts and different feedstock gases. It was demonstrated that the growth terminates rapidly at a relatively low (535-600 °C) and high (800-900 °C) temperatures, showing a relatively narrow temperature window for optimal growth of long VAA-MWNTs (up to 2-4 mm) around 700 °C using Al/Fe/Mo catalyst and C<sub>2</sub>H<sub>2</sub> feedstock gas, at a growth rate of about 0.2 - 0.5 μm/s. Nanotube lengths were controlled by rapid evacuation of the chamber. The monitoring of long, up to 2-4 mm VAA-MWNTs during growth was performed which allowed us for the first time to determine the long time growth and growth termination kinetics, and discover a new phenomenon of cooperative effect in the VAA-MWNT growth: shrinkage of VAA-MWNTs when the growth stops. A simple kinetic model was considered to explain the observed growth kinetics and to discuss the main processes responsible for the growth of VAA-MWNTs. This research was sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

#### 10:45 AM HH1.7

##### **Combinatorial Method to Find Proper Thickness of Submonolayer Metals to Catalyze Growth of Single-Walled Carbon Nanotubes.** Suguru Noda<sup>1</sup>, Yoshiko Tsuji<sup>1</sup>, Yoichi

Murakami<sup>2</sup> and Shigeo Maruyama<sup>2</sup>, <sup>1</sup>Department of Chemical System Engineering, The University of Tokyo, Tokyo, Japan; <sup>2</sup>Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan.

The approach to disperse pre-prepared metal catalyst nanoparticles on substrates for the growth of single-walled carbon nanotubes (SWNTs) by chemical vapor deposition (CVD) often suffers from the aggregation and coarsening of nanoparticles at elevated temperatures. On the other hand, it is well known that nanoparticles spontaneously form on substrates by vapor deposition processes. Metal atoms and/or islands diffuse over substrate surfaces and approach equilibrium structure, i.e. single islands, within their surface diffusion lengths. If metals of proper thickness are prepared, they will spontaneously form nanoparticles under the CVD conditions with a size suitable to catalyze the growth of SWNTs. Because it is difficult to estimate the surface diffusion lengths for most metal/substrate systems, in this work, a combinatorial method is proposed and applied to prepare a library of Co patterns. Co patterns with nominal thicknesses from 0.001 to 1 nm were prepared on an a-SiO<sub>2</sub>/Si substrate by magnetron sputtering with "combinatorial masked deposition (CMD)" method [1], and SWNTs were grown on it by alcohol catalytic CVD [2]. Micro-Raman spectroscopy revealed that high quality SWNTs were formed by submonolayer Co catalysts of nominal thicknesses between 0.01 and 0.3 nm. Field emission scanning electron microscopy (FE-SEM) revealed that thick Co patterns yielded thick bundles of SWNTs with nanoparticles whereas thin Co patterns yielded thinner bundles or separated SWNTs with smaller and fewer nanoparticles. It would be noteworthy that catalyst preparation condition, i.e. Co thickness, was determined by only one experimental run. The combinatorial method developed in this work can be applied to a wide variety of metal/substrate systems and CVD conditions. Furthermore, the catalyst preparation conditions, i.e. nominal thicknesses of metals, derived by this method are expected to be applicable to other catalyst preparation methods including wet processes. [1] S. Noda, Y. Kajikawa and H. Komiyama, Appl. Surf. Sci. 225, 372 (2004). [2] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi and M. Kohno, Chem. Phys. Lett. 360, 229 (2002).

#### 11:00 AM HH1.8

**Catalyzed Epitaxial Growth of Single Wall Carbon Nanotubes from Seed Nanotubes.** Yuhuang Wang<sup>1</sup>, Myung Jong Kim<sup>1</sup>, Hongwei Shan<sup>1</sup>, Carter Kittrell<sup>1</sup>, Bernie Ochoa<sup>1</sup>, Hua Fan<sup>1</sup>, Robert H. Hauge<sup>1</sup>, Richard E. Smalley<sup>1</sup>, Sivaram Arepalli<sup>2</sup>, Gyula Eres<sup>3</sup>, Alex A. Puzos<sup>3</sup> and David B. Geohegan<sup>3</sup>, <sup>1</sup>Carbon Nanotechnology Laboratory, Rice University, Houston, Texas; <sup>2</sup>G.B. Tech/NASA-Johnson Space Center, Houston, Texas; <sup>3</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee.

(n, m) controlled synthesis of single wall carbon nanotubes (SWNTs) is a major challenge toward fulfilling their full potential. Here we demonstrate the continued growth of SWNTs from seed nanotubes in a way analogous to molecular epitaxy. The SWNTs grow preferentially along the same direction of the aligned SWNT seeds and, as Raman spectra suggested, inherit the same diameters and chirality from the seeds. The details of our approach and analysis will be reported.

#### 11:15 AM HH1.9

**Identification of a Primary Precursor for Single Wall Carbon Nanotube Synthesis and the Growth of Vertically Aligned Single Wall Carbon Nanotube Films.** Gyula Eres, Anika Kinkhabwala, Hongtao Cui, Puzos Alex and Geohegan David; Condensed Matter Sciences Division, Oak Ridge National Laboratory,

Oak Ridge, Tennessee.

Chemical vapor deposition (CVD) is a promising method for the synthesis of single wall carbon nanotubes (SWCNT) because it can be used for fabrication of individual nanoelectronic devices as well as for mass production of bulk SWCNTs. Currently CVD is performed under extreme conditions and along with SWCNTs it also produces a large fraction of undesirable side products. These side products result from secondary reactions involving intermediate reaction products. The simplest way to suppress the secondary reactions is to use precursors and reaction conditions that facilitate direct transformation into SWCNTs. In this paper we describe experiments that identified acetylene as a primary precursor. We demonstrate that the availability of a primary precursor leads to more efficient SWCNT growth enabling the deposition of vertically aligned (VA) SWCNT films. The VA-CNT films were characterized by SEM, Raman spectroscopy and TEM.

#### 11:30 AM HH1.10

##### **Growth of Multiwalled-Carbon Nanotubes using Vertically Aligned Carbon Nanofibers as Templates/Scaffolds: Process Development and Improved Field Emission Properties.**

Hongtao Cui<sup>1</sup>, Xiaojing Yang<sup>2</sup>, Larry R. Baylor<sup>3</sup> and Douglas H.

Lowndes<sup>1</sup>, <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; <sup>3</sup>Fusion Energy Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Multiwalled-carbon nanotubes (MWCNTs) are grown using vertically aligned carbon nanofibers (VACNFs) as templates/scaffolds via microwave plasma enhanced chemical vapor deposition (MPECVD). The VACNFs are grown previously in a direct-current plasma enhanced chemical vapor deposition reactor using nickel catalyst. A layer of carbon-silicon materials is deposited on the VACNFs and the nickel catalyst particle is broken down into smaller Ni nanoparticles during an intermediate reactive ion plasma deposition step. The nickel particles nucleate and grow MWCNTs in the following MPECVD process. Field emission measurements show that the MWCNTs greatly improve the field emission properties of the VACNFs. Our results suggest that VACNFs can be used as templates/scaffolds for growth of MWCNTs for both electric field emission and scanning probe applications.

#### 11:45 AM HH1.11

##### **Low Temperature Synthesis of Vertically Aligned and Very Dense Single-Walled Carbon Nanotubes by Antenna-type Microwave Plasma Chemical Vapor Deposition.**

Takayuki Iwasaki<sup>1</sup>, Tsuyoshi Yoshida<sup>1</sup>, Takumi Aikawa<sup>1</sup>, Ryota Hosaka<sup>1</sup>, Kotaro Honda<sup>1</sup>, Guofang Zhong<sup>1</sup>, Yukio Furukawa<sup>1</sup>, Iwao Ohdomari<sup>1,2</sup> and Hiroshi Kwarada<sup>1,2</sup>, <sup>1</sup>School of Science and Engineering, Waseda University, Tokyo, Japan; <sup>2</sup>COE, Tokyo, Japan.

It is very important to control the growth orientation of CNTs on substrates for some applications such as field emission devices and CNT based FETs. As many papers reported, chemical vapor deposition (CVD) is the most reliable way for this purpose because of the precise control of the growth parameters. However few papers have been reported for vertically aligned SWNTs. In this study, we demonstrate the low temperature synthesis of dense SWNTs with very good vertical alignment deposited by CVD. Substrates were Si wafers coated with very thin Al and Fe by sputter. Al layers were oxidized after the sputter. On the substrates, vertically aligned and very dense single-walled carbon nanotubes (SWNTs) were synthesized at a low temperature of 600°C by Antenna-type Microwave Plasma CVD, which was used to deposit multi-walled carbon nanotubes (MWNTs) in our previous study. The height of CNTs is more than 170 μm for 40 min and all of them are vertically aligned. Raman spectra of as-grown CNTs have the radial breathing mode (RBM) of SWNTs at the low frequency. From the RBM and the TEM observation, most of CNTs are single-walled and their diameters range from 1.0 to 3.0 nm. The cracks observed in SEM images are probably created by the van der Waals force among SWNTs due to the very high density.

SESSION HH2: Synthesis and Growth II  
Monday Afternoon, November 29, 2004  
Room 312 (Hynes)

#### 1:30 PM \*HH2.1

##### **Low Temperature Plasma Enhanced Chemical Vapour Deposition of Carbon Nanotubes and Nanofibres.**

John Robertson<sup>1</sup>, Stephan Hofmann<sup>1</sup>, Britta Kleinsorge<sup>1</sup>, V. G. Golovko<sup>2</sup>, J. Geng<sup>2</sup>, C. Ducati<sup>3</sup>, Bojan Boskovic<sup>1</sup>, Mirco Cantoro<sup>1</sup> and Brian F. G. Johnson<sup>2</sup>; <sup>1</sup>Engineering, Cambridge University, Cambridge, United Kingdom; <sup>2</sup>Chemistry, Cambridge University,

Cambridge, United Kingdom; <sup>3</sup>Materials Science, Cambridge University, Cambridge, United Kingdom.

Aligned carbon nanofibres and nanotubes have been grown down to temperatures as low as 120C in silicon and plastic substrates by plasma enhanced chemical vapour deposition. This was the first deposition at such a low, controlled substrate temperature. A sputtered Ni catalyst and DC PECVD is used in an acetylene/ammonia gas mixture. The growth rate is Arrhenius with a low activation energy of 0.23 eV, which accounts for why growth is still possible at such low temperatures. The plasma is shown to restructure the thin Ni layer into Ni nanoclusters. The ammonia etches away the unwanted amorphous carbon. Ni or Co catalyst can also be delivered to surfaces as inverse micelle structures (colloids), Ni formate solution and as organo-metallic clusters of 20-40 atoms. This is combined for the first time with PECVD to allow low temperature growth onto substrates of complex shape such as foams, cloths and mats. The low temperature deposition onto plastics such as polyimide allows the use of fragile substrates. These results open up another avenue of applications for CNTs.

## 2:00 PM HH2.2

### Growth and Characterization of Isolated Single-walled Carbon Nanotubes using Liquid Precursors. Gayatri Keskar<sup>1</sup>,

Rahul Rao<sup>2</sup> and Apparao M. Rao<sup>2</sup>; <sup>1</sup>School of Materials Science and Engineering, Clemson University, Clemson, South Carolina; <sup>2</sup>Physics and Astronomy, Clemson University, Clemson, South Carolina.

Isolated single wall carbon nanotubes (SWNTs) were prepared on bare quartz and oxidized silicon substrates using chemical vapor deposition (CVD) in which a liquid precursor, such as xylene, was used as the carbon source. The density of isolated SWNTs was controlled by adjusting the concentration of iron (III) nitrate nonahydrate/2-propanol solution which provided the Fe seed catalyst particles. Micro-Raman measurements using the 514.5 and 647.1 nm excitation showed tangential bands around 1590 cm<sup>-1</sup>. The radial breathing mode (RBM) frequencies ranged from 150 - 240 cm<sup>-1</sup> and the estimated tube diameters are in good agreement with those obtained from atomic force microscope (AFM) images. Our synthesis technique facilitates controlled doping of isolated SWNTs with nitrogen by mixing appropriate amount of acetonitrile with xylene. As the nitrogen concentration in the feed increased from 0-10 at. %, the RBM intensity decreased while the intensity of the D-band increased relative to that of the G-band. Interestingly, the D/ band was observed for the first time in the Raman spectrum of carbon nanotubes when the nitrogen concentration reached 3 at. %.

## 2:15 PM HH2.3

### Efficient and Systematic Exploration of Catalysts for Nanomaterials Synthesis. Hans Christen<sup>1</sup>, Alex Puzosky<sup>1,2</sup>,

Hongtao Cui<sup>1</sup>, Kalayu Belay<sup>3</sup>, Jeremy Jackson<sup>3</sup>, Pam Fleming<sup>1</sup>, Ilia Ivanov<sup>1,2</sup>, David Geohegan<sup>1</sup> and Douglas Lowndes<sup>1</sup>; <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; <sup>3</sup>Department of Physics, Florida A&M University, Tallahassee, Florida.

The physical properties of nanomaterials in general, and of carbon nanotubes in particular, are known to depend strongly on the chemical composition of the catalyst particles from which they are grown. It is therefore important to develop means to systematically investigate this correlation, both in order to gain fundamental physical insights into catalytic mechanisms and in order to optimize the properties of nanomaterials. We have developed a pulsed-laser deposition (PLD) approach to form orthogonally overlapping metallic gradients ('wedge'-shaped thickness profiles) as catalysts for the chemical vapor deposition of vertically-aligned carbon nanotubes from acetylene. In this approach, the effects of catalyst composition and layer thickness are studied simultaneously on a single substrate, allowing us to visualize broad trends efficiently and reliably. The sub-monolayer deposition rate control in this PLD approach further enables us to 'zoom in' very accurately to specific ranges of parameters. Here we describe the technical challenges of the approach and discuss the broad applicability to a variety of catalytic-growth studies. Results showing the discovery of a particularly efficient catalyst in the Fe-Mo system for the rapid growth of vertically-aligned carbon nanotubes (exceeding 1 mm/hr) are presented as a specific example illustrating the method's strengths. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

## 2:30 PM HH2.4

**Carbon Microtubes: Tuning the Internal Diameters and Morphologies.** Gopinath Bhimarasetti and Mahendra K. Sunkara; Chemical Engineering, University of Louisville, Louisville, Kentucky.

Carbon nanotubes offer tremendous promise in nano-fluidics, but the

progress in this area has been limited due to the extremely small internal diameters. Here, we describe a synthesis technique for tuning the internal diameters of carbon tubular structures from a few nm to a few microns, thus controlling the morphology. The strategy uses in-situ gas phase compositional variations to impact the growth interface. A variety of hollow curved carbon morphologies have been synthesized: cones, tubes, funnels, tube-on-cone, Y-junctions, dumbbells and multi-staged tubules<sup>1</sup>. We envision that the above morphologies would find unique applications as throttle valves, micro-reactors, flow and distribution channels in nano-fluidic devices. Our synthesis concept is based on our ability to change the wetting behavior of gallium with carbon using different gas phase compositions. The growth experiments were conducted in a microwave plasma reactor on a substrate covered with molten gallium. Gallium droplets that form during plasma exposure, mediate the growth of carbon shell around the droplet. The contact angle between gallium and the carbon wall determines the conical angle of the structure. The contact angle can now be varied by using different gas phase chemistries. In the presence of oxygen or nitrogen, gallium wets carbon, thus reducing the contact angle. Using different dosings of oxygen and nitrogen we were able to control the conical angles of the tubular structures. For example, using increasing nitrogen dosing we were able to tune the conical angles from 30° to -15°. With oxygen dosing, we could synthesize straight tubes (conical angle = 0°), as oxygen is more aggressive than nitrogen in changing the contact angle. Adopting an 'n-step' dosing sequence at various stages of growth, we were able to synthesize 'n-staged' morphologies. The detailed tube-growth mechanism involved in the growth of these structures will be discussed. The walls of the described morphologies exhibit a very unique structure. Unlike multi-walled carbon nanotubes, the graphene sheets are not arranged in concentric cylinders or as a scroll structure. Instead, the wall is comprised of nanocrystals of graphite in the size range of 10-20 nm, oriented with respect to the wall surface. The orientation of these nanocrystals depended on the angle gallium makes with the carbon wall. Selected area electron diffraction and nanodiffraction analysis will be presented to discuss the wall structure and the microscopic tube-growth mechanisms involved. **Acknowledgments** : The authors gratefully acknowledge late Prof. J. M. Cowley for his input and discussions during this work. **References** 1. G. Bhimarasetti, M. K. Sunkara, U. M. Graham, B. H. Davis, C. Suh, K. Rajan, "Morphological control of tapered and multi-junctioned carbon tubular structures", *Advanced Materials*, 15 (19), 1629 (2003).

## 2:45 PM HH2.5

### Optimization of growth conditions for the synthesis of vertically aligned arrays of single wall carbon nanotubes.

Kalayu Belay<sup>3</sup>, Jeremy Jackson<sup>3</sup>, Alex Puzosky<sup>1,2</sup>, David Geohegan<sup>1</sup>, Hans Christen<sup>1</sup> and Hongtao Cui<sup>1</sup>; <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; <sup>3</sup>Department of Physics, Florida A&M University, Tallahassee, Florida.

In this study we explored the possibility of growing vertically aligned arrays of single wall carbon nanotubes (VAA-SWNT) using evaporated metal catalyst films and a chemical vapor deposition (CVD) process. The evaporated catalyst films approach allows us to grow vertically aligned nanotubes in the patterned structures as required in different functional devices based on carbon nanotubes. Recently we have shown that for the Al/Fe/Mo catalyst system the number of walls in the VAA-MWNTs decreases when the growth temperature increases. For example, we were able to grow preferentially double wall carbon nanotubes with a fraction of SWNTs at T<sub>g</sub>700 °C using C<sub>2</sub>H<sub>2</sub> as feedstock gas. The goal of this study is to maximize the fraction of SWNTs in the vertically oriented arrays of nanotubes by optimizing the catalyst films, the growth conditions and the feedstock gas. Al/Co and Al/Mo/Co films deposited at different thicknesses and compositions were explored for this purpose, with ethanol vapor as the feedstock. To find the optimum growth temperatures for different catalyst films we used a time-resolved in-situ reflectivity technique which allowed us to perform rapid screening of the different catalyst films. The optimal growth conditions for vertically aligned arrays of SWNTs will be presented and discussed. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

## 3:30 PM HH2.6

### The effect of adhesion between catalyst thin film and a substrate on the growth behaviors of vertically aligned carbon nanotubes. Seonghoon Lee<sup>1</sup> and Jung Inn Sohn<sup>2</sup>;

<sup>1</sup>Chemistry, Seoul National University, Seoul, South Korea; <sup>2</sup>Materials Science & Engineering, Kwangju Institute of Science and Technology, Gwangju, South Korea.

The growth behaviors of carbon nanotubes can be largely grouped

into a base growth-mode and a top-growth mode. The correlation between the growth mechanism of vertically aligned carbon nanotube (CNT) grown by thermal chemical vapor deposition (CVD) and the adhesion of catalyst particles to the Si substrates has been investigated using transmission electron microscopy and scanning electron microscopy. In order to obtain different adhesions of catalyst particles to the substrates, the Ni films with thickness of 10 nm are deposited by pulsed laser deposition (PLD), sputtering, and electron beam evaporation (e-beam evaporation), respectively. We find that CNTs grown on Ni nanoparticles deposited by PLD have no encapsulated Ni particles at the tip, whereas CNTs with metal tips are grown on catalyst particles deposited by sputtering and e-beam evaporation. It is shown that the growth mode of CNTs strongly depends on the adhesion of catalyst particles to the Si substrates.

### 3:45 PM HH2.7

#### Experimental Estimate of the Free Energy of Formation for Single Walled Carbon Nanotubes (SWNT). Larry M. Wagg<sup>1</sup>,

Anne C. Dillon<sup>1</sup>, Philip A. Parilla<sup>1</sup>, Kim M. Jones<sup>1</sup>, Jeffrey L. Blackburn<sup>1</sup>, G. L. Hornyak<sup>2</sup>, Leonid Grigorian<sup>3</sup> and Michael J. Heben<sup>1</sup>; <sup>1</sup>Basic Sciences, National Renewable Energy Lab, Golden, Colorado; <sup>2</sup>Physics and Astronomy, University of Denver, Denver, Colorado; <sup>3</sup>Honda America R&D, Southfield, Michigan.

Single walled carbon nanotubes (SWNT) were synthesized by methane CVD on a supported mixed transition metal catalyst. Gas feed composition and reaction temperature were varied to identify the threshold conditions of temperature and gas concentrations for the growth of SWNT. Raman spectroscopy and TEM imaging were used to confirm the formation of SWNT. Threshold growth conditions were used to calculate the experimental equilibrium constant  $K^*(T)$  and  $\Delta G^*(T)$ , the apparent free energy of reaction for methane decomposition  $CH_4 \Rightarrow C_{SWNT} + H_2$  using literature values for the graphite equilibrium constant  $K_g(T)$  and the expression  $\Delta G^*(T) = -RT \ln[K^*(T) / K_g(T)]$ . These data were then compared to literature  $\Delta G_f(T)$  data for graphite, diamond, and carbides of the metal catalysts. The differential compared to graphite was found to be between 13.4 and 15.2 kJ/mol over the temperature range 740 to 1000° C. The experimental value  $\Delta G^*(T)$  exceeds  $\Delta G_f(T)$  for all relevant carbon containing species over the temperature range where SWNT growth is observed. These data represent the first experimental estimate of the free energy of formation for SWNT.

### 4:00 PM HH2.8

#### Bulk Synthesis of Helical Coiled Carbon Nanostructures.

Wei Wang<sup>1</sup> and Apparao M. Rao<sup>2</sup>; <sup>1</sup>School of Materials Science and Engineering, Clemson University, Clemson, South Carolina; <sup>2</sup>Physics and Astronomy, Clemson University, Clemson, South Carolina.

3D helical coiled carbon nanostructures have attracted much interest recently. Due to their fascinating morphologies, they are expected to exhibit unique structural, mechanical and electrical properties. Here we report a bulk process for preparing helical coiled carbon nanostructures including coiled nanowires and coiled nanotubes on bare quartz substrates. These nanostructures were synthesized at ambient pressure using a thermal chemical vaporization deposition (CVD) process in which xylene and acetylene were used as the primary carbon source. A multi-metal catalyst formed from a mixture of ferrocene, indium isopropoxide and tin isopropoxide served as the seed to initiate the growth of these helical coiled nanostructures. Importantly, no pre-formed substrates are required in our process. The as-synthesized coiled nanowires and nanotubes are pure without the presence of amorphous carbon nanoparticles. Further, by precisely controlling the atomic ratio of In/(Fe+In), coiled nanowires or coiled nanotubes can be synthesized exclusively. The diameters of the as-grown coiled nanowires vary from several tens to several hundreds nanometers, whereas the diameters of the coiled nanotubes are around 20 nm. Structural, electrical and mechanical properties of these nanostructures revealed using SEM, TEM, HR-TEM and AFM will be presented.

### 4:15 PM HH2.9

#### Match-Stick Carbon Nanotubes : Structure Control and Properties.

Vincent Jourdain<sup>1</sup>, Matthieu Paillet<sup>1</sup>, Odile Stephan<sup>2</sup>, Annick Loiseau<sup>3</sup> and Patrick Bernier<sup>1</sup>; <sup>1</sup>Universite Montpellier, Montpellier, France; <sup>2</sup>Universite Paris Sud, Orsay, France; <sup>3</sup>ONERA, Chatillon, France.

We formerly demonstrated an original type of carbon nanotube growth, namely "sequential catalytic growth" [1]. This growth mechanism allows the formation of periodic nanofilaments whose elementary unit is a multiwall carbon nanotube with an open end and the other end filled with a nanoparticle (Fig. 1). These objects were named "match-stick carbon nanotubes". The activation of this type of growth is shown to be directly related to the co-catalytic action of phosphorus mixed with catalyst metal particles : Fe, Ni-Fe or Co-Fe. A mechanism of sequential growth, based on a kinetic mismatch

between the carbon supplying and consuming steps, inducing a periodic fluctuation of the carbon concentration in the catalyst particle, has been proposed [2]. A morphology study by TEM micrograph analysis confirms the predictions of the proposed mechanism concerning the existence of two distinct growth regimes, depending on the size of the catalyst particle and the reactant supply. The possibility to invert the growth regimes is demonstrated, opening the way to the control of the inter-particle distances. The match-stick nanotubes exhibit original mechanical properties. The thin inter-unit junctions constitute preferential bending and breaking points. They can be broken by a simple sonication process. The periodic insertion with magnetic nanoparticles also makes them potentially very interesting objects for new spintronics nanodevices. Magnetic characterisation of the inserted nanoparticles by MFM will be reported. 1) V. Jourdain et al., Chem.Phys.Lett., 364, 27, 2002. 2) V. Jourdain et al., Adv. Mat., 16, 447, 2004.

### 4:30 PM HH2.10

#### Residual Gas Analysis of Multi-walled and Single-walled Carbon Nanotube Growth.

Brett A. Cruden<sup>1</sup> and M. Meyyappan<sup>2</sup>; <sup>1</sup>Center for Nanotechnology, NASA Ames UARC, Moffett Field, California; <sup>2</sup>NASA Ames Center for Nanotechnology, Moffett Field, California.

We report a chemical characterization of downstream products produced in an Atmospheric Pressure Chemical Vapor Deposition reactor for Carbon Nanotube Growth. Single-walled nanotubes are prepared by thermal decomposition of methane using a Al/Fe/Mo catalyst below the pyrolysis temperature. Multi-walled nanotubes are produced by a similar process with ethylene and an Al/Fe and Cr/Fe catalysts. In both systems, a residual gas analyzer is connected downstream of the tube furnace and used to analyze downstream product species. Data collected in the residual gas analyzer is used to extract relative densities of reaction products, including many high mass species and hydrogen. Reaction products are monitored as a function of temperature between 600-1025 C for both chemistries and comparisons are made with and without catalyst present. An increase in many of the reaction products is observed when catalyst is introduced into the system, and these changes are used to estimate surface reaction rates of the catalyst.

### 4:45 PM HH2.11

#### Formation of Carbon Nanostructures by Metal Dusting.

Paulo J. Ferreira<sup>1,2</sup>, John B. Vander Sande<sup>2</sup> and Peter Szakalos<sup>3</sup>; <sup>1</sup>Materials Science and Engineering Program, University of Texas at Austin, Austin, Texas; <sup>2</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Swedish Institute for Metals Research, Stockholm, Sweden.

Despite the extraordinary properties of carbon nanotubes, a great technological impact will depend on the possibility of producing carbon nanotubes in large scales. As a consequence, researchers around the world have been devising methodologies to synthesize carbon nanotubes. One route that could become promising in the near future for the generation of carbon nanotubes is the phenomenon of metal dusting. Simply, metal dusting is the disintegration of metallic alloys by corrosion, which is initiated by exposure of the alloys to strongly carburizing atmospheres. The result of the decomposition is a mixture of metal particles and carbon structures. In this work, a high-purity iron sample is exposed to a reaction gas composed by CO, H<sub>2</sub>O and H<sub>2</sub> in two periods, 48h and 100h at 650 C, and subsequently observed in a Field Emission Gun Scanning Electron Microscope (SEM) and a JEOL 2010FX Transmission Electron Microscope (TEM). The research produced so far shows that upon exposing the sample to the reaction gas, both carbon nanotubes and carbon nanorods, of various diameters and lengths, and nanoparticles of various shapes are present in the coke formed during metal dusting. A careful examination of these nanoparticles confirm that they are orthorhombic cementite (Fe<sub>3</sub>C). SEM and TEM observations show that the cementite nanoparticles are closely associated with the presence of carbon nanotubes and nanorods, and dictate the final diameter of these carbon nanostructures. Further TEM examinations show that the carbon nanotubes and carbon nanorods grow in either a straight or twisted configuration.

SESSION HH3: Poster Session  
Monday Evening, November 29, 2004  
8:00 PM  
Exhibition Hall D (Hynes)

### HH3.1

#### Growth of the Open-Networked Carbon Nano-Structures at Low Temperature by Microwave Plasma Electron Cyclotron Resonance Chemical Vapor Deposition.

Chi-Hwa Wu<sup>1,2</sup> and David R. Harding<sup>1,2</sup>; <sup>1</sup>Laboratory for Laser Energetics, University of

Rochester, Rochester, New York; <sup>2</sup>Department of Chemical Engineering, University of Rochester, Rochester, New York.

The deposition of open-networked carbon nano-structures has been developed on catalyst-assisted Si substrates using microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD) system at temperature as low as 300 °C. Different types of carbon materials were synthesized on well-dispersed Co or Fe catalyst with a gas mixture of hydrogen and methane. The results were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and showed that the deposited structures can include amorphous carbon films, carbon nano-foams (pore size from 20-500 nm), and tube-like nano-structures. The morphologies of these producing nano-structures depend strongly upon the processing conditions: including substrate temperature, substrate bias, catalyst materials and the processing pressure. The dependence of the nano-structures growth on those parameters will be discussed. In addition, the properties of the carbon nano-structures including density, hardness, and Young's modulus measured by X-ray radiography, nanoindentation, and thermal mechanical analysis will be presented.

### **HH3.2**

**Growth Mechanisms of Aligned CNT in Anode Sheath of DC Discharge.** Alexander Pal<sup>1</sup>, Anatoly V. Filippov<sup>1</sup>, Nikolay Suetin<sup>2</sup> and Mikhail Timofeev<sup>2</sup>; <sup>1</sup>Troitsk Institute for Innovation and Fusion Research, Troitsk, Moscow region, Russian Federation; <sup>2</sup>Institute of Nuclear Physics, Lomonosov Moscow State University, Moscow, Russian Federation.

Plasma enhanced chemical vapour deposition (PECVD) is a key growth technology to produce arrays of vertically aligned carbon nanotubes (CNT) on patterned surfaces. Such CNTs are suitable for fabrication of different electronic devices, field emitters, sensors etc. Since such a technology is in its rather early stage, there is a general lack of understanding of mechanisms of aligned growth. DC discharges are widely used in PECVD for aligned CNT growth. When a substrate holder is a cathode the deposited film is exposed to intensive bombardment by an ion beam that is formed in the cathode layer. Such bombardment on the one hand leads to the formation of defects, and on the other hand, the great anisotropy of the angle distribution function of ions leads to the formation of the oriented structures, for example, carbon nanotubes. The preferential orientation along the line of ion anisotropy is due to more effective destruction of non-oriented structures by ions. The other factor which result in aligned CNT growth is strong electric field in a cathode layer. To exclude the influence of the ion bombardment upon the CNT properties we carried out the deposition process on the anode of the DC glow discharge. The deposition was performed in the methane-hydrogen mixture under the pressure of 100-140 Torr and the temperature of 960-1080 C on silicon substrates of 1.5x1.5 cm<sup>2</sup> in size, the substrates had previously been coated with a catalyst modified to nanoparticles of 20-30 nm. This work resulted in the successful growth, including the selective one, of highly aligned CNT arrays. To understand the processes in the anode layer of the DC discharge and to explain the effect of the electrical field upon the CNT growth the model was developed for transport processes of charged particles in the anode layer under the conditions of the CNT growth with the electron energy distribution function non-locality taken into consideration. It was found out that the oriented carbon CNT grew in the field with the strength up to 1500 V/cm. Growing CNT array moves an anode sheath along electric field direction. The consideration of possible mechanisms for the influence of the electrical field upon the growth of the oriented CNT showed that the effect of ordering the CNT massive was due to the collective Coulomb interaction of the surface charges induced on CNT heads by the external field. The termination of the CNT growth after achieving the size of 100 μm can occur due to the catalyst poisoning, one of the reasons for which can be heating the CNT top by the electron current while the thermal conductivity decreases with the increase in the tube length.

### **HH3.3**

**Growth of Aligned Carbon Nanotubes on Annealed Nickel Dots.** Zhongping Huang<sup>1</sup>, David Carnahan<sup>1</sup>, J. Rybczynski<sup>2</sup>, Z. F. Ren<sup>2</sup>, K. Kempa<sup>2</sup> and M. Sennett<sup>3</sup>; <sup>1</sup>NanoLab Inc., Newton, Massachusetts; <sup>2</sup>Department of Physics, Boston College, Chestnut Hill, Massachusetts; <sup>3</sup>Materials Science Team, U.S. Army Soldier and Biological Chemical Command, Natick Soldier Center, Natick, Massachusetts.

The aligned growth of carbon nanotubes by chemical vapor deposition is now relatively well understood, but the techniques for patterning catalytic materials are still in development. Hemispherical nickel dots are nearly ideal shapes for nanotube catalysis, and the hemisphere diameter should be smaller than 200 nm. One approach that NanoLab has developed for catalyst deposition is based on a self-assembled hexagonally close packed polystyrene sphere monolayer. Sputtering

through on such a monolayer deposits roughly triangular shapes on the substrate, at the interstitial point where three spheres meet. The size of the triangle has a geometrical relationship to the sphere size, as does the spacing between triangles. In our experiments, where we deposited nickel through a sphere mask, these triangles nucleated multiple nanotubes during CVD. Our goal was to nucleate a single nanotube at each site, so those secondary nanotubes disturb the periodicity of the primary carbon nanotubes. When the spheres are small, the corresponding triangle is small enough to nucleate a single nanotube, but when the spheres exceed 1-2 microns in size, the nickel deposit routinely nucleates multiple nanotubes. This problem limits the applicability of sphere lithography, which overall is a low cost method to fabricate large scale periodic arrays of carbon nanotubes. Our group investigated thermal annealing steps to reshape the triangular nickel deposits into hemisphere-like dots, which could be used to nucleate single aligned carbon nanotubes. Because the tungsten filament in the plasma enhanced chemical vapor deposition system was used as the thermal source for annealing, the two processes of nickel dot annealing and carbon nanotube growth can be completed within the same system sequentially. In our study, glass, silicon, and titanium substrates were tested with the sphere masking process. Our study showed that the annealing can reliably reshape the nickel triangles into hemispherical dots, and therefore the available periodicity for the sphere mask technique can be extended. Nickel thickness played an important role in nickel dot reshaping process, since it not only controls the dot size and therefore the carbon nanotube diameter, but it also affects the aggregation rate of the original nickel triangle. After annealing and aligned nanotube growth, scanning electron microscopy showed that individual carbon nanotubes were grown from each annealed nickel dot in the periodic array and that the nanotubes were well aligned and were uniform in both length and diameter.

### **HH3.4**

**Fabrication and Application of Vertically Aligned Carbon Nanofibers by Microwave Plasma-enhanced Chemical Vapor Deposition.** Zhenqing Xu<sup>1,2</sup>, Arun K. Sikder<sup>1</sup>, Arun Kumar<sup>1</sup> and Ashok Kumar<sup>1,2</sup>; <sup>1</sup>Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; <sup>2</sup>Department of Mechanical Engineering, University of South Florida, Tampa, Florida.

Vertically aligned carbon nanofibres (CNFs) have been fabricated by microwave plasma-enhanced chemical vapor deposition (MPECVD) method. Thin Ni layer around 25 nm was coated by E-beam evaporation on the Si substrate as the catalyst layer. Experiment was carried out in a flowing mixture of hydrogen and methane in the low temperature of 450 °C. Selective growth of CNFs has been produced by patterning the Ni catalyst layer. The thickness of the catalyst layer was found very critical to form vertically aligned carbon nanofibers. Only randomly oriented nanofibers had grown when using thicker Ni layer (40nm). Scanning electron microscopy (SEM) shows that nanofibers were vertically aligned perpendicular to the substrate. The electrical self-bias imposed on the substrate surface appears to be the primary mechanism responsible for the vertically alignment. The Transmission electron microscopy (TEM) and Raman spectroscopy were used to characterize the samples. Diameter of the fiber is less than 200 nm and the length is around a few microns. Field emission characteristics for the nano-rope films were observed. In the present work, functionalized CNFs were explored for drug delivery application. The CNFs were derivatized by using free radical addition method. Alkyl group terminated with carboxylic acid is used for functionalization of CNFs and further it covalently linked with drug molecules to deliver the drug.

### **HH3.5**

**Directional Growth of Single-Walled Carbon Nanotubes for Nanotube-on-Insulator Applications.** Xiaolei Liu, Song Han and Chongwu Zhou; EE-Electrophysics, University of Southern California, LA, California.

Dense arrays of highly aligned carbon nanotubes were synthesized by chemical vapor deposition on flat crystalline substrate surfaces. 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/SiO<sub>2</sub> substrates. These nanotubes are commonly tens of micrometers long, and the inter-tube spacing is typically around 200 nm, which can be controlled to certain degree. 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.

### HH3.6

**Carbon Nanotube Growth on Metal-catalyzed Substrates in Laser Oven Apparatus.** Yoshiyuki Suda, Akihide Tanaka, Maria Antoaneta Bratescu, Atsushi Okita, Yuki Hayakawa and Yosuke Sakai; Graduate School of Information Science and Technology, Hokkaido University, Sapporo, Japan.

Since carbon nanotube (CNT) has excellent physical properties, e.g., field emission property, high electrical conductivity and high tensile strength, various applications of CNT in nanotechnology field are expected. We have been studied laser ablation technique for CNT growth. Though laser ablation produces CNT in gas phase, we recently observed CNT growth also on metal-catalyzed substrates (Ni/SiO<sub>2</sub>/Si and Fe/SiO<sub>2</sub>/Si) located inside a laser oven apparatus [1]. It is thought that ablated carbon atoms and molecules were supplied on the substrates and developed into CNT. In this report, dependence of CNT growth on catalyst film thickness was examined. The experimental setup was illustrated in the previous report [1]. Focused ArF excimer laser beam (wavelength=193 nm, pulse duration=20 ns, fluence=3 J/cm<sup>2</sup>, repetition rate=10 Hz) was irradiated on Ni/Co catalyst-contained graphite target inside quartz tube operating at 1373K. Ar gas was flowed in the same direction of the laser irradiation with a flow rate of 750 sccm. The pressure was kept at 500 Torr. Ni and Fe were deposited on SiO<sub>2</sub>/Si substrate with thickness of 1-10 nm by DC sputtering. These substrates were placed 30 mm downstream the target. The experiment was continued for 120 min. The grown CNT was observed by SEM (Scanning Electron Microscopy, Hitachi, S-4300) and Raman spectroscopy (JASCO, NRS-1000HS (632.8 nm)). The grown CNT on Fe/SiO<sub>2</sub>/Si substrates was examined by SEM. We confirmed the CNT growth on Ni/SiO<sub>2</sub>/Si substrates as well. When the film thickness decreased, length, diameter and number density of CNT decreased. This tendency is a similar to that of Wei et al [2] and indicates that CNT was grown on the substrates. References [1] Y. Suda, K. Utaka, M. A. Bratescu, Y. Sakai, J. Tsujino, and K. Suzuki, *Appl. Phys. A*, in press [2] Y.Y. Wei, G. Eres, V.I. Merkulov, and D.H. Lowndes, *Appl. Phys. Lett.*, 78 (2001) 1394

### HH3.7

**Formation of Well-Aligned Carbon Nanotube on Glass Substrate by RF Plasma CVD Method at Growth Temperature of 500°C.** Yoshiyuki Show<sup>1</sup>, Yutaka Yabe<sup>1</sup>, Tomio Izumi<sup>1</sup> and Hidehiko Yamauchi<sup>2</sup>; <sup>1</sup>Dept. of Electrical and Electronic Engineering, Tokai University, Hiratsuka, Kanagawa, Japan; <sup>2</sup>Eiko Engineering Company Limited, Yamazaki, Ibaraki, Japan.

Carbon nanotube is one of the promising material for a cold cathode of the field emission display (FED), because it emits electrons at low electric field from its tip with high aspect ratio. For commercial FED, glass substrate should be used to reduce its fabrication cost. In this presentation, we present formation of well-aligned carbon nanotube on corning glass (7059) by RF plasma CVD method. The radio frequency (RF) plasma CVD method allows well-aligned carbon nanotube to grow on the glass substrate with large area at low temperature of 500 °C. This method is a promising technique to fabricate the cold cathode of FED using carbon nanotube. The well-aligned carbon nanotube was grown by using the RF plasma CVD equipment. First, Fe catalysis thin film was deposited on the glass substrate by the sputtering method. The sputtering was carried out in the chamber of the RF plasma CVD equipment. Next, acetylene gas diluted in hydrogen at 10 % was introduced into the CVD chamber. Few oxidation of the Fe catalysis took place during this process, because the Fe catalysis was not exposed to air. And then the plasma was ignited. The RF power was 100 W. The growth pressure and the temperature were 0.7 Pa and 500 °C, respectively. The growth time was 1 hour. The well-aligned carbon nanotube with length of 5 μm was grown on the glass substrate. The density of the carbon nanotube on the glass substrate was 1200 /μm<sup>2</sup>. The TEM investigation suggested that the carbon nanotube is 6 and 3 nm in an outside and an inside diameter, respectively. Moreover, the electron diffraction pattern indicated that the carbon nanotube had graphite structure.

### HH3.8

**The Characteristics of Carbon Nanotubes with Electroless Plating Deposited Ni Catalysts.** Bohr-Ran Huang, Chien-Sheng Huang, Chia-Ching Wu and Chih-Yuan Lin; Electronic Engineering Department, National Yunlin University of Science and Technology, Touliu, Yunlin, Taiwan.

We have synthesized multi-walled carbon nanotubes (MWNTs) on nickel-deposited n-type silicon substrates by thermal chemical vapor deposition (Thermal CVD). The electroless plating method was adopted in the deposition of the Ni catalytic layer. Sulfuric acid solution was used as a buffer to adjust and maintain pH value at 4.6. Both the deposition time of the nickel catalyst layer and the growth time of MWNTs were adopted to control the length and density of MWNTs. From the scanning electron microscopy (SEM) images, it

showed that the density of carbon nanotubes increased as the deposition time of nickel catalyst layer increased. The formation of nickel nucleation becomes rich as the immersion time of the substrate in electroless plating solution was longer, and this benefited the growth of carbon nanotubes. In addition, the Raman spectrum demonstrated that the ID/IG ratio of MWNTs decrease as the deposition time and the growth time increase. It indicated that more graphenes were formed of MWNTs. Transmission electron microscopy (TEM) was also used to explore the configuration and crystalline of the as-grown MWNTs. By comparison to Raman spectrum, the relation of geometric structure and ID/IG ratio would be presented.

### HH3.9

**Carbon Nanotubes Grown on Carbon Cloth and Their Field Emission Characteristics.** Sung-Ho Jo<sup>1</sup>, Dezhi Wang<sup>1</sup>, Jianyu Huang<sup>1</sup>, Guangyong Xiong<sup>1</sup>, Wenzhi Li<sup>2</sup>, Krzysztof Kempa<sup>1</sup> and Zhifeng Ren<sup>1</sup>; <sup>1</sup>Department of Physics, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Department of Physics, Florida International University, Miami, Florida.

Carbon nanotubes are grown on carbon cloth by using thermal CVD with methane/hydrogen, and their field emission characteristics are investigated. Multi-walled carbon nanotubes are grown by sputtering the thin layer of stainless steel as a catalyst on the carbon cloth. The catalysts for the single walled carbon nanotubes growth are formed by dipping the carbon cloth in the iron sulfate solution. An extremely low electric field of less than 0.4 V/μm is required to reach an emission current density of 1 mA/cm<sup>2</sup> from the carbon cloth covered with carbon nanotubes. This ultra-low operating electric field of carbon nanotubes grown on carbon cloth is mainly due to a very high field enhancement factor of 1.882×10<sup>4</sup>, which is the combined result of geometrical configuration of the carbon nanotubes and the carbon cloth substrate.

### HH3.10

**Effective Growth of Vertically-Aligned Carbon Nanotubes.** Vijaya Kayastha and Yoke Khin Yap; Physics, Michigan Technological University, Houghton, Michigan.

Rapid and continuous growth of carbon nanotubes (CNTs) are still unachievable due to the lack understanding of the growth mechanism. Ideally, CNTs will continue to grow if every carbon atom that deposits on the catalyst's surface becomes incorporated within the CNT's structure. Such an ideal condition has not been achieved. Here, we report the growth of vertically aligned multiwall carbon nanotubes (VA-MWNTs) with an initial growth rate as high as 300 μm/hour. We found that with an appropriate addition of carrier gas, optimum growth temperatures and catalyst film thickness can convert a saturated growth into a continuous mode. This effective growth is due to the balance between the decomposition of hydrocarbon molecules and the subsequent diffusion and segregation processes on the catalytic nanoparticles. We have performed a systematic study to elucidate these relations by a thermal CVD method. The catalytic Fe films used in our experiments were coated on SiO<sub>2</sub>/Si substrates in a pulsed-laser deposition (PLD) system. These films had a thickness of 4 nm (10 mJ pulsed laser for 3 minutes) as verified by atomic force microscopy (AFM). These Fe/SiO<sub>2</sub>/Si substrates were then inserted into the quartz tube of our thermal CVD system. Pretreatment was carried out for one hour in the flow of hydrogen and nitrogen at 800°C before the growth in acetylene and argon for 15 min. All samples were then examined under field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Effective growth occurred at 650°C and resulted in high density vertically aligned MWNTs at a rate of 300 μm/hour. Both growth temperatures and catalyst film thickness are critical for these effective growths. The growth rate and the degree of alignment of the MWNTs decreased beyond these optimum parameters. These MWNTs continued to grow for at least one hour. Our results show that a rapid growth rate of CNTs is achievable even without the use of ammonia (as reported by many others) for both the pretreatment and the growth. Our new finding could facilitate continuous growth of carbon nanotubes in the future. Details of these results and the modified growth model will be discussed in the meetings.

### HH3.11

**A Dual-RF-Plasma Approach for Controlling the Graphitic Order and Diameters of Vertically-Aligned Multiwall Carbon Nanotubes.** Jitendra Menda<sup>1</sup>, Kumar Lakshman Vanga<sup>1</sup>, Benjamin Ulmen<sup>1</sup>, Yoke Khin Yap<sup>1</sup>, Zhengwei Pan<sup>2,3</sup>, Iliia N. Ivanov<sup>2,3</sup>, Alex A. Puzetzy<sup>2,3</sup> and David B. Geohegan<sup>3</sup>; <sup>1</sup>Physics, Michigan Technological University, Houghton, Michigan; <sup>2</sup>Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; <sup>3</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Plasma enhanced chemical vapor deposition (PE-CVD) is the only known technique for growing vertically-aligned multiwall carbon

nanotubes (VA-MWNTs) at controllable tube densities. This technique is considerably important for the low temperature growth of MWNTs at desired locations and orientations. However, the graphitic order of these MWNTs is inferior to those grown by laser ablation, arc discharge, and thermal CVD techniques. VA-MWNTs grown by PE-CVD are usually called carbon nanofibers (CNFs) and have highly distorted structures. Previously, these CNFs were grown by a one-plasma approach (DC, microwave etc), either for gas decomposition or substrate biasing. Here, we describe a dual-RF-plasma CVD technique that offers unique capability for controlling the graphitic order and diameters of VA-MWNTs. We decoupled two plasmas in a parallel-plate configuration. One of these plasmas is applied on the top electrode and responsible for the decomposition of the hydrocarbon gas. The second plasma was applied on the substrates and initiated a negative dc bias voltage that induced in-situ ion bombardment on the growth surface. The substrates are heated independently by a controlled heating element. Previously, we have demonstrated the growth of VA-MWNTs to an area as large as 25 cm<sup>2</sup> at a substrate temperature as low as 540 °C. Here, we describe the function of these plasmas on the graphitic order, diameters, and minimum growth temperatures of VA-MWNTs. Ni catalyst films were deposited on Si/SiO<sub>2</sub> substrates by pulsed laser deposition before the growth of MWNTs in the CVD system. Methane (CH<sub>4</sub>) was used for the growth of the MWNTs at a pressure of 0.2 torr. Various parameters such as catalyst film thickness, growth temperatures, and plasma configurations were extensively studied. Results indicate that the diameters of VA-MWNTs increased with the increase of RF forward power to the top electrode. An increase of substrate biasing also resulted in greater tube diameters however, diameters decreased when excessive biasing was applied. These were explained by both plasma heating and catalyst re-sputtering, respectively. In addition, we found that VA-MWNTs can be grown at substrate temperatures as low as 400 °C at a reduced substrate biasing. According to high-resolution transmission electron microscopy (HRTEM), these MWNTs have relatively high graphitic order as compared to some CNFs produced by other PE-CVD. Raman spectroscopy indicates that both the top plasma and substrate biasing contribute to these structural properties. There is a minimum substrate biasing and RF forward power required for the growth of MWNTs with enhanced graphitic order. Details of these results will be discussed in the meetings.

### HH3.12

#### Arc-Discharge Evaporation of Silver-Plated Graphite Rod.

Mojtaba Vaziri, Computer Science, Engineering Science, and Physics, University of Michigan-Flint, Flint, Michigan.

Nanotubes and nanosized particles have attracted considerable interest because of their novel physical and chemical properties and their potential applications in nanotechnology. A variety of methods has been used to synthesize these materials; to date, no study using metal-plated graphite rods for the arc-discharge production of these materials has been reported. In this work, several silver-plated graphite rods have been evaporated using the dc-arc discharge technique in the presence of helium quenching gas. The evaporated materials deposited on the cathode and the chamber walls were characterized using scanning electron microscopy (SEM), x ray diffraction (XRD), and transmission electron microscopy (TEM). It was found that the deposited materials contain high concentrations of long carbon nanotubes and encapsulated silver crystals. These results, along with how a silver-plated rod influences the growth conditions, will be discussed. This work was supported by grants from the Research Initiative and Faculty Development Awards programs of the University of Michigan-Flint.

### HH3.13

#### Site-selective Organization of Single Wall Carbon Nanotube Forest Assemblies.

Haoyan Wei<sup>1,2</sup>, Sang Nyon Kim<sup>1,3</sup>, Harris L. Marcus<sup>1,2</sup> and Fotios Papadimitrakopoulos<sup>1,3</sup>, <sup>1</sup>Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Chemistry, Polymer Program, Nanomaterials Optoelectronics Laboratory, University of Connecticut, Storrs, Connecticut.

Aligning the shortened SWNT vertically in controlled pattern, especially nano-needles, is very important to many applications such as electron field emitters and sensors. To achieve this objective a low energy (500eV) electron beam was used to modify the surface to assist in localizing our metal-assisted self-assembly technique. The Si substrate was modified with an ultrathin Nafion film (20nm), followed by direct ebeam writing to produce the pattern for SWNT forest self-assembly. FTIR-ATR results indicate the hydrophilic sulfonate groups within Nafion were removed during irradiation resulting in the exposed areas less hydrophilic than the unexposed regions as documented with friction force microscopy. Controlled deposition of metal irons via dipping within the nonirradiated region was confirmed

by Auger mapping and AFM measurement. This provided the basis for SWNT to achieve site-selective self assembly on the Si substrate as demonstrated by AFM in topography images.

### HH3.14

#### Catalyst Design for Carbon Nanotubes and for SiC Whiskers

Production. Vladimir L. Kuznetsov, Anna N. Usoltseva and Ilya N. Mazov; Borekov Institute of Catalysis, Novosibirsk, Russian Federation.

Catalysts design for carbon nanotube production is usually based on empirical approaches. An understanding of the formation mechanism of carbon deposits on metal surfaces is very crucial for the development of carbon nanotubes and filaments. The analogies with well developed catalytic processes can be used for the analysis of the development strategy of catalyst for production of new products. Here we consider the common features of the formation mechanisms of carbon deposits and silicon carbide whiskers on metal catalyst surfaces, namely: (1) the formation metal particle alloy oversaturated with carbon and/or silicon and carbon atoms and (2) the nucleation of corresponding deposits on the metal surface. We have demonstrated that the classic nucleation theory combined with phase diagram approach can be used for the description of different scenarios of carbon and/or SiC deposits formation and for the development of the main principles of catalyst and promotor design.

### HH3.15

#### Growth Kinetics Changes of Vertically Aligned Carbon Nanostructures Synthesised at Low Substrate Temperatures.

Guan Yow Chen, Chun Hwa Patrick Poa, Vlad Stolojan, Simon J. Henley and S.R.P. Silva; University of Surrey, Guildford, Surrey, United Kingdom.

Carbon nanotubes and nanofibers are typically synthesised at conditions where the substrate temperatures are above 600°C. We investigate the influence of substrate temperature and plasma conditions on the growth of vertically aligned carbon nanostructures using DC plasma Chemical Vapour Deposition (CVD) below 550°C. These nanostructures are synthesised using a C<sub>2</sub>H<sub>2</sub> based plasma and nickel thin film as the catalyst. We found that preferential deposition of amorphous carbon takes place as the synthesis temperature is lowered below 500°C. The lowering of carbon concentration in gas feedstock (<2% conc.) allows for the nucleation of nanofiber-like structures while balancing the build-up of amorphous carbon. This method allows the synthesis of vertically aligned structures at low temperatures (min. 230°C) without intentional heating, while still achieving reasonable average growth rates up to 25 nm/min. The only heating was provided by the plasma, which typically consumes 4 W/cm<sup>2</sup>. To highlight the importance of plasma, it was found that by varying the applied plasma bias during growth (high temperature synthesis) could vary the growth rate from 0 to 165 nm/min. Based on the observations of experimental process variations and the morphology of the synthesised structures, we propose a growth mechanism for such low temperature growth and examine the resulting morphology changes.

### HH3.16

#### Control of the Amount of Defects in Single Wall Carbon Nanotube Nanoneedles and Their Effect on Peroxidase Based Biosensor Sensitivity.

Sang Nyon Kim<sup>1</sup>, Xin Yu<sup>2</sup>, James F. Rusling<sup>2,3</sup> and Fotios Papadimitrakopoulos<sup>1,2</sup>, <sup>1</sup>Nanomaterials Optoelectronics Laboratory (NOEL), Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Pharmacology, University of Connecticut, Storrs, Connecticut.

Regular orthogonal arrays of organized Single Walled Carbon Nanotubes (SWNTs) have attracted significant interests for the past few years. Our group have demonstrated the self-assembly based arrays of SWNTs by using substrate-SWNTs hydrophilic interactions and SWNTs-SWNTs hydrophobic interactions.[1] More recently we have revealed the feasibility of these nanotube forests to peroxidase based biosensors.[2] This presentation will highlight some of our recent results in controlling the amounts of defects in the assembled SWNTs. Such control was imparted by carefully monitoring the Raman D-band as a function of aging time in a variety of solvents. The effect of these SWNTs perfection to the sensitivity of biosensor obtained from attaching peroxidases to the carboxylated ends of the nanotube forests will be discussed. Moreover, application to amperometric peroxidase-linked immunoassays will be presented as a prospective application for these nanosized needle-like assemblies. [1]. Chattopadhyay, D., Galeska, I. & Papadimitrakopoulos, F. Metal-Assisted Organization of Shortened Carbon Nanotubes in Monolayer and Multilayer Forest Assemblies. *Journal of the American Chemical Society* 123, 9451-9452 (2001). [2]. Yu, X., Chattopadhyay, D., Galeska, I., Papadimitrakopoulos, F. & Rusling, J. F. Peroxidase



activity of enzymes bound to the ends of single-wall carbon nanotube forest electrodes. *Electrochemistry Communications* 5, 408-411 (2003).

### HH3.17

**Determination of the Separation Efficiencies of Single Wall Carbon Nanotubes by Raman Scattering.** D. Nezych<sup>1</sup>, V. W. Brar<sup>1</sup>, Ge. G. Samsonidze<sup>3</sup>, Shin Grace Chou<sup>2</sup>, M. S. Dresselhaus<sup>3,1</sup> and G. Dresselhaus<sup>4</sup>; <sup>1</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>4</sup>Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

One goal of the carbon nanotube research community is to isolate tubes of a single diameter and chirality. Toward this end it is necessary to determine the effectiveness of various procedures which selectively separate as-grown ensembles of tubes by finding the effect of these procedures upon the diameter distribution and metal to semiconductor ratio. As is evident from the Kataura plot of interband transition energies vs. nanotube diameter, the radial breathing mode (RBM) of Raman spectra of nanotubes can be used to determine both the diameter of an excited tube and whether the tube is metallic or semiconducting. The resonant nature of the Raman process in nanotubes allows the sampling of small subsets of tubes within a sample containing many tubes, but it also requires a knowledge of the exact interband transition energies and the width of the resonance window for all tubes in order to make an accurate determination of the original distribution. Changing the distribution of diameters or the metal to semiconductor ratio changes the environment of a nanotube, to which the electronic structure, and consequently the optical analysis, are very sensitive. The present work develops a method by which Raman spectra taken at certain excitation energies may be used to account for environmental effects, allowing the diameter distribution and the metal to semiconductor ratio to be determined. The primary focus of our study is upon samples with a small average tube diameter, where there are a small number of unique (n,m) tube types present. Procedures to analyze Raman spectra for large diameter distributions which can be treated as semi-continuous are also discussed. A criterion for determining the preferable method for a given initial distribution is presented. D. Nezych acknowledges support from the Lester Wolfe fellowship through the Physics department at the Massachusetts Institute of Technology.

### HH3.18

**NMR Investigation of n-Alkylamine Self-Organization Along the Sidewalls of Single-Wall Carbon Nanotubes (SWNTs).** Sang Yong Ju<sup>1,2</sup>, Marcel Utz<sup>2,3</sup> and Fotios Papadimitrakopoulos<sup>1,2,4</sup>; <sup>1</sup>Nanomaterials Optoelectronics Laboratory (NOEL), University of Connecticut, Storrs, Connecticut; <sup>2</sup>Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Physics, University of Connecticut, Storrs, Connecticut; <sup>4</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Single wall carbon nanotubes (SWNTs) have drawn considerable attention from the scientific community due to their unique 1-D electronic and optical properties. Type (semiconducting (sem-) vs. metallic (met-)), diameter and chirality have played key role in these properties. Several methodologies have come forward to sep. sem- from met-SWNTs. Recently our group has been able to attain bulk sepn. by type from a differential solubilization technique based on the preferential affinity of amines towards sem-SWNTs. It has been argued that stable dispersions of sem-SWNTs with surfactant-amines originate from the organization of the aliph. chain along the nanotube sidewalls, along with a small amt. of zwitterions. We hereby present a careful design of these surfactant amines to impart differentiation in the <sup>1</sup>H and <sup>13</sup>C NMR chem. shifts of the various carbon atoms along the linear alkyl chain. This permitted us to det. the localized environment along the surfactant alkyl chains as a function of distance from the nanotube, as well as the chemical affinity of the amine functionality towards the sem-SWNTs. Our findings indicate the firm attachment of these amines to the surface of sem-SWNTs (or their bundles thereof), while the carbons at the opposite end of the surfactants exhibit substantial mobility.

### HH3.19

Abstract Withdrawn

### HH3.20

**Chemical Processing and the Infrared-Active Vibrational Modes of Single-Walled Carbon Nanotubes.** Un Jeong Kim<sup>1</sup>, Xiaoming Liu<sup>1</sup>, Clascidia A. Furtado<sup>2</sup>, Gugang Chen<sup>1</sup>, Humberto R. Gutierrez<sup>1</sup>, Richiro Saito<sup>3</sup>, Jie Jiang<sup>3</sup>, Mildred S. Dresselhaus<sup>4</sup> and Peter C. Eklund<sup>1,5</sup>; <sup>1</sup>Physics, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Centro de Desenvolvimento da

Tecnologia Nuclear, CDTN/CNEN, Belo Horizonte, MG, Brazil;

<sup>3</sup>Department of Physics, Tohoku University, Sendai, Japan;

<sup>4</sup>Department of Physics, MIT, Cambridge, Massachusetts;

<sup>5</sup>Department of Materials Science, Pennsylvania State University, University Park, Pennsylvania.

The IR-active vibrational modes of single-walled carbon nanotubes (SWNTs) have been observed by optical transmission through thin films of bundled single-walled carbon nanotubes. The SWNT IR modes, 6 first order and 3 second order, are very weak, and have not been reported to date. Because IR-active chemical functional groups, e.g., -COOH, -OH, might also be attached to the tube walls and contribute additional spectral features, we have also studied the effects of chemical purification and long-term high-temperature vacuum annealing on the IR spectrum. Through comparison with theory, we are able to assign most of the sharp features observed in our IR spectra to particular symmetry nanotube vibrational modes; features that were removed via high temperature annealing are assigned to specific attached chemical groups.

### HH3.21

**Field Emission and Conductivity of Individual Carbon Nanotube Measured by a STM Probe Inside a TEM.**

Jianguo Huang, Shuo Chen, Sung-Ho Jo and Zhifeng Ren; Department of Physics, Boston College, Chestnut Hill, Massachusetts.

The field emission and conductivity of individual carbon nanotube (CNT) was studied by using a scanning tunneling microscopy (STM) probe integrated inside a high resolution transmission electron microscope (HRTEM). We can simultaneously image the microstructure of CNT at an atomic scale and measure the physical properties, such as field emission and conductivity, by using the TEM-STM holder. This enables us to correlate the physical properties of individual CNTs with its microstructure directly. The physical properties of individual CNT were compared with that obtained from CNT films, and possible field emission and conductivity mechanisms are suggested.

### HH3.22

**Production and Characterization of Suspensions of Single-Wall Carbon Nanotubes.** Richard Matthew Russo and David E. Luzzi; Materials Science and Engineering, 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, have confirmed that nanotubes and nanotube bundles can stably exist in suspension for extended time periods. Measuring steady-state emission suggests 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 100fs-resolution transient absorption spectroscopy. The 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.

### HH3.23

**On the Flexural Characteristics of Multi-walled Carbon Nanotubes.** Rong Bai, R. Byron Pipes and Justin Molenaar; Polymer Engineering, University of Akron, Akron, Ohio.

The effective engineering properties of carbon nanotubes have been the subject of considerable interest since their discovery by Iijima [1]. In an earlier publication [2] one of the authors (RBP) treated the effective properties of single-walled carbon nanotubes and their hexagonal arrays and developed relationships for the prediction of the effective density and modulus, as well as, mixing rules for conversion of weight fraction to volume fraction. Implicit in these relationships was the perspective that, in mixtures, the effective engineering properties must account for the entire volume occupied. Since carbon nanotubes may be viewed as hollow cylindrical elements at the nano-scale, the volume occupied by the carbon atoms provides the stiffness and mass for the entire system, but in computing effective engineering properties the volume contained inside the hollow cylinder must also be considered when computing effective density and

modulus. In the present work, the authors develop relationships for prediction of the effective flexural modulus of multi-walled carbon nanotubes. Based on an analytical solution for the bending of orthotropic coaxial cylinders [3], the solution for the bending, tensile and torsional response is determined for two inter-tube conditions: no slip and no friction. These results provide an insight into the contributions of the van der Waals forces for multi-walled carbon nanotubes in bending. In addition, the warpage of the cross-section is evaluated for typical nanotube geometries in order to determine the applicability of the Bernoulli-Euler hypothesis in determining the flexural response of multi-walled carbon nanotubes.

### HH3.24

**Dispersion and Alignment of Carbon Nanotubes in an Elastomer Matrix.** Samit Ahir, Guillaume Lagubeau, Ali Tajbakhsh and Eugene Terentjev; Physics, Cambridge University, Cambridge, United Kingdom.

Dispersion of nanotubes in any given medium is a topic of active research attracting widespread interest not least because a homogeneously dispersed filler can impart near-perfect composite properties. Here we investigate the nature of nanotube aggregation and its break-up, and attempt to quantify the dispersion achieved in a polymer matrix. We use the crosslinkable PDMS matrix so that the resulting composite is an elastic rubber. We determine the mixing time  $t^*$ , defined and quantified as a function of local shear stress (itself a function of effective viscosity and the mixing shear rate, as well as the nanotube parameters), such that for  $t > t^*$  a full homogeneous dispersion is achieved for given mixing conditions. The results are directly applicable to nanotube dispersion in any media. The second aim of this work is the study of alignment of well-dispersed tubes in the polymer matrix, achieved by mechanical stretching of the gel before the final crosslinking. Furthermore, we measure the bulk electric resistivity, in equilibrium and as a function of applied strain, in elastomer-nanotube composites. This gives information about the percolation point, for the given tube aspect ratio, and its dependence on the orientational distribution (isotropic or uniaxially biased under strain). The connection between nanotube alignment, dispersion and resistivity is scrutinized. The experiments are carried out with a range of SWNT, MWNT and nanofibre structures, with a variety of shear mixing; structural information is obtained with mainly TEM/SEM imaging.

### HH3.25

**Homogeneous Dispersion of the Surface Modified MWNTs in the PU Matrix and Electrical Conductivity of the MWNTs/PU Composites.** Yoon Jin Kim, Yong Gyun Jang, June Whan Choi and Ho Gyu Yoon; Division of Materials Science and Engineering, Korea University, Seoul, South Korea.

In the recent years, the studies for the practical application of carbon nanotube (CNT) have been focusing on polymeric CNT composite because of the reduction of unit cost of production. However, CNT deposits are incompatible with most organic solvents and polymers, which results in poor dispersion in the polymer matrix. We report here that dispersion characteristics of the surface modified multiwalled nanotubes (MWNTs) in the polyurethane (PU) matrix and electrical conductivity of the MWNTs/PU composites are investigated using SEM and Dielectric analyzer with respect to the chemical treatment of MWNTs, the kind of surfactants, their content, and the tail length of hydrophobic group. Several chemical treatments of the MWNTs' surfaces were performed with the acids type, acidic concentration, treatment temperature, and oxidation time. All the surface of modified MWNTs are negatively charged and functionalized with carboxylic group; however, the external walls of some MWNTs were severely damaged so that they were frequently thinned and partially cracked. Compared to those of the composites without the addition of surfactant, the surfactant embedded into composites show much better dispersion of the MWNTs and higher electrical conductivity, these results are in good agreement with the two step adsorption model of cationic surfactants proposed by Y. Gao [1]. Both the optimized MWNTs and cationic surfactant filled PU composites show very low percolation threshold,  $\rho_c = 0.0089 \pm 0.007$  vol. %, and relatively higher conductivity after percolation than other carbon nanotubes composite systems reported elsewhere. [1] Y. Gao et al., *J. Chem.Soc.FaradayTrans.* **1**, 2671(1987).

### HH3.26

**Charge Transport and Metal-Insulator Transition in Multiwalled Carbon Nanotube-poly (methyl methacrylate) Composites.** Heon Mo Kim<sup>1</sup>, Min Ki Kim<sup>1</sup>, Jinsoo Joo<sup>2</sup>, Haeyong Kang<sup>2</sup>, Won Kang<sup>2</sup>, Sin Je Cho<sup>3</sup> and Ho Sang Yoon<sup>4</sup>; <sup>1</sup>Physics, Korea University, Seoul, South Korea; <sup>2</sup>Physics, Ewha Womans University, Seoul, South Korea; <sup>3</sup>Iljin Nanotech Co., Seoul, South Korea; <sup>4</sup>Novatems Inc., Anyang, Kyongki-Do, South Korea.

We report electrical properties and metal-insulator transition in thin

films of multiwalled carbon nanotube (MWCNT)-poly (methyl methacrylate) (PMMA) composites. MWCNTs were synthesized by chemical vapor deposition method. Free-standing thin films of various weight concentrations of MWCNTs were homogeneously dispersed in PMMA matrix using high power sonication. Scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy were used to study homogeneity and structure of composites. DC conductivity ( $\sigma_{DC}$ ) and its temperature dependence [ $\sigma_{DC}(T)$ ] were measured in the range of 0.3 K – 300 K to study charge transport mechanism in composites. The  $\sigma_{DC}$  of composites at room temperatures increased as MWCNT concentration increased, which shows typical percolation behavior with percolation threshold ( $p_c$ ) at 0.4 wt.% of MWCNTs. Above  $p_c$ ,  $\sigma_{DC}(T)$  of the composites showed the metallic behavior. We assigned low temperature metallic behavior in  $\sigma_{DC}(T)$  to the formation of one-dimensional conducting MWCNT networks in insulating PMMA matrix. The metal-insulator transition in the composites ( $p_c > 0.4$  wt.%) was observed between 1 K – 10 K based on the analysis of the reduced activation energy. The  $\sigma_{DC}(T)$  of the composites with MWCNT concentrations above  $p_c$  were compared with that of the composites below  $p_c$ . AC conductivity ( $\sigma_{AC}$ ) was also measured in the frequency range of 10 Hz – 2 MHz and in the temperature range of 77 K – 300 K, in which we observed the percolation behavior for the systems. We observed the different frequency dependence of  $\sigma_{AC}$  of the composites above and below  $p_c$ .

### HH3.27

**Assembly of Polystyrene Grafted Single-Walled Carbon Nanotube in Polystyrene-Polyisoprene-Polystyrene Tri-Block Copolymer Film.** Kai Tang, Craig A. Breen, Timothy M. Swager and Edwin L. Thomas; ISN, MIT, Cambridge, Massachusetts.

Atom transfer radical polymerization (ATRP) technique was used to graft Polystyrene (PS) on the surface of Single wall carbon nanotube (SWNT) by "Grafting from" method. The spatial and orientational ordering of single wall carbon nanotube was obtained by sequestering polystyrene grafted SWNT (Ps-g-SWNT) into a SIS triblock copolymer matrix that was globally oriented using a roll-cast technique. Due to the alignment of the guest SWNT by the block copolymer template, polarized absorbance is observed from the guest-host system. This approach can produce long range order of aligned PS-g-SWNT over the entire film area (over 100cm<sup>2</sup>).

### HH3.28

**Surface Characteristics and Wetting Behavior of Carbon Nanotubes.** Asa H. Barber<sup>1</sup>, Luqi Liu<sup>1</sup>, Sidney R. Cohen<sup>2</sup> and H. Daniel Wagner<sup>1</sup>; <sup>1</sup>Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; <sup>2</sup>Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel.

Carbon nanotubes show promise as a reinforcing phase for polymer composites due to the excellent mechanical properties of the nanotubes themselves. Previous work [1, 2, 3] has shown that the interface between carbon nanotubes and various polymers may be sufficiently strong to allow effective stress transfer from the polymer matrix to the nanotube reinforcement. Generally, it is accepted that a requirement for strong reinforcement-polymer adhesion is effective wetting of the solid reinforcement by the liquid polymer during composite processing. In this work we experimentally measure the wetting forces between various organic liquids and single multi-wall carbon nanotubes (MWCNTs) due to the liquid surface tension acting on the nanotube. This is achieved by attaching single MWCNTs to the end of an AFM tip and lowering the tip towards the liquid surface. Wetting forces (F) act on the nanotube upon contact with the liquid surface, which can be recorded from deflections in the AFM cantilever [4]. Contact angles can be derived from a simple force balance considerations to evaluate the wetting behavior of carbon nanotube surfaces using  $F = \gamma \pi d \cos \theta$  where  $\gamma$  is the liquid surface tension,  $d$  is the outer nanotube diameter and  $\theta$  is the liquid contact angle with the nanotube surface. We also extend this technique to evaluate the surface of chemically modified carbon nanotubes. As an example, the liquid-nanotube interaction force (Fr) can be increased by using modified carbon nanotubes that are more compatible with the wetting organic liquid. Furthermore, changes in carbon nanotube diameter and the type of carbon nanotubes used (either chemical vapor deposition or arc-discharge grown) also show an influence on the nanotube wetting behavior because of the presence of surface defects in the nanotube surface. References 1. O. Lourie, D. M. Cox & H. D. Wagner, Phys. Rev. Lett., **81** (1998) 1638 2. C. A. Cooper, S. R. Cohen, A. H. Barber and H. D. Wagner, Appl. Phys. Lett., **81** (2002), 3873 3. A. H. Barber, S. R. Cohen and H. D. Wagner, Appl. Phys. Lett., **82** (2003), 4140 4. A. H. Barber, S. R. Cohen and H. D. Wagner, Phys. Rev. Lett., **92** (2004), 186103

### HH3.29

**Dispersion Quality and Corresponding Electrical Conductivity of Functionalized Carbon Nanotubes in**

**Polymer Resins.** Heather J. Dowty and Max D. Alexander; Polymer Branch, Air Force Research Laboratory, Dayton, Ohio.

There has been great interest of recent, in creating high quality dispersions of nanotubes in polymer resin systems. These materials can be used to create highly conductive nanocomposites with can be molded in to useful forms, spray coated, or dip coated conformably onto highly complex surfaces. Here we report on series of techniques to disperse nanotubes with various surface functionalities and the corresponding effect on electrical conductivity and mechanical properties. The volume content of the functionalized nanotubes was varied from 0.1% to 20% to characterize the percolation behavior of the system. DC electrical characterization was performed at room and elevated temperatures as a function of polymer elongation.

**HH3.30**  
**Homogeneous Carbon Nanotube/polymer Composites for Electrical Applications.** Rajagopal Ramasubramaniam and Jian Chen; Zyvex Corporation, Richardson, Texas.

Carbon nanotubes, due to their high-aspect ratio, small diameter, lightweight, high-mechanical strength, high-electrical and thermal conductivity, high-thermal and air stability, are recognized as the ultimate carbon fibers for high performance, multifunctional composites. However, smooth carbon nanotube surfaces (i.e., sidewalls) are incompatible with most solvents and polymers, which result in poor dispersion of nanotubes in the polymer matrix. We report here that homogeneous nanotube polymer composites can be fabricated using noncovalently functionalized, soluble single-walled carbon nanotubes (SWNTs)<sup>1</sup> and these composites show dramatic improvements in electrical conductivity with very low percolation threshold (0.05-0.1 wt% of SWNT loading). In contrast to previous techniques, our method is applicable to various host polymers and does not require lengthy sonication. By significantly improving the dispersion of SWNTs in commercial polymers, we show that only a very small amount of SWNTs are needed to achieve conductivity levels required for different electrical applications without compromising the host polymer's other desired physical properties and processability. The electrically conductive carbon nanotube/polymer composites will find various applications such as electrostatic dissipation, electromagnetic interference (EMI) shielding, printable circuit wiring, and transparent conductive coatings. Reference: 1. Chen, J. et al. J. Am. Chem. Soc. 2002, 124, 9034-9035.

**HH3.31**  
**Thermal Conductivity of Single-Walled Carbon Nanotube/PMMA Nanocomposites.** Csaba Guthy<sup>1</sup>, Fangming Du<sup>2</sup>, John E. Fischer<sup>1</sup> and Karen I. Winey<sup>1,2</sup>; <sup>1</sup>Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Due to their exceptional thermal properties single-wall carbon nanotubes (SWNT) are considered as very promising filler materials for improving the thermal conductivity of conventional polymers. We carefully investigated the thermal conductivity of SWNT/PMMA nanocomposites with SWNT loading in the range up to 10 wt% using the comparative technique. The samples were prepared by coagulation method. We demonstrated moderate improvement in the composites' thermal conductivity of about 200% at 10wt%. The experimental results were analyzed using the versatile Nielsen model, which takes into account many important factors, like the fillers aspect ratio and maximum packing fraction. The aspect ratio of SWNT material used to prepare our composites was determined by AFM and careful image analysis in order to use it as an input parameter in the Nielsen model. We obtained good agreement between our experimental results and the predictions of the Nielsen model. Based on our analysis we concluded that higher aspect ratio of filler material was needed to achieve better improvement in the composites thermal conductivities. One should also take steps in order to improve the thermal contact between the SWNT network and the matrix material.

**HH3.32**  
**Carbon Nanotube and Organic Composite Thin Film Transistors.** Xiang-Zheng Bo<sup>1,2</sup>, Michael Strano<sup>3</sup>, Colin Nuckolls<sup>2</sup> and Graciela B. Blanchet<sup>1</sup>; <sup>1</sup>DuPont Central Research & Development, Wilmington, Delaware; <sup>2</sup>Chemistry, Columbia University, New York, New York; <sup>3</sup>Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Organic thin film transistors (TFTs) have been of great interest due to their low cost, mechanical flexibility, and large area coverage in applications of flat panel displays, radio frequency identification tags, and integration with organic optoelectronics [1-3]. Solution-processable polymers can be potentially used in a reel-to-reel

production process of TFTs, thus reducing manufacture cost further compared with vacuum deposited organic films [3]. However, solution-based organic materials have low field-effect mobilities ( $10^{-3}$  to  $10^{-6}$  cm<sup>2</sup>/Vs). In this work, we present paths towards increasing conductivity or mobility by designing single wall carbon nanotube (SWCNT) composite materials. TFTs using the composite as either source/drain or transport channel have been fabricated. Results show that the conductivity of the conducting composites can be enhanced by  $10^9$  and that the mobility of the semiconducting composites increases by 30 relative to the host matrices. [1]. H. Siringhaus, et al, Science, 280: 1741 (1998). [2]. P. F. Baude, et al, Appl. Phys. Lett., 82: 3964 (2003). [3]. G. B. Blanchet, et al, Appl. Phys. Lett., 20: 463 (2003).

**HH3.33**  
**Thermal Properties of vertically aligned arrays of SWNT and MWNT and their Polymer Composites.** Iliia N. Ivanov<sup>2</sup>, Alex A. Puzetky<sup>2</sup>, Gyula Eres<sup>1</sup>, Stephen Jesse<sup>2</sup> and David B. Geohegan<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Tennessee, Oak Ridge, Tennessee; <sup>2</sup>Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>3</sup>Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Thermal properties measurements were performed for long, vertically aligned multiwall and single wall carbon nanotubes (VA-SWNT and VA-MWNTs) and their polymer composites. Polymer composites were obtained by infiltrating VA-SWNT and MWNT arrays with aminoepoxy resin, preserving their alignment. The thermal properties of these systems were tested using an IR-camera in vacuum. The Aligned VA-MWNT in aminoepoxy at less than 2 wt. % loading were found to have higher thermal diffusivities than randomly-oriented CNT fibers at loadings of 40 wt.%, and thermal diffusivity improvements by a factor of 20 compared to the pure polymer. Similar measurements were done on composites with randomly distributed SWNT and MWNT. Advantage of the composites with continuous NT compared to randomly distributed NT for enhanced thermal properties of systems will be discussed. This research was sponsored by NASA-Langley Research Center, DARPA, the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and the Laboratory-Directed Research and Development Program at ORNL.

**HH3.34**  
**Finite-Temperature Effects in Carbon Nanotubes.** Nicolas Mounet<sup>1</sup>, Young-Su Lee<sup>2</sup> and Nicola Marzari<sup>2</sup>; <sup>1</sup>Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Materials Science & Engineering and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We study the finite-temperature properties of carbon nanostructures using a combination of density-functional perturbation theory and ab-initio molecular dynamics. The phonon dispersions of bulk diamond, graphene, graphite, and zigzag and armchair nanotubes are first obtained at the DFT-PBE level, showing on average an excellent agreement with experiments. Thermal expansion coefficients are determined by a minimization of the vibrational free energy in the quasi-harmonic approximation. Finally, the effects of thermal disorder on the ballistic transport of nanotubes are calculated from ensemble averages on microstates obtained from extensive ab-initio molecular dynamics simulations, highlighting the role of disorder in opening small gaps in the massless bands at the Fermi energy.

**HH3.35**  
**Significant Effects of Confinement and Catalysis in Formation of Tubular Structures from Peapod Structures.** Haibin Su, Adri van Duin and William A. Goddard; Caltech, Pasadena, California.

A large number of experimental and theoretical studies have been reported on buckyballs-containing nanotubes (a.k.a. peapod) structures since the discovery of these materials. It was observed that self-assembled buckyballs with nearly uniform centre-to-centre distances and resemble a nanoscopic peapod. The endofullerenes coalesce into longer capsules by either the electron irradiation or thermal annealing. We applied the recently developed Reactive Force Field (ReaxFF) to study the growth dynamic process starting from C60-buckyball/nanotube peapod structures. We found that the space confinement provided by the single wall nanotube encapsulating the buckyballs, is of critical importance on the coalescence reaction. Furthermore, we also simulated the effects of a Ni-particles on the coalescence process and found a significant reduction on the reaction initiation temperature in the presence of these catalysts. One related quantity is the energy barrier of forming a 4-member ring between adjacent buckyballs. We chose both corannulenes (C20H10) and C60 to compute this energy barrier from quantum mechanic and ReaxFF. The good agreement between these two methods encouraged us to investigate the effect of catalysis on this energy barrier. It turned out

that this barrier is lowered by 40% with the aid of catalysis. The piece of research work can help the community to gain better understanding of the complicated growth process in fullerene systems.

### **HH3.36**

**Irradiation of Carbon Nanotube and Polymer Carbon Nanotube Composites.** Sharon Kay Pregler and Susan B. Sinnott; Materials Engineering, University of Florida, Gainesville, Florida.

Polyatomic ion-beam deposition on polymer substrates to induce surface chemical modification is an important process used to achieve thin film growth, surface etching, and nano-texturing of the surface. Previous atomistic simulations have shown that particle beam deposition can induce crosslinking between unfunctionalized carbon nanotubes and polymer chains in situ resulting in increased composite strength and toughness. In this work, we investigate the effect of atomic and electronic irradiation of nanotube bundles and nanotube-polymer composites. In particular, the simulations consider the effect of incident angle in the polyatomic ion beam irradiation of nanotube-polymer composites, the electron irradiation of multi-walled carbon nanotubes, and the ion beam irradiation of multi-walled nanotubes. The approach is classical molecular dynamic simulations using reactive empirical bond-order potentials and the primary knock-out atom approach to model the effects of electron irradiation. The objectives of this study are to further predict the responses of carbon nanotube-based materials to electron and ion beam irradiation and analyze the resulting structural changes. The predicted outcomes are compared to new and published experimental studies. This work is supported by the National Science Foundation (CHE-0200838).

### **HH3.37**

**Transport through SWNT cross junctions.** Serhat Sahakalkan and Siegmund Roth; Max Planck Institute for Solid State Research, Stuttgart, Baden-Württemberg, Germany.

In two successive steps nanotubes are deposited onto a Si/SiO<sub>2</sub> substrate, where they lie on top of each other and form a crossbar. These structures are contacted at the ends of their legs with Pd leads using electron beam lithography. In a four point probe configuration the contact resistance at the cross junctions between the tubes and its temperature dependence is measured. The same measurements are also done on suspended tubes, which are fabricated by etching some nanometers of the oxide layer. The results are discussed in terms of electromechanical switching at the cross junction.

### **HH3.38**

**Coupling of Surface Acoustic Waves to Single-Walled Carbon Nanotubes.** Viktor Siegle<sup>1</sup>, Franz-Joseph Ahlers<sup>2</sup> and Siegmund Roth<sup>1</sup>;

<sup>1</sup>MPI for Solid state research, Stuttgart, Germany; <sup>2</sup>Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

There have been increasing efforts to study quantized charge transport in low-dimensional systems. These systems are static quantum dots based on GaAs in the majority of cases. In recent publications a coupling between surface acoustic waves (SAW) and electrons in a metallic single-walled carbon nanotube (SWCNT) has been predicted[1]. The SAW is induced through the piezoelectric effect. Its coupling to the electrons is given by the electronic structure in the nanotubes. The aim of the present work is to give an overview of recent publications and theoretical predictions. Also an outline of existing experiments will be given together with reasons for SWCNTs as the preferable system. The progress in building the devices suitable for detecting the predicted effect will be reported. [1] V.I. Talyanski, D.S. Novikov, B.D. Simons, and L.S. Levitov, Phys Rev Lett 87, 27, 2001

### **HH3.39**

**Electronic Transport in Bucky-Paper, Thin Networks and Individual Single Wall Nanotubes.** Viera Skakalova, Martti Kaemppgen, Yun Sung Woo, Serhat Sahakalkan and Siegmund Roth; Solid State Research, Max Planck Institute, Stuttgart, Germany.

The exciting electronic properties observed for an individual single wall carbon nanotube (SWNT) molecule like a ballistic electron transport and Coulomb blockade effects, are not observed when the subject of the study is a dense network of nanotubes, a bucky-paper. For bucky-paper, the electrical transport is dominated by weak Van der Waals intermolecular interactions. To study the mechanism of electron transport in SWNT-system, thin networks of a various number of SWNT-layers were prepared. Temperature dependences of normalized electrical conductivity of the thin networks were compared to those of individual SWNT on one hand, and of a bucky-paper on the other hand. A systematic change of the shape of the curves due to the size of the SWNT-system was found. The results obtained were interpreted in the frame of a model combining metallic conduction of highly conductive regions (intra-tube conduction) with inter-tube tunneling or hopping. In a very thin network similar to an individual

SWNT, non-linearity in I-V characteristics at low temperatures was observed. Keywords: nanotube, transport, networks

SESSION HH4: Characterization, Processing,  
Separation  
Tuesday Morning, November 30, 2004  
Room 312 (Hynes)

### **8:30 AM \*HH4.1**

**Field Emission from Semiconducting Quasi-One Dimensional Materials.** Jun Chen<sup>1,2</sup>, S. Z. Deng<sup>1,2</sup>, N. S. Xu<sup>1,2</sup>, Weixin Zhang<sup>4</sup>, Xiaogang Wen<sup>4</sup> and Shihe Yang<sup>4</sup>; <sup>1</sup>State Key Laboratory of Optoelectronic Materials and Technologies, Guangzhou, China; <sup>2</sup>Guangdong Province Key Laboratory of Display Materials, Guangzhou, China; <sup>3</sup>Technology School of Physics and Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou, China; <sup>4</sup>Department of Chemistry, Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Kowloon, Hong Kong.

Recently, there is a growing interest in studying field emission from semiconducting quasi one-dimensional materials. The field emission from both wide band-gap and narrow band-gap materials has been reported. In this paper we will present our recent results about the synthesis of various semiconducting nanomaterials and their field emission properties. Quasi-one dimensional silicon carbide, cupric oxide, copper sulphide nanomaterials with different morphologies have been synthesized by thermal evaporation, gas-solid reaction and liquid-solid reaction methods, respectively. Their structure and field emission characteristics, including emission current-applied field characteristic, emission site distribution and emission current stability, have been studied. Stable field emission from these materials at low field has been obtained. The effects of temperature and illumination on field emission have also been explored. The potential application of this novel type of field emitter will also be discussed.

### **9:00 AM HH4.2**

**NEXAFS Investigations of Nanotube-Based Systems.**

Tirandaj Hemraj-Benny<sup>1</sup>, Sarbajit Banerjee<sup>1</sup>, Mahalingam Balasubramanian<sup>2</sup>, Sharadha Sambasivan<sup>3</sup>, Daniel A. Fischer<sup>3</sup>, James A. Misewich<sup>2</sup> and Stanislaus S. Wong<sup>1,2</sup>; <sup>1</sup>Chemistry Department, Stony Brook University, Stony Brook, New York; <sup>2</sup>Materials and Chemical Sciences, Brookhaven National Laboratory, Upton, New York; <sup>3</sup>Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

Gaining insight into chemical issues, such as oxidative processes including the solution-phase ozonolysis in carbon nanotubes (CNTs); and structural issues, such as order in nanotube systems, is of fundamental importance in devising applications of these tubes in field emission applications as well as for components of composite materials. It has been shown that near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is a particular useful and effective technique for studying the electronic structure and chemical composition of pristine, wet-air oxidized and side-walled-ozonized nanotubes. In addition, we have been able to obtain qualitative and quantitative analysis of the order in a wide range of carbon based systems, including graphite, single-walled carbon nanotubes (SWNT) powder, SWNT films, and multi-walled carbon nanotubes.

### **9:15 AM HH4.3**

**TEM combined with Transport, Raman and AFM on the same individual Carbon Nanotubes and New Ways to Free-standing Nanostructures.** Jannik Christian Meyer<sup>1</sup>, Dirk

Obergfell<sup>1</sup>, Matthieu Paillet<sup>2</sup>, Jean-Louis Sauvajol<sup>2</sup>, Georg S. Duesberg<sup>3</sup>, Po-Wen Chiu<sup>1</sup> and Siegmund Roth<sup>1</sup>; <sup>1</sup>Max-Planck Institute for solid state research, Stuttgart, Germany; <sup>2</sup>Groupe de Dynamique des Phases Condensées, Université de Montpellier II, Montpellier, France; <sup>3</sup>Infineon Technologies CPR NP, Munich, Germany.

A new method has been developed which makes it possible to create arbitrary free-standing nanostructures by lithography in such a way that they can be investigated by transmission electron microscopy (TEM). By incorporating carbon nanotubes into these structures, we are able to combine TEM investigations with various other experimental techniques on the very same carbon nanotube. We have carried out transport measurements with gate characteristics at liquid helium temperatures, AFM studies on free-standing tubes, or Raman spectroscopy, and afterwards TEM imaging of the same nanotube. Furthermore, these well-defined structures permit novel types of in-situ investigations in the TEM.

### **9:30 AM HH4.4**

**Comparison of the Nanotube Properties, Purification and Separation Method.** Jiri Cech and Siegmund Roth; MPI-FKF, Stuttgart, Germany.

Single wall carbon nanotubes produced by laser ablation, arc-discharge, and CVD (HiPCO), respectively have been characterized and purified by various methods. In particular, heating in oxidative atmosphere (air and oxygen flow), refluxing in HNO<sub>3</sub>, boiling in HCl, centrifugation and several combinations thereof have been employed. The efficiency of purification is monitored by weight loss data, X-ray diffraction and Raman and optical spectroscopy as well as by measuring the electrical conductivity of buckypaper prepared from the purified material. In addition we present preliminary results of tests to separate metallic and semiconducting SWCNT. The possibility of reliable and efficient separation opens new windows of applications.

#### 9:45 AM HH4.5

##### **Diameter Dependent Enrichment along with the Bulk Separation of Metallic from Semiconducting Single Walled Carbon Nanotubes.** Fotios Papadimitrakopoulos<sup>1,2</sup>, Zhengtang

Luo<sup>1</sup>, Sang Nyon Kim<sup>1</sup>, Sang-Yong Ju<sup>1</sup>, Rongfu Li<sup>1</sup>, Mathew Mathai<sup>1</sup>, SanthiSagar Vaddiraju<sup>1</sup>, Kushan Biswas<sup>2</sup>, G.G. Samsonidze<sup>3</sup>, Shin Grace Chou<sup>4</sup>, V. W. Brar<sup>5</sup>, G. Dresselhaus<sup>6</sup> and M. S. Dresselhaus<sup>3,5</sup>; <sup>1</sup>Nanomaterials Optoelectronics Laboratory, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Boston, Massachusetts; <sup>4</sup>Department of Chemistry, Massachusetts Institute of Technology, Boston, Massachusetts; <sup>5</sup>Department of Physics, Massachusetts Institute of Technology, Boston, Massachusetts; <sup>6</sup>Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Boston, Massachusetts.

The diversity of diameters in single walled carbon nanotubes (SWNTs) and corresponding chirality and type (i.e. semiconducting (sem-) vs. metallic (met-)), obtained from various synthetic methods, contribute to the limited understanding of these nanostructures. Utilizing the preferential affinities of amines towards sem-SWNTs, substantial separation according to type has been achieved based on a differential solubilization technique. A resonance Raman radial breathing mode (RBM) lineshape analysis has been developed to evaluate such a degree of separation. Such analysis indicated the preferential enrichment of larger diameters in the supernatant of HiPCo-based samples. In order to understand the above, a combination of <sup>1</sup>H and <sup>13</sup>C NMR along with optical, calorimetric, X-Ray and thermal desorption characterization measurements were conducted in order to quantify the localized environment along the SWNT-physisorbed surfactants. These were furthermore correlated with RBM band construction in order to elucidate the effects of aggregation and environmental contaminants.

#### 10:00 AM HH4.6

##### **Single-Walled Carbon Nanotubes in Sulfuric Acid: Intercalation and Partly Ordered H<sub>2</sub>SO<sub>4</sub>\*.** W. Zhou<sup>1</sup>, Hua Fan<sup>2</sup>, P. A. Heiney<sup>3</sup> and J. E. Fischer<sup>1</sup>; <sup>1</sup>MSE Dept., U. Penn., Philadelphia, Pennsylvania; <sup>2</sup>CNST, Rice U., Houston, Texas; <sup>3</sup>Dept. of Physics and Astronomy, U. Penn., Philadelphia, Pennsylvania.

The ideal nanotube suspension would yield isolated tubes in any desired concentration. In contrast to common surfactants, stable superacid suspensions as high as 10 wt% are by now routine. Here we use x-ray scattering from well-aligned, swollen nanotube fibers to investigate the unique interaction between nanotubes and sulfuric acid. The 2-D scattering pattern from dry nanotube fibers has two components: intense Bragg reflections with azimuthal preferred orientation from aligned nanotubes in crystalline ropes; and strong small-angle diffuse intensity from nanopores. After swelling by immersion in 102% sulfuric acid (2% excess SO<sub>3</sub>) in a dry box, the intensities of both components essentially disappear. This indicates that H<sub>2</sub>SO<sub>4</sub> molecules readily intercalate into nanotube ropes in a disordered manner, smearing out the triangular lattice; individual tubes in a rope are not completely separated but no coherent inter-tube structure remains. Consequently, acid intercalation increases the electron density of the ropes to a value similar to that of the acid. More interestingly, the scattering from sulfuric acid becomes greatly enhanced and highly anisotropic in the presence of nanotubes. The degree of anisotropy is about the same as the dry fiber (FWHM = 31°). These striking results suggest that H<sub>2</sub>SO<sub>4</sub> molecules align along the nanotube axis and form cylindrical "shells" wrapped around nanotubes and ropes. The charge transfer between nanotube  $\pi$  electrons and H<sub>2</sub>SO<sub>4</sub> molecules is responsible for the intercalation, and for the unique partly ordered H<sub>2</sub>SO<sub>4</sub> structure around nanotubes. Similar behavior is not found in other solvents (H<sub>2</sub>O, benzene etc.) in which strong nanotube-solvent interactions do not exist. \*in collaboration with Smalley group at Rice Univ.

#### 10:30 AM HH4.7

##### **Progress on Tailoring SWNT / Superacid Phase Behavior for**

##### **Improved Fiber Properties.** Virginia Angelica Davis<sup>2,1,3</sup>, A.

Nicholas Gerrado Parra-Vasquez<sup>2,1,3</sup>, Valentin Prieto<sup>2,1</sup>, Pradeep Rai<sup>2,1</sup>, Robert H. Hauge<sup>3,1,4</sup>, Richard E. Smalley<sup>1,3</sup> and Matteo Pasquali<sup>2,1</sup>; <sup>1</sup>Center for Nanoscale Science & Technology, Rice University, Houston, Texas; <sup>2</sup>Chemical Engineering, Rice University, Houston, TX, Texas; <sup>3</sup>Carbon Nanotechnology Laboratory, Rice University, Houston, TX, Texas; <sup>4</sup>Department of Chemistry, Rice University, Houston, Texas.

We have demonstrated that the phase behavior of SWNT / superacid dispersions is similar to that of lyotropic nematogenic solutions of rod-like polymers used for the production of high performance fibers such as Kevlar (Davis et al. 2004, Ramesh et al. 2004). This phase behavior has enabled us to produce highly aligned macroscopic neat SWNT fibers with promising properties (Zhou et al. 2004, Ericson et al., submitted). This work represents a critical step in the development of SWNT fiber applications such as quantum wires of all metallic nanotubes and light-weight high-modulus fibers. Continued improvements in understanding SWNT morphology, phase behavior, and processing are expected to result in further improvements in fiber properties. We are using principles of colloid chemistry to understand and control the phase behavior of SWNTs in superacids, in order to develop more easily processable dispersions. For example, the addition of potassium persulfate has been demonstrated to improve dramatically SWNT dispersion in methanesulfonic acid (Ramesh et al., 2004). Factors currently being explored for their impact on SWNT phase behavior include SWNT length, polydispersity of length, degree of surface oxidation, and presence of additives (e.g. salts, other acids) which increase electrostatic and/or steric stabilization.

#### 10:45 AM HH4.8

##### **Biomolecules as Selective Dispersants for Carbon Nanotubes.**

Simon Moulton<sup>1</sup>, Andrew Minett<sup>2</sup>, Rob Murphy<sup>2</sup>, Kevin Ryan<sup>2</sup>, Denis McCarthy<sup>2</sup>, Jonathan Coleman<sup>2</sup>, Werner Blau<sup>2</sup> and Gordon Wallace<sup>1</sup>; <sup>1</sup>Intelligent Polymer Research Institute, ARC Centre for Nanostructured Electromaterials, Wollongong, New South Wales, Australia; <sup>2</sup>Materials Ireland Polymer Research Centre, Department of Physics, Trinity College Dublin, Dublin 2, Ireland.

The arc discharge technique remains the most popular route in fabricating high quality nanotube material. Unfortunately the product (soot) from the arc discharge process, like most other techniques, includes other non-nanotube material in the form of graphitic particles (GPs). Using a variety of water soluble biomolecules we have been able to selectively suspend multiwalled carbon nanotubes (MWNTs) in solution while leaving the GPs behind in the precipitate. The biomolecules used in this work were Salmon Sperm DNA (MWt 3.0x10<sup>6</sup>) Chondroitin Sulfate Sodium Salt (MWt 7.5x10<sup>4</sup>) and Chitosan Hydrolysate Oligomer (MWt 1.5-3.0x10<sup>5</sup>). The amount of suspended MWNTs was determined using electron paramagnetic resonance (EPR). All of these biomolecules exhibited better selectivity of MWNT over GPs than that previously reported for the organic soluble synthetic polymer poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV). Of the three biomolecules investigated the best results were obtained with the Chitosan Hydrolysate oligomer, where at a 1:1 biomolecule to soot ratio, 60% of the available MWNTs in the soot were selectively suspended. The previous result for PmPV at 1:1 polymer to soot ratio was only 19% of the available MWNTs in the sample were selectively suspended. Our method provides an aqueous based one-step, nondestructive purification process that facilitates the formation MWNT dispersions of high purity. The ability to produce such dispersions is of interest since products obtained from them such as carbon nanotube fibres could find application in a range of bio-area

#### 11:00 AM HH4.9

##### **Carbon Nanotubes with Prescribed Lengths and Unaltered Properties.** Bibiana Onoa<sup>1</sup>, Michael Walsh<sup>2</sup>, Thomas B. O'Reilly<sup>2</sup> and Henry I. Smith<sup>2</sup>; <sup>1</sup>CR&D, DuPont, Wilmington, Delaware; <sup>2</sup>NanoStructures Laboratory, MIT, Cambridge, Massachusetts.

The potential application of carbon nanotubes in the fabrication of Field effect transistors, field emitter displays, sensors, and other devices is currently limited by the variability in both chirality and length of the nanotubes. Although significant progress has been made to control these two important variables either during or after the manufacturing process, the field still lacks a robust technology that allows the production of single chirality or uniform length distributions of nanotubes, without introducing undesired functionalization and/or damage to the Nanostructures. We present a simple and scalable lithography technology that permits one to produce single-walled nanotubes with prescribed lengths, while preserving to high degree the pristine properties of the starting material. Interference lithography allows us to expose in photoresist grating patterns having linewidths that range from 30 nm to microns, on surfaces previously coated with dispersed nanotubes. Reactive ion-etching techniques then allow the cutting of the nanotubes. The

resulting product consists of solutions of carbon nanotubes with prescribed length and unaltered chemical or physical properties as demonstrated by microscopic and spectroscopic characterization.

#### 11:15 AM HH4.10

**A Simple Chemical Route to Selectively Eliminate Metallic Carbon Nanotubes in Nanotube Network Devices.** Lei An, Qiang Fu, Chenguang Lu and Jie Liu; Chemistry, Duke University, Durham, North Carolina.

Semiconducting-only single-walled carbon nanotube (SWNT) network field effect transistors (FETs) have been fabricated by selectively reacting all the metallic SWNTs in the devices with diazonium reagents in a controlled manner. The concentration of diazonium reagents being used turns out to be crucial for selectively eliminating metallic SWNTs and keeping semiconducting ones intact. An excessive amount of diazonium reagents can indiscriminately react with both metallic and semiconducting SWNTs and thus degrade the performance of the devices. This new technique will undoubtedly facilitate the process of fabrication of high performance SWNT-based electronic devices.

#### 11:30 AM HH4.11

**Characterization of Single-Walled Carbon Nanotube Fibers and Correlation with Stretch Alignment.** Michelle Chen<sup>1</sup>, Csaba Guthy<sup>1</sup>, John E. Fischer<sup>1</sup>, Stephane Badaire<sup>2</sup>, Cecile Zakri<sup>2</sup>, Philippe Poulin<sup>2</sup>, Vincent Pichot<sup>3</sup> and Pascale Launois<sup>3</sup>; <sup>1</sup>Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>CRPP-CNRS, Av. Schweitzer, Pessac, France; <sup>3</sup>GPS, University de Paris Sud, Orsay, France.

Single-walled carbon nanotube (SWNT) fibers are a macroscopic realization of the unique 1-D nano-scale SWNT characteristics. We applied structural, electrical and thermal methods to characterize these materials, with post-extrusion stretching as the independent variable. Hipco SWNTs are dispersed in water using sodium dodecyl sulfate (SDS), and then co-extruded with polyvinyl alcohol (PVA)/water through a long syringe into a rotating water/PVA coagulation bath. Partial axial alignment is thereby achieved, and further enhanced by applying tension to the flexible green fibers in the coagulation bath. X-ray diffraction shows that the full width at half maximum (FWHM) of the Bragg peaks decreases from 55 (as-extruded) to less than 30 degrees by 80% elongation. Resistivity vs. stretch ratio shows a rapid initial decrease followed by saturation; essentially all the improvement in electronic transport is obtained once alignment of 40 degrees FWHM is achieved. Annealing in vacuum at 1000°C is performed to drive out PVA, improve inter-tube and inter-bundle contacts, and to heal damages on the tube walls. Such annealing is found to increase 300 K conductivity by 20,000 fold. Below 25 K, resistivity vs. temperature is well-represented by Coulomb gap variable range hopping (CG-VRH). It is rationalized that the Coulomb interactions in disordered systems open a gap at the Fermi energy. Above 25 K, thermal activation is more likely than correlated electron hops since the thermal energy is greater than the Coulomb gap. We also measure the thermal conductivity of the fibers and find that stretching measurably increases the thermal conductivity. Moreover, stretching is found to increase the Young's Modulus. Finally, the above characterization is compared with the known results of other SWNT fibers.

#### 11:45 AM HH4.12

**Reference standard for carbonaceous impurity measurements in carbon nanotubes.** Pavel Nikolaev<sup>1</sup> and Sivaram Arepalli<sup>2</sup>; <sup>1</sup>G.B.Tech Inc./NASA-JSC, Houston, Texas; <sup>2</sup>G.B.Tech Inc. / NASA-JSC, Houston, Texas.

Near-infrared spectroscopy is a convenient tool for measuring nanotube / carbonaceous impurities ratios in carbon nanotube samples [1]. These measurements are based on separation of contributions from nanotubes and impurities to the near-infrared absorption of samples dispersed in DMF, and sample purity is expressed relative to some reference sample. In the current work we produced a reference standard for NIR measurements using purified laser nanotubes. The sample was oxidized slowly using a Temperature Programmed Oxidation (TPO) setup in 2% oxygen / 98 % helium atmosphere. In these conditions, the sample oxidized in several steps, which were attributed to carbonaceous impurities, nanotubes and graphitic shells based on TEM and Raman observations. Stopping oxidation at 625 C (this temperature is sample-specific) allowed us to produce a sample with no carbonaceous impurities and well-defined ratio of nanotubes, graphite and metal catalyst. Since carbonaceous impurities no longer hold nanotubes and particles together, further centrifuging allowed us to remove particles and use this sample as a reference standard in NIR measurements. 1. M. E. Itkis, et al. Nano Lett, 3, 309 (2003)

#### 1:30 PM \*HH5.1

**Strange, Useful, and Problematic Mechanical Properties of Carbon Nanotube Sheets and Fibers.** M. Zhang<sup>1</sup>, K.R. Atkinson<sup>2</sup>, L. Hall<sup>1</sup>, J.A. Levinson<sup>1</sup>, S.R. Shah<sup>3</sup>, R. Raj<sup>3</sup>, S. Collins<sup>1</sup>, A.B. Dalton<sup>1</sup>, J.P. Ferraris<sup>1</sup>, E. Munoz<sup>1</sup>, J. Razal<sup>1</sup>, V. Ebron<sup>1</sup>, A.A. Zakhidov<sup>1</sup>, R. Hou<sup>1</sup>, M. Kozlov<sup>1</sup>, R. Capps<sup>1</sup>, G.M. Spinks<sup>4</sup>, G.G. Wallace<sup>4</sup>, J.N. Barisci<sup>4</sup>, J.N. Coleman<sup>5</sup> and Ray H. Baughman<sup>1</sup>;

<sup>1</sup>Department of Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson, Texas; <sup>2</sup>CSIRO Textile & Fibre Technology, Belmont, Queensland, Australia; <sup>3</sup>University of Colorado at Boulder, Boulder, Colorado; <sup>4</sup>University of Wollongong, Wollongong, New South Wales, Australia; <sup>5</sup>Trinity College Dublin, Dublin, Ireland.

This talk describes various unusual properties that we have observed for carbon nanotube fibers and sheets, and their structural origin. These properties include nanotube assemblies that have (1) negative Poisson's ratios, meaning the ability to laterally expand when uniaxially stretched; (2) over ten times higher ability to absorb mechanical energy (toughness) than any previously known organic fiber; and (3) the ability to deform elastically over ten percent, combined with high mechanical strength. We also find that nanotube sheets and fibers creep, and that the rate of this creep in nanotube artificial muscles depends on the applied potential. In some cases these properties arose from the use of special spinning methods that we have developed, which will be described, and in other cases they have resulted from the discovery of new properties for previously made materials. Progress in engineering other novel mechanical properties into carbon nanotube fibers will also be described, such as negative linear compressibilities - the ability to expand when hydrostatically compressed with a non-penetrating fluid.

#### 2:00 PM HH5.2

**Plasma Coating and Magnetic Alignment of Carbon Nanotubes in Polymer Composites.** Donglu Shi<sup>1</sup>, Peng He<sup>1</sup>, Jie Lian<sup>2</sup>, Rodney Ewing<sup>2</sup>, Xavier Chaud<sup>3</sup>, Robert Tournier<sup>3</sup>, Eric Beaunon<sup>3</sup> and Lumin Wang<sup>2</sup>; <sup>1</sup>Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; <sup>2</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>3</sup>CRETA, CNRS, Grenoble, France.

In order to well disperse carbon nanotubes in polymer composites, they have been coated by a unique plasma polymerization method. In this presentation, we will present our recent experimental results on the plasma coating of carbon nanotubes. An extremely thin layer of polymer film has been coated onto both outer and inner surfaces of the nanotubes. Due to surface modification, the dispersion of nanotubes in the polymer matrix is significantly enhanced. HRTEM images, SIMS results of coated surface films on nanotubes, and mechanical properties of the composites will be presented. For fundamental study and novel engineering applications, carbon nanotubes also need to be aligned along certain specified directions. Single wall carbon nanotubes, due to small amount of catalyst elements such as Ni and Co, can be well aligned in a magnetic field. However, the extremely small magnetic susceptibility of multi wall carbon nanotubes is not sufficient to induce a magnetic alignment. In this study, we present a novel method by which these nanotubes can be well aligned in a polymer matrix at moderate magnetic field. Both TEM and SEM results show clear evidence of well aligned nanotubes in the polymer composite. Mechanical testing results have also shown pronounced anisotropy in tensile strength in directions normal and parallel to the applied field, confirming an alignment of the nanotubes in the sample matrix. The magnetic alignment mechanism is discussed.

#### 2:15 PM HH5.3

**Carbon Nanotube-Polystyrene Nanocomposites for Electromagnetic Interference Shielding.** Yonglai Yang<sup>1</sup>, Mool C. Gupta<sup>1</sup>, Kenneth L. Dudley<sup>2</sup> and Roland W. Lawrence<sup>2</sup>; <sup>1</sup>Applied Research Center, Old Dominion University, Newport News, Virginia; <sup>2</sup>Electromagnetics Research Branch, NASA Langley Research Center, Hampton, Virginia.

This study reports a nanocomposite consists of conductive carbon nanotubes dispersed within an insulating polymer matrix [polystyrene (PS)], and its electrical conductivity and electromagnetic interference (EMI) shielding properties. The homogeneous polymer nanocomposites were fabricated by ultrasonic dispersion of carbon nanotubes in a polystyrene solution followed by spraying to cast films. These films were then hot-pressed to form thick structures of 25.4 mm in diameter and 1.0 mm in thickness. SEM images of the fractured surface of the nanocomposite reveal that nanotubes are well dispersed and embedded uniformly throughout the PS matrix. The uniform

microstructure of the nanocomposite is attributed to the solution spraying technique in the formation of composite films, which allows the solvent to evaporate quickly and reduces the possibility of sedimentation and aggregation of the carbon nanotubes. DC volume electrical conductivity versus carbon nanotube mass fraction of the nanocomposite was measured at room temperature. The conductivity increases with increasing carbon nanotube loading in the nanocomposite. A sharp increase in the conductivity is observed between 0.2 and 1.0 wt. % nanotube loading. When the loading of the carbon nanotubes reaches 1.0 wt. %, the conductivity of the nanocomposite is 11 orders of magnitude larger than that of the pure PS matrix, indicating that the nanocomposite is electrically conductive. It is evident that carbon nanotubes form a homogeneous network structure within the PS matrix, thereby establishing electrical conduction pathways throughout the nanocomposite, leading to good electrical conductivity. Also, the very low percolation threshold is the signature of the excellent dispersion of nanotubes within the PS matrix. EMI shielding properties of carbon nanotube-PS nanocomposites were investigated by using a HP 8510 vector network analyzer within X-band (frequency range: 8.2 GHz - 12.4 GHz). The experimental data show that the addition of carbon nanotubes to the polystyrene has a dramatic effect on the measured EMI shielding properties of nanocomposites. The EMI shielding properties of the nanocomposites enhanced with increasing the carbon nanotube content in the nanocomposite. Comparing the pure PS matrix, the shielding effectiveness of the nanocomposite with 5.0 wt. % carbon nanotube loading is found to increase by a factor of 160. The primary EMI shielding mechanism of this nanocomposite is by reflection of electromagnetic radiation. For example, the nanocomposite containing 5.0 wt. % nanotubes provides transmitted radiation level of 0.45 % and absorbed level of less than about 10.0 %. The principal amount of the EM radiation is reflected by the nanocomposite. In summary, an effective method of fabricating carbon nanotube-PS nanocomposite was achieved. This nanocomposite exhibited good electrical conductivity and excellent EMI shielding properties at a very low loading of carbon nanotubes.

#### 2:30 PM HH5.4

**Morphology and Mechanical Properties of High-Performance Nylon-6 Composites Reinforced by Multiwalled Carbon Nanotubes.** Tianxi Liu<sup>1</sup>, Wei-De Zhang<sup>2</sup>, In Yee Phang<sup>2</sup>, Lu Shen<sup>2</sup> and Shue Yin Chow<sup>2</sup>; <sup>1</sup>Institute of Advanced Materials, Fudan University, Shanghai, China; <sup>2</sup>Institute of Materials Research & Engineering, Singapore, Singapore.

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, increasing attention has been attracted to this newly emerging material due to its remarkable mechanical and electrical properties. Based on their unique and excellent physical properties, many structural and smart applications of CNTs have been proposed including transistors, sensors, and field emission devices, as well as lighter, smaller and higher performance structures for aerospace and many other industrial fields. Among them, one of the most intriguing applications of CNTs is the polymer/CNTs nanocomposites. However, the challenges for developing high performance CNTs/polymer nanocomposites are: (i) homogeneous dispersion of CNTs in the polymeric matrix, and (ii) strong interfacial interactions so as to effect efficient load transfer from the polymeric matrix to the CNTs. In this study, multiwalled carbon nanotubes (MWNTs)/nylon-6 (PA6) nanocomposites with different MWNTs loadings have been successfully prepared by simple melt-compounding approach. A fine and homogeneous dispersion of MWNTs throughout PA6 matrix is observed by transmission electron microscopy. Scanning electron microscopy observation on the fracture surfaces of the composites shows not only a uniform dispersion of MWNTs but also strong interfacial adhesion with the matrix, as evidenced by the presence of many broken but strongly embedded CNTs in the matrix and by the absence of debonding of CNTs from the matrix. A number of bead-like morphology is also observed along the stretched CNTs and their bundles, probably indicating the anchoring locations of the CNTs defects (within the beads) along the tubes where PA6 matrix has strong interfacial interactions with the CNTs, thus being favorable to stress transfer from polymer to CNTs. Mechanical testing (by tensile and nanoindentation tests as well as dynamic thermal analysis) shows that, compared with neat PA6, the elastic modulus and the yield strength of the composites are greatly improved by about 214% and 162%, respectively, with incorporating only 2 wt % MWNTs. Therefore, the mechanical properties of MWNTs/PA6 composite are substantially superior to those of neat PA6 due to (i) the reinforcement of evenly dispersed high-performance MWNTs nanofillers throughout the matrix, and (ii) strong interfacial interaction between MWNTs and PA6 matrix. In addition, a unique crystallization and melting behavior of MWNTs/PA6 composites is observed and discussed by combining differential scanning calorimetry and X-ray diffraction, that is, only the a-form crystals are observed in MWNTs/PA6 composites, which is totally different from the case observed in PA6/clay nanocomposites, probably due to the difference

in geometry or morphology of nanofillers used. A tentative model is proposed to interpret this "abnormal" crystallization phenomenon.

#### 2:45 PM HH5.5

**Property Studies of Plasma Pressure Compacted B4C-CNTs Nanocomposites.** Shuo Chen<sup>1</sup>, B. Klotz<sup>2</sup>, M. Koslowski<sup>3</sup>, Dezhi Wang<sup>1</sup>, Jianyu Huang<sup>1</sup>, R. Dowding<sup>2</sup> and Z. F. Ren<sup>1</sup>; <sup>1</sup>Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Army Research Laboratory, Aberdeen Proving Ground, Maryland; <sup>3</sup>NanoLab, Inc., Newton, Massachusetts.

Nanocomposites were prepared by plasma pressure compaction of mixtures of boron carbide (B4C) and carbon nanotubes (CNTs). The mixtures were formed through a reaction between magnesium diboride (MgB2) and carbon nanotubes with bamboo-like structure. Different ratios of B4C nanoparticles (<100 nm) and CNTs were obtained using different ratios of starting components of MgB2 and CNTs, which solved the problem of both making nano size B4C particles and mixing them uniformly with CNTs, two major challenges facing the nanocomposites field. Archimedes density measurement technique, x ray diffraction, scanning electron microscope, and transmission electron microscope studies have also been applied to characterize the samples. It was found that there was no significant grain growth. Samples with high density showed good mechanical properties including hardness and toughness due to the high hardness of nano B4C and high Young's modulus of the high quality CNTs left after the reaction.

#### 3:30 PM HH5.6

**Morphological and Mechanical Properties of Carbon Nanotube/Polymer Composites via Melt Compounding.** William Edward Dondero and Russell E. Gorga; College of Textiles (TECS Dept.), NC State University, Raleigh, North Carolina.

The mechanical properties and morphology of multi-wall carbon nanotube/polypropylene nanocomposites were studied as a function of nanotube orientation and concentration. Through melt mixing followed by melt drawing, using a twin screw mini-extruder with a specially designed winding apparatus, the dispersion and orientation of multi-wall carbon nanotubes was optimized in polypropylene. Tensile tests showed an increase of about 70% for the average tensile toughness from 64 MJ/m<sup>3</sup> to 109 MJ/m<sup>3</sup>. The modulus remained consistent with the virgin material processed under the same conditions. X-ray diffraction and transmission electron microscopy were used to quantify nanotube orientation and dispersion. In addition, unique morphologies as a function of nanotube concentration and orientation were revealed, indicating potential use as barrier materials. These nanocomposite materials have a unique combination of properties (strength and barrier properties) suitable for advanced fiber applications.

#### 3:45 PM HH5.7

**Modification of Single-Walled Carbon Nanotubes through controlled/"living" radical polymerization.** Hyun-jong Paik<sup>1</sup>, Jin Hwan Choi<sup>1</sup>, Saet Byeol Oh<sup>1</sup>, Jun Ho Chang<sup>1</sup>, Chang-Sik Ha<sup>1</sup>, Il Kim<sup>1</sup> and Bog G. Kim<sup>2</sup>; <sup>1</sup>Department of Polymer Science and Engineering, Pusan National University, Busan, South Korea; <sup>2</sup>Department of Physics, Pusan National University, Busan, South Korea.

Single-walled carbon nanotubes (SWNTs) have been attracting considerable interest due to their unique shape and outstanding mechanical and electrical properties. In efforts to utilize these properties, we focus on developing new chemical modification methods to introduce covalently attached well-defined polymer on the surface of SWNTs. For example, polystyrene was grafted from the sidewall of SWNTs via surface-initiated Nitroxide-Mediated Polymerization or Atom Transfer Radical Polymerization (ATRP). Furthermore, formation of block copolymers on SWNTs was studied by chain-extending grafted-polystyrene with second monomers including t-butyl acrylate. Functionalized SWNTs were characterized by Thermal Gravimetric Analysis, Transmission Electron Microscopy, FT-IR, 1H NMR, and Raman spectroscopy. This polymer-SWNT composite is expected to have distinct nanostructure, resulting in novel material having marked properties. In the future, these methods will become new avenue in preparing carbon nanotube-based novel materials.

#### 4:00 PM HH5.8

**Pure Carbon Nanotube Filaments Spun by Twisting.** Mei Zhang<sup>1</sup>, Ray H. Baughman<sup>1</sup> and Ken R. Atkinson<sup>2</sup>;

<sup>1</sup>Chemistry/NanoTech Institute, The University of Texas at Dallas, Richardson, Texas; <sup>2</sup>Textile Research & Development, CSIRO Textile and Fibre Technology, Belmont, Victoria, Australia.

Twist spinning is an ancient process for making continuous filaments from short fibers. The present work downscales the diameters of fibers

used for spinning by a factor of a thousand to the nanoscale and discovers surprising and useful mechanical and electronic properties for resulting spun carbon nanotubes filaments and composites thereof. We used chemical vapor deposition process to grow multiwalled carbon nanotubes forests several hundred micrometers high on Si substrate. A continuous ribbon of pure nanotubes was easily formed by pulling on the forest in the plane of the substrate. By introducing twist and making multiple ply, torque stabilized filaments, the strength can be increased a thousand fold to over 400 MPa. Compared with previous fibers having comparable strength, the twisted nanotube filaments are super elastic-deforming largely reversibly over a large strain range (10%) and having toughness (15 J/gm) comparable to fibers used for bullet proof vests. Creep resistance, the ability to retain false twist, and high electrical conductivity are advantages of these filaments, which are largely retained when special methods are used to convert the twisted filaments to composite filaments having increased strength (up to 850 MPa).

#### 4:15 PM HH5.9

**Polymer-free Carbon Nanotube Fibers.** Mikhail Kozlov, Ryan Capps, Von Howard Ebron, Vignesh Seker, William Sampson, Laura Grigsby, Kyle Martin, John Ferraris and Ray Baughman; NanoTech Institute, University of Texas at Dallas, Richardson, Texas.

Carbon nanotube fibers free of any polymer binder have been prepared by a flocculation spinning process. Dispersions of nanotubes of different types were spun in a flow of polymer-free flocculating agent. The latter was removed and stabilization of the carbon nanotube material was achieved by post-spinning treatment. The prepared fibers exhibit large electrical conductivity (over 140 S/cm at room temperature), high specific capacitance in an electrolyte (over 100 F/g) and an electromechanical actuation. Substantial degree of alignment of carbon nanotubes in the material is observed using polarized Raman measurements. The electromechanical response was measured using custom made force transducer operating in an isometric mode. The measurements were carried out at room temperature in aqueous and organic electrolytes; square-wave potential of variable amplitude was applied with a potentiostat. Composite fiber made by filling as spun fiber with poly(vinyl alcohol) as binder shows high strength (about 750 MPa/g/cm<sup>3</sup>), and high toughness (about 100 J/g). Possible applications of the fibers in electronic textile, supercapacitor and actuator areas are discussed.

#### 4:30 PM HH5.10

**SWNT-polymer composite films made by layer-by-layer assembly.** Bong Sup Shim, Nicholas A. Kotov, Tang Zhiyong and Vladimir A. Sinani; Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Single wall carbon nanotube (SWNT) composite films are fabricated by layer-by-layer (LBL) assembly technique with poly(vinyl alcohol) (PVA) and poly(styrene-4-sulfonate) (PSS) as assembly partners. The combination of electrostatic, hydrogen and van der Waals interactions results in efficient bonding of SWNT with the polymer matrix. SWNTs wrapped by PSS, are evenly dispersed in the PVA matrix to produce composites with exceptional uniformity. Structure of as-prepared films has been observed by a variety of techniques including Raman spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM), while the composition was analyzed by thermogravimetric analysis (TGA) and UV-vis absorption. The material performance of the multilayer composites was evaluated by nanoindentation, direct tensile strength and electrical conductivity measurements. The resulting composite film exhibits semiconducting characteristics and high mechanical strength. Among all possible applications, the use of such films in biomedicine, particularly in neuroprosthetics, is targeted in this research. The preliminary characterization of multilayers as implantable biomaterials is being carried out. The first example of SWNT and PVA hybrid films made by LBL technique opens a door toward the production of SWNT-polymer composites with high loading amount of SWNTs, extreme uniformity and multiple functionalities.

#### 4:45 PM HH5.11

**Investigation of the Mechanical Properties of Multi-walled Carbon Nanotubes (MWNTs) Produced by CVD.**

Jay Gaillard, Malcom Skove and Apparao M. Rao; Physics and Astronomy, Clemson University, Clemson, South Carolina.

We have measured the bending modulus of several different CVD grown MWNTs using a vibrating reed technique. The MWNTs were produced from a thermal decomposition of three different precursors: (i) xylene/ferrocene, (ii) xylene/ferrocene/melamine (nitrogen-doped), and (iii) trimethylamine/ferrocene. The first two precursors were used to compare the mechanical properties of typical CVD-grown to bamboo-type MWNTs. Nanotubes prepared using the third precursor showed relatively fewer walls and defects compared to those prepared

from xylene-ferrocene mixture. The resonant vibrational frequencies of these nanotubes were measured both optically and electronically in air using a darkfield light microscope. The diameters of these nanotubes ranged between 50 - 160 nm as determined from the TEM images and the average length was 10 microns. For the xylene/ferrocene and trimethylamine/ferrocene tubes, the average bending modulus is estimated to be 0.3 and 0.8 TPa, respectively. However, the bending modulus for the nitrogen-doped tubes was 9 GPa which is significantly lower compared to regular MWNTs implying that the bending modulus decreases with an increase in wall defects. These findings are in reasonable agreement with those reported previously by Wang et al.[1]. The effect of wall thickness on the bending modulus is still under investigation. A summary of the higher frequency modes will also be presented. I. Z. L. Wang et al., Adv. Eng. Mat. 3, 657 (2001)

SESSION HH6: Composites, Fibers, and Mechanical Properties II  
Wednesday Morning, December 1, 2004  
Room 312 (Hynes)

#### 8:30 AM \*HH6.1

**Nanoscale Intralaminar Reinforcement for Biomimetic Toughening of Bismaleimide Composites.** T. Tiano<sup>1</sup>, M.

Roylance<sup>1</sup>, R. Czerw<sup>2</sup> and Benjamin S. Harrison<sup>2</sup>; <sup>1</sup>Foster-Miller Inc., Waltham, Massachusetts; <sup>2</sup>Center for Nanotechnology and Molecular Materials, Wake Forest University, Winston-Salem, North Carolina.

The Foster-Miller/Wake Forest University team utilized single-walled carbon nanotubes (SWNTs) and carbon nanofibers as reinforcing elements promoting interlaminar shear strength and toughness in biomimetic carbon fiber/bismaleimide resin composites based on an insect cuticle model. The team explored three different methods of increasing the affinity of these carbon nanofillers for the BMI matrix. Treated and untreated nanofillers were applied between the layers of prepreg in BMI composite laminates using novel processing methods developed at Foster-Miller and composite laminates were fabricated using standard processing techniques. The mechanical properties of these composites were assessed using end notch flexure testing and open hole tensile testing. The results indicated that including nanofiller at the laminae interface could increase the interlaminar shear strength of carbon fiber-BMI composites by up to 58%. SEM micrographs revealed that the nanofiller successfully bridged the laminae of the composite indicating success in biomimicking the insect cuticle. Composite fabrication techniques developed on this program would have a wide variety of applications in space and aerospace structures including leading and trailing edges of aircraft wings.

#### 9:00 AM HH6.2

**Tailoring Physical Properties of SWNT-Polymer Composites by Controlling SWNT Alignment by an Electric Field.**

Cheol Park<sup>1</sup>, John Wilkinson<sup>2</sup>, Sumanth Banda<sup>3</sup>, Zoubeida Ounaies<sup>3</sup>, Sharon E. Lowther<sup>4</sup>, Peter T. Lillehei<sup>4</sup>, Emily J. Siochi<sup>4</sup> and Joycelyn S. Harrison<sup>4</sup>; <sup>1</sup>National Institution of Aerospace, Hampton, Virginia; <sup>2</sup>Virginia Tech, Blacksburg, Virginia; <sup>3</sup>Virginia Commonwealth University, Richmond, Virginia; <sup>4</sup>Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia.

Single wall carbon nanotubes (SWNTs) have been studied as multifunctional reinforcing inclusions owing to their exceptional intrinsic characteristics, namely, electrical, electronic, mechanical, and thermal properties. Tailoring physical properties of SWNT-polymer composites can be achieved by actively controlling the degree of SWNT alignment in a specific direction. In this presentation, a novel method to control physical properties of a SWNT-polymer composite by aligning SWNTs with an electric field is introduced. SWNTs were aligned dielectrophoretically under an AC electric field in an oligomer matrix, and the aligned SWNTs were immobilized by photopolymerization using a blue light. The alignment of SWNTs was controlled as a function magnitude, frequency, and time of applied electric field in order to tailor the physical properties. Degree of SWNT alignment was assessed using optical microscopy and polarized Raman spectroscopy. The morphology of the aligned nanocomposites was investigated by high resolution scanning electron microscopy. The actively aligned SWNTs enhanced mechanical properties as compared to the matrix resin and the unaligned SWNT-polymer composite. Significant increases in the electrical and dielectric properties were also observed. Furthermore, electrical and dielectric properties of the aligned nanocomposites exhibited anisotropic characteristics, which could be controlled by the applied field conditions.

#### 9:15 AM HH6.3

**Interfacial Nano-Mechanics: Stress Transfer in Carbon Nanotube-Polymer Composites.** Asa H. Barber<sup>1</sup>, Sidney R.

Cohen<sup>2</sup> and H. Daniel Wagner<sup>1</sup>; <sup>1</sup>Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; <sup>2</sup>Chemical Research



Support, Weizmann Institute of Science, Rehovot, Israel.

Carbon nanotubes are attractive candidates for reinforcing polymers due to their high tensile strength and elastic modulus. As with traditional engineering composites, stress transfer from the polymer matrix, across the interface to the nanotubes is required for effective polymer reinforcement. In principle, if the polymer-nanotube interface is relatively weak then the interfacial can failure at relatively low stresses whereas strong polymer-nanotube interfaces can allow a build up of stress in the nanotube during composite loading that can reach the failure strength of the nanotubes itself, resulting in nanotubes fracture. Previous work in our laboratory [1, 2] has shown that it is experimentally viable to measure the interfacial strength between a single carbon nanotubes and a polymer matrix. The experimental set-up consisted of a single multi-wall carbon nanotube (MWCNT) attached to the end of an atomic force microscope (AFM) tip. Single nanotube-polymer composites could then be prepared by partially embedding the nanotube within a molten liquid polymer followed by solidification of the polymer. The MWCNT could then be pulled from the solid polymer with the pullout force measured using the AFM. In this current work individual MWCNTs are embedded within an epoxy matrix at variable embedded lengths. The nanotube can then be pulled away from the polymer surface. The interfacial strength is observed to change with embedded length, indicating that a shear-lag approach [3] to nano-interfaces may be operating as in micro-composite samples. From this data, an evaluation of the shear stress at the nanotubes-polymer interface and the tensile stress in the carbon nanotubes can be made. We show that the strength of the polymer around the nanotubes in shear is considerably higher than that of the bulk, and is resilient enough to allow failure of the nanotube in preference to interfacial failure during the pullout experiment. References 1. Measurement of carbon nanotube-polymer interfacial strength, Barber, A. H., Cohen, S. R. & Wagner, H. D., *Appl. Phys. Lett.*, 82, 23 (2003), 4140-4142 2. Interfacial fracture energy measurements for multi-walled carbon nanotubes pulled from a polymer matrix, Barber, A. H., Cohen, S. R., Kenig, S. & Wagner, H. D, to appear in *Comp. Sci. & Tech* 3. The elasticity and strength of paper and other fibrous materials, Cox, H. L, *Brit. J. Appl. Phys.*, 3 (1952), 72-79

#### 9:30 AM HH6.4

##### **Chemically Engineered Carbon Nanotube-Polymer Composite Coatings for use as Remote Strain-Sensors.** Jerome Halary,

John L. Stanford, Peter A. Lovell and Robert J. Young; Manchester Materials Science Centre, UMIST, Manchester, United Kingdom.

Materials scientists are constantly called upon developing new smart structures that could be used as sensors to monitor engineering structures loaded closer to their design limits. Conventional strain sensors are often measuring global, mono-directional strains on a macro scale when measurement of local, micro, multidirectional strains is needed. Recent experimental breakthroughs revealed the great potentiality in developing new generations of strain sensors based on single-wall carbon nanotubes. Previous deformation micromechanics studies, some of which were conducted at the MMSC using a newly developed remote Raman spectrometer, demonstrated that remote polarised Raman spectroscopy can be used to monitor the optical strain sensitivity of deformed single-walled carbon nanotubes (SWNTs) composites. For this purpose, filled polyurethanes, comprising low volume fraction (0.1 wt. %) of HiPco single-wall carbon nanotubes (SWNTs), have been developed that are readily applied as strain-sensitive coatings materials on a variety of substrates (steel, plastic, etc.). The resonant disorder-induced G Raman band of single-wall carbon nanotubes (SWNTs) has its position strongly dependent on strain or stress applied to the nanotubes when its intensity is strongly dependent on the nanotube orientation thus allowing principal stresses and strains to be determined directly from stress/strain induced Raman band shifts. If quantitative correlations between Raman band shifts and applied strains had been observed for various substrates, the non linearity of the band shifts at high strains and the scatter of the initial peak position at zero strain induced a loss in sensitivity of the strain mapping technique. Chemically engineered polyurethane matrices of different hardness have then been developed from different polyols and polyols mixtures in order to get a better insight into interface properties between the nanotubes and the matrix. Results from deformation micromechanics studies using both polarised Raman spectroscopy and tensile tests or loading/unloading experiments will be presented for this purpose. Chemically engineered nanotubes have also been developed in order to improve the dispersion of the nanotubes within a monomer as well as to increase the binding energies between the nanotubes and the polymer matrix. Nitric acid oxidation treatments not only exfoliate the nanotubes from their bundles but also introduce carboxyl (-COOH) functional groups which can create covalent bonds with the polyurethane monomers (either the diisocyanate or the polyol(s)). Results from deformation micromechanics studies of those new nanostructured composites will be presented in comparison with results from previous systems.

Finally, results from stress/strain mapping around defects such as precisely machined holes in deformed plates, will be presented to emphasize the potentials of this novel high resolution non contact strain sensor system.

#### 9:45 AM HH6.5

##### **Synthesis of Carbon Nanotube Reinforced Composite Coatings.** Hao Li, Abhishek Kothari, Brian W. Sheldon, Kengqing Jian and Robert H. Hurt; Engineering Division, Brown University, Providence, Rhode Island.

The excellent mechanical properties of carbon nanotubes (CNTs) are driving research into the creation of new strong and tough nanocomposite systems. The toughening mechanism of CNT reinforced alumina matrix nanocomposites was investigated in a previous study. However, the mechanical properties of the CNTs and the alumina matrix were far from optimized. The aim of the present study is to tailor the experimental conditions to improve the mechanical properties of CNTs and the alumina matrix. Multiwall CNTs were fabricated with thermal and plasma enhanced chemical vapor deposition (CVD) in anodic alumina templates. The CNT microstructures were examined with scanning and transmission electron microscope (SEM and TEM). Plasma significantly increased the carbon growth rate on the template inner wall and also enhanced secondary CNT growth. TEM and electron diffraction show that the graphitic structures of most as-deposited CNTs were not highly ordered. Heat treatment could convert CNTs to a highly ordered graphitic layers parallel to the alumina template inner wall and could also crystallize the amorphous alumina template. Carbon nanofibers were also fabricated as reinforcement materials for composite coatings using template-mediated assembly of discotic mesophase pitch. TEM study shows that a thin CVD graphitic layer could modify the orientation of the discotic mesophase pitch and the graphitic layer, and thus influence the mechanical properties of the carbon nanofibers.

SESSION HH7: Theory  
Wednesday Morning, December 1, 2004  
Room 312 (Hynes)

#### 10:30 AM \*HH7.1

##### **Electronic Structure and Quantum Transport of Functionalized Carbon Nanotubes.** Young-Su Lee<sup>1</sup>, Marco Buongiorno Nardelli<sup>2,3</sup> and Nicola Marzari<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Physics, North Carolina State University, Raleigh, North Carolina; <sup>3</sup>CCS-CSM, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The electronic structure and the quantum conductance of pristine and functionalized carbon nanotubes have been studied with first-principles static, linear-response, and molecular dynamics simulations. Different patterns of functionalization involving covalently-attached phenyl and nitrene moieties have been investigated, highlighting the different roles that topology, charge transfer, and hybridization have in tuning or disrupting the conduction sheet of the nanotube. We also exploit our ability to map full Car-Parrinello electronic-structure simulations into a maximally-localized representation of the Kohn-Sham orbitals to study with first-principles accuracy the ballistic transport in complex nanostructures containing thousands of atoms, and to investigate the response of different tubes to different degrees of functionalization.

#### 11:00 AM HH7.2

##### **Corrections to the Optical Transition Energies in Single-Wall Carbon Nanotubes of Smaller Diameters.**

Georgii G. Samsonidze<sup>1</sup>, Riichiro Saito<sup>2</sup>, Naoki Kobayashi<sup>2</sup>, Ado Jorio<sup>3</sup>, Antonio G. Souza Filho<sup>4</sup>, Shin Grace Chou<sup>5</sup>, Gene Dresselhaus<sup>6</sup> and Mildred S. Dresselhaus<sup>1,7</sup>; <sup>1</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Physics, Tohoku University and CREST JST, Sendai, Japan; <sup>3</sup>Departamento de Fisica, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil; <sup>4</sup>Departamento de Fisica, Universidade Federal do Ceara, Fortaleza, Ceara, Brazil; <sup>5</sup>Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>6</sup>Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>7</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The Kataura plot that depicts the optical transition energies vs nanotube diameters is widely used in spectroscopic studies of single-wall carbon nanotubes (SWNTs). The Slater-Koster formalism with symmetry-based parameters fitted to experimental results along with the zone-folding scheme is a common tool for modeling the

optical transition energies and assigning the spectral features to specific SWNTs. The Slater-Koster model has proven to describe accurately SWNTs of larger diameters (1-2 nm). However, recent progress in synthesis of smaller diameter SWNTs (1 nm and below) and numerous photoluminescence (PL) and resonance Raman spectroscopy (RRS) measurements indicate the failure of the Slater-Koster model in the small diameter limit. The two major differences can be found between the experimentally observed optical transition energies (the experimental Kataura plot) and the predictions of the Slater-Koster model. (1) The observed ratio of the energy of the second band in the experimental Kataura plot to the energy of the first band is less than 2 predicted in the Slater-Koster model (the ratio problem). (2) The observed spread of the optical transition energies for different nanotubes within the same family ( $2n+m=\text{const}$ ) from a given band in the experimental Kataura plot is much larger than predicted by the Slater-Koster model (the family spread). While the ratio problem can be explained by the formation of excitonic states, the family spread is mainly attributed to the curvature effects and long-range interatomic interactions in small diameter SWNTs. In the present work we develop an extended model for description of the optical transition energies in small diameter SWNTs. Our approach is based on the symmetry-adapted scheme as proposed by Popov. The curvature effects are thus incorporated in the model as opposite to the conventional zone-folding approximation which ignores the curvature of the SWNT side-wall. The model is able to predict the family spread in the experimental Kataura plot, and furthermore, it is expected to shed light on the SWNT interaction with various surfactants and environments which result in different spreads of the optical transition energies within a given family in the experimental Kataura plot.

#### 11:15 AM HH7.3

**Atomic-scale Physics and Modeling of Schottky Barrier Effect in Carbon Nanotube Nanoelectronics.** Yongqiang Xue and Mark A. Ratner; Chemistry Department and Materials Research Center, Northwestern University, Evanston, Illinois.

Nanostructured devices based on single-wall carbon nanotubes (SWNTs) have been progressing in a fast pace. Many device concepts well known in conventional semiconductor microelectronics have been successfully demonstrated on a single-tube basis, ranging from intramolecular homo (hetero)-junctions to and field-effect transistors. Research on SWNT-based nanoelectronic devices therefore presents unique opportunities both for exploring novel device technology functioning at the nano/molecular-scale and for re-examining the physical principles of semiconductor microelectronics from the bottom-up atomistic approach. A point of continuing controversy in SWNT-based nanoelectronic devices has been the effect of Schottky barriers at the metal-SWNT interface. Since SWNTs are atomic-scale nanostructures in both the axial and the circumferential dimensions, any barrier that may form at the interface has a finite thickness and a finite width. In general a microscopic treatment of both the source/drain and gate field modulation effect will therefore be needed to account for faithfully the atomistic nature of the electronic processes in SWNT-based junction and transistor devices. In this talk, we present a Green's function based self-consistent tight-binding study of Schottky barrier effect in the configuration of metal-SWNT-metal junctions and metal-insulator-SWNT interfaces, which takes fully into account atomic-scale electronic structure and three-dimensional electrostatics. We focus on the insights obtained from such atomistic study and discuss its application in modeling SWNT-based field-effect transistors and sensors.

#### 11:30 AM HH7.4

**Kohn Anomalies in Graphite and Nanotubes.** Stefano Piscanec<sup>1</sup>, Michele Lazzeri<sup>2</sup>, Andrea Carlo Ferrari<sup>1</sup>, Francesco Mauri<sup>2</sup> and John Robertson<sup>1</sup>; <sup>1</sup>Engineering, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Laboratoire de Mineralogie-Cristallographie de Paris, Universite Pierre et Marie Curie, Paris, France.

The understanding of the physical mechanisms ruling the phonon dispersions and the electron-phonon coupling in graphite is a key step to derive the vibrational properties and the Raman intensities of carbon nanotubes. In graphite the inter-atomic force-constant matrix elements very slowly decay with the distance, and this long-range behaviour strongly affects the phonon dispersion of the upper optical branches at the  $\Gamma$  and K points. A key point to understand the phonons of graphite is the semi-metallic character of its electronic structure. In general, the atomic vibrations are partially screened by electronic states. In a metal this screening can change rapidly for vibrations associated to certain q points of the Brillouin Zone, entirely determined by the shape of the Fermi surface. The consequent anomalous behaviour of the phonon dispersion is called Kohn anomaly. We show that graphite displays two remarkable Kohn anomalies at the  $\Gamma$ -E<sub>2g</sub> and K-A<sub>1</sub> modes. We demonstrate that graphite is a very remarkable case, since a very simple mathematical description of the Kohn anomalies is possible. The anomalies are

revealed by two sharp kinks in the phonon dispersion. The slope of these kinks is proportional to the ratio of the square of the electron-phonon coupling matrix element and the p bands slope at K. It is thus impossible to derive the phonon branches at  $\Gamma$  and K by a force constant approach based on a finite number of force constants, contrary to what often done in literature. The electron-phonon coupling of the  $\Gamma$ -E<sub>2g</sub> and K-A<sub>1</sub> modes is particularly large, whilst the coupling of all the other modes at Gamma and K is negligible. This implies that the Raman D peak of graphite is due to the highest optical branch starting from the K-A<sub>1</sub> mode. The D peak dispersion with excitation energy reflects the slope of the Kohn anomaly at K. These results have immediate implications for carbon nanotubes. Due to their reduced dimensionality, metallic tubes display much stronger Kohn anomalies than graphite. This results in phonon softening, implying that folded graphite does not reproduce the phonon dispersions of metallic tubes. The presence of Kohn anomalies in metallic tubes is the reason for the difference in the Raman spectra between semiconducting and metallic tubes.

#### 11:45 AM HH7.5

**The Limit of Ballistic Transport in Metallic Nanotubes.** Michele Lazzeri<sup>2</sup>, Andrea Carlo Ferrari<sup>1</sup>, Stefano Piscanec<sup>1</sup>, Francesco Mauri<sup>2</sup>, Stephanie Reich<sup>1</sup> and John Robertson<sup>1</sup>; <sup>1</sup>University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Laboratoire de Mineralogie-Cristallographie de Paris, Universite Pierre et Marie Curie, Paris, France.

Metallic nanotubes can act as one-dimensional quantum wires with ballistic electron transport. Armchair tubes are predicted to be ballistic conductors because elastic scattering is suppressed by the symmetry of the conducting electrons and because the local potential of defects is small [1]. Due to the strong C-C bond, nanotubes can carry the highest current density of any material before they break for electromigration (self-electrolysis). The electromigration limit in nanotubes is at least 100 times higher than in Al or Cu, and this makes them to be the best candidates as wires or vias between the metallisation layers in integrated circuits. However, high field electrical transport measurements have shown that the electron scattering by optical phonons breaks down the ballistic behaviour [2,3]. Here we derive the electron phonon scattering matrix elements for metallic nanotubes. We show a simple and direct method to derive the electron phonon coupling matrix elements of graphite from the D peak dispersion of graphite or its optical phonon dispersions around  $\Gamma$  [4]. We demonstrate that the electron phonon coupling matrix elements of metallic nanotubes can be derived from the measured electron phonon coupling matrix elements of graphite. We then use the measured matrix elements to evaluate the electron mean free path for high field transport, with no need of direct transport measurements. The electron mean free path at high field is always well below 100 nm. Electron phonon coupling is thus the fundamental bottleneck for ballistic transport in metallic nanotubes. 1. C. T. White, T. N. Todorov, Nature 393, 240 (1998) 2. Z. Yao, C. L. Cane, C. Dekker, Phys. Rev. Lett. 84, 2941 (2000) 3. A. Javey, J. Guo, M. Paulsson, Q. Wang, D. Mann, M. Lundstrom, H. Dai, Phys. Rev. Lett. 92, 106840 (2004) 4. S. Piscanec, M. Lazzeri, F. Mauri, A. C. Ferrari, J. Robertson, Phys. Rev. Lett. Submitted (2004)

SESSION HH8: Electronic Properties and Devices I  
Wednesday Afternoon, December 1, 2004  
Room 312 (Hynes)

#### 1:30 PM \*HH8.1

**Electrical Transport in Aligned Carbon Nanotubes.** Wonbong Choi<sup>1</sup>, Donghun Kang<sup>2</sup>, Wanjun Park<sup>2</sup>, Eunju Bae<sup>2</sup>, Eungmin Lee<sup>1</sup> and Ju-hye Ko<sup>2</sup>; <sup>1</sup>Mechanical & Materials, Florida International University, Miami, Florida; <sup>2</sup>Samsung Advanced Institute of Technology, Keehung, South Korea.

We discuss the central issues to be addressed for realizing carbon nanotube (CNT) nanoelectronics. We focus on the selective growth, electron energy bandgap engineering and electrical transport characterization. We have introduced nanotemplate to control the selective growth, length and diameter of CNT. Vertically aligned CNTs are synthesized for developing a vertical CNT-field effect transistor (FET). The ohmic contact of the CNT/metal interface is formed by rapid thermal annealing. Diameter control, synthesis of y-shape CNT and surface modification of CNT open the possibility for energy band gap modulation. A nonvolatile memory based on the top gate structure with oxide-nitride-oxide charge trap is also presented. We suggest that the deposited memory film can be used for the quantum dot storage due to the localized electric field by nano scale CNT-electron channel. [1] Choi W B, Cheong B, Chae S, Bae E J, Lee J, Kim J, Kim J, 2003 Appl. Phys. Lett. Jan. 82 275. [2] Choi W B, Cheong B, Kim J J, Ju J, Bae E J, Chung G, 2003 Advanced Functional Materials, 13 80.

2:00 PM **HH8.2**

**Structure and Dynamics of Carbon Buckyballs Encapsulated into Single-Walled Carbon Nanotubes.** Julien Cambedouzou<sup>1</sup>, Stephane Rols<sup>1</sup>, Robert Almayrac<sup>1</sup>, Jean-Louis Sauvajol<sup>1</sup>, Helmut Schober<sup>2</sup> and Hiromichi Kataura<sup>3,1</sup> Groupe de Dynamique des Phases Condensees, Montpellier, France; <sup>2</sup>Institut Laue Langevin, Grenoble, France; <sup>3</sup>Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan.

Among the numerous potential applications for carbon nanotubes, one of the most attractive lies in the possibility of using the cylindrical hollow core of the tubes as long molecular tanks. Of special interest is the insertion of single-walled carbon nanotubes (SWNTs) by C<sub>60</sub> molecules with regards to its predicted superconducting properties upon alkaline doping<sup>1</sup>. The transmission electronic microscopy images of these so-called peapods have revealed the one-dimensional character of the C<sub>60</sub> chains confined into SWNT. In this communication, we present a recent study of both the structure and the dynamics of peapods. The structural investigation is based on diffraction techniques. The diffraction patterns are simulated and are found to be in good agreement with the experimental data, indicating a reliable characterization of the peapod sample. In particular, a high filling rate of about 80% is determined. However, the difficulty of discriminating between monomer, dimer or trimer chains of C<sub>60</sub> molecules inside SWNTs is demonstrated for a powder of peapods. The dynamical investigation is performed by inelastic neutron scattering, using the IN6 time-of-flight spectrometer at the Institut Laue Langevin. A very weak quasi-elastic signal is observed at a temperature of 480K, suggesting the free rotation of some of the C<sub>60</sub> molecules inside the tubes. The generalized phonon density of states (GDOS) of the chains of C<sub>60</sub> confined into SWNTs has also been derived from our measurements. This GDOS shows up characteristic features already observed in pure and alkaline doped C<sub>60</sub> phases. In particular, the GDOS can be decomposed into two regions separated by a gap, namely: - the [30-200 meV] intra-molecular energy range where all the observed vibrations can be attributed to intra-molecular modes. - the [0-8 meV] inter-molecular energy range where all the observed vibrations can be attributed to inter-molecular modes. Lattice-dynamical calculations have been performed and allows to calculate the GDOS of different types of stacking of confined C<sub>60</sub> (as monomers, dimers and polymers). The confrontation of the experimental GDOS with the calculated GDOS testifies to covalent bonding between a part of the C<sub>60</sub> molecules. All these results show that the confined C<sub>60</sub> molecules are partially polymerized inside the inner space of the tubes. <sup>1</sup> S.Saito and S.Okada, 3rd Symposium on Atomic-Scale Surface and Interface Dynamics 307 (Fukuoka 1999)

2:15 PM **HH8.3**

**Fabrication of N-type Field-Effect Transistors Based on Self-Assembled Thin Films of Carbon Nanotubes and Poylamidoamine (PAMAM) Dendrimers.** Caroline Woelfle and Richard O. Claus; Electrical and Computer Engineering department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Carbon Nanotubes (CNTs) are among the most promising building blocks for future nanoscale electronics due to their unique structural, mechanical, and electrical properties. Field-Effect Transistors (FETs) based on CNTs have been shown to exhibit field-effect mobilities as high as 12 cm<sup>2</sup>/Vs [1]. Recently, several electronic devices based on CNTs have been fabricated and characterized [2-5]. Most of these devices are based on individual Single-Walled Carbon Nanotubes (SWNTs) and require high-cost fabrication techniques. However, for many applications e.g., sensor devices, FETs, etc, individual SWNTs can be replaced by interconnected arrays of SWNTs. We report here on the fabrication of n-type FETs by the self-assembly of SWNTs on thin films of PAMAM dendrimer. PAMAM dendrimers possess one of the largest amount of electron donating amine groups among existing polymers, and are thus very attractive molecules to be used to change the normally p-type semi-conducting SWNTs into high performance n-type. The amount of amine groups in the molecules increases with the PAMAM dendrimer generation. As many as 4096 amine groups per molecule are present for a generation 10 PAMAM dendrimer. The electron donating capability of the amine groups changes the electrical conductance of individual SWNTs, by a shift in the Fermi Level closer to the conduction band. The scope of this study is to investigate the effect of the strong electron-donating capability of the PAMAM dendrimers on the electronic characteristics of the subsequently built FETs. References [1] Bradley, K.; Gabriel, J-P., P.; Gruner, G. Nano Letters, 3, 1353-1355, 2003 [2] Zhou, C.; Kong, J.; Yemilmez, E.; Dai, H. Science, 290, 1552-1555, 2000 [3] Tans, S.J.; Devoret, M.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. Nature, 386, 474-477, 1997 [4] Tans, S. J.; Verschueren, A. R. M.; Dekker, C., Nature, 393, 49-52, 1998 [5] Kong, J.; Dai, H. J. Phys. Chem. B, 105, 2890-2893, 2001

2:30 PM **HH8.4**

**Electronic Characteristics of DNA-Wrapped Carbon Nanotube Devices.** Frank Eugene Jones, Albert Alec Talin, Paul M. Dentinger and Francois Leonard; Sandia National Laboratory, Livermore, California.

Wrapping single-stranded DNA (ssDNA) molecules around single-wall carbon nanotubes (SWCNT) has recently been shown to yield excellent dispersions and to enable separation of nanotubes based on diameter and conductivity.[1] However, little has been reported in the way of electronic properties of these ssDNA/SWCNT hybrids and what impact the DNA may have on device properties. In this paper we report on electrical properties of metal/SWCNT/metal devices fabricated using ssDNA based suspensions. Compared to SWCNT suspensions made using Triton X-100 surfactant, making devices via AC dielectrophoresis with a ssDNA/SWCNT suspension results in cleaner devices with lesser occurrence of multiple tube bundles. However, the presence of ssDNA molecules on the carbon nanotubes does not significantly affect the electrical properties. Typical as-deposited contact resistance of 10<sup>8</sup> ohms for as-fabricated ssDNA/SWCNT devices and a decrease in the resistance by orders of magnitude following annealing at 300°C are properties consistent with suspensions of SWCNT in other surfactants. [1] M. Zheng, et al., Science, 302, 1545 (2003).

2:45 PM **HH8.5**

**Random Telegraph Noise in Individual Metallic Single-Walled Carbon Nanotubes.** SungHo Jhang<sup>1</sup>, SangWook Lee<sup>1</sup>, DongSu Lee<sup>1</sup>, Siegmund Roth<sup>2</sup>, Eleanor E. B. Campbell<sup>3</sup>, GyuTae Kim<sup>4</sup> and YungWoo Park<sup>1</sup>; <sup>1</sup>School of Physics, Seoul National University, Seoul, South Korea; <sup>2</sup>Max-Planck-Institute for Solid State Research, Stuttgart, Germany; <sup>3</sup>Department of Experimental Physics, Gothenburg University and Chalmers University of Technology, Gothenburg, Sweden; <sup>4</sup>Department of Electrical Engineering, Korea University, Seoul, South Korea.

The switching of resistance between two discrete values, known as random telegraph noise (RTN), was observed in individual metallic single-walled carbon nanotubes (SWNTs). Mean lifetimes in high- and low-current states,  $\tau_{high}$  and  $\tau_{low}$ , have been studied as a function of bias-voltage and gate-voltage as well as temperature. By analyzing the statistics and features of the RTN, we suggest that this noise is due to the random transition of defects between two metastable states, activated by inelastic scattering with ballistic electrons.

3:30 PM **\*HH8.6**

**Integration Schemes for Carbon Nanotubes into Microelectronics.** G. S. Duesberg, A. P. Graham, M. Liebau, R. Seidel, E. Unger and F. Kreupl; CPR Nano Processes, Infineon Technologies AG, Munich, Germany.

The use of carbon nanotubes (CNTs) in beyond-the-roadmap-applications has been widely investigated. It has been shown that they have outstanding current carrying capacity and thermal conductivity, which makes them potential candidates for interconnects on chips. The performance of field-effect transistors based on single walled CNTs improves continuously and outperforms silicon-based devices in many aspects. However, only a few promising schemes for integrating CNTs into products exist. Generally, nanomaterials demand new concepts and assembly techniques that have to be evaluated in terms of feasibility, yield and reproducibility. The concept of integration of nano-devices into microelectronics (hybrid electronics) makes use of the advantages of semiconductor fabrication techniques, such as lithographic structuring, therefore allowing parallel processing. The creation of vertical interconnects (Vias) and vertical transistors (VCNTFET) consisting of CNTs directly on silicon chips can be achieved by Catalytic Chemical Vapour Deposition (CCVD). To this, CNT growth has to be optimised in terms of scaleability, reproducibility, and yield. The crucial point is the catalyst design and its placement on the nanometer scale. The variation of the catalyst/substrate system and the growth conditions leads to control over the yield, density, and CNTs type, which are key issues for device fabrication. The growth of individual MWCNTs in lithographically defined positions on silicon chips has been achieved with a precision of 20 nm. For electrical characterisation these CNTs were grown from metallic underlayers and individually contacted using e-beam lithography. A current density of 4·10<sup>8</sup> A/cm<sup>2</sup> and a resistance of 7.8 kΩ were achieved for this vertical interconnect consisting of an individual multi-walled CNT. Further, advances in the synthesis of transistors based on SWCNTs are shown. The fabrication of power transistors consisting of multiple, parallel contacted SWCNTs has been achieved. The CCVD grown SWCNTs were contacted with only one lithographic step and unwanted metallic tubes were eliminated by electronic pulses. Using this CNT transistor it is possible to switch macroscopic devices such as LEDs or small motors.

4:00 PM **HH8.7**

**Carbon Nanotube p-n Junction Diodes.** Ji Ung Lee, GE Global Research, Niskayuna, New York.

We demonstrate a single-walled carbon nanotube p-n junction diode device. The p-n junction is formed along a single nanotube by electrostatic doping using a pair of split gate electrodes. By biasing the two gates accordingly, the device can function either as a diode or as an ambipolar field-effect transistor. The diode current-voltage characteristics show forward conduction and reverse blocking characteristics, i.e. rectification. For low bias conditions, the characteristics follow the ideal diode equation with an ideality factor close to one. At high bias, the current is limited by the contact resistance.

4:15 PM **HH8.8**

**Room-temperature fabrication of patterned carbon nanotube field emission cathodes by electrophoresis.** Soojin Oh<sup>1</sup>, Jian Zhang<sup>2</sup>, Yuan Cheng<sup>2</sup>, Hideo Shimoda<sup>3</sup>, Bo Gao<sup>3</sup> and Otto Zhou<sup>1,2</sup>; <sup>1</sup>Curriculum in applied and materials sciences, University of North Carolina-Chapel Hill, Chapel Hill, North Carolina; <sup>2</sup>Dept. of Physics and Astronomy, University of North Carolina-Chapel Hill, Chapel Hill, North Carolina; <sup>3</sup>Xintek, Inc., Chapel Hill, North Carolina.

S. Oh(1), J. Zhang(2), Y. Cheng(2), H. Shimoda(3), B. Gao(3) and O. Zhou(1), (2) (1) Curriculum in Applied and Materials Sciences, University of North Carolina, Chapel Hill, North Carolina 27599 (2) Department of Physics and Astronomy, University of North Carolina, Chapel Hill 27599 (3) Xintek, Inc., 308 West Rosemary Street, Chapel Hill, North Carolina 27516 Carbon nanotubes (CNTs) are being actively investigated for applications in vacuum electronic devices due to their attractive field emission properties and chemical and thermal stability. For the fabrication of field emission cathodes using CNTs, several techniques have been utilized including direct chemical vapor deposition and screen printing. Here we report a room-temperature liquid-phase method to fabricate high resolution CNT field emission cathodes by electrophoresis. Well-defined and adherent CNT patterns with 20  $\mu\text{m}$  – 300  $\mu\text{m}$  feature size were fabricated on various substrates. Their electron field emission properties were characterized and were found to compare favorably to those fabricated by other processes. Ref: S. Oh, J. Zhang, Y. Cheng, H. Shimoda, and O. Zhou, Appl. Phys. Lett. 84(19), p3738-3740 (2004)

4:30 PM **HH8.9**

**Transport and TEM on individual Nanotubes and Peapods.** Dirk Obergefell<sup>1</sup>, Jannik C. Meyer<sup>1</sup>, Shihe Yang<sup>2</sup>, Shangfeng Yang<sup>2</sup> and Siegmund Roth<sup>1</sup>; <sup>1</sup>Max Planck Institute for Solid State Research, Stuttgart, Germany; <sup>2</sup>Department of Chemistry, The Hong Kong University of Science and Technology, Hong Kong, China.

For the first time, transport measurements in field-effect transistor configuration and TEM investigations on the same individual nanotubes/nanotube peapods have been performed. So far approaches for combining transport and TEM on the same nanotube only allowed for measuring the output characteristics  $I_{sd}(V_{sd})$ , i.e. the dependence of the current  $I_{sd}$  through the tube on the bias voltage  $V_{sd}$ . Applying our new method of underetching a Si/SiO<sub>2</sub> substrate from the edge of a chip after the transport measurements, we can additionally get the transfer characteristics  $I_{sd}(V_g)$ , i.e. the gate response of the current, which provides crucial information about the electronic properties of the system investigated. After the transport measurements and the etching process the samples can be viewed in the TEM, which enables us to check, whether a contacted nanotube is really a single tube or a thin bundle and whether a tube is filled with fullerenes ("peapod"). Combined transport measurements and TEM investigations of nanotubes and nanotube peapods will be presented.

4:45 PM **HH8.10**

**Aligned Carbon Nanotubes on Indium Tin Oxide: Growth and Electro-Photo-Thermal Properties for Multifunctional Mesodevices.** Saurabh Agrawal<sup>1</sup>, P. Victor<sup>1</sup>, M. J. Frederick<sup>1</sup>, P. G. Ganesan<sup>1</sup>, O. Nalamasu<sup>1</sup>, Theo Borca-Tasciuc<sup>2</sup> and G. Ramanath<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Department of Mechanical Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Growing aligned carbon nanotubes (CNTs) on optically - and/or electrically - functional materials is essential for providing electrical contacts to CNTs, or accessing their properties through optical stimuli, to pave the way for new types of CNT - based devices. Here, we report the growth of oriented bundles of aligned multi-walled CNTs on indium tin oxide (ITO) - a transparent conductor, and demonstrate an ohmic contact with superlinear behavior at high voltages, and a novel thermoelectric response. These could be harnessed for realizing new types of CNT-based multifunctional mesoscale devices. We show that aligned CNT growth from a xylene -

ferrocene mixture is seeded at 775 °C, at an interfacial SiO<sub>2</sub> layer formed via the interaction of 40-nm-thick ITO layers and the Si substrate. The precursors migrate through nanopipes in the ITO layer and initiate CNT growth at the ITO/Si interface. This technique can be adapted to obtain multidirectional architectures of CNTs. To demonstrate the utility of *in-situ* bottom contact formation we demonstrate a test device comprised of Pt/CNT/ITO/SiO<sub>2</sub>/Si(001) stacks. ITO-contacted 100  $\mu\text{m}$  long CNT bundles exhibit ohmic response below 3 V, and a resistance of 335  $\Omega$  for a 3  $\text{cm}^2$  contact. This is several orders of magnitude higher than the theoretically calculated resistance of the CNT layer  $\mu\Omega$ , due to high contact resistance. At higher voltages we observe a superlinear behavior described by Poole Frenkel hot charge carrier injection across a 100 meV barrier. We describe this behavior in terms of electric field induced carrier emission injection from traps across a barrier at the ITO-CNT interface. The CNT-ITO structures also exhibit a thermoelectric voltages in the range a few V to 100s of meV, when exposed to heat or to photo-excitation by a 1.5  $\mu\text{m}$  wavelength laser source through the back contact. Voltage is dependent on both laser power and laser pulse frequency, while the thermal voltage varies for different top-contacts and decreases with temperature. Based on these results for several top contacts, including ITO, we present a mechanism for the thermal- and photo-excited voltages.

SESSION HH9: Electronic Properties and Devices II  
Thursday Morning, December 2, 2004  
Room 312 (Hynes)

8:30 AM **\*HH9.1**

**Carbon Nanotube Electron Sources for Electron Microscopes.** Niels de Jonge, Philips Research Laboratories, Eindhoven, 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 cap opening/closing was investigated in-situ in a transmission electron microscope (TEM). The emission properties of individual carbon nanotubes with closed caps were investigated in an ultra-high vacuum system 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 lifetime of more than 18 months. It followed that the Fowler-Nordheim model describes the emission process, 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:  $3 \times 10^9 \text{ A}/(\text{Sr}^* \text{m}^2 \text{V})$ ; 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 of 0.3 eV 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. Nitrogen doped multi-walled carbon nanotubes were investigated as well on their electron emission properties.

9:00 AM **HH9.2**

**Band-engineering of Nanotube Transistors via Selective Chemical Doping.** Xiaolei Liu, Zhicheng Luo and Chongwu Zhou; EE-Electrophysics, University of Southern California, LA, California.

A new approach to engineer the band structure of the carbon nanotube field-effect transistors (CNT-FET) is presented as an effort toward the goal of rational design and control of the CNT-FET performance. By selectively exposing either the center part or the contacts of the nanotube devices to oxidizing or reducing gases, we have achieved good control over the threshold voltage and the subthreshold swing. Our experiments reveal that for both center-exposed and contact-exposed devices, NO<sub>2</sub> shifts the threshold voltage toward higher values, while NH<sub>3</sub> lowers the threshold voltage. However, the changes of the subthreshold swing are in opposite directions for center-exposed and contact-exposed devices: while NO<sub>2</sub> improves the performance of the contact-exposed devices, NH<sub>3</sub> leads to lower subthreshold swing for the center-exposed devices. Numerical simulations have also been carried out to explain the experimental results. Our approach provides an interesting way to tailor the performance as well as the threshold voltage of CNT-FETs.

9:15 AM **HH9.3**

**One Dimensional Electrons in Carbon Nanotubes.** Adrian Bachtold<sup>1</sup>, Bertrand Bourlon<sup>1</sup>, Bo Gao<sup>1</sup>, Christian Glattli<sup>1</sup>, Csilla Miko<sup>2</sup> and Laszlo Forro<sup>2</sup>; <sup>1</sup>Ecole Normale Supérieure, Paris, France; <sup>2</sup>EPFL, Lausanne, Switzerland.

Experimental results for transport through crossed metallic single-wall nanotubes (SWNTs) are presented. The conductance is measured first in one tube while the second is left floating. The conductance decreases as the temperature or the bias is reduced, in a way very similar to that of tunneling experiments in SWNTs. Interestingly, this zero-bias anomaly disappears as the current is increased through the second tube. The relationship between these results and the predictions of two electrostatically coupled SWNTs described by Luttinger liquid theory will be discussed. Explicit calculations are able to reproduce these measurements rather well, in particular once backscattering generated by the deformation at the crossing is taken into account within each SWNT. The resemblance between our data and the theoretical predictions represents further evidence supporting the Luttinger liquid picture in SWNTs. In the second part of this talk, I report a new method to access the electronic paths in multiwalled carbon nanotubes (MWNT) which enables the first estimation of the linear intershell resistance. Using four-point measurement techniques, the voltage drop is measured between electrodes situated inside or outside the region lying between the current biased electrodes. Surprisingly, a significant nonlocal voltage drop is detected at room temperature. The nonlocal voltage drop decreases exponentially with distance. Moreover, the local voltage measured in a standard four-probe configuration is found to drop when the distance between the current biased electrodes is increased. These results are in agreement with a simple model which considers conduction through the two outermost shells and treats them as a resistive transmission line. In such a model, the intershell conductance is 100 S/m. This value is in agreement with the estimate based on electrons tunnelling through atomic orbitals of nearby shells while taking into account conservation of energy but not momentum.

#### 9:30 AM HH9.4

**Carbon Nanotube Photo-Detectors.** Matthew Scott Marcus, O. M. Castellini, J. M. Simmons and M. A. Eriksson; Physics, Univ. of Wisconsin-Madison, Madison, Wisconsin.

Carbon nanotube transistors can be photo-gated using visible and near infrared light. The transistors are fabricated on SiO<sub>2</sub>/p-Si substrates, where the p-Si is used as a gate for the nanotube channel. Light is absorbed by not only the carbon nanotube, producing photocurrents, but also in the silicon gate that produces a photo-voltage at the interface between the Si-SiO<sub>2</sub>. We observe that photo-voltages of 15mV change the channel current by up to 10pA. The small addition of the photo-voltage when the nanotube is illuminated by a modulated light source acts to probe the derivative of the channel current with respect to the gate voltage. Growing nanotubes with large channel lengths (L=500 μm), which are much larger than the laser beam diameter, we are able to study the spatial dependence of the photo-gating effect. We observe measurable photo-currents even when the laser illuminates at large distances (up to 1mm), indicating that the carriers responsible for photo-gating are mobile. The photo-gating effect provides an unusual photo-detector where the gate material determines the absorption, and the channel material determines the transport properties. In effort to isolate the nanotube-light interaction from the silicon gate, we have suspended the nanotubes on pillars above the substrate. When the length of the nanotube is short (L<1μm) the entire length of the nanotube remains suspended. This is in contrast for tubes with length (L>2μm) where the ends of the nanotubes remain pinned to the suspended pillars, but the central body of the tube drops 70nm and can stick to the substrate. For nanotubes with lengths between (1-2μm) the probability that the nanotube is stuck to the substrate increases with tube length. We propose that thermally driven oscillations of the nanotube during the CVD growth cause the nanotube to oscillate with amplitudes large enough (70nm) to touch the substrate, then stick. Using the length of the nanotubes, and the diameter distribution from the CVD growth we are able to non-invasively measure a value of Young's modulus.

SESSION HH10: Optical Properties I  
Thursday Morning, December 2, 2004  
Room 312 (Hynes)

#### 10:15 AM \*HH10.1

##### **Fluorescence of Single-walled Carbon Nanotubes.**

Sergei M. Bachilo, Dmitri Tsybolski, John-David R. Rocha, John P. Casey, Tonya K. Leeuw, Crystal E. Redden and R. Bruce Weisman; Department of Chemistry, Center for Nanoscale Science & Technology, and Center for Biological and Environment Nanotechnology, Rice University, Houston, Texas.

Since its recent discovery, the near-infrared band-gap photoluminescence (fluorescence) of semiconducting SWNT has become a valuable tool for basic and applied researchers. An overview

of nanotube fluorescence spectroscopy and its applications will be presented. The key assignment of distinct spectral features to specific (n,m) structural species will be shown. This information permits the elucidation of nanotube electronic structure through study of spectral transition frequencies and line shapes, as well as a recent extension to temperature-dependent spectral shifts. In another application designed to give detailed analysis of bulk samples containing mixtures of SWNT species, new methods will be described that can determine the chiral and diameter distributions of aqueous suspended samples within seconds. Fluorescence imaging techniques allow the observation and tracking of individual SWNT in dilute solid and fluid samples with time resolutions of ca. 2 s. Finally, spectral and near-infrared imaging methods have been developed for detecting SWNT at low concentrations in biological surroundings. This topic is illustrated with fluorescence data revealing pristine nanotubes that have been taken up by macrophage-like cells in culture. SWNT fluorescence is also observed within living *Drosophila* larvae that have been eaten food laced with nanotubes.

#### 10:45 AM HH10.2

##### **Antenna Effects and Visible Light Spectroscopy of Aligned Carbon Nanotubes.**

Yang Wang<sup>1</sup>, K. Kempa<sup>1</sup>, B. Kimball<sup>2</sup>, J. B. Carlson<sup>2</sup>, G. Benham<sup>3</sup>, W. Z. Li<sup>4</sup>, T. Kempa<sup>5</sup>, J. Rybczynski<sup>1</sup>, A. Herczynski<sup>1</sup> and Z. F. Ren<sup>1</sup>; <sup>1</sup>Physics, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>US Army, Natick Soldier Center, Natick, Massachusetts; <sup>3</sup>MegaWave Corporation, Boylston, Massachusetts; <sup>4</sup>Florida International University, Miami, Massachusetts; <sup>5</sup>Chemistry, Boston College, Chestnut Hill, Massachusetts.

Spectroscopic measurements in visible frequency has been pursued on aligned carbon nanotubes in random and periodic arrays. The nanotubes showed strong interaction to the incident light due to the antenna effects (polarization effect and length matching effect) of individual nanotubes of the random arrays and 2D hexagonal lattice structure of the periodic arrays. Each aligned carbon nanotube appears to act as a metallic pillar and respond to visible light due to its nanoscale morphology. The length matching antenna effect of the random nanotube arrays is of great potential in optoelectronics including THz and IR detectors, while the periodic nanotube arrays are ideal photonic band gap crystals for applications such as optical switching, negative index of refraction, etc.

#### 11:00 AM HH10.3

##### **Exciton Relaxation in Single Wall Carbon Nanotube by sub-20 fs Time Resolved Spectroscopy.**

Guglielmo Lanzani<sup>1</sup>, Moreno Meneghetti<sup>2</sup>, Enzo Menna<sup>2</sup>, Giulio Cerullo<sup>1</sup>, Cristian Manzoni<sup>1</sup> and Alessio Gambetta<sup>1</sup>; <sup>1</sup>physics, Politecnico di milano, Milan, Italy; <sup>2</sup>Chemical science, University of Padova, Padova.

SWNT obtained by the HiPco methodology and functionalised with PEG chains via amide bonds prepared embedded PMMA were studied with pump-probe spectroscopy by using ultra-short pulses in the visible and near infrared, with time duration of 7 fs and 20 fs respectively. The primary event of exciton relaxation was time resolved, providing a time constant of 40 plus/minus 5 fs, associated to photo-bleaching recovery, which is assigned to inter-band relaxation within semiconducting NT. Pumping in different region of the absorption spectrum provides a more complete description. The following relaxation process shows a broad distribution in time constant, consistent with the inhomogeneous broadening of the sample, in substantial agreement with previous studies. When using the shortest pulses (sub-10 fs) coherent phonons are clearly detected in the transmission difference traces. A radial breathing mode at 250 wavenumber is observed, with dephasing of 1.2 ps. Discussion on the assignment and possible future development based on the exploitation of coherent control will be presented.

#### 11:15 AM HH10.4

##### **Localized Spectral Analysis of Doped and Undoped SWNTs using Near-Field Raman Spectroscopy.**

Neil Anderson<sup>1</sup>, Achim Hartschuh<sup>3</sup>, Lukas Novotny<sup>1</sup> and Apparao M. Rao<sup>2</sup>; <sup>1</sup>Institute of Optics, University of Rochester, Rochester, New York; <sup>2</sup>Physics & Astronomy, Clemson University, Clemson, South Carolina; <sup>3</sup>Physikalische Chemie, Universitat Siegen, Siegen, Germany.

We use near-field Raman imaging and spectroscopy to study localized vibrational modes along individual single-walled carbon nanotubes (SWNTs). Our approach relies on the strongly enhanced field near a laser-irradiated gold tip. This enhanced field acts as our Raman excitation source. The spatial resolution is determined by the tip size and is on the order of 20nm. Using this technique we uniquely map spectral changes along the tubes axis for various Raman modes with high spatial resolution. Our studies focused on the effects of doping such SWNTs with elemental boron and nitrogen on the four main Raman active modes, namely the RBM, G, G' and D bands. The dopant concentration ranged from 0 to 10 at %. The incident laser intensity required to observe Raman signals (with the same S/N) ratio

increased with increasing dopant concentration. Our results show a dramatic loss of resonance with increased dopant concentration present in the nanotube. We attribute this loss in resonance scattering properties due to dopant-induced changes in the electronic properties of SWNTs.

#### 11:30 AM HH10.5

##### **Ultrafast Transient Absorption Spectroscopy Investigations of Excited State Dynamics in SWNT/Polymer Composites.**

David Styers-Barnett<sup>1</sup>, Stephen Ellison<sup>1</sup>, Cheol Park<sup>2</sup>, Kristopher Wise<sup>2</sup> and John Papanikolas<sup>1</sup>; <sup>1</sup>Chemistry, University of North Carolina-Chapel Hill, Chapel Hill, North Carolina; <sup>2</sup>National Institute of Aerospace NASA, Langley Research Center, Hampton, Virginia.

Wavelength-resolved femtosecond transient absorption spectroscopy is used to study the electronic dynamics of a series of single-walled carbon nanotube/polymer composite films in order to understand the environment's role in the excited state dynamics. Visible photoexcitation of nanotubes creates excitons through transitions between van Hove singularities. The electron - hole ( $e - h$ ) pairs give rise to sharp features in the nanotube transient spectra that decay in amplitude and exhibit rapid spectral shifts. The observed decay of these signals reflects ( $e - h$ ) recombination on both short (fs) and long (ps) time scales. Spectral shifts could reflect structural and/or electronic relaxation. The positions of these features and the rates of decay depend on the polymer environment and the type of nanotube present. Nanotubes produced from different methods have dramatically different excited state spectra, while changes in the polymer environment alter the band positions and decay rates. Solution phase data provides further information on the role of the environment in nanotube excited states. The creation of surface excitons in nanotubes offers a unique opportunity to understand how inhomogeneous surroundings affect the dynamics of the excitonic excited state.

#### 11:45 AM HH10.6

**Anisotropic Saturable Absorption of Single Wall Carbon Nanotubes Aligned in Polyvinyl Alcohol.** Aleksey G. Rozhin<sup>1</sup>, Youichi Sakakibara<sup>1</sup>, Hiromichi Kataura<sup>1</sup>, Shun Matsuzaki<sup>2</sup>, Kohtaro Ishida<sup>2</sup>, Yohji Achiba<sup>3</sup> and Madoka Tokumoto<sup>1,2</sup>; <sup>1</sup>AIST JAPAN, Tsukuba, Japan; <sup>2</sup>Tokyo Univ. Sci., Noda, Japan; <sup>3</sup>Tokyo Metropolitan Univ., Hachioji, Japan.

Recent research advances in optical functions of carbon nanotubes (CNTs) have revealed attractive novel applications for optoelectronics. Especially, the saturable absorption (SA) function of CNTs have opened up promising applications for optical telecommunication, such as mode-locker in short pulse laser [1], ASE noise suppressor [2] and all-optical switch [3]. The SA function can be further improved by a material design using alignment of CNTs. Because the optical transition moments are strongly anisotropic on the tube axis, using the aligned CNTs and the polarized excitation light can enhance the transition probability between the valence band and the conduction band. In this work, we aligned single wall carbon nanotubes (SWNTs) in a polyvinyl alcohol (PVA) film, and investigated the anisotropic optical absorption (OA) and the SA properties. For the film preparation, first we used surfactant-assisted ultrasonication of laser ablation SWNTs in water [4]. To this solution the PVA powder was added and dissolved. The resulted solution was dried for a week. The obtained freestanding film was mechanically stretched to the ratio of 6 under the heating. The film showed the semiconductor (at about 1.8 and 1.0  $\mu\text{m}$ ) and metallic (about 0.7  $\mu\text{m}$ ) SWNTs absorption bands. With a polarized light, a strong anisotropy of OA, reaching to the E(parallel)/E(normal) absorbance ratios of 5.6, 3.9 and 3.1 at 1.8, 1.0 and 0.7  $\mu\text{m}$  respectively, was observed. The anisotropic SA property was investigated by using a polarized femtosecond fiber laser (Imra Femtolite 780, B-60, pulse width 100 fs, repetition 48 MHz) at the wavelength of 1.8  $\mu\text{m}$ . The relative decrease in absorbance due to SA was measured by changing the polarization angle using the same laser intensity (190 MW/cm<sup>2</sup>). At lower polarization angles the absorbance decrease of the stretched film became larger than that of the unstretched film, and at higher angles inversely. This indicates that at the parallel configuration the stretched film has a better saturation property. [1] S. Y. Set et. al, OSA Trends in Optics and Photonics (TOPS) Vol.86, Optical Fiber Communication Conference, Technical Digest, Postconference Edition (Optical Society of America, Washington, DC, 2003), pd.44. [2] Sakakibara et. al, post-deadline paper Th.4.2.5 presented at 29th European conference on Optical Communication (ECOC'03), Rimini, Italy, 2003. [3] Y.-C. Chen et. al, Appl. Phys. Lett. 81 (2002) 975. [4] A.G. Rozhin, et.al, Thin Solid Films, in press.

SESSION HH11: Optical Properties II  
Thursday Afternoon, December 2, 2004  
Room 312 (Hynes)

#### 1:30 PM HH11.1

##### **Charge Transfers in Suspensions and Solutions of Single Wall Carbon Nanotubes, a Raman Study.** Nicolas Izard<sup>1</sup>, Alain Penicaud<sup>2</sup>, Philippe Poulin<sup>2</sup>, Pierre Petit<sup>3</sup> and Anglaret Eric<sup>1</sup>;

<sup>1</sup>GDPC, Universite Montpellier II, Montpellier, France; <sup>2</sup>CRPP, Universite Bordeaux I, Pessac, France; <sup>3</sup>Institut Charles Sadron, Strasbourg, France.

Homogeneous dispersions of single wall nanotubes in a fluid are required for optical applications and materials science. Fonctionnalization leads to changes in the structure of the nanotubes. An alternative and popular route is the preparation of aqueous suspensions in sodium dodecyl sulfate. From Raman studies, we report evidences that nanotubes are charged in such aqueous suspensions. On the other hand, a new route was recently explored to prepare solutions of nanotubes, using chemical reduction in polar organic solvents. Charge transfer in such solutions was also probed by Raman spectroscopy. We will show that doping nanotubes is an alternative way to prepare solutions of nanotubes without changing their chemical structure and length.

#### 1:45 PM HH11.2

##### **Resonance Raman Spectroscopy to Study and Characterize Defects on Carbon Nanotubes and other Nano-Graphite Systems.** Ado Jorio<sup>1</sup>, Luiz Gustavo Cancado<sup>1</sup>, Mauricio Souza<sup>1</sup>,

Cristiano Fantini Leite<sup>1</sup>, Marcos A. Pimenta<sup>1</sup>, Georgii G. Samsonidze<sup>2</sup>, Shin Grace Chou<sup>3</sup>, Gene Dresselhaus<sup>4</sup>, Mildred S. Dresselhaus<sup>2,5</sup>, Alexander Grueneis<sup>6</sup> and Riichiro Saito<sup>6</sup>; <sup>1</sup>Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Minas Gerais, Brazil; <sup>2</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>4</sup>Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>5</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>6</sup>Department of Physics, Tohoku University and CREST JST, Sendai, Japan.

The use of Resonance Raman Spectroscopy (RRS) to study and characterize single wall carbon nanotubes (SWNTs) is discussed, focusing on preliminary efforts for the development of the RRS to characterize defects on SWNTs. The disorder induced D-band as well as the intermediate frequency modes (IFMs) appearing between the RBM and the D/G spectral region are addressed. Unusual step-like dispersive behavior is observed for the IFMs, related to quantum confinement of electrons and phonons [1]. Single versus double resonance nature of the G-band spectra are addressed [2]. RRS on nano-graphite ribbons [3] and on a step-like defect on highly ordered pyrolytic graphite (HOPG) [4] sheds light into the problem. [1] C. Fantini, A. Jorio, M. Souza et al., Phys. Rev. Letters, in press. [2] M. Souza, A. Jorio, C. Fantini et al., Phys. Rev. B Rapid Communication, in press. [3] L. G. Cancado, M. A. Pimenta, A. Jorio et al., Phys. Rev. Letters, in press. [4] L. G. Cancado, M. A. Pimenta, B. R. A. Neves, M. S. S. Dantas and A. Jorio, Phys. Rev. Letters, submitted.

#### 2:00 PM HH11.3

##### **Spectroscopic Analysis of Excitons in Solubilized**

**Single-Walled Carbon Nanotubes.** Marcus Jones, Chaiwat Engtrakul, Wyatt Metzger, Arthur J. Nozik, Michael J. Heben and Garry Rumbles; National Renewable Energy Laboratory, Golden, Colorado.

Recent theory [1] has highlighted the importance of electron-hole ( $e^-h^+$ ) correlation effects and the formation of excitonic states in selected single-wall carbon nanotubes (SWNTs) that give a more accurate description of SWNT electronic structure than the alternative picture of electron and hole levels and van Hove singularities. With reference to this excitonic picture of excited states in SWNTs, we describe a detailed analysis of steady state and time-resolved photoluminescence (PL) data derived from measurements made on a broad distribution of SWNT tube species in aqueous solution. The functional form of the PL lineshape from individual SWNT species is found to contain a significant Lorentzian component and the Stokes shift is observed to be very small ( $< 8$  meV); which suggests an excitonic dephasing mechanism that is largely decoupled from surrounding solvent and surfactant molecules. The PL quantum yield (PLQY) of two SWNT species is determined to be  $10^{-5}$  when branching of carrier relaxation pathways [2] is ignored. It is suggested that this is much lower than the true value due to quenching of the PL in bundles by metallic tubes. Time-resolved PL measurements performed on a series of tube species reveal a dominant, luminescence lifetime component of 130ps which is significantly longer than previously reported [2]. These measurements yield a long natural radiative lifetime in excess of  $10\mu\text{s}$  that is inconsistent with a strong absorption coefficient and a small Stokes shift. Combining the measured PL lifetime with a predicted natural radiative lifetime of

20ns suggests that the true PLQY for an unbundled tube is  $6.5 \times 10^{-3}$ , and the ratio of the measured PLQY to this value could be a reasonable measure of the proportion of single vs. bundled SWNTs in solution. Finally, deconvoluted PL excitation spectra are produced for individual SWNT species, and the appearance of a higher-energy excitonic sub-band is discussed. These studies form a foundation for our long-term objective: to study the interactions between SWNTs and colloidal semiconductor quantum dots. [1] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, et al., *Applied Physics a-Materials Science & Processing* 78, 1129 (2004). [2] Y. Z. Ma, J. Stenger, J. Zimmermann, et al., *Journal of Chemical Physics* 120, 3368 (2004).

#### 2:15 PM HH11.4

##### Low Temperature Photoluminescence and Photoluminescence Excitation Studies of Individual Carbon Nanotubes.

Han Htoon, M. J. O'Connell, S. K. Doorn and V. I. Klimov; Los Alamos National Lab, Los Alamos, New Mexico.

Semiconducting, single walled carbon nanotubes have large potential for a wide variety of optoelectronic applications. In order to fully exploit this potential, it is essential to understand the intrinsic nature of fundamental optical excitations in nanotubes. Here we report the first low-temperature photoluminescence (PL) and PL excitation (PLE) studies of individual nanotubes. Single-nanotube PL spectra reveal atomically sharp peaks (down to 250 meV line widths) that exhibit continuous variations in the intensity and the spectral position in response to small variations in the immediate nanotube environment. The positions of the PL peaks are distributed continuously within the ensemble "single-species" PL bands that have previously been attributed to nanotubes with the same structural characteristics. This finding indicates the existence of numerous nanotube sub-species within "single-species" ensembles [1]. We observe two distinctly different PL line shapes (symmetric vs. asymmetric), which we attribute to the presence of unintentionally doped nanotubes along with undoped species. While undoped nanotubes produce symmetric lines typical of one-dimensional (1D) excitons, the emission of doped nanotubes is characterized by significant asymmetry due to the effect of the Fermi-edge singularity. We also conduct low temperature PLE studies of individual nanotubes to gain direct information on the structure of high-energy electronic states and the mechanisms for optical absorption. In the range from 0 to 550 meV (as measured with respect to the lowest, emitting state), we observe multiple absorption peaks that can be attributed to phonon assisted transitions into the ground exciton state. In nanotubes of relatively large diameters (emission wavelength longer than 1.1  $\mu\text{m}$ ), we also observed the absorption feature due to the second excitonic state. Surprisingly, the intensity of this feature is comparable to the intensity of the phonon assisted bands. Furthermore, the excited-state absorption features are characterized by significant broadening ( $>35\text{meV}$ ). Together with observations of intense phonon assisted bands, the latter result is indicative of extremely strong exciton-phonon coupling in nanotubes, which gives rise to ultra-fast relaxation of excited electronic states and hence significant lifetime transition broadening. In summary, our findings suggest that as a result of strong electron-phonon interactions, the structure of optical transitions in nanotubes is much more complex than in a simple framework, which assumes that absorption is dominated by singularities in 1D energy spectrum. [1] H. Htoon, et al., *Phys. Rev. Lett.* (July, 2004).

SESSION HH12: Functionalization and Doping  
Thursday Afternoon, December 2, 2004  
Room 312 (Hynes)

#### 3:00 PM HH12.1

##### Charge Transfer and Fermi-Level Shift in p-Doped

Single-Walled Carbon Nanotubes. J. E. Fischer, W. Zhou, J. Vavro and N. M. Nemes; MSE Dept., U. Penn., Philadelphia, Pennsylvania.

The electronic properties of chemically p-doped single-walled carbon nanotubes (SWNTs) were studied using multiple techniques. Raman spectroscopy, resistivity, thermoelectric power and reflectivity measurements give consistent results for the charge transfer and Fermi-level shift ( $\Delta E_F$ ) of acid doped nanotubes. We find  $\Delta E_F$  approximately 0.35 eV in nitric acid doped SWNT and approximately 0.5 eV in sulfuric acid doped SWNT. Using these  $\Delta E_F$  values in a detailed Raman data analysis, we show that the change of Raman spectra upon chemical doping can be relatively well explained by the variation in Raman resonance condition as  $E_F$  is varied. In particular, we find no evidence for selective doping based on tube diameters or distinguishing metallic and semiconducting tubes.

#### 3:15 PM HH12.2

##### Atomic-Level Investigation of Fluorination and Defluorination

of Carbon Nanotubes. Dharmpal Takhar<sup>1</sup>, Zhenning Gu<sup>2</sup>, John L. Margrave<sup>2</sup> and Kevin F. Kelly<sup>1</sup>; <sup>1</sup>ECE, Rice University, Houston, Texas; <sup>2</sup>Chemistry, Rice University, Houston, Texas.

There is a great deal of interest in the functionalization, in particular fluorination, of carbon nanotubes for solvation and subsequent chemical reactions. Previous investigations used STM to monitor the percentage of sidewall fluorination of laser-vaporized single-walled carbon nanotubes, revealing that the fluorine produced circumferentially banded domains across the nanotube. We have performed STM investigations of similarly fluorinated HiPCO-formed nanotubes and found a similar banding structure. The atomic-scale fluorine coverage on the fluorinated SWNTs was observed as function of fluorine content. Since recent research suggests that high temperature annealing of fluorinated nanotubes may be a method for controlled cutting, we have annealed fluorinated nanotubes in ultra-high vacuum and observed nanometer scale changes in their morphology. Annealing at a temperatures from 250 C upwards initiates defluorination in large areas on the nanotubes which continues to 700 C. Continued annealing results in the total removal of fluorine from the tubes, while leaving behind a large number of small defect sites. We believe such sites are where the cutting of the nanotubes is initiated.

#### 3:30 PM HH12.3

##### Property control of carbon nanotubes by fluorination.

Hidekazu Touhara<sup>1</sup>, Shinji Kawasaki<sup>2</sup>, Fujio Okino<sup>1</sup> and Hiromichi Kataura<sup>3</sup>; <sup>1</sup>Department of Chemistry, Shinshu University, Ueda, Japan; <sup>2</sup>Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Japan; <sup>3</sup>Nanotechnology Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Introduction Fluorination is one of most effective chemical methods to modify and control structural and physical properties of carbon materials. Fluorination of carbon nanotubes (CNTs) is also effective for their property control. In this paper, we report fluorination reaction of single-walled carbon nanotubes (SWNTs), structure, electrochemical and thermal properties. Fluorination of single-walled carbon nanotubes, and structure of fluorotubes. High purity end-closed SWNTs (C-SWNTs) were prepared by the laser-ablation method using a metal-carbon composite rod as a target. The diameter of the tubes was 1.4-1.5 nm. Open-end SWNTs (O-SWNTs) were obtained by a heat treatment of C-SWNTs at 698 K in the air. Fluorination was carried out using 1 atm elemental fluorine in a temperature range RT-523 K. The composition of the open-end fluorotubes, fluorinated at 301, 473, and 523 K were CF0.28, CF0.45 and CF0.51, respectively. TEM examinations showed that bundle structure and tubular morphology of pristine SWNTs were preserved up to 473 K fluorination. Further fluorination at 523 K led to the breaking of C-C bonds and, hence, the partial destruction of tubes were observed. Upon fluorination, the triangular lattice constant a 1.74 nm of pristine tube increased up to ca. 2 nm. It is noteworthy that the lattice constants of closed-end fluorotubes always larger than those of open-end fluorotubes. This result indicates a simultaneous fluorination of both external and internal surfaces of O-SWNTs dose occur. The changes in Raman spectra of C-SWNTs and O-SWNTs also support the different fluorination process between closed- and open-end tubes. RBMs were observed for all the open-end fluorotubes whereas closed-end tubes with F/C=0.48 showed no RBMs. Electrochemical and thermal properties of fluorotubes. The discharging performance of fluorotubes was studied on Li/1M-LiClO<sub>4</sub>-(ECD+EC)/ F-SWNTs cells (F-SWNTs=fluorotubes prepared by RT-473K fluorination of HiPco-tubes) under a current density of 100  $\mu\text{A}/\text{cm}^2$ . The OCV value of fluorotubes are ca. 0.7 V higher than that of graphite fluoride (CF)<sub>n</sub>, which vividly reflects the lower C-F bond energy in the fluorotubes. The discharge potential of the fluorotubes decreases with increasing the cathode utilization. In comparison, (CF)<sub>n</sub>, as is well known, the discharge potential of electrode is flat until the cathode utilization reaches 80 %. It was also observed that the OCV of fluorotubes decreases with increasing the cathode utilization. These results clearly indicate that the discharge reaction of fluorotubes is quite different from that of (CF)<sub>n</sub>, and that the discharge of fluorotube electrode proceeds homogeneously, forming discharged product CF<sub>0.51-0.5x</sub>, where the fluorine concentration decreases with the discharge ratio  $x(0.0 \leq x \leq 1.0)$ . Thermal property and reversible defluorination of fluorotubes to pristine SWNTs will also be reported.

#### 3:45 PM HH12.4

##### Noncovalent Engineering of Carbon Nanotube Surfaces.

Jian Chen<sup>1</sup>, Rajagopal Ramasubramaniam<sup>1</sup> and Haiying Liu<sup>2</sup>; <sup>1</sup>Zyveq Corporation, Richardson, Texas; <sup>2</sup>Department of Chemistry, Michigan Technological University, Houghton, Michigan.

Single-walled carbon nanotubes (SWNTs), due to their novel structural, thermal, electrical, mechanical and optical properties, are expected to find applications in many fields. In order to take

advantage of the full potential of SWNTs, it's necessary to address the fundamental issues (cutting, solubilization, chemical functionalization, purification, manipulation, and assembly) in molecular engineering of carbon nanotubes. Pristine SWNTs are generally insoluble in common solvents, and difficult to functionalize controllably. We recently reported a non-wrapping approach to noncovalent engineering of carbon nanotube surfaces by short, rigid functional conjugated polymers, poly(aryleneethynylene)s (PPE) (Ref. 1). This method enables the superior control of the relative placement of functionalities on the nanotube surface while still preserving nearly all of the nanotube's intrinsic properties. We report here that the rich functional chemistry of PPE allows us to prepare various SWNTs with tunable functionalities and solubilities. The PPE-functionalized SWNTs can be solubilized in various organic solvents and water. The soluble SWNTs with specific functionalities can be used as novel gelators that can gelate various organic solvents such as chloroform, 1-methyl-2-pyrrolidinone etc. The resulting SWNT gel may find applications in high strength nanotube fibers and high surface area catalyst supports. Our new approach can introduce various neutral and ionic groups onto the carbon nanotube surfaces. We will also report the defunctionalization of PPE-functionalized SWNTs. We will discuss our acid-free, nonchromatographic approach towards the large-scale separation of metallic from semiconducting SWNTs. The Raman, Vis-NIR spectra as well as electrical conductivity measurement show that it's possible to separate metallic from semiconducting SWNTs by noncovalent functionalization chemistry. Reference: 1. Chen, J. et al. *J. Am. Chem. Soc.* 2002, 124, 9034-9035.

#### 4:00 PM HH12.5

**Covalent Bonding of Nano-entities with NH<sub>2</sub> Groups onto Multi-walled Carbon Nanotubes.** Kuiyang Jiang<sup>1</sup>, Xinjie Zhang<sup>2</sup>, Linda S. Schadler<sup>1</sup> and Richard W. Siegel<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Hyperion Catalysis International Inc., Cambridge, Massachusetts.

Carbon nanotubes exhibit remarkable structural, electrical and mechanical properties, while proteins and dendrimers have exclusive selectivity or optical properties. The combination of their properties could result in a wide range of applications in biosensors, bio-fuel cells, biodetectors and light-electricity converters. To realize these applications, controlled structures have to be assembled as required. In this study, we report the controlled assembly of some novel nanostructured materials using ferritin, bovine serum albumin (BSA), and PAMAM dendrimer as examples. These nano-entities were chemically bonded onto multi-walled carbon nanotubes (MWNTs) through a two-step process of diimide-activated amidation. First, carboxylated MWNTs were activated by N-ethyl-N'--(3-dimethylaminopropyl) carbodiimide hydrochloride (EDAC), forming a stable active ester in the presence of N-hydroxysuccinimide (NHS). Second, the active ester was reacted with the amine groups on the ferritin or BSA proteins, or the PAMAM dendrimers, forming an amide bond between the MWNTs and the nano-scale entities. This two-step process avoids intermolecular conjugation and guarantees the uniform attachment on carbon nanotubes. TEM and AFM measurements clearly confirmed the successful attachment. This approach provides a universal and efficient method to attach nano-entities with NH<sub>2</sub> groups to carbon nanotubes at ambient conditions. This work was supported in part by the Nanoscale Science and Engineering Initiative of the U.S. National Science Foundation under NSF Award Number DMR-0117792.

#### 4:15 PM HH12.6

**Self-Organization of Semiconductor Quantum Nanocrystals on Carbon Single-Wall Nanotubes into Close-Packed Linear Arrays.** Chaiwat Engrakul<sup>1</sup>, Jovan M. Nedeljkovic<sup>1</sup>, Yong-Hyun Kim<sup>1</sup>, Marcus Jones<sup>1</sup>, Randy J. Ellingson<sup>1</sup>, Mark C. Hanna<sup>1</sup>, Scott P. Ahrenkiel<sup>1</sup>, Kim M. Jones<sup>1</sup>, Mark F. Davis<sup>1</sup>, Timothy J. McDonald<sup>1</sup>, Kale J. Franz<sup>1</sup>, Thomas Gennett<sup>2</sup>, Anne C. Dillon<sup>1</sup>, Katherine H. Gilbert<sup>1</sup>, Philip A. Parilla<sup>1</sup>, Jeff L. Alleman<sup>1</sup>, Shengbai Zhang<sup>1</sup>, Olga I. Micic<sup>1</sup>, Garry Rumbles<sup>1</sup>, Arthur J. Nozik<sup>1</sup> and Michael J. Heben<sup>1</sup>; <sup>1</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>2</sup>Chemistry, Rochester Institute of Technology, Rochester, New York.

The aim of our research is to provide a detailed understanding of the optical and electronic properties of semiconductor nanocrystal / carbon single-walled nanotube hybrid nanostructures. The integration of semiconductor nanocrystals (NCs) onto carbon nanotubes (CNTs) affords a method for combining a wide range of chemical systems with CNTs to potentially do useful photochemical work. In order to utilize the properties of these nanostructures, the spatial configurations of NCs on carbon single-walled nanotube (SWNT) surfaces, i.e., inter-NC distance and NC orientation, must be controlled in a straightforward manner. Recent progress in our program has involved the development of a synthetic method for constructing well-defined and organized NC / SWNT assemblies. The synthetic protocol avoids the need for covalent chemical modification of the CNT surface and

utilizes purified, laser grown SWNTs, and several different types of NCs. Specifically, InP and CdSe NCs were found to strongly adsorb onto the surfaces of SWNTs due to favorable van der Waals forces. Transmission electron microscopy was used to characterize the NC / SWNT assemblies, and revealed that the surfaces of the SWNT bundles template the adsorption of the NCs from solution into linear arrays. The energetics of binding and linear ordering were modeled using an atomistic pair-wise summation of the Lennard-Jones 12-6 potentials for the NC-SWNT and NC-NC interactions. In addition, efforts to determine the nature and degree of coupling between the NC and SWNT surfaces have led to methods for combining dispersions of surfactant-stabilized SWNTs with water-soluble NCs. These stable NC / SWNT dispersions are amenable to time-resolved and steady-state spectroscopic investigations.

#### 4:30 PM HH12.7

**N- and B-Doped Carbon Nanotubes and Nanostructures via Pyrolysis of Aerosols.** Nicole Grobert, <sup>1</sup>Department of Materials, Oxford University, Oxford, United Kingdom; <sup>2</sup>Max-Planck-Institut für Metallforschung, Stuttgart, Germany.

In recent years, various carbon nanotube synthesis techniques have been reported. With the development of the aerosol pyrolysis it is now possible to produce large quantities of pure and aligned high quality carbon nanotubes. Furthermore, depending on the precursor, modified carbon nanotubes can also be generated. For example, the pyrolysis of homogeneously dispersed aerosols generated from benzylamine/ferrocene solutions at 950 C using an ultrasonic spraying device yields large quantities (several grams/30 min) of pure and well-aligned CN<sub>x</sub> nanotubes (30-130 microns long, 10-200 nm outer diameter). Scanning and transmission electron microscopy (SEM, TEM) reveal that the products are generally arranged in carpet-like flakes containing high yields of bamboo-like nanotubes and are almost free of any by-products, such as polyhedral particles or amorphous carbon. High-resolution electron energy loss spectroscopy (HREELS) line-scans and elemental mapping studies reveal that the carbon nanotubes are uniformly doped with N. In addition, the spray-pyrolysis of ferrocene/xylene/triethylborane -based mixtures at 900 C results in a novel sea-cucumber-like structure containing carbon and boron. SEM studies show that these structures are hollow structures with diameter between 100 and 500 nm and lengths varying from 30 to 40 microns. HRTEM and EELS studies show that the hollow structures are partly filled with iron. They are formed by a more graphitic internal core, which hardly contains any B. This core is coated by a more disordered B-containing C material. The amount of B in this coating is around 3 at.% of B, as determined by EELS. In addition, at this pyrolysis temperature, the growth of open-ended tubular nanostructures (30-40 nm diameter; 100-200 nm length) on the surface of the sea-cucumber-like structure is observed. These tubular nanostructures are not very graphitic and they present a similar composition to the coating of the sea-cucumber-like structure (around 3 at.% of B). The study of different pyrolysis temperatures show that the growth of these tubular nanostructures and the boron content are depending on the pyrolysis temperature. Finally, preliminary results corresponding to oxidation resistance studies are presented. With this method it is now possible to explore the chemical and physical properties of CN<sub>x</sub> nanotubes and B-doped carbon nanostructures and their composite materials.

#### 4:45 PM HH12.8

**Selective End Functionalization of Carbon Nanotubes by Sidewall Protection in Aligned Membrane Structures.** Nitin Chopra, Mainak Majumder and Bruce Jackson Hinds; Chemical and Materials Engineering, Univ. of Kentucky, Lexington, Kentucky.

Carbon Nanotubes (CNTs) are ideal building blocks for novel functional nanostructures. It is critical to functionalize only the ends of CNTs, so that they can be self-directed within patterned device architectures. Ideally each end of the CNT should have different chemical function, and hence selectively connect between two chemically complementary structures. Surfactants and moderately oxidative chemistry affect the entire length of the CNTs making their controlled placement a challenge. To functionalize only the ends of CNTs, we have developed a vertically aligned array of CNTs are impregnated with polystyrene film. Water plasma process selectively oxidizes surface polymer and CNT tips resulting in a membrane structure. Importantly the sidewall length of the CNTs is protected from the oxidation process by the polystyrene film, resulting in CNT oxidation only at their ends. Functionalization chemistry can be performed on the membrane surface, affecting only CNT tips. In fact each side of the membrane can be treated with different functional chemistry, allowing for each end of CNTs to have different chemical functionality. Dissolution of such membranes in toluene and purification results in CNTs with end-functionalization. We demonstrate selective CNT tip-gold nanoparticle hetero structures utilizing well established carbodiimide chemistry by reacting -COOH groups at CNT tips with -NH<sub>2</sub> group of cysteamine (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>2</sub>-SH)



which in turn covalently links to 10 nm diameter gold nanoparticles. Nanoparticles of gold are particularly easy to see by TEM studies, and prove the presence of thiol functional groups. TEM studies showed average nanoparticle density decreases from 526 per  $\mu\text{m}^2$  at the tip to negligible values ( $<7/\mu\text{m}^2$ ) at a location beyond 700 nm, which is about 7% of the total length. EDS of nanoparticle-CNT junctions show a strong peak of S at 2.3 KeV proving functionalization of CNT tips with cysteamine. In addition, FT-IR studies conducted in range of 500 - 4000  $\text{cm}^{-1}$  confirmed presence of carbonyl groups (1630  $\text{cm}^{-1}$ ) from plasma oxidized CNTs as compared to raw CNTs. Cysteamine functionalized CNTs showed a shoulder at 1654  $\text{cm}^{-1}$  indicative of amide bond formation. The ability to functionalize one end of a CNT with thiol functionality and the other end with only carboxyl functionalization was also demonstrated.

SESSION HH13: Poster Session  
Thursday Evening, December 2, 2004  
8:00 PM  
Exhibition Hall D (Hynes)

#### HH13.1

##### **Control of Interfacial Energy between SWNTs and a Silicon Dioxide Substrate by Chemical Surface Modification using SAM Films.**

Yuji Miyato<sup>1</sup>, Kei Kobayashi<sup>2</sup>, Toshihisa Horiuchi<sup>1</sup>, Hiroyumi Yamada<sup>1,3</sup> and Kazumi Matsushige<sup>1,2</sup>; <sup>1</sup>Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; <sup>2</sup>International Innovation Center, Kyoto University, Kyoto, Japan; <sup>3</sup>Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Kyoto, Japan.

Carbon nanotubes (CNTs), especially single wall carbon nanotubes (SWNTs), have been intensively studied for their applications to electronic devices. In fact, a large number of investigations have been made on carbon nanotube field effect transistors (CN-FETs) these years, where silicon substrates with dioxide thin film are used in most cases. However, CNTs adhere to a silicon dioxide substrate so strongly that the physical and the chemical properties of CNTs can be changed. To avoid this problem, CNTs are sometimes suspended in space between electrodes or pillars. Nevertheless, the contact geometry of CNTs lying on the substrate is remarkably important in terms of not only mechanical stability but also the electronic control of CNTs by changing the substrate bias. In this study we propose a new solution to decrease the CNT interfacial interaction by chemical surface modification of the substrate. Surface energy of the  $\text{SiO}_2$  substrate can be decreased by covering it with a suitable self-assemble monolayer (SAM) film. We used hexamethyldisilazane (HMDS) in this experiment. HMDS vapor reacts with hydroxyl groups on the  $\text{SiO}_2$  surface and then trimethylsiloxane (TMS) monolayer film are made. We fabricated several pairs of metal electrodes on the silicon dioxide substrate in advance. Then we put this substrate with a small cup of liquid HMDS into a sealed container and heated them. Finally TMS films were formed on the substrate except the areas of the electrodes. In addition, we studied the control of the orientation of SWNTs using the AC dielectrophoresis method, where SWNTs in solvent can be extended along an applied AC external electrical field because of their induced dipole moment. After the solvent evaporated, SWNTs were deposited and bridged over the electrodes to which we applied the ac voltage. One of the advantages in this method is that device fabrication processes do not include any high-temperature one. We successfully bridged SWNTs between a certain pair of electrodes even after the TMS film deposition on the substrate. We evaluated the effect of the surface chemical modification, making a comparison between SWNTs on ordinary substrate and modified one. We manipulated SWNTs on both  $\text{SiO}_2$  and SAM-modified substrates by contact-mode Atomic Force Microscopy (AFM) and studied the minimum contact load required to move SWNTs. The contact load was increased while the tip was scanned over SWNTs. We also checked whether or not SWNTs were removed from the substrate by ultrasonic cleaning for both substrates. Furthermore, the electrical properties of SWNTs on the modified substrate were investigated. We measured I-V characteristics of SWNTs bridged over the electrodes and mapped surface potential along the SWNTs with a DC bias voltage by Kelvin probe force microscopy (KFM).

#### HH13.2

**Synthesis and characterization of Y-junction singlewall carbon nanotubes.** Young Chul Choi and Wonbong Choi; Mechanical and Materials Engineering, Florida International University, Miami, Florida.

Y-junction singlewall carbon nanotubes (SWNTs) are synthesized on thermally oxidized Si substrates by chemical vapor deposition. Mo-doped Fe nanoparticles supported by aluminum oxide particles are used as catalysts for the growth of Y-junction singlewall carbon nanotubes. Most of synthesized nanotubes are found to have branches,

forming Y-junctions. Transmission electron microscopy confirmed the formation of singlewalled structures with diameters of 2-5 nm. A Y-junction consists of three individual SWNTs with different diameters. Radial breathing mode peaks in Raman spectra show that our sample has both metallic and semiconducting nanotubes, indicating the possible formation of Y-branching with different electrical properties. The different electrical properties of branch and stem, caused by different diameters, can be utilized in nanoscale three-terminal electronic devices. The growth mechanism of Y-junction is proposed based on experimental results.

#### HH13.3

**Integration Of Carbon Nanotubes Into Device Structures.** Bert Lagel, Joshua David Schumacher, Nhan Nguyen, Bojana Zivanovic and Rudy Schlaf; Electrical Engineering, University of South Florida, Tampa, Florida.

Carbon nanotubes have shown promising properties for applications in electronic circuits and other device structures. Several device structures have been demonstrated in recent years by manual manipulation of single nanotubes. The intergration of large numbers of nanotubes on wafer size substrates, however, has been a challenge. Our approach addressing this issue utilizes nano-patterning methods in combination with plasma enhanced chemical vapor deposition (PECVD) to directly assemble carbon nanotubes on wafer structures. A secondary formation step is used to actually form device structures connecting the nanotubes to electrode structures. We present first results demonstrating the feasibility of our approach. Electrode structures were prepared using multi-step electron beam lithography processes. Carbon nanotubes were grown in pre-defined locations, and contact formation procedures were carried out to establish two and three-terminal contact structures.

#### HH13.4

**Direct Measurement of Band Bending across Metal-Carbon Nanotube Interface from Carbon Nanotube Field Effect Transistors.** Youngsik Song and Jaewu Choi; Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

The characteristics of carbon nanotube FET are very unique unlike conventional Si based metal oxide semiconductor field effect transistor (MOSFET). In particular, metal and carbon nanotube interface plays an important role in the transport properties. The influence of the interface to the electrical transport behaviors are studied from carbon nanotube FET. Carbon nanotube FET was fabricated by directly growing carbon nanotube between two metal electrodes. The metal electrodes consist of multi stacked metal layers where catalyst layer is in between two metal layers. Growth direction was controlled by applying in-situ electric field during thermal chemical vapor deposition. Chemical composition is analyzed by x-ray photoemission spectroscopy. Band offset at the interface is measured by scanning tunneling spectroscopy. Finally, band bending along the carbon nanotube is studied by scanning tunneling spectroscopy. From these studies, we directly observe Schottky barrier height and depletion width. This agrees with parameters found out from curve fitting of transport data.

#### HH13.5

**Light Emission and Sublimation of Carbon Nanotubes Induced by Field Electron Emission from Oriented MWCNT Arrays.** Anvar A. Zakhidov<sup>1</sup>, Alex Zakhidov<sup>2</sup>, Alexander N. Obraztsov<sup>2</sup>, Rashmi Nanjundaswamy<sup>1</sup>, Sergei Lee<sup>1</sup>, Austin Cunningham<sup>1</sup>, Mei Zhang<sup>1</sup> and Mike Sampson<sup>1</sup>; <sup>1</sup>Physics, University of Texas at Dallas, Richardson, Texas; <sup>2</sup>Physics, Moscow State University, Moscow, Russian Federation.

The spark-type emission of light accompanied by sublimation of nanotubes from cathode has been detected above threshold electron emission currents from oriented arrays of multiwalled carbon nanotubes (MWCNT). The spectrum of emitted light has been recorded at different electric fields and has been found to depend on the type of applied voltage. DC voltage shows different spectra of emitted light, compared to ac voltage. The spectrum of spark-emitted light taken during the sublimation process shows the presence of iron catalyst lines in the blackbody background. The temperature of nanotubes overheated by emission currents of 100 mA is estimated from light emission spectra to be in the range of 4000-4500 C. Mechanisms of spark light emission and the process of CNT sublimation are proposed and discussed.

#### HH13.6

**A Schottky Photoconductive Diode Based on an Individual C/CN<sub>x</sub> Multi-walled Nanotube Junction.** Yunqi Liu, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

Herein we demonstrate the possibility of creating Schottky-type photoconductive diodes based on an individual C/CN<sub>x</sub> nanotube

junction, and propose a scheme for a phototransistor in which the electric current is governed by light instead of an electric field or magnetic field in conventional electronic devices (e.g., the silicon-based field-effect transistor, FET). The light could make the C/CNx nanotube generate and carry electric current. The nanotube photoconductivity could be modulated by the light intensity. This allows switching the nanotubes between OFF and ON states. In these experiments, the C/CNx multi-walled nanotubes were grown via a continuous chemical vapor deposition (CVD) two-stage process developed in our lab. Their diameters range from 50 to 70 nm. A Schottky-type photoconductive diode or transistor was fabricated on single C/CNx nanotube. An absorption spectrum of a C/CNx nanotube film deposited on slide quartz exhibits a broad absorption band in the visible range. Experiments using the Xe lamp with various filters gave the similar effect. The photocurrent is a function of light wavelengths selectively ranged from 400 nm to 800 nm for the devices. The light-induced conductivity of the C/CNx nanotubes is very sensitive to the intensity and shows a broad maximum around 720 nm. This is positively evident that photocarriers are not intrinsically generated. With the dark insulating state as OFF and the white-exposed conducting state as ON, the photoresponse is a function of time when the lamp is switched on and off. Depending on the power of illumination, the conductivity of nanotube can be reversibly changed by 3 to 4 orders of magnitude without damaging the nanotubes. The photoconductivity response time of the nanotube is shorter than 50 ms. Additionally a continuous excitation of 5 min did not cause any thermal hysteresis. Obviously the photocurrent results from electron-hole pairs excited resonantly in the nanotube channels, rather than thermal effects. The I-V curves at forward current showed an approximately power law dependence, indicating the existence of distribution of charge carrier traps. The power law dependence is a characteristic of space charge limited (SCL) photocurrent. When the exciting light intensity is low, the thermal detrapping dominates the detrapping processes and the SCL photocurrent will be the same as in the dark. When the light intensity is increased to such a level that the optical detrapping becomes predominant, then the current depends on the light intensity. In the visible wavelength range, the photoconductivities of individual-C/CNx-nanotube devices were measured. Upon the generation of photocurrents its operation was governed by light intensity. Large changes in the current could be brought about through ON/OFF switching of a light intensity.

#### HH13.7

Abstract Withdrawn

#### HH13.8

**Field Emission of Double-Walled Carbon Nanotubes on Silicon Substrates.** Guangyong Xiong, Song-Ho Jo, Dezhi Wang and Zhifeng Ren; Dept. of Physics, Boston College, Chestnut Hill, Massachusetts.

Double-walled carbon nanotubes (DWNTs) are proved to have excellent field emission properties. Some simple and effective methods have been developed to control the density of DWNTs on the silicon substrates. The emission current density of 1 mA/cm<sup>2</sup> can be reached at a very low electric field of 1.2 V/μm. Several factors that affect the field emission properties have been studied, such as the geometrical configuration of DWNTs and substrates, the distribution of DWNTs and the roughness of the substrates. Field emission stability of DWNTs is also studied.

#### HH13.9

**Combining Nanotubes and Chromophores for Broadband Optical Limiting.** Nicolas Izard<sup>1,2</sup>, Cecilia Menard<sup>3</sup>, Eric Doris<sup>3</sup>, Charles Mioskowski<sup>3</sup>, Didier Riehl<sup>2</sup> and Anglaret Eric<sup>1</sup>; <sup>1</sup>GDPC, Universite Montpellier 2, Montpellier, France; <sup>2</sup>Departement laser-optiq, Centre Technique d'Arcueil DGA, Arcueil, France; <sup>3</sup>Service de Marquage Moleculaire et de Chimie Bioorganique, CEA-Saclay, Gif sur Yvette, France.

New systems are required for optical limiting against broadband laser pulses. We demonstrate that the association of non-linear scattering from single-wall carbon nanotubes and multiphoton absorption from organic chromophores is a promising approach to extend performances of optical limiters over broad spectral and temporal ranges [1,2]. Stable composite suspensions can be prepared, using functionalized nanotubes. Such composites display high linear transmission and good neutral colorimetry and are particularly efficient in the nanosecond regime due to cumulative effects. [1] D. Riehl, N. Izard, L. Vivien, E. Anglaret, E. Doris, C. Menard, C. Mioskowski, L. Porres, O. Mongin, M. Charlot, M. Blanchard-Desce, R. Anemian, J.C. Mulatier, C. Barsu, C. Andraud, Proceedings of SPIE 5211, 124 (2003). [2] N. Izard, C. Menard, D. Riehl, E. Doris, C. Mioskowski, E. Anglaret, Chem. Phys. Lett. 391, 1241 (2004).

#### HH13.10

Abstract Withdrawn

#### HH13.11

**Functionalized Carbon Nanotubes through Mechanically Bound and Rigid Organometallic Complexes.** Jordan Poler<sup>1,2</sup>, Tom D. Dubois<sup>1,2</sup> and Tom A. Schmedake<sup>1,2</sup>; <sup>1</sup>Chemistry, UNC Charlotte, Charlotte, North Carolina; <sup>2</sup>Center for Optoelectronics and Optical Communications, UNC Charlotte, Charlotte, North Carolina.

Carbon nanotubes and nanowires are important materials for new nanotechnology devices and sensors. Future optoelectronic devices can be made from assemblies of nanostructured materials. One difficulty in preparing these assemblies from nanotubes is the lack of site-specific points of contact and the subsequent compliance of the linkage between nanoparticles. Using molecular mechanics and dynamics calculations, we have modeled the assembly process of two-dimensional and three-dimensional structures of carbon nanotubes. The linkers between the nanotubes consist of novel metalodendrimers. These dendrimers have multiple binding sites with chemically specified chirality. Most importantly, they are mechanically rigid. This enables the multidimensional constraints and geometry, required for advanced electronic and optoelectronic devices. These computational results and the implied 3D nanostructures that are derived will be presented. Moreover we have synthesized several novel silicon based analogues of the same molecular motif. By combining these molecular systems with the Ru based supramolecular systems we can tailor their electron transfer capabilities into the carbon nanotubes. This results in the potential for optically altering the carrier density, and therefore the transport properties of the nanotubes.

#### HH13.12

**Environmental Effect on the Raman Spectra of Individual Single Wall Carbon Nanotubes.** Hyungbin Son<sup>1</sup>, E. Barros<sup>1</sup>, Y. Hori<sup>1</sup>, Shin Grace Chou<sup>1</sup> and M. S. Dresselhaus<sup>1,2</sup>; <sup>1</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

An enhanced Raman signal is demonstrated from individual suspended SWNTs and from isolated SWNTs grown on a *n* doped polysilicon film. The radial breathing modes (RBM) of the Raman spectra taken from suspended SWNTs exhibit narrow linewidths, which indicate a relatively unperturbed environment for suspended SWNTs. Rich intermediate frequency spectra in the frequency range of 520 to 1200cm<sup>-1</sup> are observed at the single nanotube level, which might allow a new method for the detailed study of the phonon band structure of individual SWNTs.

#### HH13.13

**Optical Characterizations of DNA wrapped Carbon Nanotubes Hybrids.** Shin Grace Chou<sup>1</sup>, Henrique Bucker Rubeiro<sup>2</sup>, Eduardo B. Barros<sup>3</sup>, Adelina P. Santos<sup>4</sup>, Georgii G. Samsonidze<sup>6</sup>, Marcos A. Pimenta<sup>2</sup>, Ado Jorio<sup>2</sup>, Flavio Plentz Filho<sup>2</sup>, Mildred S. Dresselhaus<sup>5,6</sup>, Riichiro Saito<sup>7</sup>, Ming Zheng<sup>9</sup>, G. Bibiana Onoa<sup>9</sup>, Ellen D. Semke<sup>9</sup>, Anna K. Swan<sup>10</sup>, M. S. Unlu<sup>10</sup> and Bennet B. Goldberg<sup>11,10</sup>; <sup>1</sup>Chemistry, MIT, Cambridge, Massachusetts; <sup>2</sup>Physics, Universidade Federal de Minas Gerais and Desenvolvimento, Belo Horizonte-MG, Brazil; <sup>3</sup>Physics, Universidade Federal do Ceara, Fortaleza-CE, Brazil; <sup>4</sup>Chemistry, Centro de Desenvolvimento da Tecnologia Nuclear, CDTN/CNEN, Belo Horizonte-MG, Brazil; <sup>5</sup>Physics, MIT, Cambridge, Massachusetts; <sup>6</sup>EECS, MIT, Cambridge, Massachusetts; <sup>7</sup>Physics, Tohoku University and CREST JST, Sendai, Japan; <sup>8</sup>Francis Bitter Magnet Laboratory, MIT, Boston, Massachusetts; <sup>9</sup>Dupont Central Research and Development, Wilmington, Delaware; <sup>10</sup>ECE, Boston University, Boston, Massachusetts; <sup>11</sup>Physics, Boston University, Boston, Massachusetts.

Optical characterization of DNA-wrapped CoMoCAT carbon nanotube hybrids (DNA-CNT) and semiconductor-enriched DNA-CNT were carried out using resonant Raman spectroscopy (RRS) and photoluminescence (PL) experiments. The  $\omega_{RBM}$  values were found to be relatively insensitive to the type of wrapping agents surrounding the nanotube. The values of  $\omega_{RBM}$  and the first and second resonant interband transitions,  $E_{11}$  and  $E_{22}$ , for a particular (n,m) tube for all samples types in RRS and PL measurements are found to correspond to the values obtained for SDS-dispersed nanotubes measured with PL, but with a shift in  $E_{ii}$  ranging from 10 to 80meV. The DNA-wrapping has shown not only to provide good isolation to the individual nanotube in a bundle, but the DNA wrapping mechanism for the CoMoCAT sample has also been shown to be diameter selective.

#### HH13.14

**Quantitative evaluation of physiochemical environment variation by the RBM resonance Raman spectra Reconstruction.** Zhengtang Luo<sup>1</sup>, Rongfu Li<sup>1</sup>, Sang Nyon Kim<sup>1</sup> and

Fotios Papadimitrakopoulos<sup>1,2</sup>; <sup>1</sup>Nanomaterials Optoelectronics Laboratory, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut.

The radial breathing mode (RBM) region of the resonance Raman spectra of HiPco single walled carbon nanotubes (SWNTs) was investigated as a function of aggregation and presence of environmental contaminants. This was modeled using an energetic deviation term ( $\Delta E$ ), imparted to the optical transitions ( $E_{ii}(n,m)$ ) by the change in SWNT physicochemical environment. Three sets of  $E_{ii}(n,m)$  values were used to reconstruct these RBM profiles, based on: (i) photoluminescence (PL) measurements, (ii) a simple tight-binding (TB) model, and (iii) a set of modified, TB-based  $E_{ii}(n,m)$  values to account for the underestimation of the influence of chiral angle to SWNTs for diameters below 1 nm. The simulation revealed that the PL-determined  $E_{ii}(n,m)$  set provided a good fit in terms of peak position as opposed to TB-calculated values. Moderate improvement was attained using the third data set of  $E_{ii}(n,m)$  values, indicative of the importance of both curvature and chirality effects. Providing an accurate set of  $E_{ii}(n,m)$  values becomes available, the RBM profile reconstruction methodology discussed herein could greatly enhance our ability to model a range of physicochemical changes to the immediate environment of SWNTs.

#### **HH13.15**

**Comparison Study of the Vibrational and Electronic Properties of Single-Wall Carbon Nanotubes Suspended and on a Silicon Oxide Substrate.** Eduardo B. Barros<sup>2,1</sup>, H. Son<sup>1</sup>, S. B. Cronin<sup>4</sup>, Shin Grace Chou<sup>1</sup>, A. K. Swan<sup>3</sup>, G. Dresselhaus<sup>1</sup> and M. S. Dresselhaus<sup>1</sup>; <sup>1</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Departamento de Física, Universidade Federal do Ceara, Fortaleza, Cear, Brazil; <sup>3</sup>Electrical and Computer Engineering Department, Boston University, Boston, Massachusetts; <sup>4</sup>Department of Physics, Harvard University, Cambridge, Massachusetts.

The electronic and vibrational properties of Single Wall Carbon (SWNTs) isolated on silicon oxide substrates have been widely studied. The fact the nanotubes remain attached to the substrate surface suggests a significant interaction between the nanotube walls and the surface. Possible applications of carbon nanotubes to electronic devices would require nanotubes placed on silicon-based substrates. Therefore, it is of great importance to understand how the interaction between the nanotube and the substrate affects the nanotube properties. In this work we present a resonance Raman spectroscopy study on SWNTs deposited on a silicon oxide Holey TEM grid. Some of the SWNTs were found to be suspended across the 1-50  $\mu\text{m}$  pores of the Holey film. Moving the Raman probe along the nanotube length from the region where the nanotube is freely suspended to the region where the tube is sitting on the silicon oxide film, the effects of the silicon oxide substrate to the vibrational and electronic properties of the SWNTs could be identified for several different (n,m) assigned nanotubes. The authors acknowledge support from NSF grant DMR-01-16042 and Intel Corporation.

#### **HH13.16**

**NMR Investigations on alkali intercalated carbon nanotubes.** Michael Schmid<sup>1,2,3</sup>, Christophe Goze-Bac<sup>2</sup>, Michael Mehring<sup>3</sup>, Patrick Bernier<sup>2</sup> and Siegmund Roth<sup>1</sup>; <sup>1</sup>Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, Germany; <sup>2</sup>GDPC, Universite Montpellier II, Montpellier, France; <sup>3</sup>2. Physik. Inst., Universitaet Stuttgart, Stuttgart, Germany.

Single-wall carbon nanotubes (SWNT) exhibit outstanding electronic properties that promise to open up wide opportunities for nanoscale applications. Intercalation of SWNT bundles with various alkali metals is expected to modify the electronic band structure and to shift up the Fermi level. Therefore it is possible to tune and control the electronic properties of these novel carbon materials via alkali metal intercalation. In this paper we report results from <sup>13</sup>C- and alkali-NMR measurements on alkali intercalated SWNT. Alkali metals like Li, Rb and Cs were reversibly intercalated in SWNT with different stoichiometries. By performing temperature dependent <sup>13</sup>C-NMR measurements, the density of states at the Fermi level  $N(E_F)$  is determined and compared for pristine and intercalated SWNT. We demonstrate that upon intercalation a pure metallic nanotube system with up to  $N(E_F) = 0.12$  states / (eV spin atom) can be obtained. In a second step temperature dependent alkali-NMR was performed. NMR lineshape-analysis as well as investigation of relaxation effects give evidence for dynamics of alkali ions in the SWNT. The results are discussed in context with structural simulations of Cs-ions intercalated in SWNT.

#### **HH13.17**

**Effect of Doping on the Resonant Raman Scattering in Metallic Single-Walled Carbon Nanotubes (SWNTs).**

Rahul Rao<sup>1</sup>, Gayatri Keskar<sup>1</sup>, Mildred S. Dresselhaus<sup>2</sup> and Apparao M. Rao<sup>1</sup>; <sup>1</sup>Physics and Astronomy, Clemson University, Clemson, South Carolina; <sup>2</sup>Department of Physics and Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Boron-doped SWNT bundles and nitrogen-doped isolated SWNTs were synthesized by the pulsed laser vaporization and CVD methods, respectively. The nominal dopant concentration in the target (for boron-doped SWNT bundles) or the liquid-precursor (for nitrogen-doped isolated SWNTs) was varied between 0 - 10 at. %. Resonant micro-Raman spectra were excited with the 514.5 and 647.1 nm laser lines, and the spectra were collected using the ISA 550 TRIAX spectrometer coupled with a Leica DL/LM microscope. The radial breathing mode (RBM) intensity in the Raman spectrum of the boron-doped metallic tubes was a maximum when the boron concentration in the target reached 3 at. %. With increasing boron concentration of the target, the RBM intensity decreased and finally disappeared when it reached 4 at. %. Similarly, in the metallic nitrogen-doped isolated SWNTs, an increase in intensity of the RBM was seen when the nitrogen concentration reached 2 at. %. These intensity enhancements are attributed to dopant-induced changes in the electronic structure of doped nanotubes. Additional evidence for their modified electronic structure comes from thermopower studies.

#### **HH13.18**

**Polystyrene-Grafted SWNTs prepared by Atom Transfer Radical Polymerization.** Hyun-jong Paik<sup>1</sup>, Jin Hwan Choi<sup>1</sup>, Saet Byeol Oh<sup>1</sup>, Jun Ho Chang<sup>1</sup>, Ho Soo Hwang<sup>2</sup>, Jong Hun Han<sup>2</sup>, Sang-Woo Joo<sup>3</sup>, Gue-Hyun Kim<sup>4</sup>, Hyung-Kook Kim<sup>5</sup> and Bog G. Kim<sup>5</sup>; <sup>1</sup>Department of Polymer Science and Engineering, Pusan National University, Busan, South Korea; <sup>2</sup>ILJIN Nanotech Co., Ltd., Seoul, South Korea; <sup>3</sup>Department of Chemistry, Soongsil University, Seoul, South Korea; <sup>4</sup>Department of Chemical and Biomolecular Engineering, Dongseo University, Busan, South Korea; <sup>5</sup>Department of Physics, Pusan National University, Busan, South Korea.

Polymer-functionalized Single-Walled Carbon Nanotubes (SWNTs) were prepared using Atom Transfer Radical Polymerization (ATRP). Hydroxyl groups on SWNTs were introduced through Friedel-Crafts alkylation of chloroform. Subsequent esterification with 2-chloro-propionyl chloride introduced ATRP initiator on the side wall of SWNTs. Modified SWNTs in each functionalization step was characterized by FT-IR, Raman, <sup>1</sup>H NMR spectroscopy, transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA). The degree of functionalization on SWNTs was estimated to be 20% on the basis of TGA analysis. In comparison with the pristine SWNTs, polymer-functionalized SWNTs were soluble in various organic solvents such as THF, chloroform, dichloromethane, and alcohol.

#### **HH13.19**

**Functionalization of Beads-milled SWNTs by Nitroradical.** Hiroshi Moriyama<sup>1</sup>, Kazuhiro Kurihara<sup>1</sup>, Masahiko Saibara<sup>1</sup>, Toshihiro Ishii<sup>2</sup>, Kaori Harigai<sup>2</sup>, Atsushi Yusa<sup>3</sup> and Terumasa Kondo<sup>3</sup>; <sup>1</sup>Department of Chemistry, Toho University, Funabashi, Japan; <sup>2</sup>Ashizawa Finetech Co., Ltd., Narashino, Japan; <sup>3</sup>Hitachi Maxell Co., Ltd., Tsukuba, Japan.

Carbon nanotubes (CNTs) are attractive for building blocks of the future electronic devices. However, compared to the molecular-based materials, robust nature of CNTs with no solubility would be obstacle for the manipulation of CNTs in solution phase from the viewpoint of fabrication due to the chemical transformation. To overcome this situation, recent efforts have been devoted to functionalize CNTs using various kinds of reactions. Here, we report the facile functionalization of SWNTs by means of the radical reaction applicable to fullerene C<sub>60</sub>. Chiang reported that hexanitrofullerene was produced by the reaction of C<sub>60</sub> and nitroradical [1]. According to this method, beads-milled SWNTs suspended in toluene were subjected to nitroradical generated from Cu and conc. nitric acid under nitrogen atmosphere. The polynitro-SWNTs obtained as yellow tar were characterized by IR, UV-vis, and TEM. The product were rather soluble in ordinary organic solvents and some applications will be presented using this functionalized SWNTs. [1] V. Anantharaj, et al. J. Chem. Soc., Perkin Trans. 1, 31-36 (1999).

#### **HH13.20**

**Interactions of Lanthanide Metal Complexes with Single-walled Carbon Nanotubes.** Tirandai Hemraj-Benny<sup>1</sup>, Sarbajit Banerjee<sup>1</sup> and Stanislaus S. Wong<sup>1,2</sup>; <sup>1</sup>Chemistry, Stony Brook University, Stony Brook, New York; <sup>2</sup>Materials and Chemical Sciences, Brookhaven National Laboratory, Upton, New York.

Oxidized, cut single-walled carbon nanotubes (SWNTs) have been reacted with lanthanide salts containing Eu, La, and Tb. These studies are not only aimed at developing a fundamental understanding of the coordination chemistry of metal ions and of metal ion

complexes onto the surfaces of nanotubes but also to improve the reactive selectivity of CNTs, and thus, solubility in a variety of solvents. We found that the lanthanide ions likely coordinate to these tubes through the increased number of oxygen atoms, forming predominantly ionic bonding arrangements. Metal coordination occurs through disruption of hydrogen bonding in bundles of oxidized SWNTs. The adducts were analyzed using FTIR, Raman, and photoluminescence spectroscopies and were structurally characterized using atomic force microscopy (AFM) and transmission electron microscopy (TEM), along with energy-dispersive X-ray spectroscopy (EDS).

#### **HH13.21**

**Room Temperature Ozone Oxidation of Single-walled Carbon Nanotubes.** Jason Simmons<sup>1</sup>, B. M. Nichols<sup>2</sup>, Matthew S. Marcus<sup>1</sup>, O. M. Castellini<sup>1</sup>, R. J. Hamers<sup>2</sup> and M. A. Eriksson<sup>1</sup>; <sup>1</sup>Department of Physics, University of Wisconsin - Madison, Madison, Wisconsin; <sup>2</sup>Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin.

The covalent functionalization of carbon nanotubes is desired for a wide variety of applications. To achieve this, the normally unreactive graphite lattice needs to be disrupted, typically by oxidation, to create attachment points for subsequent reactions. The most common oxidation processes, namely nitric acid reflux and high temperature air oxidation, are primarily bulk processes and require either long process times or elevated temperatures. An alternative method uses room temperature ozone treatment, which has the benefit of being relatively fast due to the high reactivity of ozone. Using core-level and valence-band photoelectron spectroscopy, as well as near edge X-ray absorption spectroscopy, we have studied the effect of ozone on the chemical and electronic structure of single walled carbon nanotubes. The spectroscopies indicate the formation of oxidized carbon species which remove electronic states near the Fermi level. The decreased density of states near the Fermi level causes an increased resistance, which is detected in transport measurements. Further, Raman spectroscopy shows a large reduction of the G-band tangential phonon modes, as well as an increase in defect density as measured by the ratio of the disorder induced D-band to the G-band. The spectroscopy and transport measurements indicate that the ozone etches the sidewalls of the nanotubes, eventually leading to the destruction of the nanotube structure. The time evolution of the reaction of ozone with the nanotubes is presented in order to study the mechanisms present.

#### **HH13.22**

**Polymer Functionalized Carbon Nanotubes for Sensor Application.** Narasimha Harindra Vedala, Young Chul Choi and Wobong Choi; Mechanical and Materials Engineering, Florida International University, Miami, Florida.

The present study employs the surface modification of carbon nanotubes for chemical and humidity sensing. Both single-wall and multiwall carbon nanotubes in vertically aligned as well as random orientation were grown on a 1 cm<sup>2</sup> silicon dioxide substrate using chemical vapour deposition. The surfaces of these nanotubes were functionalized by using polyvinyl alcohol. This surface functionalization changes the hydrophobic nature of carbon nanotube to hydrophilic, thus increasing its sensitivity towards humidity, as well as biological, and chemical molecules. Electrical characterization of these carbon nanotubes will be performed since it is expected that by adapting molecules onto the modified carbon nanotubes, the electrical transport property may be changed. Effect of changes in the geometry of nanotubes and film thickness on the sensor is also presented. Moreover charge transport mechanism in these functionalized nanotubes will also be proposed.

#### **HH13.23**

**Integrated Study of Ion Irradiated Singlewall and Multiwall Carbon Nanotubes by Spectroscopic Methods.** Mariya Brzhezinskaya<sup>1</sup>, Eugen Baitinger<sup>1</sup>, Vladimir Shnitov<sup>2</sup> and Aleksey Smirnov<sup>2</sup>; <sup>1</sup>Physics, Chelyabinsk State University of Education, Chelyabinsk, Russian Federation; <sup>2</sup>Ioffe Physico-Technical Institute of the Russian Academy of Sciences, St. Petersburg, Russian Federation.

The results of experimental study of single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs) are presented. They were obtained by X-ray photoelectron spectroscopy (XPS), reflection energy loss spectroscopy (EELS) and Auger electron spectroscopy. The samples of SWNTs and MWNTs were periodically irradiated by argon ions (Ar<sup>+</sup>) in situ in the spectrometer chamber. The Ar<sup>+</sup> energy was 1 keV. The maximum dose (Q) of Ar<sup>+</sup> irradiation was 360  $\mu\text{C}/\text{cm}^2$ . Each irradiation of a sample was followed by Auger spectra measurement in order to determine the concentration of argon absorbed in the near surface region of the sample. The process of Ar absorption by SWNTs and MWNTs reveals nonlinear character. CNTs accumulate Ar more quickly at small values of Q. The XPS

measurements were carried out using ultra-high vacuum electron spectrometer PHI-5500 (produced by Perkin-Ermler) using Mg K<sub>2</sub> line. Absolute energy resolution was 0.2 eV, when the transmission energy was 10 - 25 eV. Influence of ion irradiation on the energy of C 1s peak and on its full width at half maximum (FWHM) was determined. The C 1s peak energy increases and the plasma peak broadens slightly with the increase of the dose Q of Ar<sup>+</sup> irradiation. The satellite photoelectron peak located at higher binding energies (the binding energies from 284.5 eV to about 330 eV) changes essentially under Ar<sup>+</sup> irradiation. It was found out that the energy of  $\pi$ -plasmon peak decreases and it broadens essentially under Ar<sup>+</sup> irradiation; the  $\pi+\sigma$ -plasmon peak has a doublet shape and changes essentially under Ar<sup>+</sup> irradiation, also. EELS studied the influence of ion irradiation on the  $\pi$ -plasmon energy  $E_\pi$  and the FWHM of the plasma peak  $\delta E_\pi$  were studied. The determined dependence of the  $\pi$ -plasmon energy  $E_\pi$  on the dose Q of ion irradiation can be approximated by hyperbola, although the hyperbola coefficients are different for SWNTs and MWNTs. Furthermore, it was found that the hyperbola coefficients are different at small values of Q ( $Q < Q_0 = 30 \mu\text{C}/\text{cm}^2$ ) and at large values of Q ( $Q > Q_0$ ) for SWNTs and MWNTs: accumulation of defects is slower at the beginning of irradiation. In this presentation, possible causes of the observed effects are discussed. Phenomenologically, it is possible to use the model of the damped harmonic oscillator for quasi-one-dimensional system of carbon nanotubes. The microscopic model is proposed. The observed effects have been explained by narrowing of  $\pi$ -bands caused by field of charged defect and by decrease of energy of interband transitions in carbon nanotubes under ion irradiation. This work was supported by the Russian Ministry of Education under grant No.PD02-1.2-170.

#### **HH13.24**

**Solubility and electrical response of single walled carbon nanotubes with thiolate mediated gold nanoparticle attachment.** Jingbiao Cui, Charles Daghlain and Ursula Gibson; Dartmouth College, Hanover, New Hampshire.

Dodecanethiol-stabilized-Au nanoparticles are successfully attached to the sidewall of as-grown single walled carbon nanotubes (SWCNTs) via sonication. This provides a straightforward method to functionalize and dissolve SWCNTs of full length in a solvent. A correlation between the solubility and an absorption peak at 335 nm was found, which may be used as a fingerprint for the nanotube modification. The modified nanotubes exhibit dramatic increase in the resistance and strong gate dependence with a memory effect. The modified SWCNTs demonstrate preferential orientation when deposited by Langmuir-Blodgett technique if there are excess Au nanoparticles in the source materials. The anisotropic transport properties of the nanotube monolayers are reported. The mechanism for Au particle attachment is shown to be via dodecanethiol groups.

#### **HH13.25**

**Transparent Carbon Nanotube Coatings.** Martti Kaempgen and Siegmund Roth; von Klitzing, Max-Planck-Institute for Solid State Research, Stuttgart, Germany.

Conductivity and high aspect ratio of Carbon Nanotubes (CNT) are basic properties in order to get conductive composites. A very low percolation threshold can be reached with a minimum of material. This feature is used to get transparent and conductive networks. Such CNT networks are simply sprayed on glass or plastic in order to get conductive transparent coatings. They are compared with a standard material for transparent electrodes (Thin doped Indium Oxide, ITO) in terms of transparency and conductivity at RT. In contrast to ITO, CNT coatings keep their properties under flexible conditions, even after folding the substrate. For same transparency, the conductivity of CNT networks is about one order of magnitude less than of ITO due to high contact resistance between the CNT. However, since the preparation is very simple transparent conductive coatings based on CNT become interesting for all applications where the high conductivity of ITO is not require

#### **HH13.26**

**Magnetic Properties of Randomly Oriented Flakes of Aligned Fe-Filled-CNx Nanotubes.** Emilio Munoz-Sandoval, Florentino Lopez-Urias, Marisol Reyes-Reyes, Julio Alejandro Rodriguez-Manzo, Humberto Terrones and Mauricio Terrones; Advanced Department, Instituto Potosino de Investigacion Cientifica y Tecnologica A. C., San Luis Potosi, San Luis Potosi, Mexico.

The magnetic properties of flakes of aligned Fe-partly-filled CNx nanotubes, randomly oriented, are investigated using SQUID magnetization measurements. We find: a) that the temperature dependence of magnetic coercivity above 10 K is linear, except probably near room temperature, and b) a larger hysteresis when compared to two-dimensional arrays of aligned nanotubes filled with Fe particles. We attributed the latter behavior to the small currents formed within nanotubes responsible of affecting the magnetic

properties of nanowires. Theoretical calculations supporting these results will be also presented.

#### **HH13.27**

**Enhanced P-Type Conduction in SWNT by Protein Coated Microspheres.** Pil Sun Na<sup>1,3</sup>, Jeong-O Lee<sup>2</sup>, Jinhee Kim<sup>3</sup> and Hyojin Kim<sup>1</sup>; <sup>1</sup>Matrical Engineering, ChungNam National Univ., Daejeon, South Korea; <sup>2</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, South Korea; <sup>3</sup>Electronic Device Group, Korea Research Institute of Standard and Science, Daejeon, South Korea.

Rapid progress in modern biotechnology and medical science reveals the existence of marker proteins that are specific for certain diseases. This knowledge about marker proteins combined with nanotechnology gave birth to new concept biosensors that are highly sensitive and are possible to miniaturize. Here, we present a nanoscale biosensor that employs a single wall carbon nanotube field effect transistor as a signal transducing element. Selective binding of analyte with immobilized probe molecule on a single carbon nanotube field effect transistor can act as external gate, which results in a change of conductance. Extremely high surface to volume ratio that comes from the one-dimensional nature of a single carbon nanotube makes it possible to expect high sensitivity to detect even a single molecule. Here, we propose to use protein coupled nanoparticles to improve signal detection and easier visualization. We have immobilized streptavidin coated microspheres on the side wall of single wall carbon nanotube devices built on Si/SiO<sub>2</sub> substrate. About 100 nm sized polystyrene particles immobilized with streptavidin were used for the experiment. After the reaction with microspheres, samples were cleaned with buffer solution and blow dry with dry N<sub>2</sub> gas. When we compare the electrical signal from the tube before and after the reaction with microspheres, strong p-type enhancement has observed after the reaction. As a control experiment, we have immobilized streptavidin molecules, and streptavidin coupled 10 nm Au nanoparticles on single wall nanotube devices. While only a small conductance change occurred with samples incubated with streptavidin, strong p-type enhancement observed from the samples incubated with streptavidin coupled 10 nm Au particles. We will explain this with the work function of the carbon nanotubes. In summary, we have observed strong p-type enhancement in the conduction of single wall nanotube devices coupled with protein-microspheres. Since this can results in a very sensitive detection of analyte and easier to monitor protein binding, we believe that we can go one step forward to single molecule detection with this technique

#### **HH13.28**

**Transport Properties through Functionalized Aligned Carbon Nanotube Membranes.** Mainak Majumder, Nitin Chopra and Bruce Jackson Hinds; Chemical and Materials Engineering, Univ. of Kentucky, Lexington, Kentucky.

Controlling the pore size of membranes in the 1 -10 nm range is critical to many biological chemical separations. Recently we have synthesized vertically aligned carbon nanotube membranes with inner core diameters of 7 nm. Reported here is the functionalization of the entrances to CNT cores with aliphatic amines of different lengths (1.14nm, 2.8 nm), negatively charged dye molecules (2.6 nm) and an aliphatic amine elongated by spacers containing peptide bonds (5.2 nm) using well known carbodiimide chemistry. This allows us to precisely decrease the pore size by molecular length increments. FTIR studies of functionalized membranes showed a peak at 1630 cm<sup>-1</sup> and shoulder at 1654 cm<sup>-1</sup> indicative of amide bond formation. Transport of two differently sized but similarly charged molecules through aligned CNT membrane were studied. A equimolar (0.5mM) solution Ruthenium bi-pyridine (diameter 1.18 nm) and Methyl Viologen (length 1.09 nm, breadth 0.32 nm) in aqueous medium was in contact with with 0.3 cm<sup>2</sup> of membrane area in a U-tube set up. Flux into analyte cell is quantified by UV-VIS spectroscopy. Typical Ru-(bi-py)<sub>3</sub> flux through CNT membrane was found to be 8 nanomoles/cm<sup>2</sup>-hr. Methyl Viologen/Ruthenium bi-pyridine selectivity (alpha) through a non-functionalized membrane was 1.7, which is close to the ratio of their bulk aqueous diffusivities. Methyl Viologen/Ruthenium bi-pyridine selectivity (alpha) increased to 3, when 1.14nm long nonyl amine was attached to the carbon nanotube membrane. The Ru-(bi-py)<sub>3</sub> flux decreased by a factor of 2.5 when a 2.8 nm long aliphatic amine was attached to the membrane. However the (alpha) was 1.98 thus indicating that selectivity depends upon the solubility of the attached molecule in water and not only their length. When a water-soluble negatively charged dye molecule of 2.6 nm length was attached, the flux increased 4 times, (alpha) was 2.12, larger than the long chain aliphatic amine of comparable length. The carbon nanotubes were finally functionalized by a 5.2 nm long molecule containing peptide bonds, which are water soluble. In this case, Ru-(bi-py)<sub>3</sub> flux decreased about 14 times and (alpha) was 3.6. An increase in separation selectivity by increasing chain length and solubility of functional molecules indicate that pore size reduction by

molecular increments can be achieved in aligned carbon nanotube membrane architecture.

#### **HH13.29**

**Electrophoretic Deposition of Carbon Nanotubes into Device Structures: A Novel Approach to Sensors for Environmental Applications.** Madhuri Guduru and Tabbetha Amanda Dobbins; Institute For Micromanufacturing, Louisiana Tech University, Ruston, Louisiana.

Carbon Nanotubes (CNTs) will open the door to host new capabilities in environmental studies because of their high surface area and ability to act as host structures for many elemental clusters and compounds. Particularly, their ability to intercalate alkali metals, nitrides, and oxides, generates promise for their potential use as sensors and detectors. In this work, changes in the electronic properties, electrophoretic mobility and opto-electronic properties of carbon nanotubes are explored upon chemical intercalation of different elements and compounds. A sensing platform for environmental contaminants in aqueous solution based upon changes in the aforementioned properties of carbon nanotubes (before and after intercalation) is discussed. The design and fabrication of the device structure for electronic conduction measurement is also presented. Beginning with commercially available single walled CNTs and a pre-form (made by standard microfabrication methods); single-walled CNTs are electrophoretically deposited (EPD) onto electrode pads. The electrophoretic deposition is done onto different types of electrode pads— including W, Cu, Au, and Al. For the potential stability of colloidal systems, the surface charge should be less than -30mV and greater than 30mV. Our results show that the surface charge of undoped single walled CNTs ranges beyond 30mV at pH less than 2 and below -30mV at pH greater than 9. We have performed EPD onto positively and negatively charged electrodes. The intercalation of Cr(VI) compounds and actinide series oxides into the CNTs before EPD placement into the device structure will be also discussed.

#### **HH13.30**

**Carbon Nanotube Gas Sensors and Actuators.** Mikhail Kozlov<sup>1</sup>, Ali Aliev<sup>1</sup>, Dong-Seok Suh<sup>1</sup>, Richard Margolin<sup>1</sup>, Miles V. Selvidge<sup>1</sup>, Steve Collins<sup>1</sup>, Sergey Lee<sup>1</sup>, Edgar Munoz<sup>2</sup>, Anvar Zakhidov<sup>1</sup> and Ray Baughman<sup>1</sup>; <sup>1</sup>NanoTech Institute, University of Texas at Dallas, Richardson, Texas; <sup>2</sup>Instituto de Carboquimica, CSIC, Zaragoza, Spain.

Dimensional changes have been observed in carbon nanotube sheets (buckypaper) and nanotube fibers exposed to vapors of various chemical agents. The latter included common solvents (acetone, methanol, ethanol etc) and halogens. The changes in dimensions of the material were found to be reversible and accompanied by significant weight uptake. They also resulted in actuator-type behavior of samples detected in tensile and cantilever geometry. The phenomenon was monitored with IR spectrometer that revealed intense bands caused by vapors adsorbed on nanotube surface. Based on our measurements a design of nanotube sensor capable of discrimination of different gases has been proposed. A mechanism of vapor adsorption/desorption and charge transfer on nanotubes is discussed.

#### **HH13.31**

**Micro IR Study of Peptide-Nanotube Membranes.** Mikhail Kozlov<sup>1</sup>, Tiffany Lin<sup>1</sup>, Alfonso Ortiz<sup>2</sup>, Gregg R. Dieckmann<sup>2</sup>, Inga H. Musselman<sup>2</sup> and Rockford K. Draper<sup>2</sup>; <sup>1</sup>NanoTech Institute, University of Texas at Dallas, Richardson, Texas; <sup>2</sup>Department of Chemistry, University of Texas at Dallas, Richardson, Texas.

Thin free standing membranes were prepared from aqueous dispersions of single walled carbon nanotubes (CNT) and amphiphilic peptide. It was found that the membranes exhibit unusual coloration consisting of a number of well-defined color spots if observed in optical microscope using reflected light. The micro-infrared (IR) investigation of the color spots revealed significant variation in shape and intensity of IR transmittance and reflectance. Based on collected data, regions with various peptide/CNT ratios were identified. The recorded IR spectra evidenced existence of bio-CNT interaction that depended on the peptide-CNT ratio. The spectra were consistent with SEM measurements, showed substantial deviation from IR data of pristine peptide and revealed important conformation sensitive features. The origin of peptide-CNT interaction in the membrane will be discussed. Possible bio-sensing and other applications of the membranes will be proposed.

#### **HH13.32**

**Guided Neurite Growth on Patterned Carbon Nanotubes.** Cengiz Sinan Ozkan, Mechanical Engineering, University of California at Riverside, Riverside, California.

The failure of the mammalian spinal cord to regenerate following injury is not absolute, but appears to be amenable to therapeutic

manipulation. Promotion of axonal growth and support for long distance regeneration are the two requirements in the various experimental strategies for spinal cord repair. The onus of achieving these goals in-vitro is on the substrate that functions the basis for the formation of neural bridges with high signal to noise ratio for efficient signal transmission. Biomaterials thus become an important factor in developing successful guiding strategies. Patterned vertical carbon nanotube arrays are experimentally demonstrated as functional scaffolds for guiding neurite growth and forming synaptically communicative networks. Neuron bridging behavior is characterized based on the substrate geometry for potential prosthetic applications.

#### **HH13.33**

**A New Carbon Nanotubes Based Field Enhanced Thermionic Cathode.** Feng Jin and Chris Day; Department of Physics and Astronomy, Ball State University, Muncie, Indiana.

We have developed a new type of thermionic cathode that is based on field enhancement effect from carbon nanotubes. It has strong field enhanced thermionic emission at least an order of magnitude higher than conventional thermionic cathodes. This cathode consists of a metal substrate with carbon nanotubes grown on top of its surface. The carbon nanotubes are coated with thermionic emission materials (BaO/SrO/CaO). This unique cathode structure takes advantage of both the field enhancement effect from carbon nanotubes and high electron emissions capability of thermionic materials. The electron emission properties of this new thermionic cathode, particularly the field enhancement factor and effective work function are compared with the conventional thermionic cathodes that are made of same oxides coating.

#### **HH13.34**

**Carbon Nanotubes as Bio-Functional Substrates.** Evan Goulet and David E. Luzzi; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

The carbon nanotube (CNT) offers a quasi-one-dimensional structure that can be utilized as a bio-functional substrate. The graphene walls of as-produced CNTs are relatively non-reactive with most biological molecules, but through chemical functionalization the CNTs can be made more receptive to biological molecules. We report the production of stable, functionally-gradient coatings on CNTs using organic promoter molecules and inorganic sol-gel processing. CNTs ranging in diameter from 20 nm to 100 nm have been coated. Important parameters such as thickness and porosity of the coating are controlled through the chemistry and kinetics of the synthesis process and through the use of colloidal particles. Throughout the synthesis process, biocompatible conditions are used such that the coated CNTs can be combined with enzymes, resulting in the immobilization of the enzymes via steric entrapment or covalent linkage. The synthesis protocol and the flexibility provided through the integration of colloids comprise a versatile platform for the immobilization of a wide variety of enzymes. The relative activity of the immobilized enzymes will be presented.

#### **HH13.35**

**Fabrication and Characterization of a Carbon Nanotube-Embedded Silicon Nitride Membrane.** Jason Holt, Alexandr Noy, Thomas Huser, David Eaglesham and Olga Bakajin; Biosecurity and Nanosciences Laboratory, Lawrence Livermore National Laboratory, Livermore, California.

A membrane consisting of multiwall carbon nanotubes embedded in a silicon nitride matrix was fabricated for use in studying fluid mechanics on the nanometer scale. Characterization by fluorescent/isotopic tracer diffusion and scanning electron microscopy suggests that the membrane is void-free near the silicon substrate on which it rests. An upper limit to the diffusive flux of D<sub>2</sub>O of 2.4x10<sup>-5</sup> mole/m<sup>2</sup>-s was determined, based on the sensitivity of the isotope measurement technique. By contrast, hydrodynamic calculations of water flow across a nanotube membrane of similar specifications (10 nm inner diameter, 10 μm thick, with a porosity fraction of 0.03) give a molar flux of 0.061 mole/m<sup>2</sup>-s for a 1 atm pressure drop. Molecular dynamics simulations<sup>1</sup> predict an even larger value of 0.29 mole/m<sup>2</sup>-s. These carbon nanotube membranes are used to make nanoporous silicon nitride membranes, fabricated by sacrificial removal of the carbon. Nitrogen flow measurements on these structures give a membrane permeance of 4.7x10<sup>-4</sup> mole/m<sup>2</sup>-s-Pa (mass flux of 0.47 mole/m<sup>2</sup>-s at a pressure drop of 1000 Pa) at a pore density of 4x10<sup>10</sup> cm<sup>-2</sup>. The average pore size of this membrane is estimated to be 33 nm, using a Knudsen diffusion model. References [1] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, Nature 414, 188 (2001).

#### **HH13.36**

**Enhancement of Conductivity of Bucky Paper by Chemical Modification.** Urszula Dettlaff-Weglikowska<sup>1</sup>, Viera Skakalova<sup>1</sup>, Ralf Graupner<sup>2</sup>, Sung Ho Jhang<sup>3</sup>, Byung Hoon Kim<sup>3</sup>, Hyun Jung Lee<sup>3</sup>,

Lothar Ley<sup>2</sup>, Yung Woo Park<sup>3</sup>, Savas Berber<sup>4</sup>, David Tomanek<sup>4</sup> and Siegmund Roth<sup>1</sup>; <sup>1</sup>Max Planck Institute for Solid State Research, Stuttgart, Germany; <sup>2</sup>Institute of Technical Physics, University of Erlangen, Erlangen, Germany; <sup>3</sup>School of Physics and Condensed Matter Research Institute, Seoul National University, South Korea; <sup>4</sup>Physics and Astronomy Department, Michigan State University, East Lansing, Michigan.

Purified single wall carbon nanotubes have been chemically modified by thionyl chloride, SOCl<sub>2</sub>. This treatment changes significantly the electrical and mechanical properties of the resulting entangled nanotube network. Four-probe measurements indicate a conductivity increase by up to a factor of 5 at room temperature, and an even more pronounced increase at lower temperatures. This chemical functionalization also improves the mechanical properties of SWNT networks. Whereas the pristine sample shows an overall semiconducting character, the functionalized material behaves as a metal. The effect of SOCl<sub>2</sub> is studied in terms of functionalization reactions and incorporation of cross-linking functionalities into the nanotube network. We identified the microscopic origin of these changes using XPS, NEXAFS, EDX and Raman spectroscopy measurements, and by *ab initio* calculations. We interpret the SOCl<sub>2</sub>-induced conductivity increase by *p*-type doping of the pristine material. This conclusion is based on the temperature dependence of the thermopower and on the electronic structure calculations, which indicate a shift of the Fermi level to the valence band.

#### **HH13.37**

**Process of Making Local Back Gate for SWNTs Device.**

Hao Lin and Yong Wook Park; Applied Physics, Cornell University, Ithaca, New York.

Single-walled carbon nanotubes have been widely researched for applications in electronics and photonics area. Previously single-carbon nanotube field effect transistors (CNTFETs) has suffered from many drawbacks of using silicon substrate as common back gate to address each transistors. Although single top gate has recently been fabricated to locally control each device, it lost the benefit of exposing carbon nanotubes to the ambients such that it can be otherwise potentially used for single-molecule electronic sensor or other photonic device applications. Here in this paper we report the process of fabricating single-walled carbon nanotube local back gate devices, including single back gate field effect transistor and double back gates diode. The difficulty of making local back gate comes from the planarization of the back gate and surrounding dielectric material such as silicon dioxide. As well developed in the microelectronic industry, damacene process has been proved to successfully planarize different levels of metal interconnects so that it lend itself to the integration of back gate in the CNTFET devices. With this method, both polysilicon and tungsten can be used as gate material. We started with bulk silicon wafer and grew 1 μm thick silicon oxide on the substrate. By using stepper, patterns of back gate can be lithographically transferred onto the substrate followed by RIE etching so that 200nm-300nm trenches was formed in the oxide. Subsequently, either highly doped polysilicon or tungsten can be deposited onto the substrate with LPCVD or sputtering respectively. With Chemical Mechanical Polishing (CMP) technique, both polysilicon and tungsten will be polished down to the oxide level and the surface of the remaining gate material will be flush with the surrounding silicon oxide surface. For polysilicon gate, a thin (8-10nm) polysilicon oxide can be grown to be used as gate dielectrics; while for tungsten gate a thin layer ( 5nm) of SiO<sub>2</sub> can be evaporated. In addition to that, this method does not limit us from depositing other high k dielectric material if needed. The growth of single-walled carbon nanotube with CVD is followed and finally metal contact to the gate and to the tube is made with liftoff process.

SESSION HH14: Sensors, Adsorption, Other Applications  
Friday Morning, December 3, 2004  
Room 312 (Hynes)

#### **8:30 AM \*HH14.1**

**Capillarity-driven Assembly of Cellular Carbon Nanotube**

**Foams.** Nirupama Chakrapani<sup>2</sup>, Binqing Wei<sup>3</sup>, Alvaro Carrillo<sup>1</sup>, Pulickel M. Ajayan<sup>2</sup> and Ravi S. Kane<sup>1</sup>; <sup>1</sup>Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; <sup>3</sup>Electrical and Computer Engineering, Louisiana State University, Baton Rouge, Louisiana.

Carbon nanotubes have numerous potential applications as a result of their outstanding mechanical and electronic properties. The pursuit of these applications is hindered by the difficulty of manipulating these nanomaterials and organizing them into macroscopic structures. We

use capillary forces to direct the assembly of carbon nanotubes into cellular foams. We will describe the mechanisms by which these structures are formed. We will also discuss methods for controlling the length scale, orientation, and shape of the cellular structures. Applications of these nanostructured materials will also be discussed.

#### 9:00 AM [HH14.2](#)

**Carbon Nanotube Solid Filters.** Anchal Srivastava<sup>1</sup>, O. N. Srivastava<sup>1</sup>, Saikat Talapatra<sup>3</sup>, R. Vajtai<sup>4</sup> and Pulickel M. Ajayan<sup>5</sup>;

<sup>1</sup>Department of Physics, Banaras Hindu University, Varanasi, India; <sup>2</sup>Department of Physics, Banaras Hindu University, Varanasi, India; <sup>3</sup>Department of MS & E, Rensselaer Polytechnic Institute, Troy, New York; <sup>4</sup>Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; <sup>5</sup>Department of MS & E, Rensselaer Polytechnic Institute, Troy, New York.

Over the last decade of nanotube research, a variety of organized nanotube architectures have been fabricated using chemical vapor deposition. The idea of using nanotube structures in separation technology has been proposed. However, building macrostructures of nanotubes having controlled geometric shapes, density and dimensions for specific applications still remains a challenge. In order to perform various separation applications with nanoscale structures in a practical way, appropriate large-scale structures need to be designed and built with nanoscale units. By using a continuous spray pyrolysis method we have, for the first time, synthesized macroscale hollow carbon cylinders as large as centimeters in diameter and several centimeters long, with walls (ranging from 300 nm -500nm thick), consisting of micron length aligned multiwalled nanotubes. These cylindrical membranes are used as filters in the demonstration of two important applications. First, they are used as filters for effectively eliminating multiple components of heavy hydrocarbons from petroleum, a crucial step in post-distillation of crude oil, with a single step filtering process. Second, the filters are found to be efficient in the bio-filtration of bacterial contaminants such as E-Coli from water and nanometer sized polio virus (25nm). These macro filters can be cleaned for repeated filtration process through ultrasonication and autoclaving. The exceptional thermal, and mechanical stability of nanotubes, and the high surface area, ease and cost-effective fabrication of the nanotube membranes may allow them to compete with ceramic and polymer based separation membranes used commercially.

#### 9:15 AM [HH14.3](#)

**Vibrational Spectroscopic Studies of Gas Adsorption in Carbon Nanotube Bundles.** Christopher Matranga<sup>1</sup>, Liang Chen<sup>2</sup>,

Karl Johnson<sup>2</sup> and Bradley Bockrath<sup>1</sup>; <sup>1</sup>National Energy Technology Laboratory - U. S. Dept. of Energy, Pittsburgh, Pennsylvania; <sup>2</sup>Dept. of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Understanding the adsorption of molecules on single-walled carbon nanotube (SWNT) bundles is a fundamental step for using these materials in chemical sensing, storage, or membrane applications. In particular, we need to understand how different molecules access the various adsorption sites in SWNT bundles and how processing/purification procedures affect this access. By using Fourier Transform Infrared Spectroscopy (FTIR) and grand canonical Monte Carlo (GCMC) simulations, the adsorption of CO<sub>2</sub> and its displacement by Xe are studied. The FTIR experiments show that CO<sub>2</sub> physisorption at 77 K produces an infrared peak at 2330 cm<sup>-1</sup> for endohedral physisorption and at 2340 cm<sup>-1</sup> for groove/external surface physisorption. Exposure to Xe causes a sequential displacement of CO<sub>2</sub> from these sites as shown by an intensity loss of the 2330 cm<sup>-1</sup> peak, which precedes the loss at 2340 cm<sup>-1</sup>. The GCMC simulations on heterogeneous and homogenous bundles show that CO<sub>2</sub> in endohedral sites is initially displaced by Xe before that in groove/external surface sites. The CO<sub>2</sub> populations in each site of the bundle are taken from the GCMC simulations and used to model the FTIR intensity variations as a function of Xe pressure. The qualitative agreement between the simulated and experimental intensity changes is good, suggesting that the intensity changes seen in the experiments are related to CO<sub>2</sub> displacement from the sites indicated in the simulations. This agreement also serves as strong evidence that the adsorption site assignments of the IR peaks at 2330 and 2340 cm<sup>-1</sup> are indeed correct. We use these IR assignments to study the displacement of CO<sub>2</sub> by other IR active gases, such as CO. By correlating the intensity decreases for specific CO<sub>2</sub> peaks with the intensity increases seen for CO when it displaces CO<sub>2</sub>, we are able to make strong arguments for the physisorption site for CO and other gases.

#### 9:30 AM [HH14.4](#)

**Preparation of Tailor-Designed Carbon Nanotube Atomic Force Microscopy Probes for Critical Dimensions Applications.** Joshua David Schumacher<sup>1</sup>, Yusuf Emirov<sup>1</sup>, Bert

Lagel<sup>1</sup>, Nhan Nguyen<sup>1</sup>, Benjamin Rossie<sup>2</sup> and Rudy Schlaf<sup>1</sup>;  
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The continuously shrinking dimensions of integrated semiconductor circuits progressively render standard metrology techniques insufficient for process control and quality assurance. Critical dimension atomic force microscopy (CD-AFM) is increasingly used by the semiconductor industry to address these challenges. The current state-of-the-art, precision-etched or high-aspect ratio Si probes have longevity issues. Carbon nanotubes (CNT) are promising structures for AFM probes for use in high aspect ratio critical dimension metrology (CDM). The high mechanical strength of carbon nanotubes at sub 100 nm diameters makes them ideal high-resolution probes for narrow and deep features. Currently, manual attachment is the most often used method for construction of a CNT-enhanced AFM cantilever. This method has issues with control of the carbon nanotube attachment angle and is labor intensive. We report about our progress in developing a process for the direct growth of CNT from the tip of a modified cantilever using plasma-enhanced chemical vapor deposition (PECVD). This technique has produced CNT probes with defined length, diameter and nanotube orientation. AFM images and data taken with the prototype CNT-enhanced cantilevers demonstrate an improvement in resolution and accuracy compared to a standard cantilever.

#### 10:15 AM [\\*HH14.5](#)

**Carbon Nanotube Field Effect Transistors and Sensors Based on Nanotube Networks.** Jean-Christophe P. Gabriel, Nanomix, Emeryville, California.

The mission of Nanomix is to develop and commercialize chemical and biological sensors based on a technology platform that integrates carbon nanotubes into silicon microelectronics. Nanomix has developed a new sensing technology based on nanoelectronic components. Each device contains carbon nanotube network based FET sensors that are modified to respond specifically to various chemical or biological species. The nanosensor chip features state-of-the-art performance in a tiny package that consumes very little power. These inexpensive nanosensors will enable a new generation of research tools and the deployment of wireless sensor networks to replace more costly chemical sensors in many applications. In this presentation we will report the progress of Nanomix toward the production and commercialization of our generic platform for the development of new sensors (work supported by NSF SBIR grant 0340484) as well as more fundamental results on the use of this platform for the study of gas and liquids. For recent publications see: Electronic Detection of Specific Protein Binding Using Nanotube FET Devices. A. Star, J.-C. P. Gabriel, K. Bradley, G. Grüner, Nano Letters, 3(4) 459 - 463, 2003. Influence of Mobile Ions on Nanotube Based FET Devices. K. Bradley, J. Cumings, A. Star, J.-C. P. Gabriel, G. Grüner, Submitted Nano Letters, 3(5) 639-641, 2003. Flexible nanotube transistors. K. Bradley, J.-C. P. Gabriel, G. Grüner Nano Letters 3(10) 1353, 2003. Interaction of Aromatic Compounds with Carbon Nanotubes: Correlation to the Hammett Parameter of the Substituent and Measured Carbon Nanotube FET Response. A. Star, T.-R. Han, J.-C. P. Gabriel, K. Bradley, G. Grüner Nano Letters 3(10) 1421, 2003 Short-channel effects in contact-passivated nanotube chemical sensors. K. Bradley, J.-C. P. Gabriel, A. Star, G. Grüner Applied Phys. Lett., 83(18) 3821-3823, 2003. Charge transfer from ammonia physisorbed on nanotubes. K. Bradley, J.-C. P. Gabriel, M. Briman, A. Star, G. Grüner Phys. Rev. Lett. 91(21) 218301, 2003.

#### 10:45 AM [HH14.6](#)

**Carbon Nanotube Substrates for Electrochemical Biomedical Sensors.** Alexander V. Neimark<sup>1</sup>, Konstantin Kornev<sup>1</sup>, Gerardo Callegari<sup>1</sup>, Peter Ravikovitch<sup>1</sup>, Sigrid Ruetsch<sup>1</sup>, Plamen Atanassov<sup>2</sup> and Vijaykumar Rajendran<sup>2</sup>; <sup>1</sup>TRI/Princeton, Princeton, New Jersey; <sup>2</sup>University of New Mexico, Albuquerque, New Mexico.

Recent advances in fabrication of nanoporous fibers and membranes from various polymer precursors and carbon nanotubes make possible development of novel nanofluidic devices. We report on a new application of the SWCN composite substrates as supports for electrochemical biosensors. SWCN composite substrates, which are made in the form of fibers or webs, possess a hierarchical pore architecture. Using the methods of capillary condensation and droplet absorption, we demonstrated that they have high surface area and open porosity. This provides a significant absorption capacity and selective permeability that can be tailored by controlling pore openings. Employing horseradish peroxidase (HRP), we examined Direct Electron Transfer (DET) on SWCN nanoporous substrates as a signal generation mode in electrochemical biosensing. The high surface area allows for HRP immobilization by adsorption and the resulting surface complex exhibits DET behavior. The dependence of the current on the HRP concentration is non-linear suggesting a

kinetic controlled response. We discuss different designs of biosensors to exploit specific hydrodynamic and adsorption properties of SWNT on nanoporous substrates.

#### 11:00 AM [HH14.7](#)

**Double Wall Carbon Nanotubes as Molecular Sensors in Gases, Liquids and Polymers.** Ayman Bassil<sup>1</sup>, Pascal Puech<sup>1</sup>, Wolfgang S. Bacsa<sup>1</sup>, Sophie Barrau<sup>2</sup>, Philippe Demont<sup>2</sup>, Hannes Hubel<sup>3</sup>, David J. Dunstan<sup>3</sup>, Revathi Bacsa<sup>4</sup>, Emmanuel Flahaut<sup>4</sup>, Alain Peigney<sup>4</sup> and Christophe Laurent<sup>1</sup>; <sup>1</sup>Physique, LPST, Toulouse, France; <sup>2</sup>LPP, CIRIMAT-UPS, Toulouse, France; <sup>3</sup>Physics, Queen Mary University of London, London, United Kingdom; <sup>4</sup>LCMIE, CIRIMAT-UPS, Toulouse, France.

Apart of using functionalisation of nanotubes to incorporate them in a polymer matrix, one can use surfactants to increase the adhesion of nanotubes to couple them with the polymeric matrix. Moreover, surfactant should increase the quantity of debundled nanotubes in the polymer. Raman spectral bands are sensitive to their environment and can in return be used to sense the local environment e.g. the D\* band shifts up to 20 cm<sup>-1</sup> [1]. We show how double wall carbon nanotubes can be used to separate the effect on the external tube in interaction of the environment from the internal tube, which is only in interaction with the external tube and which does not depend on the environment [2]. Pressure experiment in alcoholic pressure-transmitting medium on 80% of double wall carbon nanotube reveals a new band associated to the outer tube. This additional spectral band, observed in high pressure Raman experiments, are also observed for nanotubes in polymer matrix composites and is unambiguously associated to a large blue shift of the G band. A large Raman mapping on several samples with constant percentage of CNT and various concentration of surfactant will be presented. The analysis of the bands (new bands and frequency shift due to their environment) can be tentatively correlated with the electric properties. [1] J. R. Wood and H.D. Wagner, Appl. Phys. Lett. 76, 2883 (2000) [2] P. Puech, H. Hubel, D. Dunstan, R.R. Bacsa, C. Laurent, W.S. Bacsa, submitted to Phys. Rev. Lett.

#### 11:15 AM [HH14.8](#)

##### **SWNT Network for Biomolecule Detection.**

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Nanosized materials have the potential to revolutionize the analytical tools in the field of biotechnology. The fascinating physical and chemical properties of carbon nanotubes have encouraged us to utilize them for development of a nano-biosensor. We report the application of single wall carbon nanotube (SWNT) for detection of biomolecules (streptavidin). The change in the electrical properties and mass modification of a network of carbon nanotubes on non-covalent binding of protein molecules on the sidewalls of carbon nanotubes has been observed. Commercially available SWNT (70% pure) produced by arc discharge technique were used for the experiments. A 1% solution by weight of carbon nanotubes in chloroform was prepared by dissolving SWNT and sonification of the mixture. In order to remove the nickel catalyst residue filtration of the solution was performed using 20nm Whatman anotops. SWNT network was formed on a pretreated glass substrate by dip-coating technique. AFM was employed to study the distribution of the SWNT on the glass slide. It was observed that the diameter of the nanotubes is 1.4nm with a length of 3-5  $\mu$ m. The Raman spectrum of the SWNT network shows the characteristic G-band and D-band peaks of carbon nanotubes. In order to study the electrical characteristics of the network, microelectrodes with 60  $\mu$ m spacing were formed by shadow masking technique. The electrical characteristics suggested that the network was semiconducting in nature. The change in electrical characteristics of the network when biomolecules were bound on the sidewalls of SWNT was monitored. The electrical response of the SWNT network shows a decrease from 97  $\mu$ A to 61  $\mu$ A in current due to binding of 20  $\mu$ l of streptavidin (conc. 1  $\mu$ M). In order to quantitatively estimate the mass of the biomolecules bound to the SWNT, Quartz Crystal Microbalance (QCM) was employed. The principle of QCM is based on the shift in the resonant frequency that can be attributed to the mass bound on the sensor membrane. The mass bound on the surface is calculated from the well-established Sauerbrey equation. QCM measurements were performed on the network of SWNT formed on RF sputtered gold surface of quartz crystals. Frequency shifts due to the increase of mass on the immobilization of protein molecules on the walls of carbon nanotubes were monitored. The QCM measurements of the carbon nanotubes show a frequency shift 120 Hz which corresponds to binding of 1 $\mu$ M of streptavidin on the carbon nanotubes sidewalls that is in agreement with the AFM studies. These results give a valuable insight to the development of a new generation of biomolecular assay.

#### 11:30 AM [HH14.9](#)

**Direct Attachment of Au Nanoparticles to Single Walled Carbon Nanotubes.** Saleem Ghaffar Rao<sup>1</sup>, Peng Xiong<sup>1</sup> and Seunghun Hong<sup>2</sup>; <sup>1</sup>Physics, Florida State University, Tallahassee, Florida; <sup>2</sup>Physics, Seoul National University, Seoul, South Korea.

Individual carbon nanotube-based devices have demonstrated great potential as high performance nanoscale electric components. The production of large scale integrated nanoelectronic circuits, however, has faced the difficulties of directed assembly of single walled carbon nanotubes (SWCNT) into regular array or onto predefined templates is thus of great interest. We recently reported that chemically functionalized surface with polar molecules can be used to align large number of SWCNT over macroscopic areas [1]. Here we report that bare Au surface, without any polar molecules, can be used to precisely align SWCNT. The bonding of SWCNT to bare Au surface appears to be even stronger than to polar molecules. Furthermore, we show that Au nanoparticles can be robustly attached directly to SWCNT without any chemical treatment of the SWCNT surface. We demonstrate this via precise alignment of SWCNT on patterns of Au nanoparticles and high resolution TEM. [1] Saleem Rao et al., Nature 425, 36 (2003)