SYMPOSIUM HH
Functional Carbon Nanotubes

November 29 - December 3, 2004

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* Invited paper
SESSION HH1: Synthesis and Growth I
Monday Morning, November 29, 2004
Room 312 (Hynes)

8:30 AM *HH1.1
Abstract Not Available. P. Bernier

9:00 AM HH1.2
Cheng-Xin Wang, Qiu-Xiang Liu, Yi-Hua Yang and Guo-Wei Yang; State key laboratory of optoelectronic materials and technologies, School of Physics Science & Engineering, Zhongshan University, Guangzhou 510275, P. R. China, Guangzhou, China.

One-dimensional nanostructures such as wires, rods, belts, and tubes have become the focus of intensive research owing to their unique applications in mesosopic physics and fabrication of nanoscale devices. Due to unique properties including extreme high hardness, very high thermal conductivity, large band gap, and chemical inertness, etc., diamonds are expected to be an important semiconductor material for high-temperature and high-power microelectronics device, and UV-light emitting optoelectronics. Very recently, one-dimensional nanostructures of diamond have received increasing interest in theoretical. For example, due to stronger than fullerene nanotubes, diamond nanorods are expected to be an important and viable candidate for synthesis. The energy band gap of diamond nanowires (DNWs) is significantly reduced by Barnar products and growth kinetic approach in theoretical, with respect to the effect of nanosize-induced surface tension, for the formation of DNWs inside CNTs upon CVD. Thermodynamic analyses show that the diamond nucleation inside a CNT would be preferable to that on the flat surface of silicon substrate due to the effect of surface tension induced by the nanosize curvature of CNTs. Meanwhile, the capillary effect of the nanosize curvature of diamond nuclei can drive the metastable phase region of diamond nucleation into a new stable phase region in the carbon thermodynamic equilibrium phase diagram. Kinetic analyses indicate that the growing rate of DNWs would go to much higher once nuclei formed inside CNTs, due to the same mechanism of growth termination, etc. which hampers their applications. Different methods have been used to fabricate DNWs, including chemical vapor deposition (CVD), microwave plasma enhanced CVD, and catalyst-assisted chemical vapor deposition (ACCVD). However, no detailed parametric study of this method has been undertaken. In this report, we present a detailed analysis of the growth properties of SWNTs as functions of growth time, deposition temperature, flow rate, type of alcohol (i.e. ethanol versus methanol) and catalyst concentration (Fe-Co-Mo acetate ratio). We have analyzed the as-grown SWNTs with high resolution transmission electron microscopy (HRTEM), field-emission scanning electron microscope (FE-SEM), Raman spectroscopy and atomic force microscopy (AFM). Nucleation and growth of SWNTs occurs within seconds after introduction of the alcohol vapor. The results show that although multi-walled nanotubes can be grown at 450°C, high quality SWNTs with a narrow diameter distribution without amorphous carbon can be grown using Co acetate catalyst doped with Mo acetate above 700°C. The HRTEM analysis revealed defective nanotubes at low and high temperatures with the optimum temperature being 500°C. The concentration and quality of SWNTs (determined by Raman and TEM) are also improved when methanol vapor was used. In brief, our work is a step towards optimizing SWNTs growth conditions using ACCVD. [1] S. Maruyama, R. Kojima, Y. Mynmachi, S. Chisashi, M. Kohno, Chemical Physics Letters 360 (2002) 229.

9:15 AM HH1.3
Single Wall Carbon Nanotube by Microwave Plasma CVD.
Roy Gat1, Matt Maschmann2, A. Goyn3, Zafar Iqbal4 and Tim S. Fisher1, 2Skeletchnotron USA, Somerville, Massachusetts; 3Mechanical Eng, Purdue University, West Lafayette, Indiana; 4Chemistry, New Jersey Institute of Technology, Newark, New Jersey.

Microwave plasma enhanced CVD has reproducibly yielded Single wall Carbon Nanotube (SWCNT) deposition. The tubes deposited in bundles containing 5-10 individual tubes each tube was either 1.3 um or 0.5 in diameter. The reactor used was an AFX-500/1 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 a new source of opportunity for better control over nanotube properties. Deposition temperature was 800-900°C. Gas mixture was methane and hydrogen. The catalysts was bimetallic Mo-Co supported on MgO and dispersed on a silicon wafer. Raman, AFM and TEM were used to characterize the tubes results will be reported.

9:30 AM HH1.4
Controllable Growth of Single Wall CNTs on Nanotemplates Prepared from Amphiphilic Diblock Copolymers.
Jennifer Lu1, Nick Mor1, Daniel Roitman1, Qiang Fe2, Jie Liu1, David Ritter3, Ian Manns3 and Mitch Winnick1; 1Nanoscience and Nanodevices, Lash Miller Chemical Labs, University of Toronto, Toronto, Ontario, Canada; 2Chemistry Department, Duke University, Durham, North Carolina; 3Chemistry Department, Lash Miller Chemical Labs, University of Toronto, Toronto, Ontario, Canada.

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

9:45 AM HH1.5
Parametric Study of Single Wall Carbon Nanotubes using Alcohol Catalytic Chemical Vapor Deposition. Huson Enam Ul Islam and Manash Chhowalla; Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

The unique structural, mechanical, and electrical properties of single-wall carbon nanotubes (SWNTs) have made these structures highly appealing for investigators. Different methods have been used for the synthesis of SWNTs, including alcohol catalytic chemical vapor deposition (ACCVD). However, no detailed parametric study of this method has been undertaken. In this report, we present a detailed analysis of the growth properties of SWNTs as functions of growth time, deposition temperature, flow rate, type of alcohol (i.e. ethanol versus methanol) and catalyst concentration (Fe-Co-Mo acetate ratio). We have analyzed the as-grown SWNTs with high resolution transmission electron microscopy (HRTEM), field-emission scanning electron microscope (FE-SEM), Raman spectroscopy and atomic force microscopy (AFM). Nucleation and growth of SWNTs occurs within seconds after introduction of the alcohol vapor. The results show that although multi-walled nanotubes can be grown at 450°C, high quality SWNTs with a narrow diameter distribution without amorphous carbon can be grown using Co acetate catalyst doped with Mo acetate above 700°C. The HRTEM analysis revealed defective nanotubes at low and high temperatures with the optimum temperature being 500°C. The concentration and quality of SWNTs (determined by Raman and TEM) are also improved when methanol vapor was used. In brief, our work is a step towards optimizing SWNTs growth conditions using ACCVD. [1] S. Maruyama, R. Kojima, Y. Mynmachi, S. Chisashi, M. Kohno, Chemical Physics Letters 360 (2002) 229.

10:30 AM HH1.6
In situ Optical Monitoring of Vertically-Aligned Multiwall Carbon Nanotube Array Growth During Chemical Vapor Deposition.
Alex A. Purzycki2, David B. Geoghegan2, Stephen Jesse1, Hongtao Cui1, Jeremy Jackson3, Ilia Ivanov2, Gyula Eros1; 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.

Vertically aligned arrays of multiwall carbon nanotubes (VAA-MWNT) can be synthesized using chemical vapor deposition (CVD) method, but little is known about: the growth mechanism, identity of the precursor species, growth rates and kinetics, the mechanism of growth termination, etc. which hampers their applications. A detailed experimental investigation of vertically aligned arrays of multi-wall carbon nanotubes (VAA-MWNT) growth by chemical vapor deposition (CVD) based on time-resolved reflectivity (TRR) throughout the first 10 microns of growth and direct remote microwave imaging at longer VAA-MWNT lengths using a diagnostic to measure and control the length of VAA-MWNTs in situ was performed. Attenuation of a reflected HeNe laser beam and Fabry-Perot fringes were used to measure the length of VAA-MWNT arrays throughout the first 10 microns of growth, providing in situ...
growth rates and permitting the kinetics and termination of the growth to be studied. The VAA-MWNT growth was investigated between 500°C on Si substrates with evaporated different multi- catalysts and different feedstock gases. It was demonstrated that the growth terminates rapidly at a relatively low (535-600°C) and high (800-900°C) temperatures, showing a relatively narrow range of growth. The growth of long VAA-MWNTs (up to 5-4 nm) around 700°C using Al/Pt/Mo catalyst and C_2H_2 feedstock gas, at a growth rate of about 0.2 - 0.5 μm/s. Nanotube lengths were controlled by rapid evacuation of the chamber. The heights of long VAA-MWNTs 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 metal/substrate systems, in this work, a combinatorial method is proposed and applied to prepare a library of Co patterns with nominal thicknesses from 0.01 to 1 nm were prepared on an a-SiO_2/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 catalysis 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 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 [1][S. Noda, Y. Kajikawa and H. Komiyama, Appl. Surf. Sci. 225, 372 (2004).] [2] S. Maruyama, R. Kojima, Y. Miyaschi, S. Chiashi and M. Kohno, Chem. Phys. Lett. 360, 229 (2002)


(n, m) controlled synthesis of single wall carbon nanotubes (SWNTs) is a major challenge toward fulfilling their potential. Here we demonstrate the controlled 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.


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 gases that facilitate direct transformation into SWNTs. 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.


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 material 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 aggregate and coarsen at elevated temperatures. The rate of particle aggregation and coarsening is a major challenge toward fulfilling their full potential. Here we describe the low temperature synthesis of dense SWCNTs in very high vertical alignment deposited by CVD. Substrates were Si wafers coated with very thin Al and Fe by sputter. Al layers were oxidized after the sputter. On the substrates, vertically aligned and very dense single-walled carbon nanotubes (SWNT) were synthesized at a low temperature of 600°C by Antenna-type Microwave Plasma CVD, which was used to deposit multi-walled carbon nanotubes (MWNts) in our previous study. The height of CNTs is more than 170 μm for 40 nm and all of the CNTs 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 1.9 to 3.6 nm. The cracks observed in SEM images are preferentially generated by the van der Waals force among SWNTs due to the very high density.

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. Takanori Inazaki, Tsuyoshi Yoshida, Takumi Aikawa, Ryota Hoshina, Kotaro Honda, Guofang Zhong, Yukio Furukawa, Iwao Odomori and Hiroshi Kawarada, 1School of Science and Engineering, Waseda University, Tokyo, Japan; 2COE, Tokyo, Japan.

It is very important to control the growth orientation of CNTs on substrates for some applications such as field emission devices and CNT-based FETs. As many papers reported, chemical vapor deposition (CVD) is the most reliable way for this purpose because of the precise control of the growth parameters. However few papers have been reported for vertically aligned SWCNTs. In this study, we demonstrate the low temperature synthesis of dense SWNTs with very vertical alignment deposited by CVD. Substrates were Si wafers coated with very thin Al and Fe by sputter. Al layers were oxidized after the sputter. On the substrates, vertically aligned and very dense single-walled carbon nanotubes (SWNT) were synthesized at a low temperature of 600°C by Antenna-type Microwave Plasma CVD, which was used to deposit multi-walled carbon nanotubes (MWNts) in our previous study. The height of CNTs is more than 170 μm for 40 nm and all of the CNTs 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 1.9 to 3.6 nm. The cracks observed in SEM images are preferentially generated by the van der Waals force among SWNTs due to the very high density.
Carbon nanotubes offer tremendous promise in nano-fluidics, but the progress in this area has been limited due to the extremely small internal diameters. Here, we describe a synthesis technique for tuning the internal diameters of carbon tubular structures from a few nm to a few microns, thus controlling the morphology. The strategy uses in-situ gas phase compositional variations to impact the growth interface. A variety of hollow curved carbon morphologies have been synthesized: cones, tubes, Y-junctions, dumbbells and multi-staged tubules. We envision that the above morphologies would find unique applications as throttle valves, micro-reactors, flow and distribution channels in nano-fluidic devices. Our synthesis concept is based on our ability to change the wetting behavior of gallium with carbon using different gas phase compositions. The growth experiments were conducted in a microwave plasma reactor on a substrate covered with molten gallium. Gallium droplets that form during exposure, mediate the growth of carbon shell around the droplet. The contact angle between gallium and the carbon wall determines the conical angle of the structure. The contact angle can now be varied by using different gas phase chemistries. In the presence of oxygen or nitrogen, wet carbon, thus reducing the contact angle. Using different dosings of oxygen and nitrogen we were able to control the conical angles of the tubular structures. For example, using increasing nitrogen dosing we were able to tune the conical angles from 20° to ~15°. With oxygen dosing, we could synthesize straight tubes (conical angle ~ 0°), as oxygen is more aggressive than nitrogen in changing the contact angle. Adopting an 'in-step' dosing sequence at various stages of growth, we were able to synthesize 'staged' morphologies. The detailed tube-growth mechanism involved in the growth of these structures will be discussed. The walls of the described morphologies exhibit a very unique structure. Unlike multi-walled carbon nanotubes, the graphene sheets are not arranged in concentric cylinders or as a scroll structure. Instead, the wall is comprised of nanocrystals of graphite in the size range of 10-20 nm, oriented with respect to the wall surface. The orientation of these nanocrystals depended on the angle gallium makes with the carbon wall. Selected area electron diffraction and nanodiffraction analysis will be presented to discuss the wall structure and the microscopic tube-growth mechanisms involved. Acknowledgments: The authors gratefully acknowledge Prof. J. M. Cowley for his input and discussions during this work. References 1. G. Bhimarasetti, M. K. Sunkara, U. M. Grahama, B. H. Davis, C. Suh, K. Rajan, "Morphological control of nanotube growth and multi-junctioned carbon tubular structures", Advanced Materials, 15 (19), 1629 (2003).
into a base growth-mode and a top-growth mode. The correlation between the growth mechanism of vertically aligned carbon nanotube (CNT) growth, grown by thermal chemical vapor deposition (CVD) and the adhesion of catalyst particles to the Si substrates has been investigated using transmission electron microscopy and scanning electron microscopy. In order to obtain different adhesions of catalyst particles to the substrates, the Ni film 10 nm are deposited by pulsed laser deposition (PLD), sputtering, and electron beam evaporation (e-beam evaporation), respectively. We find that CNTs grown on Ni nanoparticles deposited by PLD have an encapsulated Ni particle at the tip, whereas CNTs with metal tips are grown on catalyst particles deposited by sputtering and e-beam evaporation. It is shown that the growth mode of CNTs strongly depends on the adhesion of catalyst particles to the Si substrates.

3:45 PM HH2.7
Experimental Estimate of the Free Energy of Formation for Single Walled Carbon Nanotubes (SWNT). Larry M. Wagg1, Anne C. Dillon1, Philip A. Paulin2, Kim M. Jones1, Jeffrey L. Blackburn1, G. L. Hornyak2, Leonid Grigorian3 and Michael J. Heben1,1
Basic Sciences, National Renewable Energy Lab, Golden, Colorado; 2Physics and Astronomy, University of Denver, Denver, Colorado; 3Honda America R&D, Southfield, Michigan.

Single walled carbon nanotubes (SWNT) were synthesized by methane CVD on a supported mixed transition metal catalyst. Gas feed composition and reaction temperature were varied to identify the threshold conditions of temperature and gas concentrations for the growth of SWNT. Raman spectroscopy and TEM imaging were used to confirm the formation of SWNT. Threshold growth conditions were used to calculate the experimental carbon containing constant (\( G^*(T) \)) and \( \Delta G^*(T) \), the apparent free energy of reaction for methane decomposition \( \text{CH}_4 \rightarrow \text{C}_x \text{H}_y + \text{H}_2 \) using literature values for the graphite equilibrium constant \( K_0^* \) and the expression \( \Delta G^*(T) = -RT \ln K_0^*(T) \). These data show that the comparison of surface reaction rates of the catalyst.

4:00 PM HH2.8
Bulk Synthesis of Helical Coiled Carbon Nanostructures. Wei Wang1 and Apparao M. Rao2,1
School of Materials Science and Engineering, Clemson University, Clemson, South Carolina; 2Physics and Astronomy, Clemson University, Clemson, South Carolina.

3D helical carbon nanostructures have attracted much interest recently. Due to their fascinating morphologies, they are expected to exhibit unique structural, mechanical and electrical properties. Here we report a bulk process for preparing helical coiled carbon nanostructures including coiled nanowires and coiled nanotubes on bare quartz substrates. These nanostructures were synthesized at ambient pressure using the thermal chemical vapor reaction deposition (CVD) process in which xylene and acetylene were used as the primary carbon source. A multi-metal catalyst formed from a mixture of ferrocene, indium isopropoxide and tin isopropoxide served as the seed to initiate the growth of these helical coiled nanostructures.

4:15 PM HH2.9
Match-Stick Carbon Nanotubes : Structure Control and Properties. Vincent Jourdain1, Matthieu Pailet1, Odile Stephan2, Annick Loiseau2 and Patrick Bernier1,1 Universite Montpellier, Montpellier, France; 2Universite Paris Sud, Orsay, France; 3ONERA, Chatillon, France.

We formerly demonstrated an original type of carbon nanotube growth, namely "match-stick" carbon nanotube. A mechanism of sequential growth, based on a kinetically mismatch between the carbon supplying and consuming steps, inducing a periodic fluctuation of the carbon concentration in the catalyst particle, has been proposed. A morphology study with STEM 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-unit junctions constitute preferential bending and breaking points. They can be broken by a simple mechanical process. The aromatic insertion with magnetic nanoparticles also makes them potentially very interesting objects for new spintronics nanodevices. Magnetic characterization of the inserted nanoparticles by MFM will be reported.

4:45 PM HH2.11
Formation of Carbon Nanostructures by Metal Dusting. Paulo J. Ferrerias1,2, John B. Vander Sande2 and Peter Szakalos3,1 Materials Science and Engineering, 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 for the generation of carbon nanotubes is the phenomenon of metal dusting. Simply, metal dusting is the disintegration of metallic alloys by corrosion, which is initiated by exposure of the alloys to strongly carburizing atmospheres. The result of the decomposition is a mixture of metal carbides, and carbon nanotubes. 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 shapes 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 presence of carbon nanotubes and nanorods, and depend on the final diameter of these carbon nanostructures. Further TEM examinations show that the carbon nanotubes and carbon nanorods grow in either a straight or twisted configuration.

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

HH3.1
Growth of the Open-Networked Carbon NanoStructures at Low Temperature by Microwave Plasma Electron Cyclotron Resonance Chemical Vapor Deposition. Chi-Hwa Wai1,2 and David R. Harding1,2, Laboratory for Laser Energetics, University of
The deposition of open-networked carbon nano-structures has been developed on catalyst-assisted Si substrates using microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD) system. Carbon nanotubes (CNT) were grown at a temperature as low as 300 °C. Different types of carbon catalytic materials were synthesized on well-dispersed Co or Fe catalyst with a gas mixture of hydrogen and methane. The results were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and showed that the deposited structures can include amorphous carbon films, carbon nano-foams (pore size from 20-50 nm), and tube-like nano-structures. The morphologies of these producing nano-structures depend strongly upon the processing conditions: including substrate temperature, substrate bias, catalyst amount, thickness of the substrate, and the processing pressure. The dependence of the nanosystems growth on those parameters will be discussed. In addition, the properties of the nano-structures including density, hardness, and Young's modulus measured by X-ray radiography, nano-indentation, and thermal mechanical analysis will be presented.

**HH3.2 Growth Mechanisms of Aligned CNT in Anode Sheath of DC Discharge.** Alexander Pal 1, Anatoly V. Filippen 1, Nikolay Suev 1 and Mikhail Timofeev 2, 1Traktor Institute for Innovation and Fusion Research, Troitsk, Moscow region, Russian Federation; 2Institute of Nuclear Physics, Lomonosov Moscow State University, Moscow, Russian Federation.

Plasma enhanced chemical vapour deposition (PECVD) is a key growth technology to produce arrays of vertically aligned carbon nanotubes (CNT) on patterned surfaces. Such CNTs are suitable for fabrication of different electronic devices, field emitters, sensors etc. Since some key problems like in its earlier stage, there is still a lack of understanding of mechanisms of aligned growth. DC discharges are widely used in PECVD for aligned CNT growth. When a substrate holder is a cathode the deposited film is exposed to intensive bombardment by an ion beam that is formed in the cathode layer. Such bombardment on the one hand leads to the formation of defects, and on the other hand, the great anisotropy of the angle distribution function of ions leads to the formation of the oriented structures, for example, carbon nanotubes. The preferential orientation is due to more effective destruction of non-oriented structures by ions. The other factor which result in aligned CNT growth is strong electric field in a cathode layer. To exclude the influence of the ion bombardment on the CNT properties we carried out the deposition process on the anode of the DC glow discharge. The deposition was performed in the methane-hydrogen mixture under the pressure of 100-140 Torr and the temperature of 950-1080 °C on silicon substrates of 1.5x1.5 cm² in size, the substrates had previously been coated with a catalyst modified to nanoparticles of 20-30 nm. This work resulted in the successful growth, including the selective one, of highly aligned CNT arrays. To understand the processes in the anode layer of the DC discharge and to explain the effect of the electrical field upon the CNT growth the model was developed for transport processes of charged particles in the anode layer under the conditions of the CNT growth with the charged species energy distribution function non-locality taken into consideration. It was found out that the oriented carbon CNT grew in the field with the strength up to ~1000 V/cm. Growing CNT array moves an anode sheath along electric field direction. The consideration of possible mechanisms for the influence of the electrical field upon the growth of the oriented CNT showed that the effect of ordering the CNT was due to the collective Coulomb interaction of the surface charges induced on CNT heads by the external field. The termination of the CNT growth after the size of 100 nm can occur due to the catalyst poisoning, one of the reasons for which can be heating the CNT top by the electron current while the thermal conductivity decreases with the increase in the tube length.

**HH3.3 Growth of Aligned Carbon Nanotubes on Annealed Nickel Dots.** Zhongping Huang 1, David Carnahan 2, J. Rybczynski 2, Z. F. Ren 2, K. Kempa 2 and M. Sennett 3, 1NanoLab Inc., Newton, Massachusetts; 2Department of Physics, Boston College, Chestnut Hill, Massachusetts; 3Materials Science Team, U.S. Army Soldier and Biological Chemical Command, Natick Soldier Center, Natick, Massachusetts.

The aligned growth of carbon nanotubes by chemical vapor deposition is now relatively well understood, but the techniques for patterning catalyst materials are still in development. Planar carbon nanotube dots are nearly ideal shapes for nanotube catalysis, and the hemisphere diameter should be smaller than 200 nm. One approach that NanoLab has developed for catalyst deposition is based on a self-assembled hexagonally close packed polyethylene sphere monolayer. Sputtering through on such a monolayer deposits roughly triangular shapes on the substrate, at the interstitial point where three spheres meet. The size of the triangle has a geometrical relationship to the size of the triangle, as does the spacing between triangles. In our experiments, where we deposited nickel through a sphere mask, these triangles nucleated multiple nanotubes during CVD. Our goal was to nucleate a single nanotube at each site, so those secondary nanotubes disturb the periodicity of the primary carbon nanotubes. When the spheres are small, the corresponding triangle is small enough to nucleate a single nanotube, but when the spheres exceed 1-2 microns in size, the nickel deposits multiple nanotubes. This lack of understanding of mechanisms for the influence of the electrical field upon the growth of CNT has previously been coated with a catalyst modified to nanoparticles of 20-30 nm. This observation, as a contrast to the randomly oriented growth of nanotubes on Si/SiO2 substrates, is now relatively well understood, but the techniques for patterning catalyst materials are still in development. Hemispherical nickel dots with a diameter should be smaller than 200 nm. One approach that NanoLab has developed for catalyst deposition is based on a self-assembled hexagonally close packed polyethylene sphere monolayer. Sputtering
Carbon Nanotube Growth on Metal-catalyzed Substrates in Laser-Induced Vacuum Arc Process: Yoshiyuki Show, Yutaka Yabe, Japan.

Both growth is required to reach an expected. We have studied laser ablation technique for CNT growth. Though laser ablation produces CNT in gas phase, we expect that CNT will growth on catalyst film thickness was examined. The experiment was continued for 120 min. The grown CNT was observed by SEM (Scanning Electron Microscopy, Hitachi, S-4300) and Raman spectroscopy (JASCO, NRS-1000HS (632.8 nm)). The grown CNT on Fe/SiO2/Si substrates was examined by SEM. We confirmed the CNT growth on Ni/SiO2/Si substrates was examined by SEM. The film thickness decreased, length, diameter and number density of CNT decreased. This tendency is a similar to that of Wei et al [2] and indicates that CNT was grown on the substrates. References [1] Y. Suda, K. Utaka, M. A. Bratescu, Y. Sakai, J. Tsujino, and K. Suzuki, Appl. Phys. Lett., 81 (2001) 1394

Formation of Well-Aligned Carbon Nanotube on Glass Substrate by RF Plasma CVD Method at Growth Temperature of 500°C: Yoshiyuki Shioi, Yutaka Yabe, 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 FE, glass substrate should be used to reduce its fabrication cost. In this presentation, we present formation of well-aligned carbon nanotube on corning glass (7059) by RF plasma CVD method. The radio frequency (RF) plasma CVD method allows well-aligned carbon nanotube to grow on the glass substrate with large area at temperature of 500°C. This method is a promising technique to fabricate cathode of FED using carbon nanotube. The well-aligned carbon nanotube was grown by the RF plasma CVD equipment. First, Fe catalytic thin film was deposited on the glass substrate by the sputtering method. The sputtering was carried out in the chamber of the RF plasma CVD equipment. Next, acetylene gas diluted in hydrogen was introduced into the CVD chamber. Then the growth of carbon nanotube on the glass substrate was confirmed by atomic force microscopy (AFM). The grown carbon nanotube showed hexagonal pattern indicated that the carbon nanotube have graphite structure.

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

We have synthesized multi-walled carbon nanotubes (MWNTs) on nickel-deposited n-type silicon substrates by thermal chemical vapor deposition (TH-CVD). The electroless plating method was adopted in the deposition of the Ni catalytic layer. Sulfuric acid solution was used as a buffer to adjust and maintain pH value at 4.6. Both the deposition time of the nickel catalyst layer and the growth time of MWNTs were adopted to control the length and density of MWNTs. 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 multi-walled tube is the immersion time. The MWNTs deposited on the nickel plating solution was longer, and this benefited the growth of carbon nanotubes. In addition, the Raman spectrum demonstrated that the D/I ratio of MWNTs decreases as the deposition time and the growth time increase. It indicated that more graphenes were formed of MWNTs. Transmission electron microscopy (TEM) was also used to explore the configuration and crystalline of the m-grown MWNTs. By comparison to Raman spectrum, the relation of geometrical structure and D/I ratio would be presented.

Carbon Nanotubes Grown on Carbon Cloth and Their Field Emission Characteristics: Sung Ho Jo, Doo Hwan Wang, Jin Hyung Hong, Guang Yong Chong, Wenzhi Li, Krzysztof Kempa and Zhi-feng Ren, 1Department of Physics, Boston College, Chestnut Hill, Massachusetts; 2Department of Physics, Florida International University, Miami, Florida.

Carbon nanotubes are grown on carbon cloth by using thermal CVD with methane/hydrogen, and their field emission characteristics are investigated. Multi-walled carbon nanotubes are grown by sputtering the thin layer of stainless steel as a catalyst on the carbon cloth. The catalysts for the single walled carbon nanotubes growth are formed by dipping the carbon cloth in the iron sulfate solution. An extremely low electric field of less than 4.9 V/um is required to reach an emission current density of 1 mA/cm² from the carbon cloth covered with carbon nanotubes. This ultra-low operating electric field of carbon nanotubes grown on carbon cloth is mainly due to a very high field enhancement factor of 1.8x10², which is the combined result of geometrical configuration of the carbon nanotubes and the carbon cloth substrate.

Rapid and continuous growth of carbon nanotubes (CNTs) are still unachievable due to the lack understanding of the growth mechanism. Ideally, CNTs will continue to grow if every carbon atom that deposits on the catalyst’s surface becomes incorporated within the CNT structure. Such an ideal condition has not been achieved. Here, we report the growth of vertically aligned multiwall carbon nanotubes (VA-MWNTs) with an initial growth rate as high as 300 μm/hour. We found that with an appropriate addition of carrier gas, optimum growth temperatures and catalyst film thickness can convert a saturated growth into a continuous mode. This effective growth is due to the balance between the decomposition of hydrocarbon molecules and the subsequent diffusion and segregation processes on the carbon nano-particles. We have shown that this system is ready to elucidate 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) reactor. Then they were treated by ion-beam etching with 4 nm (10 mJ pulsed laser for 3 minutes) as verified by atomic force microscopy (AFM). 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). Effective growth occurred at 650°C and resulted in high density, vertically aligned MWNTs at a rate of 300 μm/hour. Both growth temperatures and catalyst film thickness are critical for these effective growths. The growth rate and the degree of alignment of the MWNTs decreased beyond these optimum parameters. These MWNTs continued to grow for at least one hour. Our results show that a rapid growth rate of CNTs is achievable even without the use of ammonia (as reported by many others) for both the pretreatment and the growth stage.


A Dual-RF-Plasma Approach for Controlling the Graphitic Order and Diameters of Vertically-Aligned Multiwall Carbon Nanotubes: Infandra Menda, Kumar Lakshman Vanga, Benjamin Ulmen, Yoke Khin Yap, Zhenwei Pan, Alex A. Puretzky, and David B. Geohegan; 1Physics, Michigan Technological University, Houghton, Michigan; 2Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 3Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Plasma enhanced chemical vapor deposition (PECVD) is the only known technique for growing vertically-aligned multiwall carbon
nanotubes (VA-MWNTs) at controllable tube densities. This technique is considerably important for the low temperature growth of MWNTs and carbon nanotube forests. However, the graphitic order of these MWNTs is inferior to those grown by laser ablation, 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.) for gas decomposition or substrate biasing. Here, we describe a dual-RF-plasma CVD technique that offers unique capability for controlling the graphitic order and 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 25 by a substrate biasing approach. Here, we describe the function of these plasmas on the graphitic order, diameters, and minimum growth temperatures of VA-MWNTs. The lowering of carbon concentration in gas is very important to many applications such as in the fields of electronics and sensors. To highlight the importance of plasma, it was found that by applying the plasma on the substrates and initiating a negative bias voltage (high temperature heating was provided by the plasma, which typically consumes 4 kW) to the substrate, the plasma could be used to produce high-quality carbon nanotubes at substrate temperatures as low as 400 °C. The deposited materials contain high concentrations of carbon deposits and silicon carbide whiskers on metal catalyst particles, as demonstrated by Auger mapping and AFM measurement. This provided the basis for SWNT to achieve site-selective self assembly on the Si substrate as demonstrated by AFM topography images.

**HH3.14 Catalyst Design for Carbon Nanotubes and for SiC Whiskers Production**

Mojtaba Vaziri, Vladimir N. Ulyanova, and Ilya N. Mazov; Borelskov 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 crucially important for the development of carbon nanotubes and filaments. The analogies with well-developed catalytic techniques can be used for the analysis of the development strategy of catalyst for production of new products. Here we consider the common features of the formation mechanisms of carbon deposits and silicon carbide whiskers on metal catalyst surfaces, namely: (1) the formation of a metal particle oversaturated with carbon and/or silicon and carbon atoms and (2) the nucleation of corresponding deposits on the metal surface. We have demonstrated that the classic nucleation theory combined with phase diagram approach can be used for the description of different scenarios of carbon and/or SiC deposits formation and for the development of the main principles of catalyst and promotor design.

**HH3.15 Growth Kinetics Changes of Vertically Aligned Carbon Nanostructures Synthesised at Low Substrate Temperatures.**

Guan You Cheng, Chun Hsu, Patrick Fos, Vlad Stolosan, Simon J. Harvey 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 RF plasma CVD method. We find that lower temperatures (min. 200°C) without intentional heating can be used for the synthesis of SWNTs of high quality and diameters less than 10 nm. The lowest temperature growth condition is considerably important for the low temperature growth of carbon nanotubes and carbon nanofibers. These nanostructures are synthesised using a C2H2 based plasma and nickel thin film as the catalyst. We found that preferential deposition of amorphous carbon takes place as the synthesis temperature is lowered below 500°C. The lowering of carbon concentration in gas feedstock (c2% conc.) allows for the nucleation of nanofiber-like structures while balancing the build-up of amorphous carbon. This method allows the synthesis of vertically aligned structures at low temperatures (min. 200°C) without intentional heating. This is a significant improvement as it is known that carbon nanotubes grow at high temperature, achieving reasonable average growth rates up to 25 nm/min. The only heating was provided by the plasma, which typically consumes 4 W/cm². To highlight the importance of plasma, it was found that by varying the applied plasma bias during growth (high temperature synthesis) could vary the growth rate from 0 to 165 nm/min. Based on the observations of experimental process variations and the morphology of the synthesised structures, we propose a growth mechanism for such low temperature growth and examine the resulting morphology changes.

**HH3.16 Control of the Amount of Defects in Single Wall Carbon Nanotube Nanoneedles and Their Effect on Peroxidase Based Biosensor Sensitivity.**

Sang Nyon Kim1,2, Xin Yu3, James F. Rusing3,5 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; 5Department of Materials Engineering, University of Connecticut, Storrs, Connecticut.

Regular orthogonal arrays of organized single walled Carbon Nanotubes (SWNTs) have attracted significant interests for the past few years. Our group has demonstrated the self-assembly based nanotubes using SWNTs having defects (SWNTs-SWNTs hydrophobic interactions) and SWNTs-SWTWs hydrophobic interactions.[1] More recently we have revealed the feasibility of these nanotube forests to peroxidase based biosensor.[2] This presentation will highlight some of our recent results in controlling the amount of defects in the assembled SWNTs. This was achieved by carefully controlling 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 peroxidase to the carboxylated ends of the nanotube forests will be discussed. Moreover, application to amperometric peroxidase-linked immunoassays will be presented as a prospective application for these organized nanotube forests. [1] Chattopadhyay, D., Galeska, I. & Papadimitrakopoulos, F. Metal-Assisted Organization of Shortened Carbon Nanotubes in Monolayer and Multilayer Forest Assemblies. Journal of the American Chemical Society 123, 9550-9552 (2001). [2] Yu, X., Chattopadhyay, D., Galeska, I., Papadimitrakopoulos, F. & Rusing, 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. Nezich1, V. W. Brisco1, C. A. Furtado2, G. G. H. Smith3, A. A. Gutierrez4, M. S. dresselhaus1,2, and G. Dresselhaus1, 1Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; 4Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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

HH3.18 NMR Investigation of α-Alkylamine Self-Organization Along the Sidewalls of Single-Wall Carbon Nanotubes (SWNTs), Sang Yong Ju1,2, Marcel Utz3, and Fotios Papadimitrakopoulos1,2,3, 1Nanomaterials Optoelectronics Laboratory (NOEL), University of Connecticut, Storrs, Connecticut; 2Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 3Department of Physics, University of Connecticut, Storrs, Connecticut; 4Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Single wall carbon nanotubes (SWNTs) have drawn considerable attention from the scientific community due to their unique electronic properties. With the discovery of metallic (−) and semiconducting (+) SWNTs, diameter and chirality have played key roles in these properties. Several methodologies have come forward to separate sem- from met-SWNTs. Recently our group has been able to attain bulk electron microscopy (HRTEM). We can simultaneously image the linear alkyl chain. Measuring steady-state emission suggests that nanotubes may be viewed as hollow cylindrical elements at the nanoscale, but in computing effective properties of single-walled carbon nanotubes and their suspensions contain some individual, surfactant-coated SWNTs. In the present work, we investigate the evolution of SWNTs from a template to final rope structures to individual tubes and study a range of experimental parameters are used for the centrifugation and concentration 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.

HH3.19 Abstract Withdrawn

HH3.20 Chemical Processing and the Infrared-Active Vibrational Modes of Single-Walled Carbon Nanotubes, Xinming Liu1, Clascidia A. Furtado2, Gugang Chen3, Humberto R. Gutierrez2, Richicho Saito4, Jie Jiang5, Mildred S. Dresselhaus1, and Peter C. Eklund1,6, 1Physics, Pennsylvania State University, University Park, Pennsylvania; 2Centro de Desenvolvimento da Tecnologia Nuclear, CDTN/CNEN, Belo Horizonte, MG, Brazil; 3Department of Physics, Tohoku University, Sendai, Japan; 4Department of Physics, MIT, Cambridge, Massachusetts; 5Department of Materials Science, Pennsylvania State University, University Park, Pennsylvania.

The IR-active vibrational modes of single-walled carbon nanotubes (SWNTs) have been observed by optical transmission through thin films of bundled single-walled carbon nanotubes. The SWNT IR modes, 5 first order and 3 second order, are very weak, and have not been reported to date. In this work, we have observed the IR-active chemical functional groups, e.g., −COOH,−OH, might also be attached to the tube walls and contribute additional spectral features, we have also studied the effects of chemical purification and long-term high-temperature vacuum annealing on the IR spectrum. Through comparison with theory, we are able to assign most of the sharp features observed in our IR spectra to particular symmetry nanotube vibrational modes; features that were removed via high temperature annealing are assigned to specific attached chemical groups.

HH3.21 Field Emission and Conductivity of Individual Carbon Nanotube Measured by a STM Probe Inside a TEM, Jianyu Huang, Sho Chen, Sung-Ho Jo and Zhifeng Ren; Department of Physics, Boston College, Chestnut Hill, Massachusetts.

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


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 surfactant-bonded carbon nanotubes can stably exist in suspension for extended time periods. Measuring steady-state emission suggests that the suspensions contain some individual, surfactant-covered SWNTs. In the present work, we investigate the evolution of SWNTs from a template to final rope structures to individual tubes and study a range of experimental parameters are used for the centrifugation and concentration 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. Hong Bai, R. Byron Pipes and Justin Molenaur; Polymer Engineering, University of Akron, Akron, Ohio.

The effective engineering properties of carbon nanotubes have been a 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 arrays and development 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 be also considered when computing effective density and...
In the present work, the authors develop relationships for prediction of the effective flexural moduli of multi-walled carbon nanotube (MWNT) nanocomposites by analytical methods. The Bernoulli-Euler hypothesis of orthotropic coaxial cylinders [3], the solution for the bending, tensile and torsional response is determined for two inter-tube conditions: no slip and no friction. These results provide an insight into the contributions of the bending, tensile, and torsional responses to the effective flexural moduli of multi-walled carbon nanotubes in bending. In addition, the warpage of the cross-section is evaluated for typical nanotube geometries in order to determine the applicability of the Bernoulli-Euler hypothesis in determining the flexural response of multi-walled carbon nanotubes.

We report electrical properties and metal-insulator transition in thin films of multiwalled carbon nanotube (MWCNT)-poly (methyl methacrylate) (PMMA) composites. MWCNTs were synthesized by chemical vapor deposition method. Pre-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 was used to study homogeneity and structure of composites. DC conductivity ($\sigma_{DC}$) and its temperature dependence ($\sigma_{DC}(T)$) were measured in the range of 0.3 K - 300 K to study charge transport mechanism in composites. The $\sigma_{DC}$ of composites at room temperatures increased as MWCNT concentration increased, which shows typical percolation behavior with percolation threshold ($\phi_c$) at 0.4 wt % of MWCNTs. Above $\phi_c$, $\sigma_{DC}(T)$ of the composites showed the metallic behavior. We assigned low temperature metallic behavior to the formation of one-dimensional conducting MWCNT nets in insulating PMMA matrix. The metal-insulator transition in the composites ($\phi_c > 0.4$ wt %) was observed between 1 K - 10 K based on the analysis of the reduced activation energy. The $\sigma_{DC}(T)$ of the composites at MWCNT concentrations above $\phi_c$ were compared with that of the composites below $\phi_c$. AC conductivity ($\sigma_{AC}$) was also measured in the frequency range of 10 Hz - 2 MHz and in the temperature range of 77 K - 360 K, in which we observed the percolation behavior for the systems. We observed the different frequency dependence of $\sigma_{AC}$ of the composites above and below $\phi_c$.

Dispersion and Alignment of Carbon Nanotubes in an Elastomer Matrix: Scheme Al. 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 crosslinking 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 the 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 tube 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.

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

In the recent years, the studies for the practical application of carbon nanotube (CNT) have been focusing on polymeric CNT composite because of the reduction of unit cost of production. However, CNT dispersion is a new and complicated phenomenon and poor results which provide poor dispersion in the polymer matrix. We report here that dispersion characteristics of the surface modified multiwalled nanotubes (MWNTs) in polyurethane (PU) matrix and electrical conductivity of the MWNTs/PU composites are investigated using SEM and Dielectric analyzer with respect to the chemical treatment of MWNTs, the kind of surfactants, their content, and the tail length of hydrophobic group. Several chemical treatments of the MWNTs/PU surfaces were performed with the acidic type, sodium concentration, treatment temperature, and oxidation time. All the surface of modified MWNTs are negatively charged and functionalized 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.

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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 functional 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 matrix, polarized absorbance is observed from the guest-host system. This approach can produce long range order of aligned Ps-g-SWNT over the entire film area (over 100nm2).


Carbon nanotubes show promise as a reinforcing phase for polymer composites due to the excellent mechanical properties of the nanotubes themselves. Previous work [1, 2, 3] has shown that the interface between carbon nanotubes and various polymers may be strongly strong to allow efficient stress transfer from the polymer matrix to the nanotube reinforcement. Generally, it is accepted that a requirement for strong reinforcement-polymer adhesion is effective wetting of the solid reinforcement by the liquid polymer during composite processing. In this work, we measure the wetting forces between various organic liquids and single multi-wall carbon nanotubes (MWCNTs) due to the liquid surface tension acting on the nanotube. This is achieved by attaching single MWCNTs to the end of an AFM tip and lowering the tip towards the liquid surface. Wetting forces (F) act on the nanotube upon contact with the liquid surface, which can be recorded from deflections in the AFM cantilever [4]. Contact angles can be derived from a simple force balance considerations to evaluate the wetting behavior of carbon nanotube surfaces using $F = \gamma \cos \theta$ where $\gamma$ is the liquid surface tension, $d$ is the outer nanotube diameter and $\theta$ is the liquid contact angle with the nanotube surface. We also extend this technique to evaluate the surface of chemically modified carbon nanotubes. As an example, the liquid-nanotube interaction force (Fr) can be increased by using modified carbon nanotubes that are more compatible with the wetting organic liquid. Furthermore, changes in nanotube diameter and the type of carbon nanotubes used (either chemical vapor deposition or arc-discharge grown) also show an influence on the nanotube wetting behavior because of the presence of surface defects in the nanotube surface. References 1. O. Lourie, D. M. Cox & H. D. Wagner. Phys. Rev. Lett., 81 (1998) 1682. 2. C. A. Cooper, S. R. Cohen, A. H. Barber and H. D. Wagner. Appl. Phys. Lett., 81 (2002), 3873. 3. A. H. Barber, S. R. Cohen and H. D. Wagner. Appl. Phys. Lett., 82 (2003), 4149. 4. A. H. Barber, S. R. Cohen and H. D. Wagner. Phys. Rev. Lett., 92 (2004), 186103.

Dispersion Quality and Corresponding Electrical Conductivity of Functionalized Carbon Nanotubes in...
Winey 2; Materials Science and Engineering, using wt% loading were of SWNT loading). In contrast to previous fabricated using noncovalently functionalized, soluble single-walled nanotubes for improving the thermal conductivity of conventional polymers. We carefully investigated the thermal conductivity of SWNT/PMMA nanotube/polymer composites will find various applications such as transistors. Xiang-Zheng B, Michael Strano, Colin Nuckolls University of Pennsylvania, Philadelphia, Pennsylvania; Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania. Due to their exceptional thermal properties single-wall carbon nanotubes are considered as very promising filler materials for improving the thermal conductivity of conventional polymers. We carefully investigated the thermal conductivity of SWNT/PMMA nanocomposites with SWNT loading in the range up to 10 wt% using the comparative technique. The samples were prepared by copolymerization method. We demonstrated moderate improvement in the composites' thermal conductivity of about 20–50% at 10 wt%. The experimental results were analyzed using the versatile Nielsen model, which takes into account many important factors, like the fillers aspect ratio and maximum packing factor. 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 the 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. 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 threshold (0.05–0.1 wt% of SWNT loading). In contrast to previous techniques, our method is applicable to various host polymers and does not require lengthy sonication. By significantly improving the dispersion of nanotubes in the matrix, we show that only a very small amount of SWNTs are needed to achieve conductivity levels required for different electrical applications without compromising the host 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 wiring, and transparent conductive coatings. Reference: 1. Chen, J. et al. J. Am. Chem. Soc. 2002, 124, 9039-9035. Carbon nanotube and organic composite thin film transistors, Heung-Chang Byun, Michael Strano, Colin Nuckolls and Graciel B. Blanchet. Polymeric nanostructured active layers (PNALs) and the transistors based on these materials. It was observed that self-assembled buckyballs with nearly uniform one-to-one distances and resemble a nanoscopic peapod. The endofullerenes coalesce into longer capillaries by either the electron irradiation or thermal annealing. We applied the recently developed Reactive Force Field (ReaxFF) to study the growth dynamics of C60-buckyball/nanotube peapod structures. We found that the space confinement provided by the single wall nanotube encapsulating the endofullerenes is of critical importance on the coalescence reaction. Furthermore, we also simulated the effects of a Ni-particle 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 for forming a 4-member ring between adjacent buckyballs. We chose both coronulenes (C20H10) and C60 to compute this energy barrier from quantum mechanical and ReaxFF. The good agreement between these two methods encouraged us to investigate the effect of catalysts 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.


Polymers with ion-beam deposition on polymer substrates to induce structural modification is an important process used to achieve thin film growth, surface etching, and nano-texturing of the surface. Previous atomistic simulations have showed that particle beam deposition can induce crosslinking between unfunctionalized carbon nanotubes and polymer chains in situ resulting in increased composite strength and toughness. In this work, we investigate the effect of atomic and electronic irradiation of nanotube bundles and nanotube-polymer composites. In particular, the simulations consider the effect of incident angle in the polyatomic ion beam irradiation of nanotube-polymer composites, the electron irradiation of multi-walled carbon nanotubes, and the ion beam irradiation of multi-walled nanotubes. The approach is classical molecular 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 Sahakalkan 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-walled carbon nanotube (SWCNT) has been predicted[1]. The SAW is induced through the piezoelectric effect. Its coupling to the electrons is given by the electronic structure in the 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. Talysnki, D.S. Novikov, B.D. Simon, and L.S. Levitov, Phys Rev Lett 87, 27, 2001.

HH3.39 Electronic Transport in Bucky-Paper, Thin Networks and Individual Single Wall Nanotubes. Viara Shkakunova, Martti Kaempgen, Yun Sung Woo, Serhat Sahakalkan 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 electron transport in SWNT-systems, networks of 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. The change of the shape of the curves due to the size of the SWNT-system was found. The results obtained were interpreted in the frame of a model combining metallic conduction of highly conductive regions (intra-tube conduction) with inter-tube tunneling or hopping. In a very thin network similar to an individual SWNT, non-linearity in I-V characteristics at low temperatures was observed. Keywords: nanotube, transport, networks.

SESSION HH4: Characterization, Processing, and Applications

Tuesday Morning, November 30, 2004

Room 312 (Hyne)

8:30 AM HH4.1 Field Emission from Semiconducting Quasi-One Dimensional Materials. Jun Chen1,2, Z. S. Deng1,2, N. S. Xu1,2, Weixin Zhang1, Xiangwen Wen1 and Shiehe Yang2; 1State 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 nanowires, the electron irradiation of multi-walled 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).

9:00 AM HH4.2 NEXAFS Investigations of Nanotube-Based Systems. Viana Hemraj-Benny1, Sarbajit Banerjee1, Mahalingam Bala, Sujeet Chakrabartii1, Sai Balasubramanian1, Saradha Sambasivan1, Daniel A. Fischer2, James A. Misevic3 and Stanislav S. Wong4; 1Chemistry 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 field emission applications as well as for understanding their field emission characteristics. It has been shown that near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is a particular useful and effective technique for studying the electronic structure and chemical composition of pristine, wet-air oxidized, and ozone-oxidized nanotubes. In addition, we have been able to obtain quantitative analysis of the order in a wide range of carbon based systems, including graphite, single-walled carbon nanotubes (SWNT) powder, SWNT films, and multi-walled carbon nanotubes.

9:15 AM HH4.3 TEM combined with Transport, Raman and AFM on the same individual Carbon Nanotubes and New Ways to Free-standing Nanostructures. Jannik Christian Meyer1, Dirk Obergfell1, Matthieu Puille2, Jean-Louis Sauvajol2, Georg S. Dueberg3, Po-Wen Chiu4 and Sigmar Roth5; 1Max-Planck Institute for Solid State Research, Stuttgart, Germany; 2Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland. France; 3Infinicon 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.

9:30 AM HH4.4 Comparison of the Nanotube Properties, Purification and Separation Method. Jiri Cech1 and Sigmar Roth2; MPI-FKF, Stuttgart, Germany.
Single wall carbon nanotubes produced by laser ablation, arc-discharge, CHD (HiPCO), respectively, have been characterised 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 toward separation of semiconducting and metallic SWCNT. 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. Fotos Papadimitrakopoulos, Zhengang Luo, Sang Nyon Kim, Sang-Yong Ju, Kangho Lj, Mathew Mckai, Santhikumar Vadhiraju, Kushan Bayes, G. G. Samsonidze, Shinn Grace Chou, V. W. Bray, G. Dresselhaus and M. S. Dresselhaus, NanoMaterials Optoelectronics Laboratory, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 2Department of Chemistry, University of Connecticut, Storrs, Connecticut; 3Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Boston, Massachusetts; 4Department of Chemistry, Massachusetts Institute of Technology, Boston, Massachusetts; 5Department of Physics, Massachusetts Institute of Technology, Boston, Massachusetts; 6Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Boston, Massachusetts.

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


The ideal nanotube suspension would yield isolated tubes in any desired concentration. In order to understand the above, a combination of 1H and 13C NMR along with optical, calorimetric, X-Ray and thermal desorption characterization measurements were conducted in order to quantify the localized environment along the SWNT-porphyrin surfactant. These were furthermore correlated with Raman band construction in order to elucidate the effects of aggregation and environmental contaminants.


The potential application of carbon nanotubes in the fabrication of field effect transistors, field emitter displays, sensors, and other devices is currently limited by the variability in both chirality and length distributions of nanotubes. Although significant progress has been made to control these two important variables either during or after the manufacturing process, the field still lacks a robust technology that allows the production of single chirality or uniform length distributions of nanotubes, with retention of unique electronic properties. We are using principles of colloid chemistry to understand and control the phase behavior of SWNTs in superacids, in order to develop new more easily processable dispersions. For example, the addition of potassium persulfate has been demonstrated to improve dramatically SWNT dispersion in methanesulfonic acid (Ramesh et al., 2004). Factors currently being explored for their impact on SWNT phase behavior include SWNT length, polydispersity of length, degree of surface oxidation, and presence of additives (e.g. salts, other acids) which increase electrostatic and/or steric stabilization.
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-Nanovessel Devices. Lei An, Qianga Fu, Chenguang Lu and Jie Liu; Chemistry, Duke University, Durham, North Carolina.

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

11:30 AM HH4.11

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 (including extrusion stretching as the independent variable). Hipco SWNTs are dispersed in water using sodium dodecyl sulfate (SDS), and then co-extracted with polyvinyl alcohol (PVA)/water through a long syringe into a rotating water/PVA coagulation bath. Partial axial alignment is thereby achieved, and further enhanced by applying tension to the flexible green fibers in the coagulation bath. X-ray diffraction shows that the full width at half maximum (FWHM) of the Bragg peaks decreases from 55 (as-extruded) to less than 30 degrees by 80% elongation. Resistivity vs. stretch ratio shows a rapid initial decrease followed by saturation; essentially all the improvement in electronic transport is obtained once alignment of 40 degrees FWHM is achieved. Annealing in vacuum at 1000°C is performed to drive out PVA, improve inter-tube and inter-bundle contacts, and 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). This is rationalized that the Coulomb interactions in disordered systems open a gap at the Fermi energy. Above 25 K, thermal activation is more likely than correlated electronic states 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 DMP, and sample purity is expressed relative to some reference sample. In the current work we produced a reference standard for NIR measurements using purified inner nanotubes. The sample was obtained slowly using a Temperature Programmed Oxidation (TPO) setup in 20% oxygen / 98% helium atmosphere. In these conditions, the sample oxidized in several steps, which were attributed to carbonaceous impurities, nanotubes and graphite shell C-D 

SESSION HH5: Composites, Fibers, and Mechanical Properties I
Tuesday Afternoon, November 30, 2004
Room 312 (Hynes)

1:30 PM HH5.1
Strange, Useful, and Problematic Mechanical Properties of Carbon Nanotube Sheets and Fibers. M. Zhang1, K. R. Atkinson2, L. Hall1, J.A. Levinson1, S.R. Shah1, R. Hay2, S. Collins1, A.B. Duxton1, J.P. Ferraris1, E. Munoz1, J. Razali1, V. Ebron2, A.A. Zakhidov3, R. Hou1, M. Koziol1, R. Capp3, G.M. Spijker6, G.G. Wallace1, J.N. Barisci1, J.N. Coleman7 and Ray H. Baughman8.

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

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

2:00 PM HH5.2
Plasma Coating and Magnetic Alignment of Carbon Nanotubes in Polymer Composites. Donglu Shi1, Peng He1, Jie Lina2, Rodney Ewing3, Xavier Chaud3, Robert Tourner3, Eric Beaunoun3 and Lumin Wang4; 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 dispense 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 modifications, 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 needed to be aligned along certain specified directions. Single wall carbon nanotubes, due to small amount of catalyst elements such as Ni and Co, are able to 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 polymer matrix. The magnetic alignment mechanism is discussed.

2:15 PM HH5.3
Carbon Nanotube-Polystyrene Nanocomposites for Electromagnetic Interference Shielding. Yonglin Yang1, Mool C. Gupta1, Kenneth L. Dudley2 and Roland W. Lawrence2; 1Applied Research Center, Old Dominion University, Newport News, Virginia; 2Electromagnetics Research Branch, NASA Langley Research Center, Hampton, Virginia.

This study reports a nanocomposite consists of conductive carbon nanotubes dispersed within an insulating polymer matrix [polystyrene (PS)], and its electrical conductivity and electromagnetic interference (EMI) shielding properties. The homogeneous polymer nanocomposites were fabricated by ultrasonic dispersion of carbon nanotubes in a polystyrene solution followed by spraying to cast films. These films were then hot-pressed to form thick structures of 25.4 mm in diameter and 1.0 mm in thickness. SEM images of the fractured surface of the nanocomposite reveal that nanotubes are well dispersed and embedded uniformly throughout the PS matrix. The uniform
The mechanical properties of multi-wall carbon nanotube/polypropylene nanocomposites were studied as a function of nanotube orientation and concentration. Through melt mixing followed by melt drawing, using a twin screw mini-extruder with a specially designed winding apparatus, the dispersion and orientation of multi-wall carbon nanotubes was optimized in polypropylene. Tensile tests showed an increase of about 7% for the average tensile toughness from 64 MJ/m² to 109 MJ/m². 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.

4:34 PM HH5.7
Modification of Single-Walled Carbon Nanotubes through controlled/"Living" radical polymerization. Jin Chung Park, Jin-Buk Oh, Jin-Seok Paik, Jieun Ahn, Cheol Eun Cho, Jeong Yong Lee, Chang-Suk Hy, Il Kim and Bog G. Kim. 1Department of Polymer Science and Engineering, Pusan National University, Busan, South Korea; 2Department of Physics, Pusan National University, Busan, South Korea.

Single-wall carbon nanotubes (SWNTs) have been attracting considerable interest due to their unique shape and outstanding mechanical and electrical properties. In efforts to utilize these properties, we focus on developing new chemical modification methods to introduce covalently attached well-defined polymer on the surface of SWNTs. For example, polystyrene was grafted from the sidewall of SWNTs via surface-initiated Nitroxide-Mediated Polymerization or Atom Transfer Radical Polymerization (ATRP). Furthermore, formation of block copolymers on SWNTs was studied by chain-extending grafted-poly(styrene) with second monomers including t-butyl acrylate. Functionalized-SWNTs were also used as templates for Thermal Gravimetric Analysis, Transmission Electron Microscopy, FT-IR, 1H NMR, and Raman spectroscopy. This polymer-SWNT composite is expected to have instinct nanostructure, resulting in novel material having marked properties. In the future, these methods will become new avenue in preparing carbon nanotube-based novel materials.
used for spinning by a factor of a thousand to the nanoscale and discovers surprising and useful mechanical and electronic properties for resulting spun nanotubes filaments and composites thereof. We used chemical vapor deposition process to grow multilawed carbon nanotubes forests several hundred micrometers high on Si substrate. A continuous ribbon of 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 substrate. A continuous ribbon of pure nanotubes was easily formed. The first example of SWNT and PYA hybrid films made carried out. The measurements were carried out at room temperature in aqueous and organic electrolytes; square-wave polarized Raman spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM), while the composition was analyzed by micrographs revealed that the nanofiller successfully bridged the laminae interface could increase the interlaminar shear strength of carbon fiber-BMI composites by up to 58%. SEM micrographs revealed that the nanofiller successfully bridged the lamina of the composite indicating success in biomimicking the insect cuticle. Composite fabrication techniques developed on this program would have a wide variety of applications in space and aerospace structures including leading and trailing edges of aircraft wings.

4:30 PM HH5.10
SWNT-polymer composite films made by layer-by-layer assembly. Long Shao, Shin, Nicholas A. Kotov, Tong Zhongyong and Vladimir A. Sinani, Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

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

4:45 PM HH5.11
Investigation of the Mechanical Properties of Multi-walled Carbon Nanotubes (MWCNTs) Produced by CVD. Jay Gaillard, Malcolm Sove and Apparao M. Rao; Physics and Astronomy, Clemson University, Clemson, South Carolina.

We have measured the bending modulus of several different CVD grown MWCNTs using a vibrating reed technique. The MWCNTs were produced from a mixture of three different precursors: (i) xylene/ferrocene, (ii) xylene/ferrocene/melamine (nitrogen-doped) and (iii) trimethylamine/ferrocene. The first two precursors were used to compare the mechanical properties of typical CVD-grown to bamboo-type MWCNTs. Nanotubes prepared using the third precursor showed relatively fewer walls and defects compared to those prepared from xylene-ferrocene mixture. The resonant vibrational frequencies of these nanotubes were measured both optically and electronically in air using a vibrating reed technique. The diameters of these nanotubes ranged between 50 - 100 nm as determined from the TEM images and the average length was 10 microns. For the xylene/ferrocene and trimethylamine/ferrocene tubes, the bending modulus is estimated to be 0.3 and 0.2 TPa, respectively. However, the bending modulus for the nitrogen-doped tubes was 9 GPa which is significantly lower compared to regular MWCNTs implying that the bending modulus decreases with an increase in wall defects. These findings are in reasonable agreement with those reported previously by Wang et al.[1]. The effect of wall thickness on the bending modulus is still under investigation. A summary of the higher frequency modes will also be presented. 1. Z. L. Wang et al., Adv. Eng. Mat. 3, 657 (2001)
Carbon nanotubes are attractive candidates for reinforcing polymers due to their high tensile strength and elastic modulus. As with traditional engineering composites, stress transfer from the polymer matrix, across the interface to the nanotubes is required for effective polymer reinforcement. Microscopy principle, if the polymer-nanotube interface is relatively weak then the interfacial failure can tolerate relatively low stresses whereas strong polymer-nanotube interfaces can allow a build up of stress in the nanotube during composite loading that can reach the folding stress of the nanotubes itself leading to nanotube fracture. Previous work in our laboratory [1, 2] has shown that it is experimentally viable to measure the interfacial strength between a single carbon nanotube and a polymer matrix. The experimental setup consisted of single multi-wall carbon nanotubes (MWCNTs) 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 mechanical properties of the MWCNT composite were determined 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 nanotubes-polymer interface was conducted. Stress transfer between a single carbon nanotube (SWNT) has its position strongly dependent on strain when its modulus and Young’s modulus are sufficient. The results of these studies emphasize the potentials of this novel high resolution non contact strain sensor system. Finally, results from stress/stain 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, Kening Jin 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 aluminas 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 aluminas 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 graphic 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 fabricated as reinforcement materials for composites containing using template-mediated assembly of discotic mesomeric switch. TEM study shows that a thin CVD graphitic layer could modify the orientation of the discotic mesomeric pitch and the graphitic layer, and thus influence the mechanical properties of the carbon nanofibers.
optical transition energies and assigning the spectral features to specific SWNTs. The Slater-Koster model has proven to describe accurately SWNT diameter dependencies. However, recent progress in synthesis of smaller diameter SWNTs (1 nm and below) and numerous photoluminescence (PL) and resonance Raman spectroscopy (RRS) measurements indicate the failure of the Slater-Koster model for these small diameters. Major differences can be found between the experimentally observed optical transition energies (the experimental Kataura plot) and the predictions of the Slater-Koster model. (1) The observed ratio of the energy of the first band to the second band in the experimental Kataura plot to the energy of the first band is less than 2 predicted in the Slater-Koster model (the ratio problem). (2) The observed spread of the optical transition energies for different nanotubes within the same family (2±nm interconnection) for 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 exotic states, the family spread is mainly attributed to the curvature effects and long-range interatomic interactions in small diameter SWNTs. In the present work we develop an extended model for description of the optical transition energies in small diameter SWNTs. Our approach is based on the symmetry-adapted scheme as proposed by Popov. The curvature effects are thus incorporated in the model as opposite to the conventional zone-folding approximation which ignores the curvature of the SWNT side-wall. The model is able to predict the family spread in the experimental Kataura plot, and furthermore, it is expected to shed light on the SWNT interaction with various surfactants and environments which result in different spreads of the optical transition energies within a given family in the experimental Kataura plot.

11:15 AM HH7.3
Atomic-scale Physics and Modeling of Schottky Barrier Effect in Carbon Nanotube Nanoelectronics. Yongqiang Xue and Mark A. Ratner; Chemistry Department School of Materials Research Center, Northwestern University, Evanston, Illinois.

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

11:30 AM HH7.4
Kohn Anomalies in Graphite and Nanotubes. Stefano Piscanec1, Michele Lazzero2, Andrea Carlo Ferrari1, Francesco Mauri3 and John Robertson1; 1Engineering, University of Cambridge, Cambridge, United Kingdom; 2Laboratoire de Minéralogie-Cristallographie de Paris, Université Pierre et Marie Curie, Paris, France.

The understanding of the physical mechanisms ruling the phonon dispersions and the electron-phonon coupling in graphite is a key step to derive the vibrational properties and the Raman intensities of carbon nanotubes. In graphite the inter-atomic force-constant matrix elements very weakly decay with the distance, and this long-range behaviour strongly affects the phonon dispersion of the upper optical branches at the Γ and K points. A key point to understand the phonons of graphite is the semi-metallic character of its electronic structure. In fact, the atomic vibrations are partially screened by electronic states. In a metal this screening can change rapidly for vibrations associated to certain q points of the Brillouin Zone, entirely determined by the shape of the Fermi surface. The consequence anomalous behaviour of the phonons is the so-called Kohn anomaly. We show that graphite displays two remarkable Kohn anomalies at the Γ-E2g and K-A1 mode, respectively. We demonstrate that graphite is a very remarkable case, since a very simple mathematical description of the Kohn anomalies is possible. The anomalies are revealed by two sharp kinks in the phonon dispersion. The slope of these kinks is proportional to the ratio of the square of the electron-phonon coupling matrix element and the p bands slope at K. It is thus impossible to derive the phonon branches at Γ and K by a force constant approach based on a finite number of force constants, contrary to what often done in literature. The electron-phonon coupling of the Γ-E2g and K-A1 modes is particularly large, whilst the coupling of all the other modes at Gamma and K is negligible. This implies that the Raman D peak of graphite is due to the highest optical branch starting from the K-A1 mode. The D peak dispersion with excitation energy is in the slop of the Kohn anomalous. These results have immediate implications for carbon nanotubes. Due to their reduced dimensionality, metallic tubes display much stronger Kohn anomalies than graphite. This result in phonon softening, implying that folded graphite does not reproduce the phonon dispersions of metallic tubes. The presence of Kohn anomalies in metallic tubes is the reason for the difference in the Raman spectra between semiconducting and metallic tubes.

SESSION H8H: Electronic Properties and Devices I

1:30 PM *H8H.1
Electrical Transport in Aligned Carbon Nanotubes. Wonbong Choi1, Donghun Kang2, Wanjun Park2, Eunjoo Bae2, Eungmoo Lee1 and Ju-yeol Ko2; 1Mechanical & Materials, Florida International University, Miami, Florida; 2Samsung Advanced Institute of Technology, Keung, South Korea.

We discuss the central issues to be addressed for realizing carbon nanotube (CNT) nanoelectronics. We focus on the selective growth, electron energy bandgap engineering and electrical transport characterization. We have introduced nanocomposite to control the selective growth, length and diameter of CNT. Vertically aligned CNTs are synthesized for developing CNT-based field-effect transistor (FET). The ohmic contact of the CNT/metal interface is formed by rapid thermal annealing. Diameter control, synthesis of y-shape CNT and surface modification of CNT open the possibility for energy band gap modulation. We focus on the selective growth on the top gate structure with oxide-nitride-oxide charge trap is also presented. We suggest that the deposited memory film can be used for the quantum dot storage due to the localized electric field by nano scale CNT/electron channel. [1] Cho WM, Cheong B, Choi S, Bae E J, Lee J, Kim J, Kim J, 2003 Appl. Phys. Lett. Jan. 82 275. [2] Choi W B, Cheong B, Kim J, Ju J, Bae E J, Chung G, 2003 Advanced Functional Materials, 13 80.
2:00 PM HH8.2
Structure and Dynamics of Carbon Buckyballs Encapsulated into Single-Walled Carbon Nanotubes. Julien Camboudeau1, Stephane Rols1, Robert Almaric1, Jean-Louis Sauvajol1, Helmut Scholer2 and Hiromichi Kataura2, 1Groupe de Dynamique des Phases Condensées, Service P9, Laboratoire de Physique, 2Laboratoire de Physique de la Matière Condensée, UMR CNRS 8502, INSA, INPL, Nancy, France; 3Institut Laue Langevin, Grenoble, France; 4Nanotechnology 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, which allows the study of its precipitation, etc. Interaction of covalent bonding upon alkylation 1. The transmission electronic 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 480 K, suggesting the free rotation of some of the C60 molecules inside SWNTs. The generalized 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 has been decomposed into two regions separated by a gap, namely: the [30-200 meV] inter-molecular energy range where all the observed vibrations can be attributed to intra-molecular modes. - the [0-80 meV] inter-molecular energy range where all the observed vibrations can be attributed to inter-molecular modes. 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. S. Saito and S. Okada, 3rd Symposium on Atomic-Scale Surface and Interface Dynamics 367 (Fukuoka 1998).

2:15 PM HH8.3
Fabrication of N-type Field-Effect Transistors Based on Self-Assembled Thin Films of Carbon Nanotubes and Polyamidoamine (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 the future of electronics, as their unique structural, mechanical, and electrical properties. Field-Effect Transistors (FETs) based on CNTs have been shown to exhibit field-effect mobilities as high as 12 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 c.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, making them very attractive FET-active materials to be used to fabricate 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 4000 amine groups per molecule are present for a generation 10 PAMAM dendrimer. The electron donating capability of the amine groups changes the electrical conductance of individual SWNTs, by a shift in the Fermi Level closer to the conduction band. The scope of this study is to investigate the effect of the electron donating capability of the PAMAM dendrimers on the electronic characteristics of the subsequently built FETs. References [1] Bradley, K.; Gabriel, J.-P.; Gruner, G. Nano Letters, 3, 1353-1355, 2003 [2] Zhou, C.; Kong, J.; Yenilmez, E.; Dai, H. Science, 290, 1552-1555, 2000 [3] Tao, T.; Devoret, M.; Dai, H.; Thouy, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. Nature, 386, 477-477, 1997 [4] Tao, S. J.; Verschuuren, A. R. M.; Dekker, C.; Nature, 393, 49-52, 1998 [5] Kong, J.; Dai, H. J. Phys. Chem. B, 105, 8269-8273, 2001.

2:30 PM HH8.4

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 non-conductive surfactants, ssDNA/SWCNTs dispersed in 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 Lee1, DongGyu Lee1, Siegmar Roth2, Eleanor E. B. Campbell3, GyuTae Kim4 and YungWoo Park1, 1School of Physics, Seoul National University, Seoul, South Korea; 2Max-Planck-Institut for Solid State Research, Stuttgart, Germany, 3Department of Experimental Physics, University of Gothenburg University and Chalmers University of Technology, Göteborg, 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-walled carbon nanotubes (SWNTs). Mean lifetimes in high- and low-current states, \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \), 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-chip. The performance of lead-field-effect transistors consisting of individual single-walled CNTs improves continuously and outperforms silicon-based devices in many aspects. However, only a few promising schemes for integrating CNTs into products exist. Generally, nanomaterials demand new concepts and assembly techniques that have to be evaluated in terms of feasibility, yield and reproducibility. The concept of integration of nano-devices into microelectronics (hybrid electronics) makes use of the advantages of semiconductor fabrication techniques, such as lithographic structuring, therefore allowing parallel processing. The creation of vertical interconnects (Vias) and vertical transistors (VCNTFET) consisting of CNTs directly on silicon chips has been 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/substrate system and the growth conditions leads to control over the yield, density, and CNTs type, which are key issues for device fabrication. The growth of individual MWCNTs in lithographically defined positions on silicon chips has been achieved with a precision of 20 nm. For electrical characterisation these CNTs were grown from metallic underlayers and individually contacted using e-beam lithography. A current density of 4×106 A/cm2 and a resistance of 7.8 k\( \Omega \) 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 unmasked metallic tubes were eliminated by electronic pulses. Using this CNT transistor it is possible to switch macroscopic devices such as LEDs or small motors.

3:00 PM TH8.6

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-chip. The performance of lead-field-effect transistors consisting of individual single-walled CNTs improves continuously and outperforms silicon-based devices in many aspects. However, only a few promising schemes for integrating CNTs into products exist. Generally, nanomaterials demand new concepts and assembly techniques that have to be evaluated in terms of feasibility, yield and reproducibility. The concept of integration of nano-devices into microelectronics (hybrid electronics) makes use of the advantages of semiconductor fabrication techniques, such as lithographic structuring, therefore allowing parallel processing. The creation of vertical interconnects (Vias) and vertical transistors (VCNTFET) consisting of CNTs directly on silicon chips has been 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 20 nm. For electrical characterisation these CNTs were grown from metallic underlayers and individually contacted using e-beam lithography. A current density of 4×106 A/cm2 and a resistance of 7.8 k\( \Omega \) 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 unmasked metallic tubes were eliminated by electronic pulses. Using this CNT transistor it is possible to switch macroscopic devices such as LEDs or small motors.
We demonstrate a single-walled carbon nanotube p-n junction diode device. The p-n junction is formed along a single nanotube by electrostatic doping using a pair of split gate electrodes. By observing 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.

S. Oh1, J. Zhang2, Y. Cheng2, Hideo Shimo3, Bo Gao3 and Otto Zhou1, 2, 4

Carbon nanotube p-n junction diodes on indium tin oxide (ITO) - a transparent conductor, and nitrogen-doped multi-walled carbon nanotubes were fabricated on various field emission cathodes by electrophoresis. Soojin Oh1, Jian Zhang2, Hideo Shimo3, Bo Gao3 and Otto Zhou1, 2, 4

We demonstrate a single-walled carbon nanotube p-n junction diode device. The p-n junction is formed along a single nanotube by electrostatic doping using a pair of split gate electrodes. By observing 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.

S. Oh1, J. Zhang2, Y. Cheng2, Hideo Shimo3, Bo Gao3 and Otto Zhou1, 2, 4

For the first time, transport measurements in field-effect transistor configuration and TEM investigations on the same individual nanotubes/nanotube peapods have been performed. So far approaches for combining transport and TEM on the same nanotube only allowed for measuring the output characteristics Isd(Vsd), i.e. the dependence of the current Isd through the tube on the bias voltage Vsd. Applying our new method of underetching a Si/SiO2 substrate from the edge of a chip after the transport measurements, we can additionally get the transfer characteristics Isd(Vg), i.e. the gate response of the current, which provides additional information about the electronic properties of the system investigated. After the transport measurements and the etching process the samples can be viewed in the TEM, which enables us to check, whether a contacted nanotube is really a single tube or a thin bundle and whether a tube is filled with fullerenes (“peapod”). Combined transport measurements and TEM investigations of nanotubes and nanotube peapods will be presented.

Dirk Obbergell1, Jannek C. Meyer1, Shihe Yang1, Shangfeng Yang2 and Siegmund Roth2
1Max Planck Institute for Solid State Research, Stuttgart, Germany; 2Department of Chemistry, The Hong Kong University of Science and Technology, Hong Kong, China.
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 decreases as the length of the second tube increases 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 measured voltage drop in SWNTs. In 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 configuration, the voltage drop is measured by a split differential pair situated inside or outside the region lying between the current biased electrodes. Surprisingly, a significant nolocal 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 voltage bias is increased. These results are in agreement with a simple model which considers conduction through the two outermost shells and treats them as a resistive transmission line. In such a model, the intershell conductance is 100 S/m. This value is in agreement with the estimate based on electronic tunnelling through atomic orbitals of nearby shells while taking into account conservation of energy but not momentum.

9:30 AM HH9.1 Carbon Nanotube Photo-Detectors, Matthew Scott Marcus, O. M. Castellini, J. M. Simmons and M. A. Eriksson; Physics, Univ. of Wisconsin-Madison, Madison, Wisconsin.

Carbon nanotube transistors can be photo-gated using visible and near infrared light. The transistors are fabricated on 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 determines the voltage drop of the channel current with respect to the gate voltage. Growing nanotubes with large channel lengths (L=500 μm), which are much larger than the laser beam diameter, we are able to study the spatial dependence of the photo-gating effect. We observe measurable photo-currents even when the laser illuminates at large distances (up to 1mm), indicating that the carriers responsible for photo-gating are mobile. The photo-gating effect provides an unusual photo-detector where the photo-voltage determines the transport properties. In efforts 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 shorter than the laser beam diameter, we observe the entire nanotube channel current to be suppressed. This is in contrast for tubes with lengths L=2μm, where the ends of the nanotubes remain pinned to the suspended pillars, but the central body of the tube drops 70nm and can stick to the substrate. For nanotubes with lengths between L=1-2μm, the probability that the nanotube is stuck to the substrate increases with tube length. We propose that thermally driven oscillations of the nanotube during the CVD growth cause the nanotube to oscillate with amplitudes large enough (70nm) to touch the substrate, then stick. Using the length of the nanotubes, and the diameter distribution from the CVD growth we are able to non-invasively measure a value of Young’s modulus.

SESSION HH10: Optical Properties


Sergey I. Troyanovskiy, Dmytro Sasyuk, John-David T. Rocha, John P. Casey, Thomas Keeney, Crystal E. Redden and B. Ruston Weisman; Department of Chemistry, Center for Nanoscale Science & Technology, and Center for Biological and Environment Nanotechnology, Rice University, Houston, Texas.

Since its recent discovery, the near-infrared band-gap photoluminescence (fluorescence) of semiconducting SWNT has become a valuable tool for both 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 (mixture) structural species will be shown. This information is crucial for increased understanding of nanotube photoluminescence in single and bulk environments. Some limitations of fluorescence spectroscopy as a tool for elucidating 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 nanostructural information, we present a method to use mixtures of SWNT species, new methods will be described that can determine the chiral and diameter distributions of aseptic aqueous samples within seconds. Fluorescence imaging techniques allow the observation of single nanotubes in dilute solid and liquid suspensions with time resolutions of 20 μs. Spectrally and temporally-resolved near-infrared imaging methods have been developed for detecting SWNT at low concentrations in biological suspensions. This talk is illustrated with fluorescence data revealing pristine nanotubes that have been taken up by macrophage-like cells in culture. SWNT fluorescence is also observed within living Drosofila larvae that have been eaten food laced with nanotubes.


Spectroscopic measurements in visible frequency has been pursued on aligned carbon nanotubes in random and periodic arrays. Arrays of nanotube substrates 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 Lanzani1, Moreno Meneghetti2, Enzo Menna2, Giulio Cercellio2, Cristina Manzon2 and Alessio Giambett2, 1Physics, Politecnico di Milano, Milan, Italy; 2Chemical science, University of Padova, Padova.

SWNT obtained by the HiPco methodology and functionalised with PEG chains via amide bonds prepared embedded PMMA were studied with pump-probe spectroscopy by using ultra-short pulses in the visible and near infrared, with time duration of 7 fs and 20 fs respectively. The primary event of excitation relaxation was time resolved, providing a time constant of 40 plus/minus 5 fs, associated to the exciton reaching recovery, which is assigned to intrinsic relaxation between 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 wavenumber is observed, with dephasings of 1.2 ps. Discussion on this will be presented.

11:15 AM HH10.4 Localized Spectral Analysis of Doped and Undoped SWNTs using Near-Field Raman Spectroscopy. Neil Anderson1, Achim Hartschuh1, Lukas Novotny and Apparao M. Rao1, 1Institute of Optics, University of Rochester, Rochester, New York; 2Physics & Astronomy, Clemson University, Clemson, South Carolina; 3Physikalische Chemie, Universitat Siegen, Siegen, Germany.

We use near-field Raman imaging and spectroscopy to study localized vibrational modes along individual single-walled carbon nanotubes (SWNTs). Our approach relies on the strongly enhanced field near a laser-irradiated gold tip. This enhanced field acts as our Raman “extraction source.” The key to successful extraction is detection of the characteristic Raman excitation source, 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 focus on the effects of doping such SWNTs with elemental boron and nitrogen on the four main Raman active modes, namely the RBM, G, G’ and D bands. The dopant concentration ranged from 0 to 10 at %, and the incident laser intensity required to observe Raman signals (with the same S/N) ratio.
increased with increasing dopant concentration. Our results show a dramatic loss of resonance with increased dopant concentration present in the polymer environment. We attribute this in resonance scattering properties due to dopant-induced changes in the electronic properties of SWNTs.

11:30 AM HH10.5

Wavelength-resolved femtosecond transient absorption spectroscopy is used to study the electronic dynamics of a series of single-walled carbon nanotube/polymer composite films in order to understand the environment’s role in the excited state dynamics. Visible photoexcitation of nanotubes creates excitons through transitions between Van Hove singularities. The electron-hole 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 after 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. Alexey G. Rozhin1, Youshi Sakakibara2, Hiroshi Koinuma2, Shun Matsuzaki2, Kohtaro Ishida2, Yoshi Aoyama2 and Madoka Okutomo2,1. 1AIST 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 have opened up promising applications for optical telecommunication, such as mode-locker in short pulse laser [1], ASE noise suppressor [2] and all optical switch [3]. The SA function can be further improved by a material design using alignment of CNTs. Because the optical transition moments are strongly anisotropic on the tube axis, using the aligned CNTs and the polarized excitation light can enhance the transition probability between the valence band and the conduction band. In this work, we aligned single wall carbon nanotubes (SWNTs) in a polyvinyl alcohol (PVA) film, and investigated the anisotropic optical absorption (OA) and the SA properties. For the film preparation, first we used surfactant-assisted ultrasonication of laser ablation SWNTs in water. 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) SWNTs absorption bands. With a polarized light, a strong anisotropy of OA, reaching to the E(parallel) / E(normal) absorbance ratios of 5.6, 3.9 and 3.1 at 1.8, 1.0 and 0.7 urn respectively, was observed. The excitonic dephasing mechanism that is much lower than the true value due to the excitation 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 of the long natural radiative lifetime in excess of 10ns that is inconsistent with a strong absorption coefficient and a small Stokes shift. Combining the measured PL lifetime with a predicted natural radiative lifetime of...
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The OCV value I'A/cm². pristine SWNTs will also be reported.

for a wide variety of optoelectronic applications. In order to fully spectra upon chemical doping can be relatively well explained by the structure of optical transitions in nanotubes is much more complex significant lifetime transition broadening.


Semiconducting, single walled carbon nanotubes have large potential for a wide range 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 behavior 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 (compared with respect to the lowest, emitting state), we observe multiple absorption peaks that can be attributed to phonon assisted transitions into the ground exciton state. In nanotubes of relatively large diameters (emission wavelength longer than 1.1 μm), we also observe the absorption feature due to the second excitonic state. Surprisingly, the intensity of this feature is comparable to the intensity of the phonon assisted bands. Furthermore, the excited-state absorption features are characterized by significant broadening (>25meV). 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 broadening. In summary, our findings suggest that as a result of strong electron-phonon interactions, the structure of optical transitions in nanotubes is much more complex than in a simple framework, which assumes that absorption is dominated by resonant transitions in 1D energy spectrum. [2] 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 ≈ 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 Ramsauer-Townsend 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_R is varied. In particular, we find no evidence for selective doping based on tube diameters or distinguishing metallic and semiconducting tubes.

3:15 PM HH12.2 Atomic-Level Investigation of Fluorination and Defluorination of Carbon Nanotubes. Dharmapal Takahr1, Zhenning Gu2, John L. Margrave2 and Kevin F. Kelly1; 1ECE, Rice University, Houston, Texas; 2Chemistry, Rice University, Houston, Texas.

There is a great deal of interest in the functionalization, in particular fluorination, of carbon nanotubes for solution and subsequent chemical reactions. Previous investigations used STM to monitor the performance of sidewall fluorating 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 low energy Raman spectrum and deconvoluted fluorescence 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. Hidehisa Imagawa1, Shinji Kawasuki2, Ruyko Okino3 and Hiroshige Katayama4; 1Department of Chemistry, Shinshu University, Ueda, Japan; 2Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Japan; 3Nanotechnology 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 fluorinated CNTs (C-SWNTs) were prepared by the laser-ablation method using a metal-carbon composite rod as a target. The diameter of the tubes was 1.4-1.5 nm. Open-end SWNTs (O-SWNTs) were obtained by heat treatment of C-SWNTs at 698 K in the air at 1 atm, while partial removal of fluorine from the tubes was carried out using 1 atm elemental fluorine in a temperature range RT-523 K. The composition of the open-end fluorotubes, fluorinated at 473, 523 and 523 K were CFO.29, CFO.45 and CFO.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 bond and, hence, the partial destruction of tubes were observed. Upon fluorination, the triangular lattice constant of 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 partial 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 the closed-end tubes with F/C=0.48 showed no RBMs. Electrochemical and thermal properties of fluorotubes. The discharging performance of fluorotubes was studied on Li/LiClO4 (EC/CHCl3)/ LiF-SWNTs cells (F-SWNTs=fluorotubes prepared by RT-573K 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 fluorotubes was decreased while 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 CFO.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 Chen1, Rajagopal Ramanubramaniam1 and Haiying Liu2; 13Mx 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, nanotube chemistry) 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. A rigid functional conjugated polymer, poly[aryleneethynylene]s (PPE) (Ref. 1). This method enables the superior control of the relative placement of functionalities on the nanotube surface while still preserving nearly all of the nanotube properties. We support these results with the rich functional chemistry of PPE allows us to prepare various SWNTs with tunable functionalities and solubilities. The PPE-functionalized SWNTs can be solubilized in various organic solvents and water. The soluble SWNTs with specific functional properties can be used as gels that can gelate various organic solvents such as chloroform, 1-methyl-2-pyrrolidinone etc. The resulting SWNT gel may find applications in high strength nanotube fibers and high surface area catalyst supports. One major approach would be to produce unique metal and ionic groups onto the carbon nanotube surfaces. We will also report the defunctionalization of PPE-functionalized SWNTs. We will discuss our acid-free, nonchromatographic approach towards the large-scale separation of metallic from semiconducting SWNTs. The Raman, Vis-NIR spectra as well as electrical conductivity measurements show that it’s possible to separate metallic from semiconducting SWNTs by noncovalent functionalization chemistry. Reference: 1. Chen, J. et al. J. Am. Chem. Soc. 2002, 124, 9834-9835.

4:00 PM HH12.5 Covalent Bonding of Nano-entities with NH2 Groups onto Multi-walled Carbon Nanotubes, Kuiyang Jiang1, Xujie Zhang2, Linda S. Schodler1 and Richard W. Siege1:1Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; 2Hyperion Catalysis International Inc., Cambridge, Massachusetts.

Carbon nanotubes exhibit remarkable structural, electrical and mechanical properties, while proteins and dendrimers have exclusive selectivity or optical properties. The functionalization of these properties could result in a wide range of applications in biosensors, bio-fuel cells, biotectors and light-electricity converters. To realize these applications, controlled structures have to be assembled as required. In this study, we control the uniform attachment of some nanomaterials using ferritin, bovine serum albumin (BSA), and PAMAM dendrimers as examples. These nano-entities were chemically bonded onto multi-walled carbon nanotubes (MWNTs) through a two-step process of diimide-activated amidation. First, carboxylated MWNTs were activated by N-ethyl-N-3-dimethylaminopropyl) carbodiimide hydrochloride (EDAC), forming a stable active ester in the presence of the amine groups on the ferritin or BSA proteins, or the PAMAM dendrimers, forming an amide bond between the MWNTs and the nano-scale entities. This two-step process avoids intermolecular and unwanted uniform attachment on carbon nanotubes. TEM and AFM measurements clearly confirmed the successful attachment. This approach provides a universal and efficient method to attach nano-entities with NH2 groups to carbon nanotubes at ambient conditions. This work was supported by the Nanoscale Science and Engineering Initiative of the U.S. National Science Foundation under NSF Award Number DMR-0117792.

4:15 PM HH12.6 Self-Organization of Semiconductor Quantum Nanocrystals on Carbon Single-Wall Nanotubes into Close-Packed Linear Arrays, Chaitu Engratkal1, Jovam M. Nedeljkovic1, Yong-Hyung Kim1, Marcus Jones2, Randy J. Ellison1, Mark C. Hanna1, Scott P. Ahrenkiel1, Kim M. Jones1, Mark F. Davis1, Timothy J. McDonald1, Kale J. Franz1, Thomas Gennett2, Anne C. Dillon1, Katherine H. Gilbert1, Philip A. Parilla3, Jeff L. Alleman3, Shengbai Zhang1,2,3,4,5.

5:00 PM HH12.7 N- and B-Doped Carbon Nanotubes and Nanomaterials via Pyrolysis of Aerosols, Nicole Gierke1. 1Department of Materials, Oxford University, Oxford, United Kingdom; 2Max-Planck-Institut fur Metallforschung, Stuttgart, Germany.

In recent years, various carbon nanotube synthesis techniques have been reported. With the development of the aerosol pyrolysis it is now possible to produce large quantities of pure and aligned high quality carbon nanotubes. Furthermore, depending on the precursor, modified carbon nanotubes can also be generated. For example, the pyrolysis of homogeneously dispersed aerosols generated from benzylamine/ferrocene solutions at 950 °C using an ultrasonic spraying device yields large quantities (several grams/30 min) of pure and well-aligned CNx nanotubes (30-130 microns long, 10-200 nm outer diameter). Scanning and transmission electron microscopy show that the electrospun aerosol secondary carbon nanotube assemblies, and revealed that the surfaces of the SWNTs were functionalized with tunable functionalities and solubilities. The PPE-functionalized SWNTs can be solubilized in various organic solvents and water. The soluble SWNTs with specific functional properties can be used as gels that can gelate various organic solvents such as chloroform, 1-methyl-2-pyrrolidinone etc. The resulting SWNT gel may find applications in high strength nanotube fibers and high surface area catalyst supports. One major approach would be to produce unique metal and ionic groups onto the carbon nanotube surfaces. We will also report the defunctionalization of PPE-functionalized SWNTs. We will discuss our acid-free, nonchromatographic approach towards the large-scale separation of metallic from semiconducting SWNTs. The Raman, Vis-NIR spectra as well as electrical conductivity measurements show that it’s possible to separate metallic from semiconducting SWNTs by noncovalent functionalization chemistry. Reference: 1. Chen, J. et al. J. Am. Chem. Soc. 2002, 124, 9834-9835.
Carbon nanotubes (CNTs), especially single wall carbon nanotubes (SWNTs), have been intensively studied for their applications to electronic devices. In fact, a large number of investigations have been made on the field effect transistors (FETs) in recent years, where silicon substrates with doped thin films are used in most cases. However, CNTs adhere to a silicon dioxide substrate so strongly that the physical and chemical properties of CNTs can be changed. To avoid this problem, CNTs are sometimes suspended in space between electrodes or pillars. Nevertheless, the contact geometry of CNTs lying on the substrate is remarkably important in terms of not only mechanical stability but also the electronic control of CNTs by chemical methods. 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 hexamethyldisilazane (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 into a sealed container and heated them. Finally TMS films were formed on the substrate except the areas of the electrodes. In addition, we studied the control of the orientation of SWNTs using the AC dielectric method, where SWNTs in solvent can be extended along an applied AC external electrical field because of their induced dipole moment. After the solvent evaporated, SWNTs were deposited and bridged over the electrodes to which we applied the ac voltage. We measured the 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).

HH13.3 Integration Of Carbon Nanotubes Into Device Structures.
Brett Lagem, Joshua David Schumacher, Nhan Nguyen, Bojana Zivanovic and Rudy Schlaf; Electrical Engineering, University of Florida, State University of Florida, Tampa, Florida.
Carbon nanotubes have shown promising properties for applications in electronic circuits and other devices. Recently, 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 utilizes nano-patterned 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 initial 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. Youngak 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 electric 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. Obraztsov3, Rashmi Nanjundaswamy4, Sergei Lee1, Austin Cunningham5, Mei Zhang6 and Mike Sampson7; 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 K. The mechanism of light emission and the process of CNT sublimation are proposed and discussed.

HH13.6 A Schottky Photocathode Diode Based on an Individual C/CNx Multi-walled Nanotube Junction. Yung Lai, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.
Herein we demonstrate the possibility of creating Schottky-type photocathode diodes based on individual C/CNx nanotube
Several factors that affect the junction, and propose a scheme for a phototransistor in which the field emission properties have been studied, such as the geometrical configuration of DWNTs and substrates, the distribution of DWNTs at a very low electric field of 1.2 V/\mu m. 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 photo current 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 traps in the polymer layer. The power law dependence is characteristic of space charge limited (SCL) photocurrent. When the exciting light intensity is low, the thermal detrapping dominates the detrapping process and the SCL photocurrent will be the same as in the dark. When the light intensity is increased to such a level that the optical detrapping becomes predominant, then the current depends on the light intensity. In the visible wavelength range, the photoconductivities of individual-C/CNx-nanotube devices were measured. Upon the generation of photocurrents its operation was governed by light intensity. Large changes in the current could be obtained 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 Zhuoi Peng; Dept. of Physics, Boston College; Chestnut Hill, Massachusetts.

Double-walled carbon nanotubes (DWNTs) are proved to have excellent field emission properties. Some simple and effective methods have been developed to control the density of DWNTs on silicon substrates. The threshold electric current density of 1 mA/cm² can be reached at a very low electric field of 1.2 V/\mu m. Several factors that affect the field emission properties have been studied, such as the geometrical configuration of DWNTs and substrates, the distribution of DWNTs and the roughness of the substrates. Field emission stability of DWNTs is also studied.

HH13.9 Combining Nanotubes and Chromophores for Broadband Optical Limiting. Nicolas Izard1,2, Cecilia Menard3, Eric Doris4, Charles Mioskowski5, Didier Richet6 and Anglaret Eric1, 1GDPC, Universite Montpellier 2, Montpellier, France; 2Department of Physics, Université de Lille, Lille, France; 3Service de Marquage Moleculaire et de Chimie Bioorganique, CECA-Saclay, Gif sur Yvette, France.

New systems are required for optical limiting against broadband laser pulses. We demonstrate that the association of non-linear scattering from single-wall carbon nanotubes and multiphoton absorption from organic chromophores is a promising approach to extend performances of optical limiters over broad spectral and temporal ranges. Stable composite suspensions can be prepared, using functionalized nanotubes. Such composites display high linear transmission and good neutral colorimetry and are particularly efficient in the nanosecond regime due to cumulative effects. 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, E11 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 E(r), ranging from 10 to 80 meV. 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.

HH13.10 Abstract Withdrawn

HH13.11 Functionalized Carbon Nanotubes through Mechanically Bound and Rigid Organometallic Complexes. Jordan Pottier1,2, Tom D. Dubois1,2 and Tom A. Schmedders1,2, 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 ensembles. One difficulty in preparing these assemblies from nanotubes is the lack of site-specific points of contact and the subsequent compliance of the linkage between nanoparticles. Using molecular mechanics and dynamics calculations, we have modeled the assembly process of two-dimensional and three-dimensional structures of carbon nanotubes. The linkers between the nanotubes consist of novel metalodendrimers. These dendrimers have multiple binding sites with chemically specified chirality. Most importantly, they are mechanically rigid. This enables the multidimensional constraints and geometry, required for advanced electronic and optoelectronic devices. These computational results and the implied 3D nanostructures that are derived will be presented. Moreover we have synthesized several novel silcon 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 controlled crosstalk of 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. Horii1, Shin Grace Chou1 and M. S. Dresselhaus3,4; 1Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

An enhanced Raman signal is demonstrated from individual suspended SWNTs and from isolated SWNTs grown on a doped polycrystalline film. The radial breathing modes (RBM) of the Raman spectra 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 1200 cm⁻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, Eduard B. Barroso2, Adelina P. Santos3,4, Georgii G. Samsonidze5, Marcus A. Pimenta6, Ado Jorio7, Flavio Plentz Filho7, Mildred S. Dresselhaus8,9, Richiro Saito10, Ming Zheng11, G. Bibiana Onoa1, Ellen D. Semke12, Anna K. Swan13, M. S. Ural14 and Bennet B. Goldberg14,15; 1Chemistry, MIT, Cambridge, Massachusetts; 2Department of Physics, MIT, Cambridge, Massachusetts; 3Physics, Universidade Federal de Minas Gerais and Development, Belo Horizonte-MG, Brazil; 4Physics, Universidade Federal do Cearário, Fortaleza-CE, Brazil; 5Chemistry, Centro de Desenvolvimento da Tecnologia Nuclear, CDTN, Belo-Horizonte/MG, Brazil; 6Physics, MIT, Cambridge, Massachusetts; 7ECCS, MIT, Cambridge, Massachusetts; 8Physics, Tohoku University and CREST JST, Sendai, Japan; 9Francis Bitter Magnet Laboratory, MIT, Boston, Massachusetts; 10Dartmouth Research and Development, Wilmington, Delaware; 11ECE, Boston University, Boston, Massachusetts; 12Physics, Boston University, Boston, Massachusetts.

Optical characterization of DNA-wrapped CoMoCAT carbon nanotube hybrids (DNA-CNT) and semiconductor-enriched DNA-CNT were carried out using resonant Raman spectroscopy (RRS) and photoluminescence (PL) experiments. The 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, E11 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 E(r), ranging from 10 to 80 meV. 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.
The radial breathing mode (RBM) region of the resonance Raman spectra of HiPco single walled carbon nanotubes (SWNTs) was investigated as a function of aggregation and presence of environmental contaminants. This was modeled using an energetic deviation term (ΔE), imparted to the optical transitions (Eo(n,m)) by the change in SWNT physical chemical environment. Three sets of Eo(n,m) values were used to reconstruct these RBM profiles, based on: (i) photoluminescence (PL) measurements, (ii) a simple tight-binding (TB) model, and (iii) a set of modified, TB-based Eo(n,m) values for the understanding of the influence of chiral angle on SWNTs for diameters below 1 nm. The simulation revealed that the TL-determined Eo(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 Eo(n,m) values, indicative of the importance of both curvature and chirality effects. Providing an accurate set of Eo(n,m) values becomes available, the RBM profile reconstruction methodology discussed herein could greatly enhance our ability to model a range of physicochemical changes to the immediate environment of SWNTs.

HH13.15
Comparison Study of the Vibrational and Electronic Properties of Single-Wall Carbon Nanotubes Suspended and on a Silicon Oxide Substrate. 

Eduardo B. Barros 2, H. Son 1, S. Cronin 3, Shin Grace Chou 1, A. K. Swan 4, G. Dresselhaus 5, and M. S. Dresselhaus 1.

The electronic and vibrational properties of Single Wall Carbon Nanotubes (SWNTs) isolated on silicon oxide substrates have been widely studied. The fact the nanotubes remain attached to the substrate surface suggests a significant interaction between the nanotube walls and the surface. Possible applications of carbon nanotubes to electronic devices requires a comprehensive understanding of these nanotubes. 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 solely suspended to the region where the tube is sitting on the silicon oxide film, the effects of the silicon oxide substrate to the vibrational and electronic properties of the SWNTs could be identified for several different (n,m) assigned nanotubes. The authors acknowledge support from NSF grant DMR-01-16042 and Intel Corporation.

HH13.16
NMR Investigations on alkali intercalated carbon nanotubes. 

Michael Schmid 1,2,3, Christoph Goze-Bac 1, Michael Mehring 4, Patrick Bermer 2 and Siegmund Roth 1.

1Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, Germany; 2GDPC, Universite Montpellier II, Montpellier, France; 3Physik. Inst., Universitaet Stuttgart, Stuttgart, Germany.

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

HH13.17
Effect of Doping on the Resonant Raman Scattering in Metallic Single-Walled Carbon Nanotubes (SWNTs). 

Rahul Rao 1, Gayatri Keskar 1, Mildred S. Dresselhaus 2 and Apparao M. Renu 3.

1Physics and Astronomy, Clemson University, Clemson, South Carolina; 2Physics 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 spectroscopy 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
Polymer-functionalized Single-Walled Carbon Nanotubes (SWNTs) were prepared using Atom Transfer Radical Polymerization (ATRP).

Hydroxyl groups on SWNTs were introduced through Friedel-Crafts alkylation of chloroform. Subsequent esterification with 2-chloro-propionyl chloride introduced ATRP initiator on the side wall of SWNTs. Modified SWNTs in each functionalization step was characterized by FT-IR, Raman, transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA). The degree of functionalization on SWNTs was estimated to be 20% on the basis of TGA analysis. In comparison with the pristine SWNTs, polymer-functionalized SWNTs were soluble in various organic solvents such as THF, chloroform, dichloromethane, and alcohol.

HH13.19
Functionalization of Bundles-milled SWNTs by Nitrodial.

Hiroshi Moriya 1, Kazuhiro Kurihara 1, Masahiko Saibara 1, Tooshirou Ishii 2, Kacori Harigai 2, Atsushi Yusa 3 and Terumasa Kondo 1.

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Carbon nanotubes (CNTs) are attractive for building blocks of the future electronic devices. However, compared to the molecular-based materials, robust nature of CNTs with no solubility, the density of states at the Fermi level of CNTs is lower than that of the polymeric chains. The polymeric CNTs are expected to form a scaffold 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 reaction applicable to fullerene C60. Chiang reported that hexanitrofullerene was produced by the reaction of C60 and nitric acid [1]. According to this method, bundled-milled SWNTs were intercalated with nitric acid, followed by alkaline ammonium solution. The obtained SWNTs were yellow, and it was concluded that the nanotubes were subjected to nitricaldical generated from Cu and conc. nitric acid under nitrogen atmosphere. The polymeric SWNTs obtained by this method were shown to be stable in organic solvents. These results clearly show that the functionalization of CNTs by means of the reaction applicable to fullerene C60 was successfully achieved.

HH13.20
Interactions of Lanthanide Metal Complexes with Single-walled Carbon Nanotubes. 

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Oxidized, single-walled carbon nanotubes (SWNTs) have been reported to show enhanced Eu 3+ luminescence, Ln 3+ luminescence, and Tb 3+ luminescence. These studies have been only aimed at developing a fundamental understanding of the coordination chemistry of metal ions and of metal ion binding to SWNTs, respectively.
complexes onto the surfaces of nanotubes but also to improve the reactive selectivity of CNTs, and thus, solubility in a variety of solvents. We found that the lanthanide ions likely coordinate to these carbon nanotubes, eventually leading to the destruction of the graphite lattice which is a necessary condition for the formation of oxidized carbon species predominantly ionic bonding arrangements. Metal coordination occurs through the increased number of oxygen atoms, forming covalent functionalization changes the hydrophobic nature of carbon nanotubes functionalized by using polyvinyl alcohol. This surface functionalization also allows adaptation of molecules onto the modified carbon nanotubes, the electrical transport properties may be changed. Effect of changes in the geometry of nanotubes will be performed since it is expected that by adapting molecules onto the modified carbon nanotubes, the electrical transport property may be changed. Effect of changes in the geometry of nanotubes and film thickness on the sensor is also presented. Moreover charge transport mechanism in these functionalized carbon nanotubes will also be proposed.

HH13.23 Integrated Study of Ion Irradiated Single-walled and Multi-walled Carbon Nanotubes by Spectroscopic Methods. Mariya Brzhezinskaya1, Eugen Baitinger1, Vladimir Shnitov 2, June Simmons4, 3B. M. Nichols2, Matthew S. Marcus2, O. M. Castellini1, B. J. Hames1 and M. A. Eriksson3, 1Department of Physics, University of Wisconsin - Madison, Madison, Wisconsin; 2Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin; 3Department of Physical Chemistry, Stockholm University - Stockholm, Sweden; 4Department of Chemistry, North Carolina State University - Raleigh, North Carolina.

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 advantage of being relatively fast due to the high reactivity of ozone. Using core-level and valence-band photoelectron spectroscopy, as well as near edge X-ray absorption spectroscopy, we have studied the effect of ozone on the chemical and electronic structure of single walled carbon nanotubes. The spectroscopies indicate the formation of oxidized carbon species which remove electronic states near the Fermi level. The decreased density of states near the Fermi level causes an increased resistance, which is detected in transport measurements. Further, Raman spectroscopy shows a large reduction of the G-band tangential phonon modes, as well as an increase in defect density as measured by the ratio of the 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.


Dodecanethiol-stabilized-Au nanoparticles are successfully attached to the sidewall of as-grown single walled carbon nanotubes (SWCNTs) via reaction by dodecanethiol groups. Adhesion and charge 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 carbon nanotubes will also be proposed.


Conductivity and high aspect ratio of Carbon Nanotubes (CNT) are basic properties in order to get conductive composites. A very low percolation threshold can be reached with a minimum of material. The material is used to get transparent conductive coatings which CNT networks are simply sprayed on glass or plastic in order to get transparent conductive coatings. They are compared with a standard material for transparent electrodes (Thin doped Indium Oxide, ITO) in terms of transparency and conductivity at RI. 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.
Enhanced P-Type Conduction in SWNT by Protein Coated Microspheres. Phil. Sudhakar, Jeong-O Lee, Jinhee Kim and Hyojin Kim. Material Engineering, ChungNam National University, Daejeon, South Korea; 2Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, South Korea; 3Electronic Device Group, Korea Research Institute of Standard and Science, Daejeon, South Korea.

Rapid progress in modern biotechnology and medical science reveals the existence of marker proteins that are specific for certain diseases. This knowledge has provided protein engineering with a new way of thinking. Recently we have observed new concept biosensors that are highly sensitive and are able to minimize the sample size, which results in a change of conductance. Extremely high surface to volume ratio that comes from the one-dimensional nature of a single carbon nanotube makes it possible to expect high sensitivity to detect even a single molecule. Here, we propose to use protein coupled nanoparticles to improve signal detection and easier visualization. We have immobilized streptavidin coated microspheres on the side wall of single wall carbon nanotube devices built on Si/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. As a control experiment, we have immobilized streptavidin molecules, and streptavidin coupled 10 nm Au nanoparticles on single wall nanotube devices. While only a small conductance change occurred with samples incubated with streptavidin, strong p-type enhancement observed from the samples incubated with streptavidin coupled 10 nm Au nanoparticles. We will explain this with the work function of the carbon nanotubes. In summary, we have observed strong p-type enhancement in the conduction of single wall nanotube devices coupled with protein-microspheres. Since this can results in a very sensitive detection of analyte and easier to monitor protein binding, we believe that we can go one step forward to single molecule detection with this technique.


Controlling the pore size of membranes in the 1 - 10 nm range is critical to many biological chemical separations. Recently we have synthesized and characterized single walled carbon nanotube membranes with inner core diameters of 7 nm. Reported here is the functionalization of the membranes with aliphatic amines of different lengths (1.41, 2.84 and 5.6 nm) using an amine coupling reagent (dicyclohexylcarbodimide) and an amine amine elongated by spacers containing peptide bonds (5.2 nm) using well known carbodiimide chemistry. This allows us to precisely decrease the pore size by molecular length increments. FTIR studies of functionalized aligned CNT membranes showed a peak at 1630 cm^-1 and shoulder at 1654 cm^-1 indicative of amide bond formation. Transiton of two differently sized but similarly charged molecules through aligned CNT membrane were studied. A cyanine (0.5mM) solution Ruthenium bi-pyridine (diameter 1.38 nm) and Methyl Viologen (length 1.09 nm, breadth 0.32 nm) in aqueous medium was in contact with with 0.3 cm^2 of membrane area in a U-tube set up. Flux into analyte cell is quantified by UV-VIS spectroscopy. Typical Ru(bipy)3 flux through CNT membrane was found to be 8 nanomoles/cm^2·hr. Methyl Viologen/Ruthenium bi-pyridine selectivity (alpha) through a non-functionalized membrane was 1.7, which is close to the ratio of their bulk aqueous diffusivities. Methyl Viologen/Ruthenium bi-pyridine selectivity (alpha) increased to 3, when 1.14 nm long nonyl amine was attached to spacers containing peptide bonds (5.2 nm) using well known carbodiimide chemistry. This allows us to precisely decrease the pore size by molecular length incremenents. FTIR studies of functionalized aligned CNT membranes showed a peak at 1630 cm^-1 and shoulder at 1654 cm^-1 indicative of amide bond formation. Transition of two differently sized but similarly charged molecules through aligned CNT membrane were studied. A cyanine (0.5mM) solution Ruthenium bi-pyridine (diameter 1.38 nm) and Methyl Viologen (length 1.09 nm, breadth 0.32 nm) in aqueous medium was in contact with with 0.3 cm^2 of membrane area in a U-tube set up. Flux into analyte cell is quantified by UV-VIS spectroscopy. Typical Ru(bipy)3 flux through CNT membrane was found to be 8 nanomoles/cm^2·hr. Methyl Viologen/Ruthenium bi-pyridine selectivity (alpha) through a non-functionalized membrane was 1.7, which is close to the ratio of their bulk aqueous diffusivities. Methyl Viologen/Ruthenium bi-pyridine selectivity (alpha) increased to 3, when 1.14 nm long nonyl amine was attached to the carbon nanotube membrane. The Ru(bipy)3 flux decreased by a factor of 2.5 when a 2.8 nm long aliphatic amine was attached to the membrane. However the (alpha) was 1.98 thus indicating that selectivity depends upon the solubility of the attached molecule in water and not only their length. When a water-solubly negatively charged dye molecule of 2.6 nm length was attached, the flux increased 4 times, (alpha) was 2.12, larger than the value of comparable amine (1.14 nm) length. The carbon nanotubes were finally functionalized by a 5.2 nm long molecular containing peptide bonds, which are water soluble. In this case, Ru(bipy)3 flux decreased about 14 times and (alpha) was 3.6. An increase in selectivity by increasing the molecular length of functional molecules indicate that pore size reduction by molecular increments can be achieved in aligned carbon nanotube membrane architecture.
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 conventional thermionic cathodes. This cathode consists of a metal substrate with carbon nanotubes grown on top of its surface. The carbon nanotubes are coated with thermionic emission materials (BaO/5rO/CaO). This unique cathode structure takes advantage of both the field enhancement effect from carbon nanotubes and high electron emissions capability of thermionic materials. The electron emission properties of this new thermionic cathode, particularly the field enhancement factor and effective work function are compared with the conventional thermionic cathodes that are made of same oxides coating.


The carbon nanotube (CNT) offers a quasi-one-dimensional structure that can be utilized as a bio-functional substance. 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 promoters. The CNTs are then sol-gel processed. 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 on the surface of CNTs. The immobilization of enzymes on the CNTs and the development of these CNT-based enzyme systems and materials is presented. 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.

Fabrication and Characterization of a Carbon Nanotube-Membrane, Jason Holt, Alexandre Nox, Thomas Huser, David Eaglesham and Olja Ceand; Biosecurity and Nanosciences Laboratory, Lawrence Livermore National Laboratory, Livermore, California.

A membrane consisting of multi wall 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,0 of 2.4x10-5 mole/m²-s was determined, based on the sensitivity of the isotope measurement technique. By hydrodynamic calculations, hydrodynamic water flow across a nanotube membrane of similar specifications (10 nm inner diameter, 10 μm thick, with a porosity fraction of 0.38) gives a molar flux of 0.061 mole/m²-s for a 1 atm pressure drop. Molecular dynamics simulations predict an even larger value of 0.29 mole/m²-s. These carbon nanotube membranes are used to make nanoporous carbon membrane transformers embedded in a silicon nitride matrix, fabricated by sacrificial removal of the carbon. Nitrogen flow measurements on these structures give a membrane permeability of 2x10-4 mole/m²-s Pa (mass flux of 4.77x10-4 mole/m²-s Pa at a pressure drop of 100 Pa) at a pore density of 4x1016 cm². The average pore size of this membrane is estimated to be 33 nm, using a Knudsen diffusion model. References [1] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, Nature 414, 188 (2001).

Enhancement of Conductivity of Bucky Paper by Chemical Enhancement, Urszula Dettlaff-Weglikowska1, Viera Skalakova1, J. Graupner1, Song Ho Jang2, Byung Hoon Kim3, Hyun Jung Lee4, Lothar Ley5, Yung Woo Park6, Savas Berber7, David Tomankb, and Siegmur Roth9; 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 thiolyl chloride, SOCl₂. This treatment changes significantly the electronic and mechanical properties of the resulting entangled nanotube network. Four-probe measurements indicate a conductivity increase by up to a factor of 5 at room temperature, and an even more pronounced increase at lower temperatures. This chemical functionalization also improves the mechanical properties of SWNT networks. Whereas the pristine sample shows an overall semiconducting character, the functionalized material behaves as a metal. The effect of SOCl₂ is studied in terms of functionalization reactions and incorporation of a carbon nanotube field enhancement effect from carbon nanotubes. It has strong field synthesized process, biocompatible conditions are used such that the signal transmission. Biomaterials thus become an important factor in scaffolds for guiding neurite growth and forming synaptically enhanced thermionic emission at least an order of magnitude higher than the conventional thermionic cathode. This cathode 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 conventional thermionic cathodes. This cathode consists of a metal substrate with carbon nanotubes grown on top of its surface. The carbon nanotubes are coated with thermionic emission materials (BaO/5rO/CaO). This unique cathode structure takes advantage of both the field enhancement effect from carbon nanotubes and high electron emissions capability of thermionic materials. The electron emission properties of this new thermionic cathode, particularly the field enhancement factor and effective work function are compared with the conventional thermionic cathodes that are made of same oxides coating.

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use capillary forces to direct the assembly of carbon nanotubos into cellular foams. We will describe the mechanisms by which these structures are formed, as well as the potential applications of these nanotube architectures.

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


Understanding the adsorption of molecules on single-walled carbon nanotubes (SWNT) 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 of SWNT, and how processing/purification procedures affect this access. By using Fourier Transform Infrared Spectroscopy (FTIR) and grand canonical Monte Carlo (GCMC) simulations, the adsorption of CO2 and its displacement by Xe are studied. The FTIR experiments show that CO2 in endohedral sites is initially displaced by Xe before that in groove/external surface sites. The CO2 populations in each site of the bundles are determined using GCMC simulations. The agreement between the GCMC simulations and the IR spectra 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 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 physiosorption site for CO and other gases.


The continuously shrinking dimensions of integrated semiconductor circuits progressively render standard metrology techniques insufficient for process control and quality assurance. Critical dimension atomic force microscopy (CD-AFM) is increasingly used by the semiconductor industry to address these challenges. The current state-of-the-art, precision-optical and high-aspect ratio Scanning electron microscopy have longevity issues. Carbon nanotubes (CNT) are promising structures for AFM probes for use in high aspect ratio critical dimension metrology (CDM). The high mechanical strength of carbon nanotubes at 1000 nm diameter makes them ideal high-resolution probes for narrow and deep features. Currently, manual attachment is the most often used method for construction of a CNT-enhanced AFM cantilever. This method has issues with control of the CNT attachment angle and cantilever bending. We will report on our progress in developing a process for the direct growth of CNT from the tip of a modified cantilever using plasma-enhanced chemical vapor deposition (PECVD). This technique has produced CNT probes with defined length, diameter and nanotube orientation. AFM images and data taken with the prototype CNT-enhanced cantilevers demonstrate an improvement in resolution and accuracy as compared to a standard cantilever.


10:45 AM HH14.6 Carbon Nanotube Substrates for Electrochemical Biosensor Applications. Alexander V. Neimark, Konstantin Korosec, Gerard Callegari, Peter Ravikovitch, Sigrid Ruettsch, Plamen Atanassov and Vijaykumar Rajendran; 2TRI/Princeton, Princeton, New Jersey; 3University of New Mexico, Albuquerque, New Mexico.

Recent advances in fabrication of nanofibers and membranes from various polymers precursors and carbon nanotubes make possible development of novel nanofiber devices. We report on the application of the SWCN composite substrates as supports for electrochemical biosensors. SWCN composite substrates, which are made in the form of fibers or webs, possess a hierarchical pore architecture. Using the methods of capillary condensation and droplet absorption, we demonstrated that they have high surface area and open porosity. This provides a significant absorption capacity and selective permeability that can be tailored by controlling pore functionality. Employing horseradish peroxidase (HRP) as a model enzyme, we examined Direct Electron Transfer (DET) on SWCN nanosubstrate as a signal generation mode in electrochemical biosensing. The high surface area allows for HRP immobilization by adsorption and the resulting surface complex exhibits DET behavior. The dependence of the current on the HRP concentration is non-linear suggesting a
The Raman spectrum of the SWNT network shows characteristic G-band and D-band peaks of carbon nanotubes. In order to quantitatively estimate the number of streptavidin on the carbon nanotubes, we employed to study the distribution of the SWNT on a glass slide. 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 surface can in return be used to sense the local environment e.g. the D* band can be used to separate the effect on the external tube in interaction with the external tube and which does not depend on the environment. Pressure experiment in alcoholic pressure-transmitting medium on 80% of double wall carbon nanotubes reveals a new band associated to the outer tube. This additional spectral band, observed in high pressure Raman experiments, is also observed for nanotubes in polymer matrix composites and is unambiguously associated to a large blue shift of the G band. A large Raman mapping on several samples with constant percentage of CNT and various concentration of surfactant will be presented. The analysis of the bands (new bands and frequency shift due to their environment) can be tentatively correlated with the electrical properties. [1] J. R. Wood and H. Wagner, Appl. Phys. Lett. 76, 2883 (2000) [2] P. Puech, H. Hubel, D. Dunstan, R.R. Bacsa, C. Laurent, W.S. Bacsa, submitted to Phys. Rev. Lett.

SWNT Network for Biomolecule Detection.
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Nanosized materials have the potential to revolutionize the analytical tools in the field of biotechnology. The fascinating physical and chemical properties of carbon nanotubes have encouraged us to utilize them for development of a nano-biosensor. We report the application of single wall carbon nanotube (SWNT) for detection of biomolecules (streptavidin). The change in the electrical properties and mass modification of a network of carbon nanotubes on non-covalent binding of protein molecules on the sidewalls of carbon nanotubes has been observed. Commercially available SWNT (70% pure) produced by arc discharge technique were used for the experiments. A 1% solution by weight of carbon nanotubes in chloroform was prepared by RF sputtered gold surface of quartz crystals. Frequency shifts due to the increase of mass on the immobilization of protein molecules on the walls of carbon nanotubes were monitored. The QCM measurements of the carbon nanotubes show a frequency shift 120 Hz which corresponds to binding of 1 μM 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.

Individual carbon nanotube-based devices have demonstrated great potential as high performance nanoscale electronic components. The production of large scale integrated nano-electronic circuits, however, has faced the difficulties of directed assembly of single walled carbon nanotubes (SWCNT) into regular array or onto predefined templates is 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)