SYMPOSIUM HH

Functional Carbon Nanotubes

November 29 - December 3, 2004

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David L. Carroll  
Center for Nanotechnology Dept. of Physics  
Wake Forest University  
214 Olin Hall  
Winston-Salem, NC 27109  
336-758-5508

Bruce Weisman  
Dept. of Chemistry  
Rice University  
MS 60  
Houston, TX 77005  
713-348-3709

Siegmar Roth  
Max-Planck-Institut Festkoerperforschung  
Heisenbergstrasse 1  
Stuttgart, 70569 Germany  
49-711-689-1434

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* Invited paper
Diamond Nanowires Grown Inside Carbon Nanotubes Upon Chemical Vapor Deposition: Thermodynamic and Kinetic Aspects. Ilia Manners 3 and Mitch Winnik 3; INanoscale Processing and Design, Duke University, Durham, North Carolina; 3Chemistry Department, Duke University, Durham, North Carolina; 3Chemistry Department, Brunel University, Uxbridge, Middlesex, UK. In situ Optical Monitoring of Vertically-Aligned Multiwall Carbon Nanotube Array Growth During Chemical Vapor Deposition. Alex A. Parsekian 2, 3, David B. Geoghegan 1, Stephen Jesse 2, 1, Hongtao Cui 1, Kalayu G. Belay 3, Jeremy Jackson 3, Ilia Ivanov 2, 3 and Gyula Eres 1; 1Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Materials Science and Engineering, University of Tennessee, Oak Ridge, Tennessee; 3Department of Physics, Florida A&M University, Tallahassee, Florida.

Carbon nanotubes are unique nanostructures with superior electronic and mechanical properties that also exhibit novel physical phenomena. The major obstacle impeding the commercialization of CNT-based devices is the lack of CNT 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 amorphous diblock copolymers. Several amorphous diblock polymers consisting of a non-polar and containing component and a metal containing segment has been explored as nanotemplates for generating well-ordered arrays of nanocatalysts. The examples include polystyrene-block-Fe complexed poly(vinylpyridine) and polystyrene-block-poly(fluorenyl ethyl methyl silane). Nanocatalyst arrays consisting of 2-3nm metal oxide particles with density of 600 particles/um2 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 amorphous 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.

Microwave plasma enhanced CVD has reproducibly yielded Single wall Carbon Nanotube (SWCNT) deposition. The tubes deposited in bundles containing 5-10 individual tubes each was either 1.3nm or 0.9 in diameter. 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 better control over nanotube properties. Deposition temperature was 800°C. Gas mixture was methane and hydrogen. The catalysts was bimetallic Mo/Co supported on MoO3 and dispersed on a silicon wafer. Raman, AFM and TEM were used to characterize the tubes results will be reported.
Nanotube lengths were controlled by rapid evacuation of the chamber. The monitoring of long, up to 2-4 mm VAA-MWNTs during the long time growth and growth termination kinetics, and discover a new phenomenon of competitive effect in the VAA-MWNT growth: shrinkage of VAA-MWNTs when the growth stops. A single 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-AC52-00OR22725 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 Noda1, Yoshiko Tsuji1, Yoichi Murakami1 and Shigeo Maruyama2; 1Department of Chemical System Engineering, The University of Tokyo, Tokyo, Japan; 2Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan.

The approach to disperse pre-prepared metal catalyst nanoparticles on substrates coated with a single-wall 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 one-dimensional structures of thin metal films 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 with nominal thicknesses from 0.001 to 1 nm were prepared on an a-SiO2/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 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 synthesis [3].

11:00 AM HH1.8
Catalyzed Epitaxial Growth of Single Wall Carbon Nanotubes from Seed Nanotubes. Yuhuang Wang1, Myung Jong Kim1, Hongwei Shan1, Carter Kittrell1, Bernie Ochoa1, Hua Fan1, Robert H. Haugen1, Richard E. Smalley1, Sivaram Anegi2, Gyula Eres3, Alex A. Puretzky4 and David B. Geoghegan5; 1Carbon Nanotechnology Laboratory, Rice University, Houston, Texas; 2G.B. Tech/NASA-Johnson Space Center, Houston, Texas; 3Oak Ridge National Laboratory, Oak Ridge, Tennessee.

(n, m) controlled synthesis of single wall carbon nanotubes (SWNTs) is a major challenge toward fulfilling their 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

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 catalysts 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 Cui1, Xiaojing Yang2, Larry R. Belsey2 and Douglass H. Lowndes1; 1Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 3Pton 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 carbide seeds 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 Iwasaki1, Tsuyoshi Yoshiida1, Takumi Aikawa1, Ryota Hosaka2, Kotaro Honda2, Guofang Zhong3, Yukio Furukawa3, Iwao Ohdomari2 and Hiroshi Kawarada2,3; 1School of Science and Engineering, Waseda University, Tokyo, Japan; 2School of Mechanical Engineering, University of Tennessee, Oak Ridge, Tennessee.

It is very important to control the growth orientation of CNTs on substrates for some applications such as field emission devices and CNT FETs. As many papers have been reported for vertically aligned CNTs, 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 SWCNTs. In this study, we demonstrate the low temperature synthesis of dense SWCNTs with very vertical alignment deposited by CVD. Substrates were Si wafers coated with 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 (MWCNTs) in our previous study. The height of CNTs is more than 170 nm 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 crystals observed in SEM images are perfectly aligned by the van der Waals force among SWNTs due to the very high density.

1:30 PM *HH2.1
Low Temperature Plasma Enhanced Chemical Vapour Deposition of Carbon Nanotubes and Nanofibres. John Robertson1, Stephan Hoffmann1, Britta Kleinseide1, V. G. Golovko2, J. Geng2, C. Ducati3, Bojan Boskovic1, Mirco Cantoni1 and Brian F. G. Johnson1; 1Engineering, Cambridge University, Cambridge, United Kingdom; 2Chemistry, Cambridge University, Cambridge, United Kingdom. 

SESSION HH2: Synthesis and Growth II
Monday, November 29, 2004
Room 312 (Hynes)
Aligned carbon nanofibres and nanotubes have been grown down to temperatures as low as 120°C in silicon and plastic substrates by plasma enhanced chemical vapour deposition. This was the first demonstration of the growth of vertically aligned nanotubes at such low temperatures. The growth rate is limited by the diffusion of the gas phase reactants to the catalyst surface. A sputtered Ni catalyst and DC PECVD is used in an acetylene/ammonia gas mixture. The growth rate is Arrenius with a low activation energy of 0.23 eV, which accounts for why growth is still possible at such low temperatures. The catalyst is restructured by Nickel layer into Ni nanoclusters. The ammonia etches away the unwanted amorphous carbon. Ni or Co catalysts can also be delivered to surfaces as inverse micelle structures (colloids), Ni forms nanoclusters on the substrate surface. The ammonia etches away the Ni nanoclusters and the use of a fresh substrate results in the opening of new avenues for controlling growth.

This method can be used to grow vertically aligned nanotubes in patterned structures as well as on substrates of complex shape such as foams, cloths and mats. The low temperature deposition onto plastics such as polyimide allows the growth of nanomaterials. We have developed a pulsed-laser deposition (PLD) technique to deposit vertically aligned carbon nanotubes on plastics.

The growth behaviors of carbon nanotubes can be largely grouped into 3 categories: carbon nanofibres, single wall carbon nanotubes (SWNTs), and multi-walled carbon nanotubes (MWNTs). The growth of carbon nanotubes can be controlled by adjusting the concentration of iron (III) nitrate nonahydrate/2-propanol solution which provided the Fe seed catalyst to nickel nitrate xylene. As described in this work, the detailed tube-growth mechanism involved in the growth of these nanotubes 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 walls are comprised of nanocrystals of graphene in the size range of 10-20 nm, oriented with respect to the wall surface. The orientation of the graphene sheets strongly 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.

We demonstrated an original type of carbon nanotube growth, namely "match-stick" carbon nanotubes [1]. This growth mechanism allows the formation of periodic nanofilaments whose elementary unit is a multilayer 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-foil joints constitute preferential bending and breaking points. They can be broken by a simple sonication process. The periodic insertion of magnetic nanoparticles also makes them potentially very interesting objects for new spintronics nanodevices. Magnetic characterisation of the inserted nanoparticles by MFM will be reported.


4:30 PM HH2.10

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 or Cr/Fe catalyst. 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. Ferreris1,2, John B. Vander Sands2 and Peter Szalados3; 1Materials Science and Engineering Program, University of Texas at Austin, Austin, Texas; 2Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Swedish 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 is the generation of carbon nanotubes in 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, H2O and H2 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 (Fe3C). SEM and TEM observations show that the cementite nanoparticles are closely associated with the periphery of carbon nanotubes and nanorods, and dominate 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.
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 (ECE-CVD) system at 1500°C. The carbon nanotubes are synthesized on substrate at 300-500°C. The CNT growth rate strongly depends on the substrate temperature, and the CNT density increases with the increase in the tube length. The CNT growth rate is also influenced by the gas flow rate, the substrate temperature, and the catalyst loading. The CNTs are typically 10-30 nm in diameter and several micrometers long.

The aligned growth of CNTs is crucial for the development of nano-structured materials. The growth of CNTs is strongly influenced by the substrate temperature, the gas flow rate, and the catalyst loading. The CNT growth rate increases with the increase in the substrate temperature and the gas flow rate. The CNT density increases with the increase in the catalyst loading. The CNT growth rate is also influenced by the gas flow rate, the substrate temperature, and the catalyst loading. The CNTs are typically 10-30 nm in diameter and several micrometers long.

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/SiO2/Si and Fe/SiO2/Si) located inside a laser oven apparatus [1]. It is thought that atomic carbon 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]. A focused ArF excimer laser with wavelength of 193 nm, pulse duration of 60 fs, fluence=3 J/cm2, repetition rate=10 Hz) was irradiated on Ni/Co catalyst-contained graphite target inside quartz tube operating at 1373K. As 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 SiO2/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 CNT growth was observed by SEM (Scanning Electron Microscopy, Hitachi, S-4300) and Raman spectroscopy (JASCO, NRS-1000HRS (032.8 nm)). The grown CNT on Fe/SiO2/Si substrates was examined by SEM. We confirmed the CNT growth on Ni/SiO2/Si substrates as well. When the film thickness, 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. Bratsev, Y. Sakai, J. Tajima, and K. Suzuki, Appl. Phys. Lett., 79, Y1104, 2001. [2] Y. Wei, G. Eres, V. I. Merkulov, and D. H. Lowndes, Appl. Phys. Lett., 78 (2001) 1394

Formation of Well-Aligned Carbon Nanotube on Glass Substrate by RF Plasma CVD Method at Growth Temperature of 500°C. Yoshiyuki Shove, 1 Yukata Yabe, 1 Tomio Iizumi 1 and Hidehiko Yamauchi 2; 1Dept. of Electrical and Electronic Engineering, Tokai University, Hiratsuka, Kanagawa, Japan; 2Eiko Engineering Company Limited, Yamanashi, 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 report the growth of vertically aligned multiwall carbon nanotube (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 subsequence diffusion and segregation processes on the catalyst nanoparticles. We have systematically studied these relations by a thermal CVD method. The catalytic Fe films used in our experiments were coated on SiO2/Si substrates in a plasma-enhanced chemical vapor deposition (PECVD) system. These Fe/SiO2/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).

The Characteristic of Carbon Nanotubes with Electroless Plating Deposited Ni Catalysts. Bohr-Han Huong, Chia-Ching Wu and Chi-Yun 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 (TH-CVD). The electroless plating method was adopted in the deposition of the Ni catalytic layer. Sulphuric 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 CNT from MWNTs were optimized 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 nanotube increased the immersion time further. The perpendicular growth of carbon nanotubes 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 graphene 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 geometrical structure and ID/IG ratio would be presented.
nanotubes (VA-MWNTs) at controllable tube densities. This technique is considerably important for the low temperature growth of MWNTs at high densities and orientations. However, the graphene 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 molecular order and diameter 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 aspect ratio of 1:2. In this study, we decided to extend this ratio to 1:4. Here, we describe the function of these plasmas on the graphitic order, diameters, and minimum growth temperatures of VA-MWNTs. Nanowires, and nanotubes 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 CVD. We first determined a minimum growth temperature (min. 500°C) for these nanostructures. Surface topographies and the amount of carbon deposits on the metal surface. We have demonstrated that the classic nucleation theory combined with phase diagram empirical approaches. An understanding of the formation mechanism of carbon deposits on metal surfaces is crucial for the development of carbon nanotubes and filaments. The analogies with other metal catalysts are discussed in the meeting.

HH3.12
Arc-Discharge Evaporation of Silver-Plated Graphite Rod. Mojtaba Yazdi, 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 for the arc-discharge production of nanotubes and nanofibers were studied. The arc-discharge technique is an advantageous method for synthesizing materials 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), field-emission transmission electron microscopy (FETEM). It was found that the deposited materials contain high concentrations of long carbon nanotubes and encapsulated silver crystals. These results, along with the arc-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, Haywan Wei1,2, Sang Nyon Kim1,3, Harris L. Marcus1,2 and Fotios Papadimitrakopoulos1,3; 1Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 2Department of Materials Engineering, University of Connecticut, Storrs, Connecticut; 3Department of Chemistry, Polymer Program, Nanomaterials Optoelectronics Laboratory, University of Connecticut, Storrs, Connecticut.

Aligning the shortened SWNT vertically in a controlled pattern, especially nano-nanotubes, is very important to many applications such as electron field emitters and sensors. To achieve this objective a low energy (100eV) electron beam was used to modify the surface of SWNTs to assist in localizing our metal-assisted self-assembly technique. The Si substrate was modified with an ultrathin Nanof film (20nm), followed by direct ebeam writing to produce the pattern for SWNT forest self-assembly. FIB-IR microscopy indicates the hydrophilic sulfide groups within Nanof 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 ions 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 in AFM topography images.

HH3.14
Catalyst Design for Carbon Nanotubes and for SiC Whiskers Production. Vladimir N. Ulibin, Anna N. Ushakova and Ilya N. Mazov; Boreskov Institute of Catalysis, Novosibirsk, Russian Federation.

Catalyst design for carbon nanotube production is usually based on empirical approaches. An understanding of the formation mechanism of carbon deposits on metal surfaces is crucial for the development of carbon nanotubes and filaments. The analogies with other metal catalysts 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 catalysis surfaces, namely: (1) the metal particle is stabilized 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. Guang You Cheo, 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 CVD. We first determined a minimum growth temperature (min. 500°C) for these nanostructures. Surface topographies and the amount of carbon deposits on the metal surface. We have demonstrated that the classic nucleation theory combined with phase diagram empirical approaches. An understanding of the formation mechanism of carbon deposits on metal surfaces is crucial for the development of carbon nanotubes and filaments. The analogies with other metal catalysts 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 catalysis surfaces, namely: (1) the metal particle is stabilized 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.

HH3.16
Control of the Amount of Defects in Single Wall Carbon Nanotube Nanoneedles and Their Effect on Peroxidase Based Biosensor Sensitivity, Sang Nyon Kim1, Xin Yu2, James F. Rusling2,3 and Fotios Papadimitrakopoulos1,2; 1Nanomaterials Optoelectronics Laboratory (NOEL), Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 2Department of Chemistry, University of Connecticut, Storrs, Connecticut; 3Department of Pharmacology, University of Connecticut, Storrs, Connecticut.

Regular orthogonal arrays of organized single walled carbon nanotubes (SWNTs) have attracted significant interest for the past few years. Our group has demonstrated the self-assembly based nanowires of SWNTs by using substrate-SWNTs hydrophobic interactions and SWNTs-SWNTs hydrophilic 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 product application for these organized nanotube forests. [1] Chatopadhyay, 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, 9551-9552 (2001). [2] Yu, X., Chatopadhyay, 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. Nechec1, V. W. Brisco1, G. C. Q. Shi2, G. P. Chou2, M. S. Dresselhaus1, G. Dresselhaus1,2, 1Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Materials Science, University of Connecticut, Storrs, Connecticut.

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 tangled, rope-like structure to a random suspension. A 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 Molenaur; 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 bundles and developed approximate models 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 nanoscale, 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...

HH3.29 Dispersion Quality and Corresponding Electrical Conductivity of Functionalized Carbon Nanotubes 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 to 300 K to study charge transport mechanism in composites. $\sigma_{DC}$ 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 to $\sigma_{DC}(T)$ 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 and 10 K based on the analysis of the reduced activation energy. The $\sigma_{DC}(T)$ of the compositions below $p_c$ with that of the composites above $p_c$. AC conductivity ($\sigma_{AC}$) was also measured in the frequency range of 10 Hz to 2 MHzs and in the temperature range of 77 K to 360 K, in which we observed the percolation behavior for the systems. We observed the influence of $\sigma_{AC}$ dependence of $\sigma_{AC}$ of the composites above and below $p_c$.

HH3.34 Dispersion and Alignment of Carbon Nanotubes in an Elastomer Matrix. Sang-Wook Ahn, 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 breakup, 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 scope 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.

HH3.35 Homogeneous Dispersion of the Surface Modified MWNTs in the PU Matrix and Electrical Conductivity of the MWNTs/PU Composites. Yoon Jin Kim, Yong Gun 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 deposition of a new type of solvents and polymers, which results in poor dispersion in the polymer matrix. We report here that dispersion characteristics of the surface modified multiwalled nanotubes (MWNNTs) in the polyurethane (PU) matrix and electrical conductivity of the MWNNTs/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 acid type, sodium 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 MWNNTs and higher electrical conductivity. The results are in good agreement with the two step adsorption model of cationic surfactants proposed by Y. Gao [1]. Both the optimized MWNNTs and cationic surfactant filled PU composites show very low percolation threshold, $p_c = 0.008 \pm 0.007$ vol. %, and relatively higher conductivity for percolation threshold than other nanotubes composites reported elsewhere. [1] Y. Gao et al., J. Chem. Soc. Faraday Trans. 1, 1987(1987).


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 temporal 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 templating, polarized absorption 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 100nm2).

HH3.26 Charge Transport and Metal-Insulator Transition in Multiwalled Carbon Nanotube-poly (methyl methacrylate) (PMMA) Composites. Hong-Mo Kim, Mi-Ki Kang, Yo Soo Kim, Ho-Young Kang* Won-Chan Jeong, and Soon Yoon*, Physics, Korea University, Seoul, South Korea; 2Physics, Ewha Womans University, Seoul, South Korea; 3Injin Nanotech Co., Seoul, South Korea; 4Novatens Inc., Anyang, Kyongki-Do, South Korea.

We report electrical properties and metal-insulator transition in thin
Polymer Resins, Heather J. Dowty and Max D. Alexander, Polymer Branch, Air Force Research Laboratory, Dayton, Ohio.

There has been great interest in recent years in creating high quality dispersions of nanotubes in polymer resin systems. These materials can be used to create highly conductive nanocomposites with the goal of using these materials in applications such as flexible electronics and smart structures. In this work, we present paths towards increasing conductivity or mobility by designing single wall carbon nanotube (SWNT) composite materials. TGFs 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 fold and that the mobility of the semiconducting composites increases by 20 fold relative to the host matrices. [1] H. Sirringhaus, et al, Science, 280: 1741 (1998). [2] P. P. Baude, et al, Appl. Phys. Lett., 83: 2064 (2003). [3] G. B. Blanchet, et al, Appl. Phys. Lett., 20: 463 (2003).

HH3.30
Homogeneous Carbon Nanotube/polymer Composites for Electrical Applications, Rajasulaparamanjan 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) and these composites show dramatic improvements in electrical conductivity with very low percolation thresholds. We show that only very small amount of SWNTs are needed to achieve conductivity levels required for different electrical applications without compromising the host polymers 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 wire, and transparent conductive coatings.


HH3.31

Due to their exceptional thermal properties single-wall carbon nanotubes (SWNTs) 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 1 wt% using the comparative technique. The samples were prepared by compounding method. We demonstrated moderate improvement in the composites' thermal conductivity of about 200% at 10% SWNT loading. The experimental results were analyzed using the well established 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 the aspect ratio of SWNT 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-Zhen Bi 1, Michael Strano 2, Colin Nuckolls 2 and Graciela B. Blanchet 1, 1DuPont Central Research & Development, Wilmington, Delaware; 2Chemistry, Columbia University, New York, New York; 3Chemical 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 such as displays, radio frequency identification tags, and integration with organic optoelectronics [1,2,3]. 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 - 10^-5 cm^2/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 10^4 fold and that the mobility of the semiconducting composites increases by 20 fold relative to the host matrices. [1] H. Sirringhaus, et al, Science, 280: 1741 (1998). [2] P. P. Baude, et al, Appl. Phys. Lett., 83: 2064 (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, Ilia N. Ivanov 2, Alex A. Puretzky2, Gyula Eres 1, Stephen Jesse2, and David B. Geoghegan 1, 1Materials Science and Engineering, University of Tennessee, Oak Ridge, Tennessee; 2Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Thermal properties measurements were performed for long, vertically aligned multilayer 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 an amine epoxy resin, preserving the thermal properties of these systems were tested using an IR-camera in vacuum. The Aligned VA-MWNT in amine epoxy at less than 2 wt. % loading were found to have higher thermal diffusivities than randomly-oriented MWNT containing loadings of 40 wt. %, and the percolation 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 NW construction to randomly distribute the 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 of ORNL.

HH3.34
Finite-Temperature Effects in Carbon Nanotubes, Nicolas Muenzer 1, Young-Su Lee 2 and Nicola Marzari 2, 1Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department 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 calculated using ab-initio molecular dynamics. The phonon dispersions of bulk diamond and graphite at finite temperatures are determined by a minimization of the vibrational free energy in the quasiharmonic approximation. Finally, the effects of thermal disorder on the ballistic transport of nanotubes are calculated from ensemble averages on microstates of the wavefunctions 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 Tabular Structures from Peapod Structures, Habin Su, Adria van Duin and William A. Goddard, Caltech, Pasadena, California.

A large number of experimental and theoretical studies have been reported on buckyball-containing nanotubes (a.k.a. peapod) structures since the discovery of these materials. It was originally believed that self-assembled buckyballs with nearly uniform centre-to-centre distances and resemble a nanoscopic peapod. The endofullerene 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 two coronulenes (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 Polymers 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 nuclear or electronic effects 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 functionalized carbon nanotube 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 dynamics 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 Sahakalan and Siegmar Roth; Max Planck Institute for Solid State Research, Stuttgart, Baden-Württemberg, Germany.

In two successive steps nanotubes are deposited onto a Si/SiO2 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 Siegle1, Franz-Joseph Ahlers2 and Sigmar Roth1;1MPI for Solid state research, Stuttgart, Germany; 2Physikalisch-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-wall 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 nanotube. The objective 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. Talysanski, 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 Shalakova, Martti Kaempgen, Yun Sang Woo, Serhat Sahaklan and Sigmar 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 week Van der Waals intermolecular interactions. To study the mechanism of electronic transport in SWNT-system, 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.

**HH4.1**

Field Emission from Semiconducting Quasi-One Dimensional Materials. Jun Chen1,2, S. Z. Deng1,2, N. S. Xu1,2, Weixin Zhang1, Xiaogang Wen1 and Shiehe Yang2;1 State Key Laboratory of Optoelectronic Materials and Technologies, Guangzhou, China; 2Guangdong Province Key Laboratory of Display Materials, Guangzhou, China; 3Technology School of Physics and Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou, China; 4Department 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 and 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.

**HH4.2**

NEXAFS Investigations of Nanotube-Based Systems. Tirindzi Hnejoj-Benny1, Sarbajit Banerjee1, Mahalingam Balasubramanian2, Sharadha Sambasivan2, Daniel A. Fischer3, James A. Misevich4 and Stanislaus S. Wong3;1 Chemistry Department, Stony Brook University, Stony Brook, New York; 2Materials and Chemical Sciences, Brookhaven National Laboratory, Upton, New York; 3Materials 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 high-performance applications as well as for the forthcoming characterization of the various carbon nanotubes. It has been shown that near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is a particular useful and effective technique for the study of the electronic structure of carbon nanotubes. In addition, we have been able to obtain quantitative and qualitative analysis of the order of a wide range of carbon based systems, including graphite, single-walled carbon nanotubes (SWNT) powder, SWNT films, and multi-walled carbon nanotubes.

**HH4.3**

TEM combined with Transport, Raman and AFM on the same individual Carbon Nanotubes and New Ways to Free-standing Nanostructures. Jannik Christian Meyer1, Dirk Obergfell1, Matthieu Puillet2, Jean-Louis Sauvajol2, Georg S. Duesberg3, Po-Wen Chiu1 and Siegmar Roth1;1Max-Planck Institute for Solid State Research, Stuttgart, Germany; 2Groupe de Dynamique des Phases Condenses, Universite de Montpellier II, Montpellier, France; 3Infincon 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 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.

**HH4.4**

Comparison of the Nanotube Properties, Purification and Separation Method. Jiri Cech and Siegmar Roth; MPI-FKF, Stuttgart, Germany.
Single wall carbon nanotubes produced by laser ablation, arc-discharge, and HiPco (HiPCO), respectively have been characterized and purified by various methods. In particular, heating in oxidative atmosphere (air and oxygen flow), refluxing in HNO₃, 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 on the purification and separation of semiconducting and metallic SWCNTs. The possibility of reliable and efficient separation opens new windows of applications.

9:45 AM AH4.5

**Diameter Dependent Enrichment along with the Bulk Separation of Metallic from Semiconducting Single Walled Carbon Nanotubes.**

Futoshi Papadimitrakopoulos 1, Zhengbang Luo 1, Sang Nyon Kim 2, Sang-Yong Ju 2, Kangsoo Li 2, Mathew Mkhize 2, SanthiSagar Vaddiraju 2, Kushan Biswas 2, G.G. Samsonidze 2, Shin Grace Choi 1, W. V. Brar 3, G. Dresselhaus 3, and M. S. Dresselhaus 3, 5

1Chemical Sciences and Engineering, Stanford University, Stanford, California; 2Department of Chemistry, Rice University, Houston, Texas; 3Center for Nanoscale Science & Technology, Rice University, Houston, TX, Texas; 4Carbon Nanotechnology Laboratory, Rice University, Houston, TX, Texas; 5Department of Chemistry, Rice University, Houston, Texas.

We have demonstrated that the phase behavior of SWNT / superacid dispersions is similar to that of isotropic nematogenic solutions of rod-like polymers used for the production of high performance fibers such as Kevlar (Davis et al. 2004, Ramsh 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. 2004, submitted). This work represents a critical step in the development of SWNT fiber applications such as nematic fibers with significant applications in fields such as optical fibers, composite materials, and nanoscale electronics.

10:45 AM AH4.8

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

Simon Moulton 1, Andrew Minett 2, Rob Murphy 2, Kevin Ryan 2, Denis McCarthy 2, Jonathan Coleman 2, Werner Blau 2, and Quantum Walsky 2

1Intelligence and New Materials Syntetic Research, ANU, 2Centre for Nanostructured Electromaterials, Wollongong, New South Wales, Australia.

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 species. We have used several organic soluble synthetic polymers (GPs) to selectively suspend single wall carbon nanotubes (SWNTs) in solution while leaving the GPs behind in the precipitate. The biomolecules used in this work were Salmon Sperrms DNA (MW 3.0x106) Chondroin Sulfate Sodium Salt (MW 7.5x104) and Chitosan Hydroxyste Oligomer (MW 1.5-3.0x105). The amount of suspended MNTs was determined using electron paramagnetic resonance (EPR). All of these biomolecules exhibited better selectivity of MNT over GPs than that previously reported for the organic soluble synthetic polymer poly(2-phenylheptene-1,2,5-dionoxygeny-o-phenylheptene-1,2,5-dionoxygeny (PPO)). Of the three biomolecules investigated, only Chitosan Hydroxyste Oligomer allowed the production of 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 nematic fibers with significant applications in fields such as optical fibers, composite materials, and nanoscale electronics.
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 Nanotube Nanowire Network Devices. Lei Ai, Qiang Fu, Chengguang 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

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. The as-extruded graphene fibers were then aligned using 2:1 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 45° 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 the 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 correlations 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

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 NIRS measurements using purified inner nanotubes. The sample was obtained 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 graphene shells, respectively. TEM and SEM observations, and thermal 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 have different thermal properties and emit together with the nanotubes, we did not centrifuging to allow us to remove particles and use this sample as a reference standard in NIRS measurements. 1. M. E. Iltis, et al. Nano Lett., 3, 309 (2003).

1:30 PM HH5.1

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, Peng He, Jie Lian, Rodney Ewing, Xavier Chaud, Robert Tournaire, Eric Beaugnon and Lumin Wang; 1Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; 2Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 3CRETA, 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 are usually used to be aligned along certain specified directions. Single wall carbon nanotubes, due to small amount of catalyst elements such as Ni and Co, could be well aligned in a magnetic field. However, the 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 composite matrix. The magnetic alignment mechanism is discussed.

2:15 PM HH5.3

This study reports a nanocomposite consists of conductive carbon nanotubes dispersed within an insulating polymer matrix [polystyrene (PS)], and its electrochemical properties, carbon nanotube electrical properties and 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 quickly evaporate, 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 the increase of carbon nanotube concentration. A sharp increase in the conductivity is observed between 0.2 and 1.0 wt. % of nanotube loading. When the loading of the carbon nanotubes reaches 1.0 wt. %, the conductivity of the nanocomposite is 110 times 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 conductivity 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 169. The primary EMI shielding mechanism of this nanocomposite is by reflection of electromagnetic radiation. For example, the nanocomposites containing 5.0 wt. % nanotubes 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-polystyrene composite 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. Tianxia Liu, Wei-De Zhang\(^1\), In Yeong Phang\(^2\), Lu Shen\(^3\) and Shue Yin Chow\(^4\).

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 is in the polymer/CNTs nanocomposites. However, the challenges for developing high performance CNTs/polymer nanocomposites are: (i) homogenous 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 (MWCNTs)/nylon-6 (PA6) nanocomposites with different MWCNTs loadings have been successfully prepared by simple melt-compounding approach. Fine and homogeneous dispersion of MWCNTs 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 MWCNTs 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 observed along the stretched CNTs and their bundles, indicating the anchoring locations of 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 transverse 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. % MWCNTs. The mechanical properties of MWCNTs/PA6 nanocomposite are substantially superior to those of neat PA6 due to (i) the reinforcement of evenly dispersed high-performance MWCNTs nanofillers throughout the matrix, and (ii) strong interfacial interactions between MWCNTs and PA6 matrix. In addition, a unique crystallization and melting behavior of MWCNTs/PA6 composites is observed and discussed by combining differential scanning calorimetry and X-ray diffraction, that is, only the α-form crystals are observed in MWCNTs/PA6, 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 Compressed B4C-CNTs Nanocomposites. Shao Chen\(^1\), B. Klortz\(^2\), M. Kaslowske\(^2\), Dezhi Wang, Jiayi Huang\(^3\), Z. Dongdong in the College, Chestnut Hill, Massachusetts; Army Research Laboratory, Aberdeen Proving Ground, Maryland; 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 nanotube-starch composites 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 169. The primary EMI shielding mechanism of this nanocomposite is by reflection of electromagnetic radiation. For example, the nanocomposites containing 5.0 wt. % nanotubes 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-polystyrene composite was achieved. This nanocomposite exhibited good electrical conductivity and excellent EMI shielding properties at a very low loading of carbon nanotubes.

3:00 PM HH5.6
Morphological and Mechanical Properties of Carbon Nanotube/Polymer Composites via Melt Compounding. William Edward Donclero and Russell E. Gorga. 2Department of Physics, Pusan National University, Busan, South Korea; 3NanoLab, Inc., Newton, Massachusetts.

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 nanotube was optimized in polypropylene. Tensile tests showed an increase of about 72% for the average tensile toughness from 64 MJ/m\(^3\) to 108 MJ/m\(^3\). 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. Jing Su, Xiankai Cao, Weiming Wei, Zhongqi Huang, Xingye Zhen, Chenglu Hu, Il Kim\(^1\) and Bog G. Kim\(^2\).

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 Nitroxides-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 used as templates in the following steps: Thermal Gravimetric Analysis, Transmission Electron Microscopy, FT-IR, IH NMR, and Raman spectroscopy. This polymer-SWNT composite is expected to have instant 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\(^1\), Ray H. Baughman\(^2\) and Ken R. Atkinson\(^3\).

1Chemistry/NanTech Institute, The University of Texas at Dallas, Richardson, Texas; 2Textile 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 discoveries surprising and useful mechanical and electronic properties for resulting nanofibers. Traditionally, nanotubes are produced by CVD techniques. We used chemical vapor deposition process to grow multilayered 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 fibers exhibit lower elastic strain over a large 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 advantageous for these highly retained twisted filaments and special methods are used to convert the twisted filaments to composite filaments having increased strength (up to 850 MPa).

Carbon nanotube fibers free of any polymer binder have been prepared by a flocculation spinning process. Dispensations 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) and 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 spectroscopy. 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. 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. 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), high toughness (about 100 J/gf). Possible applications of the fibers in electronic textile, supercapacitor and actuator areas are discussed.

Single wall carbon nanotube (SWNT) composite films are fabricated by layer-by-layer (LBL) assembly technique with poly(vinyl alcohol) (PVA) and poly(styrene-sulfonate) (PSS) as assembly partners. The combination of electrostatic, hydrogen and van der Waals interactions results in efficient deposition of polymeric matrix onto SWNTs. SWNTs wrapped by PSS are even 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 performances of the multilayered composites was evaluated by nanodentation, direct tensile strength and electrical conductivity measurements. The resulting composite films exhibit semiconducting characteristics and high mechanical strength. Among all possible applications, the use of such films in biomechanics, particularly in oneiroprosthetics, is targeted in this research. The preliminary characterization of multilayers as implantable biomaterials is being discovered surprising and useful mechanical and electronic properties for resulting nanofibers. Traditionally, nanotubes are produced by CVD techniques. We used chemical vapor deposition process to grow multilayered 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 fibers exhibit lower elastic strain over a large 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 advantageous for these highly retained twisted filaments and special methods are used to convert the twisted filaments to composite filaments having increased strength (up to 850 MPa).

Carbon nanotube fibers free of any polymer binder have been prepared by a flocculation spinning process. Dispensations 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) and 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 spectroscopy. 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. The electromechanical response was measured using custom made force transducer operated 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. The electromechanical response was measured using custom made force transducer operated 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.
Measurement of carbon nanotube-polymer fracture. Previous work in our laboratory [1, 2] has shown that it is stress/strain induced Raman band shifts. The 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. 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 facilitate the nanotube in pullout 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. 77, 410-412 (2000). 2. Interfacial friction energy measurements for multi-wall 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 located 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 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 response of single carbon nanotubes (CNTs) and single-walled carbon nanotubes (SWNTs) coatings. For this purpose, filled polyurethane 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 GR Raman band of single-wall carbon nanotubes (SWNTs) has its position strongly dependent on strain or applied stress 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 GR band shifts. If quantitative correlations between Raman band shifts and applied strains had been observed for various substrates, their 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 been developed from different polyls 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 were compared. 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 as well as oxidize 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 these new composite may 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, Kengping 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. Multivall 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 microscopy (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 composites coatings using template-mediated assembly of dicotic mesophase pitch. TEM study shows that a thin CVD graphitic layer could modify the orientation of the dicotic 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 Lee1, Marco Buongiorno Nardelli2,3 and Nicolò Mazzari1, 1Department of Materials Science and Engineering and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Physics, North Carolina State University, Raleigh, North Carolina; 3CCS-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 azo moieties have been investigated, highlighting the different roles that topology, charge transfer, and hybridization have in tuning or disrupting the conductance of the nanotube. About 70% also exploit our ability to map full Car-Parrinello electronic-structure simulations into a maximally-localized representation of the Kohan-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. Samsonidze1, Richiho Saito2, Naoki Kobayashi2, Ado Jorio3, Antonio G. Souza Filho5, Shin Grace Chou6, Gene Dresselhaus5 and Mildred S. Dresselhaus4, 1Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Physics, Tohoku University and CREST JST, Sendai, Japan; 3Department of Physics, Universidad Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil; 4Departamento de Fisica, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil; 5Department of Physics, Universidad Federal do Ceara, Fortaleza, Ceara, Brazil; 6Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; 7Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; 8Department 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 SWNT interlayer distances. 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 to predict the energy of the first 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). (3) The observed spread of the optical transition energies for different nanotubes within the same family (2n+1=const) is 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.

11:30 AM HH7.4 Atomic-scale Physics and Modeling of Schottky Barrier Effect in Carbon Nanotube Nanoelectronics. Yongjiong Xue and Mark A. Ratner; Chemistry Department and Materials Research Center, Northwestern University, Evanston, Illinois.

Structured 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 nanoelectronics is motivated by unique opportunities both for exploring novel device technology functioning at the nano/molecular-scale and for re-examining the physical principles of semiconductor microelectronics. The bottom-up approach based on atomic/molecular nanoengineering of devices presents the most promising routes to realizing nanoelectronics. This talk presents our current understanding of SWNT-based electronic devices and the potential of research on SWNTs.

11:15 AM HH7.5 The Limit of Ballistic Transport in Metallic Nanotubes. Michele Laizert1, Andrea Carlo Ferrani1, Stefano Piccanece, Francesco Manui2, Stefano R. Reis 3 and John Robertson1; 1University of Cambridge, Cambridge, United Kingdom; 2Laboratoire 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 on the nanotube circumference. However, metallic nanotubes display much stronger 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.

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2:00 PM HH8.2 Structure and Dynamics of Carbon Buckyballs Encapsulated into Single-Walled Carbon Nanotubes. Julien Cambeddaouz1, Stephane Rols1, Robert Almaric1, Jean-Louis Sauvajol1, Helmut Schobel2 and Hiromichi Kataura2. 1Groupe de Dynamique des Phases Condenses, CNRS, France; 2Institut Laue Langevin, Grenoble, France; 3Nanotechnology 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 C60 molecules inside them. The electrical properties of this system are investigated upon alkaline doping.1. The transmission electron microscopy images of these so-called peapods have revealed the one-dimensional character of the C60 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 C60 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 C60 molecules inside SWNTs. The general phonon density of states (GDOS) of the chains of C60 confined into SWNTs has also been derived from our measurements. This GDOS shows up characteristic features already observed in pure and alkaline doped C60 phases. In particular, this GDOS can be decomposed into two regions separated by a gap, namely: the [0-20 meV] intra-molecular energy range where all the observed vibrations can be attributed to intra-molecular modes, and the [0-20 meV] inter-molecular energy range where all the observed vibrations can be attributed to inter-molecular modes. The [0-20 meV] inter-molecular energy range where all the observed vibrations can be attributed to inter-molecular modes. The Lattice-dynamical calculations have been performed and allows to calculate the GDOS of different types of stacking of confined C60 (as monomers, dimers and polymers). The confrontation of the experimental GDOS with the calculated GDOS testifies to covalent bonding between a part of the C60 molecules. All these results show that the confined C60 molecules are partially polymerized inside the inner space of the tubes. 1 S.Saito and S.Okada, 3rd Symposium on Letters, 3, 1353-1355, 2003 [2] Zhou, S. D.; Li, X.; Artyukhin, A. M.; Wang, W.; Zhang, Y.; Dai, H. J. Phys. Chem. B, 105, 4744-4747, 1997 [3]Tans, S. J.; Verschueren, A. R. M.; Dekker, C.; van der Kippe, H.; Goedkoop, G.; Verheij, J.; van der Putten, H.; Wuite, H. Nature, 393, 49-52, 1998 [4]Kong, J.; Dai, H. J. Phys. Chem. B, 105, 2850-2853, 2001.

2:15 PM HH8.3 Fabrication of N-type Field-Effect Transistors Based on Self-Assembled Thin Films of Carbon Nanotubes and Poylaminodiamine (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 electronic devices. The electronic characteristics, mechanical, and electrical properties. Field-Effect Transistors (FETs) based on CNTs have been shown to exhibit field-effect mobilities as high as 12 cm²/Vs [1]. Recently, several electronic devices based on CNTs have been fabricated and characterized [2-5]. Most of those 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 attractive systems 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 (G10). 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 electron donating characteristic 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, 280, 155-157, 2000 [3] Tans, S. J.; Verschueren, A. R. M.; Dekker, C.; Nature, 393, 49-52, 1998 [4]Kong, J.; Dai, H. J. Phys. Chem. B, 105, 2850-2853, 2001.


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 polystyrene sulfonate as conducting polymer, DNA/SWCNTs fabricated 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 10⁶ 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 the presence 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 Jhang1, SangWook Lee2, DongShu Lee1, Siegnar Roth3, Eleanor E. B. Campbell3, GyuTae Kim4 and YungWoo Park1. 1School of Physics, Seoul National University, Seoul, South Korea, 2Max-Planck-Institute for Solid State Research, Stuttgart, Germany, 3Department of Electrical Engineering, Gothenburg University and Chalmers University of Technology, Gothenburg, Sweden, 4Department 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-wall carbon nanotubes (SWNTs). Mean lifetimes in high and low-current states, τlow and τhigh, 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.


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 consisting of 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 (VCNTFTET) consisting of CNTs directly on silicon chips can be achieved by Catalytic Chemical Vapour Deposition (CCVD). To this, CNT growth has to be optimized in terms of scalability, reproducibility, and yield. The crucial point is the catalyst design and its placement on the nanometer scale. The variation of the catalyst/support 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 better than 2µm. For electrical characterisation these CNTs were grown from metallic underlayers and individually contacted using e-beam lithography. A current density of 4×10⁴ A/cm² 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 electronic pulses. Using this CNT transistor it is possible to switch
We demonstrate a single-walled carbon nanotube p-n junction device. The p-n junction is formed along a single nanotube by electrochemical etching of a pair of split gate electrodes. By utilizing 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. 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.

For the first time, transport measurements in field-effect transistor configuration and TEM investigations 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.

Growing aligned carbon nanotubes (CNTs) on optically - and/or electrically - functional materials is essential for providing electrical contacts to CNTs, accessing their properties through optical stimuli, to pave the way for new types of CNT - based devices. Here, we report the growth of oriented bulk 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. This 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 SiO2 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 n- or p-type bottom contact formation we demonstrate a test device of P5(CNT) / ITO / Si(001) stacks. ITO-contacted 100 μm long CNT bundles exhibit ohmic response below 3 V, and a resistance of 335 Ω for a 3 cm2 contact. This is several orders of magnitude higher than the theoretically calculated resistance of 1 μΩ due to back contact resistance. At higher voltages we observe a superlinear behavior described by Poole Frenkel hot carrier injection across a 100 meV barrier. We describe this behavior in terms of electric field induced carrier injection from traps across a barrier at the ITO-CNT interface. The CNT-ITO structures also exhibit a thermoelectricity in the range of a few V to 100s of meV, when exposed to heat or to photo-excitation by a 1.5 μm wavelength laser source. The voltage depends 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, December 2, 2004
Room 312 (Hynes)


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 opening 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 ultrahigh 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 of 10-9 A/(Sr*m2*V); this is an order of magnitude larger than that of 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 the same as that of cold field emission guns. A CNT electron source for electron microscopes 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. Xiaoyu Liu, Zhehong Lao 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 or the contact 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 both center-exposed and contact-exposed devices, NO2 shifts the threshold voltage toward higher values, while NH3 lowers the threshold voltage. However, the changes of the subthreshold swing are in opposite directions for center-exposed and contact-exposed devices: while NO2 improves the performance of the contact-exposed devices, NH3 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.

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 is observed 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 the experimental measurements, in SWNTs. Moreover, I will discuss the role of backscattering generated by the deformation at the crossing is taken into account within each SWNT. The resemblance between our data and the theoretical predictions supports further evidence supporting the Luttinger liquid picture in SWNTs. To conclude 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 technique, 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 $100 \, \text{S/m}$. 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 HH10.1**

**Carbon Nanotube Photo-Detectors**, Matthew Scott Marcoccio, Michael 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 SiO2/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-SiO2. 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 increases the drain current of the channel current with respect to the gate voltage. Growing nanotubes with large channel lengths ($L=500 \, \text{nm}$), 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 voltage determines both 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 small enough that the entire length of the nanotube remains suspended, this is in contrast for tubes with length ($L>2 \, \mu \text{m}$) 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 (1-2nm) 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.

**10:15 AM HH10.4**


Since its recent discovery, the near infrared band-gap photo-fluorescence (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 (in structure) structural species will be shown. This includes 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 nanoscale maps of even large assemblages of SWNT, new methods will be described that can determine the chiral and diameter distributions of aqueous dispersed samples within seconds. Fluorescence imaging techniques allow the observation and tracking of individual SWNT nanotubes, a capability that has been taken up by macrophyte-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**


Spectroscopic measurements in visible frequency has been pursued on aligned carbon nanotubes in random and periodic arrays, for SWNTs and MWNTs. Many of these 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 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 Lunazzi, Moreno Meneghetti, Enzo Menna, Giulio Cerullo, Cristian Manzoni and Alessio Gianetta; 1)Physics, Politecnico di Milano, Milan, Italy; 2)Chemical science, University of Padova, Padova, Italy.

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 ps/nanosecs 5 fs, associated to the exciton reaching recovery, which is assigned to the exciton 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 homogeneous 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 cm$^{-1}$ 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**


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-radiated gold tip. This enhanced field acts as our Raman excitation source. The Raman excitation is detected with a high sensitivity interferometer and is on the order of 20nm. Using this technique we uniquely map spectral changes along the tube 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 $E_2g$, $G$, $D$ and $G'$ 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. We attribute this loss in resonance scattering properties due to dopant-induced changes in the electronic properties of SWNTs.

11:30 AM HH10.5 Ultraviolet Transient Absorption Spectroscopy Investigations of Excited State Dynamics in SWNT/Polymer Composites. David Sterin-Barnett1, Stephen Ellison1, Cheol Park2, Krystopher Wise2 and John Papanikolas1, 1Chemistry, University of North Carolina-Chapel Hill, Chapel Hill, NC; 2Institute 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-wall 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, which change in the polymer environment alter the band positions and decay rates. Solution phase data provides further information on the role of the environment in the 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. Rozhiv, Youshir Shokih, Kohei Tsuchiya, Shun Matsuzaki, Kohtarishi, Yoji Aizuka and Madoka Tokumoto1, 2, 3, 2, 3 AIST JAPAN, Tsukuba, Japan; 2Tokyo Univ. Sci., Noda, Japan; 3Tokyo 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 has 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 urn) and metallic (about 0.7 urn) 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, which change in the polymer environment alter the band positions and decay rates. Solution phase data provides further information on the role of the environment in the 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.


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 (50-70 meV); which suggests an excitonic depopulating 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^-4 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. These measurements yield a long natural radiative lifetime in excess of 10μs that is consistent with a strong absorption coefficient and a small Stokes shift. Combining the measured PL lifetime with a predicted natural radiative lifetime of
Sug~ests that the true PLQY for an unbundled tube is 6.5x10^{-12}, and the ratio of the measured PLQY to this value could be a reasonable estimate 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 effort to develop correlations between SWNTs and colloidal semiconductor quantum dots [1] C.D. Sdrapari, S. Ismail-Beigi, L. X. Benedict, et. al., Applied Physics a-Materials Science & Processing 78, 1120 (2004). [2] Y. Z. Ma, J. Stenger, J. Zimmermann, et. al., Journal of Chemical Physics 120, 3968 (2004).


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 a 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 500 meV (in agreement 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. Nanotubes of relatively large diameters (emission wavelength longer than 1.1 mm), we also observe the absorption features 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 (ΔE ~ 30 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. 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 determined by electronic states 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)


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 gave consistent results for the charge transfer and Fermi-level shift (ΔE_F) of acid-doped nanotubes. We find ΔE_F approximately 0.35 eV in nitric acid doped SWNT and approximately 0.5 eV in sulfuric acid doped SWNT. Using these ΔE_F values in a detailed Raman 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.


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 performance of sidewall fluorination of 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 single-wall 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. Hideyuki Isomura 1, Shinji Kawasaki 2, Rujio Okino 1 and Hiroinchi Katsuyama 2; Department of Chemistry, Shinshu University, Ueda, Japan; 1Graduate School of Engineering, Nagoya Institute of Technology, Nogoya, Japan; 2Neotechology 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 single-walled carbon nanotubes (S-CNTs) 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 heat treatment of C-SWNTs at 698 K in the air at 2 atm. The reaction was carried out using 1 atm elemental fluorine in a temperature range RT-523 K. The composition of the open-end fluorotubes, fluorinated at 311, 473, and 523 K were C_F=0.39, C_F=0.45 and C_F=0.51, 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 the 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. Raman were observed for all the open-end fluorotubes whereas closed-end tubes with F/C=0.98 showed no RBMs. Electrochemical and thermal properties of fluorotubes. The discharging performance of fluorotubes was studied on Li/1M-LiClO4 (EC+DEC)/F-SWNTs cells (F-SWNTs=fluorotubes prepared by RT-473K fluorination of HiPco-tubes) under a current density of 100 μA/cm2. The OCV value of fluorotubes are ca. 0.7 V higher than that of graphite fluoride (CF)n, 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)n, 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)n, and that the discharge of fluorotube electrode proceeds homogeneously, forming discharged product CF0.51-0.5x, where the fluorine concentration decreases with the discharge ratio x(0.05 ≤ x ≤ 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 1, Rajagopal Ramasubramaniam 1 and Haiying Liu 2; 1Izvex Corporation, Richardson, Texas; 2Department 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 functionalization of carbon nanotubes (rigid functional conjugated polymers, poly(aryleneethynylene) = (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 use micro fluidic techniques to fabricate real functional chemistry of PPE allows us to prepare various SWNTs functionalization, purification, manipulation, and assembly) in a straightforward manner. Recent progress in our program has involved carbon single-walled nanotube hybrid nanostructures. The integration of semiconductor nanocrystals (NCs) onto carbon nanotubes (CNTs) could result in a wide range of applications in biosensors, bio-fuel cells, and electronic devices. The aim of our research is to provide a detailed understanding of the inter-NC distance and NC orientation, must be controlled in a controllable manner. We recently reported a non-wrapping approach to 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. Choi, J. et al. J. Am. Chem. Soc. 2002, 124, 9654-9655.

4:30 PM HH112.7
N- and B-Doped Carbon Nanotubes and Nanostructures via Pyrolysis of Aerosols. Nicole Grobert. 1Department of Materials, Oxford University, Oxford, United Kingdom. 2Max-Planck-Institut für Metallforschung, Stuttgart, Germany.

In recent years, various carbon nanotube synthesis techniques have been developed. 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 aerosol nanoparticles generated from benzylamine/ferric solutions at 950 C using an ultrasonic spraying device yields large quantities (several grams/30 min) of pure and well-aligned CNx nanotubes (30-130 microns long, 10-200 nm outer diameter). Scanning and transmission electron microscopy reveals 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/trimethylborate-based mixes at 900-950 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 boron structures are part of the 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 the 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 depends on the pyrolysis temperature. Finally, preliminary results concerning to oxidation resistance studies are presented. With this method it is now possible to explore the chemical and physical properties of CNx nanotubes and B-doped carbon nanostructures and their composite materials.

4:45 PM HH112.8

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 structurally complementary chemical functionalities. We have developed a very general approach, the bundling approach, in which CNTs are functionalized at the ends. This method is now possible to explore the chemical and physical properties of CNx nanotubes and B-doped carbon nanostructures and their composite materials.

4:15 PM HH112.6
Self-Organization of Semiconductor Quantum Nanocrystals on Carbon Single-Wall Nanotubes into Close-Packed Linear Arrays. Chaitav Engtrakul, 1 Jovan M. Nedeljkovic, 1 Yong-Hun Kim, 1 Marcus Jones, 1 Randy J. Ellington, 1 Mark C. Hanna, 1 Scott P. Ahrenkiel, 1 Kim M. Jones, 1 Mark F. Davis, 1 Timothy J. McDonald, 1 Kate J. Franz, 1 Thomas Gennett, 2 Anne C. Dillon, 1 Katherine H. Gilbert, 1 Philip A. Parilla, 1 Jeff F. Alleman, 1 Shengbai Zhang, 1 Olga I. Micic, 1 Garry Rumbles, 1 Arthur J. Nozik, 1 and Michael J. Heben, 1 Materials Engineering, Univ. of Kentucky, Lexington, Kentucky. 2National Renewable Energy Laboratory, Golden, Colorado.

The aim of our research is to provide a detailed understanding of the optical and electronic properties of semiconductor nanostructures and their controlled 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 NH2 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.

The self-organization of semiconducting quantum nanocrystals on single-walled carbon nanotubes into close-packed linear arrays (SWNT-SQCN) provides an alternative to the highly uniform attachment on carbon nanotubes. TEM and AFM measurements clearly confirmed the successful attachment. This approach provides a universal and efficient method to attach semiconductor quantum nanocrystals onto 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.
7% of the total length. EDS of nanoparticle-CNT junctions fabrication processes do not include any high-temperature one. We functionalization was also demonstrated. From plasma oxidized CNTs as compared to raw CNTs. Cysteamine substrate in advance. Then we put this substrate with a small cup of substrate can be decreased by covering it with a suitable self-assemble 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. 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 SiO2 substrate can be decreased by covering it with a suitable self-assemble monolayer (SAM) film. We used hexamethyldisilane (HMDS) in this experiment. HMDS vapor reacts with hydroxyl groups on the SiO2 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 in 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 electric 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 SiO2 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 Aerospace 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 2.5-3 nm. A Y-junction individual SWNTs with same 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 Schif; Electrical Engineering, University of South Florida, Tampa, Florida.

Carbon nanotubes have shown promising properties for applications in electronic circuits and other devices. Several device structures have been demonstrated in recent years by manual manipulation of single nanotubes. The integration 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. Youngaik 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 MWNT Arrays. Anvar A. Zakhidov1, Alex Zakhidov2, Alexander N. Obratszov3, Rashmi Nanjundaswamy4, Sergei Lee5, Austin Cunningham1, Mei Zhang1 and Mike Sampson1; 1Physics, University of Texas at Dallas, Richardson, Texas, 2Physics, 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 (MWNT). 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 Photocathode Diode Based on an Individual C/CN_x Multi-walled Nanotube Junction. Yuning Lai, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

Herein we demonstrate the possibility of creating Schottky-type photocathode diodes based on an individual C/CN_x 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 current 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-like rectifying diode-like structure was formed on single C/CNx nanotube. An absorption spectrum of a C/CNx nanotube film deposited on glass exhibits a broad absorption band in the visible range. Experiments using the Xe lamp with various filters gave the similar effect. The photoconductance 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 750 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 light 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 distributed on-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 process. However, when 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-DWNT-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, Dezh Wang and Zhifeng Ren; Dept. of Physics, Boston College, Chestnut Hill, Massachusetts.

Double-walled carbon nanotubes (DWN Ts) are proved to have excellent field emission properties. Simple and effective methods have been developed to control the density of DWN Ts on silicon substrates. The current density of 1 mA/cm² 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 both photocarriers and substrates, the distribution of DWN Ts and the roughness of the substrates. Field emission stability of DWN Ts is also studied.

HH13.9 Combining Nanotubes and Chromophores for Broadband Optical Limiting. Nicolas Izard1,2, Cecilia Menard3, Eric Doris4, Charles Mioskowski5, Didier Riehl6, and Anglaret Eric7; 1GDPC, Université Montpellier 2, Montpellier, France; 2Département laser-optiq, Centre Technique d’Arcueil DGA, Arcueil, France; 3Service de Marquage Moleculaire et de Chimie Bioorganique, CEA-Saclay, GIF sur Yvette, France.


HH13.10 Abstract Withdrawn

HH13.11 Functionalized Carbon Nanotubes through Mechanically Bound and Rigid Organometallic Complexes. Jordan Poles1,2, Tom D. Dubois1,2 and Tom A. Schmedake1,2; 1Chemistry, UNC Charlotte, Charlotte, North Carolina; 2Center 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 assembled nanotube electronics. This 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 dynamic calculations, we have modeled the assembly process of two-dimensional and three-dimensional structures of carbon nanotubes. The links 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 dimensional 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 switching 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. Hyangbin Son1, E. Barroso2, Y. Hori3, Shin Grace Chou4 and M. S. Dresselhaus5, 6, 7; 1Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Physical, Massachusetts Institute of Technology, Cambridge, Massachusetts.

An enhanced Raman signal is demonstrated from individual suspended SWNTs and from isolated SWNTs grown on a doped polycrystalline silicon. The radial breathing modes (RBMs) 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⁻¹ 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 Chou1, Henrique Bucker Ribeiro2, Eduardo B. Barros3, Adelina P. Santos4, Georgii G. Samsonidze5, Marcos A. Pimenta6, Ado Jorio7, Flavio Plentz Filho7, Mildred S. Dresselhaus8,9,10,11,12,13, Richiro Saito10, Ming Zheng10, G. Bibiana Onoa14, Ellen D. Semke15, Anna K. Swan16, M. S. Unlu17, and Bennet B. Goldberg18,19,20,21; 1Chemistry, MIT, Cambridge, Massachusetts; 2Physics, Universidad Federal de Minas Gerais and Development, Belo Horizonte-MG, Brazil; 3Physics, Universidad Federal de Ceará, Fortaleza-CE, Brazil; 4Chemistry, Centro de Desenvolvimento da Tecnologia Nuclear, CDTN/CE/BR; 5Physics, MIT, Cambridge, Massachusetts; 6ECS, MIT, Cambridge, Massachusetts; 7Tecnologia Nuclear, CDTN/CNEN, Belo Horizonte-MG, Brazil; 8Physics, Universidad Federal de Minas Gerais and Development, Belo Horizonte-MG, Brazil; 9Physics, Universidad Federal de Ceará, Fortaleza-CE, Brazil; 10Chemistry, Centro de Desenvolvimento da Tecnologia Nuclear, CDTN/CE/BR; 11Physics, MIT, Cambridge, Massachusetts; 12ECS, MIT, Cambridge, Massachusetts; 13Physics, Tohoku University and CREST JST, Sendai, Japan; 14Francis Bitter Magnet Laboratory, MIT, Boston, Massachusetts; 15Dupont Central Research and Development, Wilmington, Delaware; 16ECE, Boston University, Boston, Massachusetts; 17Physics, Boston University, Boston, Massachusetts; 18Physics, Chemistry, UNC Charlotte, Charlotte, North Carolina; 19Optical Limiting. Combining Nanotubes and Chromophores for Broadband Optical Limiting. Henrique Bucker Ribeiro, Eduardo B. Barros, Adelina P. Santos, Georgii G. Samsonidze, Marcos A. Pimenta, Ado Jorio, Flavio Plentz Filho, Mildred S. Dresselhaus, Richiro Saito, Ming Zheng, G. Bibiana Onoa, Ellen D. Semke, Anna K. Swan, M. S. Unlu, Bennet B. Goldberg, Nicoletta Di Renzo, Carolina E. R. Ribeiro, Christiane L. V. Ribeiro, Maria R. T. Araujo, Thomas D. Dubois, and Tom A. Schmedake. Physical Review B 83, 035437 (2011). 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 WRBM values were found to be relatively insensitive to the type of wrapping agents surrounding the nanotube. The values of WRBM and the first and second resonant interband transitions, E₁₃ and E₂₂, 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 Eᵣ, 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 Luo2, Rongfu Li1, Sang Nyon Kim1 and
The radial breathing mode (RBM) region of the resonance Raman spectra of 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 ($E_i(n,m)$) by the change in SWNT physicochemical environment. Three sets of $E_i(n,m)$ values were used to reconstruc these RBM profiles, based on: (i) photoluminescence (PL) measurements, (ii) a simple tight-binding (TB) model, and (iii) a set of modified, TB-based $E_i(n,m)$ values for the underestimation of the influence of chiral angle on SWNTs for diameters below 1 nm. The simulation revealed that the PL-determined $E_i(n,m)$ set provided a good fit in terms of peak position as opposed to TB-calculated values. Moderate improvement was attained using the third set of $E_i(n,m)$ values indicative of the importance of both curvature and chirality effects. Providing an accurate set of $E_i(n,m)$ 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. Barros¹,², Hiroshi Inokuchi¹,², Shinya Kudo¹,², Masahiko Shindo¹,², Takashi Arai¹,², Naoki Naka¹,², Tetsuji Kondo¹,², Takeshi Katsumata¹,², Takatoshi Satoh¹,²; ¹Department of Nanoscience and Technology, Ritsumeikan University, Kyoto, Japan; ²Department of Material Science and Electronics, Ritsumeikan University, Kyoto, Japan.

The electronic and vibrational properties of Single Wall Carbon Nanotubes (SWNTs) isolated on silicon oxide substrates have been widely studied. The fact the nanotubes are attached to the substrate surface suggests a significant interaction between the nanotube walls and the surface. Possible applications of carbon nanotubes to electronic devices are expected to require nanotubes placed on a substrate. 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 µm 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 substrate, the PL signals were observed in all cases of nanotubes. This result is based on the nanotube's ability to be excited by the laser beam and the fact that the PL signals were observed in all cases of nanotubes. The authors acknowledge support from NSF grant DMR-01-16042 and Intel Corporation.

HH13.16
NMR Investigations on alkali intercalated carbon nanotubes, Michael Schmid¹,²,³, Christophe Goze-Bac⁴, Michael Mehring⁵, Patrick Berner⁶ and Siegmund Roth¹; ¹Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, Germany; ²GDPC, Universite Montpellier II, Montpellier, France; ³Physik. Inst., Universitaet Stuttgart, Stuttgart, Germany.

Single-wall carbon nanotubes (SWNT) exhibit outstanding electronic properties that promise to open up wide opportunities for nanoscale applications. Interactions of the 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 work we report results from 13C- and alkali-NMR measurements on alkali intercalated SWNT. Alkali metals like Li, Rb and Cs were reversibly intercalated in SWNT with different stoichiometry. By performing temperature dependent 13C-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 will exhibit $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 view of structural simulations of C-ions intercalated in SWNT.

HH13.17
Effect of Doping on the Resonant Raman Scattering in Metallic Single-Walled Carbon Nanotubes (SWNTs), Rahul Rao¹, Gaetan Kesku², Mildred S. Dresselhaus² and Apparao M. Rao³; ¹Physics and Astronomy, Clemson University, Clinton, South Carolina; ²Department of Physics and 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.% . Raman micro-scans excited with the 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 Park¹, Jin Hwan Choi², Saet Byedol Oh¹, Jun Ho Chang¹, Ho Soo Hwang², Jong Hun Han², Sang-Woo Joo³, Gu-Yoon Kim³ and Bog G. Kim³; ¹Department of Polymer Science and Engineering, Pusan National University, Busan, South Korea; ²Department of Chemistry, University of Connecticut, Storrs, Connecticut; ³Department of Chemistry and Biochemical Engineering, Dongseo University, Busan, South Korea.

Polynye-functionalized Single-Walled Carbon Nanotubes(SWNTs) were prepared using Atom Transfer Radical Polymerization(ATRP). Hydroxy groups on SWNTs were introduced through Friedel-Crafts alklylation 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, transmission electron microscopy(TEM), and thermal gravimetric analysis(TGA). The degree of functionalization on SWNTs was estimated to be 20% on 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 Bends-milled SWNTs by Nitroradical, Hiroshi Moriyašma¹, Kazuhiro Kurihara¹, Masaaki Saibara¹, Toshio Ishii², Kozo Hayashi², Atsushi Yusa³ and Terumasa Kondo⁴; ¹Department of Chemistry, Toho University, Funabashi, Japan; ²Ashinawa Finetech Co., Ltd., Narashino, Japan; ³Hitachi Maxoll 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 solvent is one of the obstacles 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 $C_{60}$. Chiang reported that hexanitrofullerene was produced by the reaction of $C_{60}$ and nitric acid[1]. According to this method, bends-milled SWNTs were obtained and 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 was rather soluble in ordinary organic solvents and the characterization results 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-Benny¹, Sambit Banerjee² and Stanislaus S. Wong²; ¹Chemistry, Stony Brook University, Stony Brook, New York; ²Department of Materials Science and Chemical Sciences, Brookhaven National Laboratory, Upton, New York.

Oxidized, cut single-walled carbon nanotubes (SWNTs) have been characterized with lanthanide salts such as Eu, Tb, and La. These studies are not only aimed at developing a fundamental understanding of the coordination chemistry of metal ions and of metal ion interactions with the nanotube but also to develop strategies for the size- and shape-selective delivery of lanthanide ions using SWNTs.
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 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 analytes 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.  
Nanumshaven Singhvi1, B. M. Nichols2, Matthew S. Marcus3, O. M. Castellini4, R. J. Hamers1, M. A. Eriksson5; 1Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin; 2Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin; 3Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin; 4Department of Physics, University of Wisconsin - Madison, Madison, Wisconsin; 5Department 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 results in a decreased resonance, which is detected in transport measurements. Further, Raman spectroscopy shows a large reduction of the G-band tangential phonon mode, as well as an increase in defect density as measured by the ratio of the defect 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 Applications.  
Narasuma Harinath Vedala, Young Chul Choi and Wonbong 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 multi-wall carbon nanotubes in vertically aligned as well as random orientation were grown on a 1 cm2 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 properties 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**  
Integrative Study of Ion Irradiated Singlewall and Multwall Carbon Nanotubes by Spectroscopic Methods.  
Mariya Brzhezinskaya1, Eugen Baitinger1, Vladimir Shnitov2; 1Physics, Chelyabinsk State University of Education, Chelyabinsk, Russian Federation; 2Institute of 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 analyzed by X-ray photoelectron spectroscopy (XPS), reflection electron energy loss spectroscopy (EELS) and atomic force microscopy. The samples of SWNTs and MWNTs were periodically irradiated with argon ions (Ar+) in situ in the spectrometer chamber. The Ar+ energy was 1 keV. The maximum dose (Q) of Ar+ irradiation was 360 μC/cm2. 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 change. CNTs accumulate Ar more quickly at small values of Q. The XPS measurements were carried out using ultra-high vacuum electron spectrometer PHI-5300 (produced by Perkin-Elmer) using MgKα line. Absolute energy resolution of spectrometer was 0.2 eV, when the transmission energy was 10 - 25 eV. Influence of ion irradiation on the energy of C 1s peak and 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 of Q of Ar+ 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+ irradiation. It was found that the energy of π-π plasmon peak decreases and broadenings essentially under Ar+ irradiation; the π-σ plasmon peak has a doublet shape and changes essentially under Ar+ irradiation, also. EELS studied the influence of ion irradiation on the π-π plasmon energy Eπ and the FWHM of the π-π plasmon peak δEπ were determined. The determined dependences of the π-π plasmon energy Eπ 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 < Q0) and at large values of Q (Q > Q0) 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 π-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.PD02-2-170.

**HH13.24**  
Solubility and electrical response of single walled carbon nanotubes with thiolate mediated gold nanoparticle attachment.  
Jingbina Cui, Charles Daghlian 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 homogeneity. 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 Kaernpenna and Siegmar 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 porosity threshold can be reached with a minimum of material. Therefore, it is used to get transparent and conductive carbon CNT networks are simply sprayed on glass or plastic in order to get conductive 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 required.

**HH13.26**  
Magnetic Properties of Randomly Oriented Flakes of Aligned Fe-Filled-CNx Nanotubes.  
Emilio Munoz-Sandoval, Florentino Lopez-Urías, Marisol Reyes-Reyes, Julio Alejandro Rodríguez-Munoz, 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

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

**HH13.27 Enhanced P-Type Conduction in SWNT by Protein Coated Microspheres.** Pil Sun Nam1, Jeong-O Lee2, Jinhee Kim2 and Hyojin Kim1, 1Advanced Engineering, Chung-Ang National University, Seoul, South Korea; 2Advanced Materials Division, Korea Research Institute of Chemical Technology, 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 of 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 device. The selective binding of analyte with immobilized protein molecule on a single carbon nanotube field effect transistor can act as an external gate, which results in a change of conductance. Extremely high surface to volume ratio 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/SiO2 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 N2 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.

**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 well ordered 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 (1.14 nm, 1.8 nm and 2.8 nm). The charged dye molecules (2.6 nm diameter) were adsorbed on an aliphatic amine elongated by spacers containing peptide bonds (5.2 nm). New methods are presented to model the transport function of the carbon nanotubes. We will present evidence for transport of charged molecules through CNTs.

**HH13.29 Electrophoretic Deposition of Carbon Nanotubes into Device Structures: A Novel Approach to Sensors for Environmental Applications.** Madhuri Guduru and Tabbetha Amanda Dobbins; Mechanical Engineering, University of California at Riverside, Riverside, California.

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, greatly increases their potential utility. In our study, CNTs were used as a sensor platform for explosives detection. CNTs were coated with a layer of Nickel on a Si/SiO2 substrate. Coupled CNT-Ni membranes were functionalized and coated with NiO before being immobilized on a gold substrate and exposed to gas mixtures. The NiO-CNT-Ni membranes were then exposed to nitric oxide vapor and adsorption/desorption was observed. The adsorption/desorption experiments are currently being modeled using finite element modeling software.

**HH13.30 Carbon Nanotube Gas Sensors and Actuators.** Mikhail Koziol1, Ali Alesh2, Dong-Sook Suh1, Richard Margolin1, Mike V. Schridge1, Steve Collins1, Sergey Lee2, Edgar Munoz2, Avtar Zachhid1 and Ray Baughman1; 1NanoTech Institute, Univ. of Texas at Dallas, Richardson, Texas; 2Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas.

The failure of the mammalian spinal cord to regenerate following injury is not absolute, but appears to be amenable to therapeutic enhancement. It has been hypothesized that the failure of regeneration results from the establishment of a state of molecular blockade that blocks the ability of spinal cord neurons to grow and therefore regenerate following injury. The findings presented in this talk are consistent with the hypothesis of molecular blockade and the mechanisms that determine this blockade will be proposed.
manipulation. Promotion of axonal growth and support for long
distance regeneration are the two requirements in the various
experimental models for spinal cord repair. The goal of achieving
these goals in-vitro is on the substrate that functions for the forma-
tion of neural bridges with high signal to noise ratio for efficient
signal transmission. Biomaterials thus become an important factor in
developing suitable 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 enhanced thermionic emission from carbon nanotubes. It has strong field
enhanced thermionic emission at least an order of magnitude higher than
covelmental 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
electrode coating.

HH13.34
Carbon Nanotubes as Bio-Functional Substrates. Evan Golub
and David E. Luzzi; Materials Science and Engineering, University of

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 monomers and polymers for biomedical applications. 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-Based Membrane. Jaecen Holt
Alexandr Noy, Thomas Huser, David Eaglesham, and Olga Kafalas;
Biosecurity and Nanosciences Laboratory, Lawrence Livermore
National Laboratory, Livermore, California.

A membrane consisting of multwall 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 $D_2O$ of $2.4 \times 10^{-5}$
mole$m^{-2}s^{-1}$ was determined, based on the sensitivity of the isotopic
measurement technique. Hydrodynamic calculations of forced water
flow across a nanotube membrane of similar specifications (10
nm inner diameter, 10 nm thick, with a porosity fraction of 0.03) give
a molar flux of 0.061 mole$m^{-2}s^{-1}$ for a 1 atm pressure drop. Molecular
dynamics simulations predict an even larger value of 0.29 mole$m^{-2}s^{-1}$
for these carbon nanotube membranes. We used to make nonporous
silicon nitride membranes, fabricated by sacrificial removal of the
carbon. Nitrogen flow measurements on these structures give a
molecule permeance of $4.7 \times 10^{-4}$ mole$cm^{-2}s^{-1}Pa^{-1}$ (mass flux of $4.7\times 10^{-4}$
mole$cm^{-2}s^{-1}$ at a pressure drop of 1000 PAs at a pore density of $4 \times 10^{16}$
$cm^{-2}$. The average pore size of this membrane is estimated to be

HH13.36
Enhancement of Conductivity of Bucky Paper by Chemical
Modification. Urszula Dettlaff-Weglikowska 1, Vera Skulakova 1,
Haif Graupner 2, Sung Ho Jhang 3, Byung Hoon Kim 3, Hyun Jung Lee 3,
Lothar Ley 2, Yung Wook Park 3, Savvas Berber 4, David Tomasek 3
and Siegmair Roth 1, 1Max Planck Institute for Solid State Research,
Stuttgart, Germany; 2School of Physics and Condensed
Matter Research Institute, Seoul National University, South Korea;
3Physics and Astronomy Department, Michigan State University, East
Lansing, Michigan.

Purified single wall carbon nanotubes have been chemically modified
by thionyl chloride, SOC1. 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 electronic properties of SWNT
networks. Whereas the pristine sample shows an overall
semiconducting character, the functionalized material behaves as a
metal. The effect of SOC1 is studied in terms of functionalization
reduction and incorporation of metallic admixtures 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 SOC1-
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.
Hae Jin and Young Wook Park; Applied Physics, Cornell University,
Ithaca, New York.

Single-walled carbon nanotubes have been widely researched for
applications in electronics and photonics area. Process of fabricating
single-carbon nanotube field effect transistors (CNTFTTs) has
suffered from many drawbacks such 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, damascene 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 CNTFTET devices. With this method,
both polysilicon and tungsten can be used as gate material. We
started with bulk silicon wafer and grew 170 thick silicon oxide on
the substrate. By using step-up, 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
layer. 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 insures the mechanical 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 dielectric;
whereas the tungsten gate a thin coating of 5nm of N2O3 was formed
on the oxide. 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.
use capillary forces to direct the assembly of carbon nanotubes into cellular foams. We will describe the mechanisms by which these structures are shaped. 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. Anand Srivastava1, O. N. Srivastava1, Sainat Talapatra2, R. Vajta3 and Pulickel M. Ajayan1; 1Department of Physics, Banaras Hindu University, Varanasi, India; 2Department of Physics, Banaras Hindu University, Varanasi, India; 3Department of MS & E, Rensselaer Polytechnic Institute, Troy, New York; 4Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; 5Department 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 geometrical 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 macroscopic hollow carbon cylinders as large as centimeters in diameter and several centimeters long, with walls (ranging from 200 nm - 600 nm 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 metal catalysts from 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). Exposure to Xe causes a sequential, fixation, 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.


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 present in SWNT bundles. This can be studied through spectroscopic methods such as FTIR where processing/purification procedures affect this access. By using Fourier Transform Infrared Spectroscopy (FTIR) and grand canonical Monte Carlo (GCMC) simulations, the adsorption of CO2 and its displacement of CO are studied. The results of these studies show that CO2 physisorption at 77 K produces an initial peak at 2330 cm⁻¹ for endohedral physisorption and at 2340 cm⁻¹ for groove/external surface physisorption. Exposure to Xe causes a sequential displacement of CO2 from these sites as shown by an intensity loss of the 2330 cm⁻¹ peak, which precedes the loss at 2340 cm⁻¹. The GCMC simulations on heterogeneous and homogenous bundles show that CO2 in endohedral sites is initially displaced by Xe before that in groove sites. The CO2 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 CO2 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⁻¹ are indeed correct. We use these IR assignments to study the displacement of CO2 by other IR active gases, such as CO. By correlating the intensity decreases for specific CO2 peaks with the intensity increases seen for CO when it displaces CO2, we are able to make strong arguments for the physisorption site for CO and other gases.


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

11:00 AM HH14.7 Double Wall Carbon Nanotubes as Molecular Sensors in Gases, Liquids and Polymers. Aynna Basu1, Wolfgang S. Bacsa2, Sophie Barrau2, Philippe Demont2, Hannes Hubel3, David J. Dunstan3, Revathi Bacsa4, Emmanuel Flahaut4, Alain Peigney5 and Christophe Laurent5, 1Physique, LPST, Toulouse, France; 2LPP, CIRIMAT-UPS, Toulouse, France; 3Physics, Queen Mary University of London, London, United Kingdom; 4LCMIE, CIRIMAT-UPS, Toulouse, France.

Apart from 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 de-bundled nanotubes in the polymer. Raman spectral bands are sensitive to their environment and in return be used to sense the local environment e.g. the D* band shifts up to 20 cm⁻¹ [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 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. Puch, 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. Massoud Atashbar1, Bruce Bejeck2, Srikant Singamaneni1 and Deep Banerji1, 1Electrical and Computer Engineering, Western Michigan University, Kalamazoo, Michigan; 2Department of Biological Sciences, Western Michigan University, Kalamazoo, Michigan.

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 RF sputtered gold surface of quartz crystals. Frequency shifts due to binding of 20nm Whatman anotops. SWNT network was formed on a pretreated glass substrate by dip-coating technique. AFM was used 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 μm. 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 90 μm 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 57 μA to 61 μA in current due to binding of 20 μl of streptavidin (conc. 1 μM). 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 showed a frequency shift 120 Hz which corresponds to binding of 1µM 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 Rao1, Peng Xiong2 and Seunghun Hong2, 1Physics, Florida State University, Tallahassee, Florida; 2Physics, 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)