

# SYMPOSIUM Z

## Making Functional Materials with Nanotubes

November 26 – 29, 2001

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SESSION Z1: PROGRESS IN SYNTHESIS AND  
PROCESSING I

Chairs: Pavel Nikolaev and Annick Loiseau  
Monday Morning, November 26, 2001  
Back Bay A (Sheraton)

**8:30 AM \*Z1.1**

**OPTIMIZING CARBON NANOTUBE GROWTH USING HIGH THROUGHPUT EXPERIMENTATION.** Alan M. Cassell, Bin Chen, Elore Corporation, NASA Ames Research Center, Moffett Field, CA; K. McGuire, A.M. Rao, Department of Physics and Astronomy, Clemson University, Clemson, SC; Goldwyn Parker II, NC State University, Raleigh, NC.

High throughput methods for optimizing catalysts used in the growth of carbon nanotubes has become an efficient technique for understanding and controlling nanotube production. For example, we have demonstrated the capability of performing nearly 1000 experiments per week for optimizing multiwalled nanotube growth using catalyst microarrays. For multiwalled carbon nanotube growth, we use scanning electron microscopy to quickly analyze the catalyst arrays for nanotube quality, and desired growth orientation. For single-walled carbon nanotube growth, we are developing high throughput Raman scattering approaches to characterize the as-grown nanotubes in addition to using scanning electron microscopy to qualitatively evaluate the yield. Our goals are to control the nanotube growth process to enable the production of nearly monodisperse diameters and types of nanotubes. The use of high throughput microarray printing methodology for exploring advanced nanotube architectures as well as efforts towards developing high throughput screening tools such as Raman spectroscopy will be discussed.

**9:00 AM \*Z1.2**

**DEVELOPMENT OF LARGE SCALE SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES AND THEIR APPLICATION.** Motoko Yumura, Satoshi Ohshima, Hiroki Ago and Kunio Uchida, Research Center for Advanced Carbon Materials, AIST, Tsukuba, JAPAN; Hitoshi Inoue, Toshiki Komatsu, Japan Fine Ceramics Center, Tokyo, JAPAN.

We have been developing the mass production methods of multi walled carbon nanotubes (MWNT). We have developed a method to produce several 10 grams of MWNT per day by continuous arc method which has the higher productivity compared with the arc discharge method used from 1996. Furthermore, aiming at proceeding research and development for the MWNT as the material for industry, we started to develop the new production method to produce several kg of the MWNT. We have developed a chemical synthesis method of MWNT by using low boiling point hydrocarbon as the raw material and ultra fine metal particle as the catalyst. We used ultra fine metal particle as a catalyst metal and benzene as a carbon source. Advantages of this method are selective production of MWNT and cost of mass production will be low. It is quite easy for this method to scale up the MWNT production. We have developed the pilot plant which is capable to produce several kg of MWNT per day. In 1999, We started to construct the large scale experimental continuous reactor in cooperation with Showa Denko Co. Ltd. as the Frontier Carbon Technology Project of Ministry of International Trading and Industry (MITI), and we succeeded in producing 200g of carbon nanotube per hour. Now, we are carrying out the experiment using this plant to make sure its possibility for industrial utilization and we are developing several industrial applications of MWNT. This work is supported by the Frontier Carbon Technology Project of the MITI.

**9:30 AM Z1.3**

**MASS-PRODUCTION OF SINGLE-WALLED CARBON NANOTUBES BY THE VERTICAL FLOATING CATALYTIC TECHNIQUE.** Hongwei Zhu, Xuesong Li, Cailu Xu, Ji Liang, Dehai Wu, Tsinghua University, Dept. of Mechanical Engineering, Beijing, P.R. CHINA.

Very long (3 - 15 cm) ropes of aligned single-walled carbon nanotubes (SWNTs) with high purity (>80%) are synthesized by the vertical floating catalyst method for the first time. N-hexane is found the better hydrocarbon than benzene for catalytic pyrolysis to produce SWNTs. Diameter distributions, microstructure and purity of the SWNTs ropes are measured by Raman spectroscopy and electron microscopy. The results show that SWNTs product has a high degree of orientation, a wide distribution of diameters (0.8 nm - 2.0 nm). Each rope is composed of many crystalline bundles of ordered tubes array. The high degree alignment and super-length of the crystalline SWNTs ropes will make them an ideal intermediary for high performance electron and composite materials. Keywords: Single-walled carbon nanotubes (SWNTs), Vertical floating catalyst method, Raman spectroscopy.

**10:15 AM \*Z1.4**

**CARBON NANOTUBE FIBERS.** Brigitte Vigolo, Philippe Poulin, Cecile Zakri, Helene Richard, Centre de Recherche Paul Pascal-CNRS, Pessac, FRANCE; Patrick Bernier, GDCP, Montpellier, FRANCE; Pascale Launois, LPS, Univ Paris Sud, FRANCE.

Carbon nanotubes can be processed into long fibers using a simple spinning-like process. The method consists in dispersing the nanotubes in a surfactant solution, re-condensing the nanotubes in the flow of a coagulating polymer solution to form a nanotube mesh, and then collating this mesh to a nanotube fiber. We discuss in this paper the main features of the process and its optimization for different types of nanotubes. Structural characterizations and physical properties of carbon nanotubes fibers will be also presented. Although far from being fully optimized, we believe that already obtained fibers are potentially useful in different applications such as sensors and actuators. In addition, carbon nanotubes fibers can be modified and improved in different ways using mechanical, chemical or thermal treatments. We present preliminary results along these directions. We hope that the simplicity of the present method and the practical use of fibers for integrating nanotubes in devices and materials will contribute in the future in making carbon nanotubes more suitable for potential applications.

**10:45 AM Z1.5**

**TOWARDS BUILDING THREE DIMENSIONAL ARCHITECTURES OF CARBON NANOTUBES.** B.Q. Wei, Y. Jung, R. Vajtai, G. Ramanath, P.M. Ajayan, Rensselaer Polytechnic Institute, Department of MS&E, Troy, NY.

It is important to develop 2D and 3D architectures of nanotubes for several applications such as field emission display, electronic circuits, and sensor arrays. This problem mandates achieving control on the nucleation sites and growth directions of nanotubes on pre-defined patterns on planar substrates. Based on our previous success of growing aligned carbon nanotubes selectively on SiO<sub>2</sub>/Si patterns, we report that we can now build 3D architectures of carbon nanotubes controllably and reproducibly on such substrates. By combining standard microfabrication techniques and chemical vapor deposition, we demonstrate the directed growth of nanotubes to produce vertically and horizontally aligned nanotube arrays, ordered fibers and structures with complex geometry and shapes. Such architectures inherit the position, shape and the size of the original patterns on the substrates and therefore, can be controlled with relative ease.

**11:00 AM Z1.6**

**MICRO-PATTERNED VERTICALLY WELL-ALIGNED CARBON NANOTUBE GROWTHS ON THE PLANE Si OR INSIDE THE TRENCHES.** Jung Inn Sohn, Seonghoon Lee, Kwangju Institute of Science and Technology (K-JIST), Department of MS&E, Kwangju, KOREA; Yoon-Ho Song, Sung-Yool Choi, Jin Ho Lee, Young-Il Kang, ETRI, Micro-Electronics Tech. Labs., Taejeon, KOREA.

The good field emission property of carbon nanotubes coupled with their high mechanical strength, chemical stability, and high aspect ratio, is ideal in building efficient and inexpensive field emission electronic devices. The fabrication process we suggest here will be of great help in developing an integrated radio frequency (RF) amplifier or field emission-controllable cold electron guns for field emission displays (FEDs). This fabrication process is compatible with present semiconductor processing technologies. We grow micro-patterned vertically well-aligned carbon nanotubes on the plane Si surface or inside the trenches in the first time, using chemical vapor deposition (CVD), photolithography, pulsed laser deposition (PLD), reactive ion etching (RIE), and lift-off methods. In detail, we grow carbon nanotubes on the plane Si(100) substrate with a pattern of squares of 20 μm by 20 μm, 10 μm by 10 μm, or 5 μm by 5 μm. We also fabricate the simple and the most desirable triode-type field emitting electronic device containing carbon nanotube field emitters in a trench of 10 μm deep and 6 μm wide as cold cathodes. This fabrication process can be widely applied for developments of electronic devices using carbon nanotube field emitters as cold cathodes and revolutionize field emitting electronic devices.

**11:15 AM Z1.7**

**FORMATION OF ALIGNED SINGLE-WALL CARBON NANOTUBE BUNDLES BY SELF-ASSEMBLY.** H. Shimoda, L. Fleming, K. Horton and O. Zhou, University of North Carolina, Chapel Hill, NC.

We report the formation of freestanding membranes containing aligned single-wall carbon nanotube (SWNT) bundles by self-assembly. Purified SWNTs were chemically etched to short bundles by ultrasonic-assisted oxidation. The processed SWNTs were dispersed in de-ionized water and were let to settle over night at room temperature. Rectangular shape membranes (~5x10mm) were found to float on the water surface. Transmission electron microscopy

measurements show that the SWNT bundles are uniaxially aligned and randomly spaced within the membrane. These results suggest that the short SWNT bundles exhibit nematic liquid crystal behavior.

#### 11:30 AM Z1.8

GROWTH OF ALIGNED CARBON NANOTUBE ARRAYS WITH CONTROLLED SITE DENSITY BY ELECTROCHEMICAL DEPOSITION. Yi Tu, Zhongping Huang, Dezhi Wang, Joel Moser, Michael Naughton, Zhifeng Ren, Boston College, Dept of Physics, Chestnut Hill, MA.

Electrochemical deposition has been used to prepare nickel nanoparticles as catalyst for growth of well-aligned carbon nanotube arrays with controlled site density. The catalyst particle size and density are controlled by the combining effect of concentration of the solution, amplitude of the pulse current, and the pulse length. With these particles, well-aligned carbon nanotube arrays with site density as low as  $10^6$  sites per  $\text{cm}^2$  by plasma-enhanced chemical vapor deposition (CVD) method have been achieved. The low density is absolutely necessary for good field emission for flat panel display devices.

#### 11:45 AM Z1.9

DIAMETER-CONTROLLED GROWTH OF CARBON NANOTUBES. Chin Li Cheung, Andrea Kurtz, Hongkun Park and Charles M. Lieber, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA.

Carbon nanotubes have many interesting electrical, chemical and mechanical properties. Nanotubes with variety diameters are beneficial for testing many theoretical predictions and for applications such as hydrogen storage, nano-electromechanical devices and atomic force microscopy (AFM) probes. Here we report the synthesis of carbon nanotubes with controlled-diameter using monodispersed iron colloids catalyst by chemical vapor deposition (CVD). Transmission electron microscopy and atomic force microscopy studies of the carbon nanotubes grown from iron colloid of 3, 9 and 13nm average diameters produced by solution-phase showed that single-walled carbon nanotubes and thin-walled multi-walled carbon nanotubes with 3, 7 and 12nm average diameters, respectively, can be synthesized. As the size of the starting catalyst particles increases, an increase in flux of hydrocarbon source is required for the growth of carbon nanotubes with similar diameters as those of the catalyst. High CVD temperature was found to increase the crystallinity of as-grown carbon nanotubes. Applications using this method for fabrication of carbon nanotube AFM probes will be discussed.

### SESSION Z2: PROGRESS IN SYNTHESIS AND PROCESSING II

Chairs: Motoo Yumura and David B. Geohegan  
Monday Afternoon, November 26, 2001  
Back Bay A (Sheraton)

#### 1:30 PM Z2.1

LASER PRODUCTION OF SINGLE-WALL CARBON NANOTUBES OF SPECIFIC SIZE AND TYPE BY VARIATION IN PEAK PULSE POWER. Anne Dillon, Jeff Alleman, Kim Jones, Philip Parilla and Michael Heben, National Renewable Energy Laboratory, Golden, CO; Thomas Gennett, Rochester Institute of Technology, Rochester, NY.

Carbon single-wall nanotubes (SWNTs) have diameters that may vary from  $\sim 0.8 - 2.7$  nm and depending on tube chirality are either semi-conducting or metallic. For certain of the many potential nanotube applications to be ultimately realized it may be important to develop methods for the controlled production of specific sizes and types of SWNTs. For example, the large-scale fabrication of nanotube based devices will depend on the assembly of very specific nanotubes. It has also recently been suggested that semi-conducting nanotubes are desirable for the optimization of nanotube hydrogen storage properties<sup>1</sup>. Here we demonstrate that for a laser vaporization process at a constant synthesis temperature of  $1200^\circ\text{C}$ , the diameter distributions of both the semi-conducting and the metallic SWNTs may be tailored through variation in peak pulse power. In each case smaller diameter nanotubes are produced with increasing peak pulse power. It is also possible to regulate the concentrations of semi-conducting or metallic tubes by varying the peak pulse power during synthesis. In this case, higher peak powers result in the production of semi-conducting SWNTs at a much higher density. However, we find that overall nanotube yields are increased for lower peak pulse powers where a vaporization regime is easily maintained. Nanotube materials produced at a peak pulse power of  $1.5\text{E}7 \text{ W/cm}^2$  contain predominantly semi-conducting tubes, but the overall SWNT content may be lowered by as much as a factor of three compared to materials produced at lower peak powers.

<sup>1</sup>A.C. Dillon, J.L. Alleman, T. Gennett, K.M. Jones, P.A. Parilla, and M.J. Heben, (in preparation).

#### 1:45 PM Z2.2

CONTROLLING DIAMETERS OF NANOTUBE FILMS FROM 5 - 300 NANOMETERS. M.P. Siegal, D.L. Overmyer, P.P. Provencio, and F.H. Kaatz, Sandia National Laboratories, Albuquerque, NM; N.J. DiNardo, Drexel University, Dept of Physics, Philadelphia, PA.

We grow multiwalled carbon nanotube films using thermal CVD at atmospheric pressure from a mixture of acetylene and nitrogen. Nanotube outer (inner core) diameters, ranging from 5 - 300 nm (2 - 15 nm), are controlled primarily by growth temperature, which varies from 630 - 790 C, respectively. Growth at lower temperatures yields no carbon structures; growth at higher temperatures yields micron-sized diameter tubular-like cluster structures from the gas phase, independent of the catalyst, that coat the inside of the furnace apparatus. These films are all grown on Si(100) using 4 nm thick sputtered Ni as the catalyst. A 50 nm thick W diffusion barrier prevents silicidation. We reduce the Ni/W/Si(100) substrates in flowing CO at 600 C for 1 hour, raise the temperature to that desired for growth in N, and then expose the samples to the growth ambient for 15 minutes. Samples furnace-cool in nitrogen. Nanotube formation is extremely uniform over the entire sample area. We will present detailed microscopy studies, both SEM and TEM, of nanotube structural properties; and AFM of the Ni catalyst layer morphology following various stages of the growth process. We will show that nanotube diameters are not solely dependent upon the Ni-catalyst grain size, but also are a function of growth time. These experiments define nanotube growth conditions which will be applied to the use of anodized Al templates with pre-determined pinhole sizes for optimal growth of aligned multiwalled carbon nanotube arrays.

\*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000.

#### 2:00 PM \*Z2.3

BORON NITRIDE NANOTUBE, NANOCONE AND NANOCABLE. Yoshio Bando, Dmitri Golberg, National Institute for Materials Science (NIMS), Tsukuba Ibaraki, JAPAN.

The boron nitride nanotubes, nanocones and nanocables have been prepared and their atomic structures are identified by using a 300kV filed emission transmission electron microscopy with the use of electron energy loss spectroscopy. Multi-walled BN nanotubes were prepared by the substitution reaction, where carbon nanotubes are heated with boric oxides at temperatures of  $1500^\circ\text{C}$  under  $\text{N}_2$  gas. C nanotubes were converted into BN nanotubes without a drastic change of morphology. The addition of catalytic oxides of  $\text{MoO}_3$  increased a yield of pure BN nanotubes. It is shown that BN nanotubes have a preferential zig-zag orientation. The bamboo-like BN nanotubes having a rhombohedral stacking were found. An efficient CVD synthetic route for bulk quantities of BN nanotubes was also developed, where a B-N-O precursor was used. BN nanocones consist of slanted walls approximately 10 nm in width separated by thin empty core (diameter 1nm). The observed apex angles were close to 39 degree, which can be explained by a model of orderly stacked 240 degree disclination. One case of a nanocone constituted of 300 degree disclinations was found, implying that the structure containing line defects of non-B-N bonds may form. The first synthesis of insulating BN nanocables were successfully carried out, where BN nanotubes were continuously filled with Fe-Ni alloy. The filled nanotube diameters ranged between 30 to 300nm, whereas the filled length of the nanotubes reached several microns.

#### 2:30 PM \*Z2.4

SINGLE-WALL BORON NITRIDE NANOTUBES : SYNTHESIS VIA LASER VAPORIZATION AND PROPERTIES. A. Loiseau, R.S. Lee, J. Gavillet, LEM, UMR 104 ONERA-CNRS, Chatillon Cedex, FRANCE; J.L. Cochon, D. Pigache, ONERA, Chemin de la Humière, Palaiseau Cedex, FRANCE; J. Thibault, SP2M: DRFCM, CENG, Grenoble Cedex, FRANCE; F. Willaime, SRMP, CEA Saclay, Gif sur Yvette Cedex, FRANCE.

Boron nitride nanotubes (BN-NTs) are attracting considerable interest due to their unique physical properties which make them a possible alternative to their carbon brethren in regards to possible applications. However, until recently, careful study of BN-NTs has been stymied by the paucity of material produced by various synthesis methods which has prevented the realization of certain experiments. Here, a new route to the successful synthesis of single wall boron nitride nanotubes (BN-NTs) in "mass" quantities is presented. It is based on the vaporisation of a BN (or pure boron) target by a continuous  $\text{CO}_2$  laser under nitrogen atmosphere [1]. High-resolution transmission electron microscopy (HRTEM) analyses have shown the synthesis deposit to be composed of almost exclusively single wall boron nitride nanotubes (BN-SWNTs) either isolated or organized in

ropes. Furthermore, very high resolution images has revealed that the majority of BN-SWNTs seem to have a zig-zag configuration. The chemical composition of the tubes was confirmed using electron energy loss spectroscopy (EELS) analysis which also determined that BN-SWNTs are capped by a boron particle, strongly supporting a root-based growth mechanism with tubes growing from boron nanoparticles issued from the target. These results are particularly interesting as they represent the first time that BN-NTs have been synthesized in quantities and quality comparable to that of carbon nanotubes with the advantage that no catalyst is needed. First characterization of the properties of these systems will be presented. [1] R. Lee et al., Phys. Rev. B(2001), in press.

### 3:30 PM Z2.5

PURIFICATION AND DIAMETER-DEPENDENT OXIDATIVE STABILITY OF SWNT SYNTHESIZED BY THE HIGH PRESSURE CARBON MONOXIDE PROCESS. Wei Zhou, Yao Hua Ooi, Richard Russo, Brian W. Smith, Satishkumar B. Chikkannanavar, Peter Papanek, David E. Luzzi, John E. Fischer, University of Pennsylvania, Dept. of Materials Science, Philadelphia, PA; Michael J. Bronikowski, Peter A. Willis, and Richard E. Smalley, Rice University, Center for Nanoscale Science and Technology, Houston, TX.

Low T oxidation followed by brief sonication in hot HCl has been optimized to remove Fe catalyst residues from HiPco material with minimal loss of SWNTs. TGA shows that one pass reduces the Fe catalyst content from typically 6 -10 at.% to 0.6 - 1.6 at.% with ~60% yield, most of which corresponds to Fe removal. In one case, a second pass reduced Fe from 1.6 to 0.4 at.%. Raman scattering reveals a broad diameter distribution with a mean of 1.0-1.1 nm. Neutron diffraction and HRTEM show a low degree of microcrystalline rope formation compared to laser ablation and carbon arc methods. Neither of these attributes are affected by purification or vacuum annealing. Fe catalyzes the oxidation of SWNT; higher oxidation temperatures can be used after the first pass without significant loss of tubes. After purification we find excellent correlation between TGA and Raman data, showing that T(oxidation) varies inversely with tube diameter. This can be explained by the larger strain associated with greater curvature of small tubes. HRTEM shows that the remaining tubes are intact with clean sidewalls, so controlled burning can be useful to narrow the diameter distribution by burning off small-diameter tubes.

### 3:45 PM Z2.6

COMPLETE ELIMINATION OF CATALYTIC IMPURITIES FROM HIPCO AND LASER ABLATED SINGLE WALL CARBON NANOTUBES. Debjit Chattopadhyay, Izabela Galeska, Fotios Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT; Ray Baughman, Honeywell Co., Morristown, NJ.

Total exclusion of entrapped catalytic impurities from single wall carbon nanotubes (SWNTs) has thus far remained elusive. Currently the as produced HIPCO tubes have a significant catalyst (Fe) incorporation (>40 w/w % as monitored by EDAX), which drastically decreases its thermal stability and processability, thereby excluding it from many of the proposed applications intended for nanotubes. A novel catalyst removal/purification process leading to a complete elimination of the metallic impurities and applicable to both laser ablated and HIPCO produced nanotubes will be presented. The multi-step process involving a combination of brief room temperature sonication in a combination of non-oxidizing acids (HF/HCl), and air oxidation results in complete elimination of the entrapped catalytic particles as evidenced by EDAX and TGA. Significantly the presence of anionic surfactants were found to be crucial in the catalyst elimination. As a result of the purification process the decomposition temperature of the HIPCO tubes increases to about 700°C as opposed to 260°C (in N<sub>2</sub>) for the as prepared HIPCO tubes. SEM and Raman investigations on the purified SWNTs clearly illustrate that the quality of the tubes are not compromised by the purification process. Additionally data on electrochemical actuators fabricated from the purified HIPCO tubes will be presented

### 4:00 PM Z2.7

VARIATION IN THE EFFECTS OF PURIFICATION ON SWNTS SYNTHESIZED BY ARC DISCHARGE, LASER ABLATION, AND THE HIPCO PROCESS. B.C. Satishkumar, Richard M. Russo, Brian W. Smith, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

While there have been many advances in single-walled carbon nanotube (SWNT) synthesis, most recently the HIPCO process, there still remains the difficult task of separating the SWNTs from amorphous carbon and catalyst impurities contained within graphitic shells. Many potential purification methods, such as acid treatment and air annealing have been explored. Often times these treatments produce inconsistent results due to the inhomogeneous morphology of

SWNTs. As well, these treatments have not been studied extensively in terms of how the SWNT surface has been chemically modified. In this report, we explore purification schemes involving pulsed laser, carbon arc, and HiPCO material. The different morphologies require purification schemes to be developed for each material. The materials are characterized both before and after purification, using high resolution transmission electron microscopy (HRTEM) to qualitatively determine the purity of the SWNTs. The thermal oxidation of SWNTs, as well as residual catalyst content, is determined by Thermogravimetric Analysis (TGA). Infrared and Raman spectroscopies are used to assess the relative amorphous carbon content in the purified SWNTs, as well as changes in the SWNT surface induced by the purification treatment. The effects of vacuum annealing over a significant temperature range on SWNT defects are also explored. Spectroscopic studies reveal that side wall defects, terminating in acid sites, are modified with increasing temperature.

### 4:15 PM Z2.8

PURIFICATION OF SWNTS USING MICROWAVE LOCAL HEATING. A.R. Harutyunyan, B.K. Pradhan, G. Chen, and P.C. Eklund, Dept. of Physics, The Pennsylvania State University, University Park, PA; J. Chang, Mat. Res. Lab., The Pennsylvania State University, University Park, PA.

Single-walled carbon nanotubes (SWNTs) are often produced as a minority constituent in the reaction product. Also present, for example, are amorphous carbon which coats the bundles walls, residual metal catalyst, and multi-shell carbon which covers the metals residue. Fundamental studies and proposed applications of SWNTs require reasonably pure material. It is a challenging problem to purify the reaction product without damaging the tubes. In the present work, we show that local heating of the carbon-encapsulated metal catalyst particles in air using microwave radiation is a very beneficial first step in general purification scheme for SWNTs. The local microwave heating, either drives the combustion of the carbon coating, or via expansion of the metal core, weakens the carbon overcoating, allowing a mild acid treatment at low temperature to remove most, if not all, of the residual metal catalyst. Transmission electron microscopy, oxidation analysis, energy-dispersive X-ray and Raman spectroscopy data are presented which reveal the benefits of the microwave processing SWNT materials.

### 4:30 PM Z2.9

MACROSCOPIC SHEET ASSEMBLIES OF MAGNETICALLY ALIGNED CARBON NANOTUBES PRODUCED IN MAGNETIC FIELDS. Michael J. Casavant, Deron A. Walters, Micah Stoutimore, Richard E. Smalley, Rice University, Houston, TX; R. Hagenmueller, J. Vavro and J.E. Fischer, University of Pennsylvania, PA.

Macroscopic samples of highly aligned SWNTs have been produced by filtration in the presence of a magnetic field. A 25 Tesla vertical bore magnet and 7 Tesla horizontal bore magnet were used. Alignment resulted from the difference in magnetic susceptibility between nanotubes parallel and perpendicular to the field. The solid mats resulting from filtration exhibit anisotropic mechanical and optical properties. Unlike similar mats composed of unordered material, the aligned mats split preferentially along the magnetic field axis. This is consistent with a lack of reinforcing fibers perpendicular to this axis. Micro-Raman scattering showed a factor of up to (4.5 ± 0.5) difference in signal intensity for orientations parallel and perpendicular to the polarization of incident radiation. This process produced aligned nanotube assemblies in the form of sheets 10 cm wide, (13.5 ± 1.5) cm long, and 10 microns thick. This promises to provide a more practical approach to achieving macroscopic aligned assemblies of nanotubes, further enabling potential applications. Post-alignment treatments will also be discussed. The in-plane alignment, as measured by x-ray diffraction, exhibits a mosaic FWHM of 30 degrees, consistent with the Raman data. The anisotropy of electrical resistance R(parallel)/R(perpendicular) varies from 8.9 to 7.9 between 1.2 K and 300 K. Both the structural and electrical anisotropy are comparable to what we found for the 26T material, suggesting that the degree of alignment is limited more by the hydrodynamics of filter deposition rather than the magnetic energy.

### 4:45 PM Z2.10

EPOXY REINFORCEMENT USING POLYMER WRAPPED SINGLE WALLED CARBON NANOTUBES. Richard A. Bley, Damian Beascoechea, Jennifer F. Clark, James B. Schutz, Eltron Research, Boulder, CO.

We are developing a method for incorporating Single Walled Carbon Nanotubes (SWNT) into epoxy thermosets to act as reinforcement. The helical structure of poly (m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) encourages this polymer to wind itself around both individual SWNTs and multiple SWNT ropes. This forms a polymer/nanotube mixture in which the polymer is mechanically anchored to the nanotube but is not chemically bound

to it. Because interaction between the PmPV and SWNTs is purely mechanical, no incursion into the bond structure of the SWNTs occurs. Placing various functional groups on the side chains of the PmPV polymer will make covalent bonding possible between this PmPV derivative and the epoxy matrix in the final composite. This will provide optimal strength in the final composites by maximizing the load transfer properties of the derivative. How well this final composite is capable of conveying the extraordinary strength and durability of the carbon nanotubes to the final PmPV/SWNT/epoxy composite as a whole will depend on the PmPV derivatives ability to transfer the applied load from the composites epoxy matrix to the SWNTs.

SESSION Z3: POSTER SESSION  
SYNTHESIS, PROCESSING, AND POLYMER  
COMPOSITES

Monday Evening, November 26, 2001

8:00 PM

Exhibition Hall D (Hynes)

**Z3.1**

**CONTROLLED SYNTHESIS OF CARBON NANOSTRUCTURES WITH CYLINDER-ON-CONE SHAPE.** Vladimir I. Merkulov, Instrumentation and Controls (I&C) Division, Oak Ridge Natl Laboratory, Oak Ridge, TN; Anatoli V. Melechko, Center for Environmental Biotechnology, University of Tennessee, Knoxville, TN; Douglas H. Lowndes, Solid State Division, Oak Ridge Natl Laboratory, Oak Ridge, TN; Michael A. Guillorn and Michael L. Simpson, Dept of Electrical and Computer Engineering, University of Tennessee, Knoxville, TN and I&C Division, Oak Ridge Natl Laboratory, Oak Ridge, TN.

The ability to control the nanoscale shape of carbon nanostructures in a large-scale synthesis process is reported for the first time. Utilizing electron beam lithography and plasma enhanced chemical vapor deposition (PECVD), nanoscale carbon tips with conical and cylinder-on-cone shapes were fabricated. The transition between the cylindrical and conical carbon nanostructures was controlled by changing the growth parameters during the PECVD process. In contrast to simple conical or cylindrical tips, the cylinder-on-cone nanotips possess both mechanical stability and the high aspect ratio needed for use in high-resolution scanning microscopy, field emission devices, biological probes, and other nanoscale devices. Since the growth process is highly deterministic in allowing large-scale synthesis of precisely engineered nanoscale components only at selected locations, the technique reported here provides an important tool for a practical nanotechnology.

**Z3.2**

**NANOTUBES OF SINGLE CRYSTALLINE TELLURIUM: SYNTHESIS, CHARACTERIZATION, AND UTILIZATION.** Brian Mayers, Younan Xia, Dept. of Chemistry, University of Washington, Seattle, WA.

We have recently demonstrated a new approach based on concentration depletion at seeds for the large-scale synthesis single crystalline nanotubes of trigonal tellurium. The diameters of these nanotubes could be controlled in the range of 50-200 nm, with their lengths up to tens of micrometers. By varying the reaction conditions, these nanotubes could also be changed into nanorods with well-controlled diameters and lengths. In this talk, we will discuss the growth mechanism (as revealed by SEM and TEM studies), and some applications for these metallic nanotubes.

**Z3.3**

**GROWTH OF SINGLE-WALLED CARBON NANOTUBES IN A CONDENSED PHASE.** Rahul Sen, Shinzo Suzuki, Takanori Tamaki, Yohji Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Hiromichi Kataura, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN.

Single-walled carbon nanotubes (SWNTs) were grown from the soot prepared by laser ablation of metal-carbon composite target at 550°C and 700°C in a condensed phase using post-annealing technique. It was found that the soot prepared only by laser ablation at such low ambient temperature did not contain SWNTs, while post-annealing of that soot at 1200°C in Ar gas atmosphere resulted in the formation of SWNTs. Interestingly, the soot prepared at room temperature and 400°C did not show any indication of SWNTs, even after post-annealing procedure. These experimental findings strongly suggest that the nucleation sites for the growth of SWNTs can be formed above a certain threshold ambient temperature (around 550°C), and the existence of these sites are required for the growth of SWNTs from the metal-carbon mixture in a condensed phase by post-annealing procedure.

**Z3.4**

**THE CATALYTIC EFFECTS OF COBALT AND COBALT SILICIDE ON CARBON NANOTUBE FORMATION.** Hui Lin Chang, Chao Hsun Lin, Cheng Tzu Kuo, Department of MS&E, National Chiao Tung University, Hsinchu, TAIWAN.

The cobalt was widely used as catalyst for nanotube growth on Si substrate. However, very few researches were able to differentiate the differences in catalytic behaviors between Co and CoSi<sub>x</sub>. In this study the carbon nanotubes were synthesized on Si substrate by MPCVD method using a mixture of CH<sub>4</sub> plus H<sub>2</sub> as source gases. The substrate was coated by four different films before nanotube growth, i.e. (1) Co, (2) SiO<sub>2</sub> and then Co, (3) CoSi<sub>x</sub> and (4) chemically etched CoSi<sub>x</sub> films. The preliminary results show the average nanotube diameters for four different substrate pretreatments under the same deposition conditions are about 18 nm, 100 nm, 40 nm and 10 nm, respectively. The pretreatment (3) indicates the best performance in field emission. In this case, the turn-on voltage can be as low as 4.6 V/μm, and the emission current density can reach 5 mA/cm<sup>2</sup> at 10 V/μm. The preliminary results also reveal that the characters of CoSi<sub>x</sub> presented or formed during deposition can reason the differences in sizes and properties of nanotubes by four different pretreatments. This is supported by Auger depth profile analyses of nanotubes for pretreatment (1), where Co and Si interdiffusion are obvious. The differences in catalytic effect between pretreatments (1) and (2) may be due to different extent of interaction of Co with Si to form CoSi<sub>x</sub>. In the cases of pretreatments (1), (3) and (4), the compositions and grain sizes of CoSi<sub>x</sub> during deposition can be different. The possible nanotube formation mechanisms will be discussed.

**Z3.5**

**PREPARATION OF SINGLE-WALLED CARBON NANOTUBES BY SIMULTANEOUS LASER ABLATION OF TWO KINDS OF TARGET.** Shinzo Suzuki, Rahul Sen, Takanori Tamaki, Yohji Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Hiromichi Kataura, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN.

Single-walled carbon nanotubes (SWNTs) were prepared by simultaneous laser ablation of a graphite target and a metal/alloy target inside a furnace at 1200°C ambient temperature with 500 Torr Ar gas atmosphere. Each target was vaporized with a different laser, respectively. Various metal targets (Ni, Co, Fe, and permalloy) were tested in order to find the difference in the resulting SWNT yield. At the moment, it seems that permalloy gives the highest yield for the SWNT formation. Also, time-resolved images of the plume by carbon and metal species after laser vaporization were collected using a high-speed video camera. These images suggest that the hot plumes due to carbon and metal species do not mix together so extensively, at least in a few hundred micro seconds after laser vaporization. Based on these experimental findings, a plausible growth mechanism for SWNTs is presented and discussed.

**Z3.6**

**GROWTH OF HIGHLY ORDERED CARBON NANOTUBE ARRAYS ON SILICON SUBSTRATE USING POROUS ALUMINA FILM AS NANO-TEMPLATE.** Zhi Chen, Wenchong Hu, Dawei Gong, Padmakar Kichambare and Craig A. Grimes, Univ of Kentucky, Dept of Electrical and Computer Engineering, Lexington, KY; Liming Yuan and Kozo Saito, Univ of Kentucky, Dept of Mechanical Engineering, Lexington, KY.

In the past several years, many researchers have attempted to grow aligned carbon nanotube (CNT) arrays with fully controlled parameters on various substrates. Among them, the most encouraging results were obtained by using anodized aluminum oxide (AAO) film as the nano-template to confine CNTs' geometry. However, previous results were achieved by using aluminum sheet as the substrate that is not favorable for silicon solid-state circuits. Experiments on CNT array growth from AAO thin film templates on silicon substrates were tried without much success. In this paper, we report, for the first time, highly ordered CNT arrays synthesized with high density and uniformity by a flame method using a porous AAO film as template on silicon wafer. The AAO template was fabricated by using anodization of aluminum film on Si substrate in 0.2M oxalic solution. The AAO template with vertically aligned nano-pores of ~50 nm were obtained. Cobalt catalyst was deposited at the bottom of the nano-pores in an aqueous solution mixed with cobalt sulfate hydrate, boric acid and ascorbic acid under AC current. The CNTs were grown on these templates by a flame method using ethylene as the carbon source. Highly-ordered carbon nanotube arrays with high density and uniformity were successfully synthesized by the flame method on silicon substrate. The diameter and length of these carbon nanotubes (CNTs) are controllable with the porous structure of template, leading to the shortest nanotubes (500 nm long) ever reported. In addition, the nanotubes were found to be open-tipped and have

strong interactions with the alumina side-walls. These results show the feasibility of integration between CNT molecular arrays and the silicon microelectronics, which may find application in smart sensor arrays or molecular electronic devices.

### Z3.7

Abstract Withdrawn.

### Z3.8

EFFECTS OF Fe FILM THICKNESS AND AMMONIA ON THE GROWTH BEHAVIOR OF CARBON NANOTUBES GROWN BY THERMAL CHEMICAL VAPOR DEPOSITION. Jung-Inn Sohn, Chel-Jong Choi, Tae-Yeon Seong, Seonghoon Lee, Kwangju Institute of Science and Technology (K-JIST), Dept of Materials Science and Engineering, Kwangju, KOREA.

Carbon nanotubes are of considerable importance because of their potential technological applications, such as gas reservoirs, battery electrodes, and field emission displays. As for field emission device applications, the synthesis of vertically aligned carbon nanotubes on commercially available low-cost substrates such as silicon is required. Several growth methods of laser vaporization, arc discharge and chemical vapor deposition (CVD) have been used to synthesize carbon nanotubes. In this work, we investigate the effects of the Fe film thickness and ammonia on the growth behavior of carbon nanotubes using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Carbon nanotubes were grown on Fe-deposited Si (001) substrates by thermal CVD. The Fe films were deposited for 20 s - 20 min by pulse-laser deposition. Ammonia was introduced to activate the Fe film prior to the CVD growth of carbon nanotubes. For some samples, Ar was used instead, in order to compare with ammonia. SEM results show that the growth characteristics of carbon nanotubes strongly depend on the Fe film deposition time. TEM results show that the CVD growth at 800°C causes the continuous Fe films to be broken up into nanoparticles 10 - 50 nm across and discontinuous islands 100 nm - 1.1 μm in size. The TEM and SEM results show that the Fe nanoparticles and the ammonia pretreatment are essentially required for the formation of aligned carbon nanotubes. It is, however, shown that although the nanotubes grown on the Ar-treated Fe films are reasonably aligned, there are amorphous graphite layers near the top surface region. Based on X-ray photoemission spectroscopy and TEM results, possible mechanisms are given to describe the growth mode and the growth behavior of carbon nanotubes.

### Z3.9

OBSERVATION OF TITANIUM OXIDE NANOTUBE-LIKE ARRAYS PREPARED BY ANODIC OXIDATION. Dawei Gong, Craig A. Grimes, Suresh Singh, Zhi Chen, University of Kentucky, Electrical and Computer Engineering Department, Lexington, KY; Wenchong Hu, Elizabeth C. Dickey, University of Kentucky, Department of Chemical and Material Engineering, Lexington, KY.

Nano-sized titanium oxide materials are desirable for catalytic and gas sensing applications. In this work, nano-sized titanium oxide structures were achieved through anodization of pure titanium sheets in diluted hydrofluoric aqueous solution. Besides the continuously nano-porous films, nanotube-like features were observed under certain anodizing conditions. These titanium oxide nanotubes were self-organized into well-aligned arrays and their diameters were controllable with anodizing voltage. In 1.5% wt HF aqueous solution, typical value of the tube diameter ranged from 30 nm to 60 nm, corresponding to anodizing voltage from 10 V to 20 V. The length of these tubes were limited to about 300 nm and did not increase with the prolonged anodization time. At the bottom of tubes, a dome-shaped barrier layer was observed, which was similar to those of anodized aluminum oxide. The SEM images of samples anodized for varying time revealed that the nanotube-like structures were developing from continuously porous film that were formed during removal of the initial compact oxide layer at surface. Some possible growth mechanisms of the nanotube-like structures are presented.

### Z3.10

STRUCTURE OF FRILLED CARBON NANOWIRES SYNTHESIZED BY SULFUR-ASSISTED CHEMICAL VAPOR DEPOSITION. Tadashi Mitsui, Takashi Sekiguchi, National Institute for Materials Science (NIMS), Nanomaterials Laboratory, Tsukuba, JAPAN; Yafei Zhang, Toshihiro Ando, CREST of JST, *c/o* NIMS, Advanced Materials Laboratory, Tsukuba, JAPAN; Mikka N.-Gamo, University of Tsukuba, Institute of Applied Physics and Center for Tsukuba Advanced Research Alliance, Tsukuba, JAPAN.

Effects of sulfur addition during the growth of carbon nanowires were studied by high-resolution transmission electron microscope (HRTEM). The carbon nanowires were synthesized by microwave plasma CVD using a gas mixture of hydrogen and methane (5000ppm) on the diamond substrate. The sulfur-assisted process

contained 2550 ppm H<sub>2</sub>S in the gas phase. The HRTEM images revealed that the nanowires grown without H<sub>2</sub>S were multi-wall carbon nanotubes (MWCNTs). The diameter of those MWCNTs was ranged from 40 to 70 nm. Contrary to this, the carbon nanowires grown with H<sub>2</sub>S was not a simple MWCNT; thin layers near the surface of the sulfur-assisted grown carbon nanowires were split as a "frill". The structure of the frills was found to be as that of a graphite multi layers. It is not clear whether the anomalous, frilled structure was yielded whether during sulfur-assisted growth process or after the formation of ordinal MWCNTs. In either case, we speculate that the chemical nature of sulfur should affect to yield the frilled structure. We may expect to modify a MWCNT intentionally into a single-wall CNT by using sulfur.

### Z3.11

CONTROLLING THE ALIGNED GROWTH OF CARBON NANOTUBES BY SUBSTRATE SELECTION AND PATTERNING. Y.J. Jung, B.Q. Wei, R. Vajtai and P.M. Ajayan, Rensselaer Polytechnic Inst, Dept of MS&E, Troy, NY.

To build nanotube based nanodevices, controlling the growth of aligned carbon nanotubes will be essential. Our group reported a method for growing aligned nanotube selectively on SiO<sub>2</sub> surfaces by thermal chemical vapor deposition (CVD) method from xylene-metallocene mixtures. Here we will describe further studies on the roles of size and thickness of patterned oxide structures for the aligned and controlled growth of carbon nanotubes. Patterned SiO<sub>2</sub>/Si substrates prepared by conventional micro fabrication techniques such as lithography and dry & wet etching methods were exposed to xylene-metallocene mixture at 800°C. By defining the size and the thickness of silicon oxide patterns we could control the orientation of nanotube growth and the degree of nanotube alignment.

### Z3.12

CFD ANALYSIS ON A VORTEX ENHANCED CVD REACTOR DESIGN. Kazunori Kuwana, Univ of Kentucky, Dept of Mechanical Engineering, Lexington, KY; Rodney Andrews, Univ of Kentucky, Center for Applied Energy Research, Lexington, KY; Eric A. Grukke, Univ of Kentucky, Dept of Chemical and Materials Engineering, Lexington, KY; Kozo Saito, Univ of Kentucky, Dept of Mechanical Engineering, Lexington, KY.

To enhance the yield of multi-walled carbon nanotubes (MWCN), a vortex enhanced CVD reactor (VECVD) design has more advantage over the conventional straight tube CVD with a flat substrate that is currently in operation in the Center for Applied Energy Research at the University of Kentucky. A commercial CFD code was applied to analyze heat and mass transfer processes without chemical reactions in order to compare the old CVD design performance with a new type. First we conducted CFD calculations on three different types of conventional CVD design. We created unstructured grids in the boundary fitted coordinate and tested three different configurations: a horizontally oriented tube with and without a substrate, and a vertically oriented tube with the bottom injection. The first design resulted in non-uniform flow along the tube, a potential cause of yielding amorphous carbon (impurity for carbon nanotubes). The second design resulted in a uniform flow pattern along the tube suggesting a better flow pattern than the first type. However, for the purpose of production effectiveness, the vertical orientation is more attractive, so the third design was tested, but no circulation was obtained. VECVD is expected to have a longer residence time by an enhanced circulation flow along the tube than the currently available straight tube CVD design. To assess the effect of fluid dynamics without heat transfer on the generation of circulation, a CFD calculation without heat transfer was performed on a vertically oriented tube with the bottom injection. The calculation showed a strong and uniform circulation along the tube with higher mass transfer rate than the conventional CVD. This CFD prediction will be tested against a laboratory scale experiment.

### Z3.13

RELIABLY MEASURED SYNTHESIS OF C<sub>60</sub>@SWNT IN 90% YIELDS. Brian W. Smith, Richard M. Russo, B.C. Satishkumar, Ferenc Stercel, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

In previous works, we have shown our discovery of C<sub>60</sub>@SWNT and first described the general mechanism of filling, which involves the vapor phase transport of C<sub>60</sub> molecules to openings in the SWNTs' walls. Here, we discuss the high-yield synthesis of C<sub>60</sub>@SWNT by refinements to our method. Yields are measured by a calibrated weight uptake technique, a methodology that is not subject to the potential pitfalls of other techniques that have been applied. At certain processing conditions, yields exceeding 90% were obtained and corroborated by transmission electron microscopy. From our data, we determine the parameters most important for creating endohedral SWNT supramolecular assemblies by the vapor phase method. Our

results pave the way for successful single-tube measurements and for high-yield filling with non-fullerenes.

### **Z3.14**

**CARBON NANOTUBE NETWORK SYNTHESIZED USING MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION.** Dajiang Yang, Qing Zhang, S.F. Yoon, J.Ahn, Sigen Wang, Nanyang Technological University, Microelectronics Centre, School of Electrical and Electronic Engineering, SINGAPORE.

A new carbon nanotube network is prepared using microwave plasma enhanced chemical vapor deposition under plasma of a mixture of methane, hydrogen and nitrogen at 720°C. The Field Emission Scan Electronic Microscopy images show that the carbon nanotube network is self-organized into netlike cylinder, different from the previously reported carbon nanotube ropes or nanofibers. The netlike cylinders are about 1 micron in diameter, more than 10 micron in length and composed of hundreds of carbon nanotubes with the diameter from 20 to 100nm, Energy Dispersive X-Ray(EDX) results confirm that the network is carbon in nature, with a small amount of Ni which was used as catalyst. Raman scattering results show G-peak ( $1583\text{cm}^{-1}$ ) and D-peak ( $1328\text{cm}^{-1}$ ) in the spectra, indicating a graphitic structure. XRD results are found to be consistent with EDX and Raman results. The correlation between the position, intensity of the peak and morphology of carbon nanotube network is also discussed.

### **Z3.15**

**FORMATION OF SINGLE-WALL CARBON NANOHORNS SUPPORTED BY METAL PARTICLES USING CO<sub>2</sub> LASER VAPORIZATION.** Daisuke Kasuya, Department of Material Science and Engineering, Faculty of Science and Technology, Meijo University, Nagoya, Aichi, JAPAN; Masako Yudasaka, "Nanotubulites" Project, Japan Science and Technology, c/o NEC, Tsukuba, Ibaraki, JAPAN; Kunimitsu Takahashi, Fumio Kokai, Institute of Research and Innovation, Kashiwa, Chiba, JAPAN; Sumio Iijima, Department of Material Science and Engineering, Faculty of Science and Technology, Meijo University, Nagoya, Aichi, JAPAN, "Nanotubulites" Project, Japan Science and Technology, c/o NEC, Tsukuba, Ibaraki, JAPAN, NEC Corporation, Tsukuba, Ibaraki, JAPAN.

A single-wall carbon nanohorn (SWNH) is a horn-shaped sheath composed of single-wall graphene sheets with diameters of 2 to 3 nm, and they form a "dahlia-like" aggregate with a diameter of about 80 nm [1]. Previous studies have confirmed that SWNHs were heat-resistant in vacuum at up to 1800°C [1], while single-wall carbon nanotubes (SWNTs) coalesced with neighbors in vacuum at 1400 or 1500°C [2]. We recently found that the size and structure of the "dahlia-like" SWNH aggregates did not change greatly when they were exposed to 760-torr O<sub>2</sub> gas at 550°C. Since SWNHs are stable carbon nanomaterials, they will become useful if they are chemically modified. In this report, we introduce a method of producing SWNHs supported by metal particles, such as Pt, Pd, and Gd. We produced SWNHs supported by metal particles by the CO<sub>2</sub> laser vaporization of metal-carbon composite in 760 torr of Ar gas at room temperature. The structures of the obtained materials were studied with transmission electron microscope (TEM) and Raman spectra. When the platinum-carbon [0.6-99.4 at%] composite was vaporized at 20 kW/cm<sup>2</sup>, most of the products were SWNHs supported by platinum particles with diameters of 5 to 10 nm. At the higher laser power density (60 kW/cm<sup>2</sup>), amorphous carbon particles supported by platinum particles with diameters of 5 to 10 nm containing a little quantity of SWNTs with diameters of about 1.2 nm were produced. This work was supported by the US Office of Naval Research (ONR-N000140010762).

References:

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### **Z3.16**

Abstract Withdrawn.

### **Z3.17**

Abstract Withdrawn.

### **Z3.18**

Abstract Withdrawn.

### **Z3.19**

Abstract Withdrawn.

### **Z3.20**

**EFFECT OF CATALYST ON GROWTH BEHAVIOR OF CARBON NANOTUBE SYNTHESIZING BY MICROWAVE HEATING THERMAL CVD PROCESS.** Yu-Chen Chang, George-C Tu, Cheng-Tzu Kuo, Department of Materials Science and Engineering, National Chiao-Tung University, Hsin-Chu, TAIWAN ROC; Jian-Yih Wang, Materials and Electro-Optics Research Division, Chung-Shan

Institute of Science and Technology, Tao-Yuan, TAIWAN ROC; I-Nan Lin, Materials Science Center, National Tsing-Hua University, Hsin-Chu, TAIWAN ROC.

Carbon nanotubes (CNTs) exhibiting good electron field emission properties have successfully synthesized using a novel chemical vapor deposition process, in which the substrates were heated up by a susceptor via the absorption of microwave. Morphology of the CNTs coated on silicon substrate varies with the form of catalyst coated. The growth behavior is also pronouncedly influenced whenever the plasma was induced in the deposition chamber. Bias applied in-situ further improved the synthesis of the aligned CNTs. Thus obtained CNTs own largest number density and exhibit largest emission current density when using sputtered Ni as catalyst. The electron field emission can be turned on at  $E_0 = 0.78 \text{ V}/\mu\text{m}$ , attaining  $J_e = 13,000 \text{ uA}/\text{cm}^2$  under 5.5 V/ $\mu\text{m}$  applied field, even though the CNTs are randomly oriented. These CNTs possess good enough electron field emission properties for applications as electron emitters in field emission display.

### **Z3.21**

**ORIENTATIONAL GROWTH OF CARBON NANOTUBE.** Shen Zhu, USRA, NASA/Marshall Space Flight Center, Huntsville, AL; Ching-Hua Su, S. Lehoczky, Microgravity Science and Applications Department, Science Directorate, NASA/Marshall Space Flight Center, Huntsville, AL; J.C. Cochran, USRA, NASA/Marshall Space Flight Center, Huntsville, AL; Y. Cuic, A. Burger, Center for Photonic Materials, Fisk University, Nashville, TN.

Since the superior properties of multi-wall carbon nanotubes (MWCNT) could improve performances of various devices such as electronics and sensors, many efforts have been made in synthesizing high quality multi-wall MWCNT. Most applications require uniform aligned MWCNT. In this presentation, a directional growth of MWCNT will be reported. Carbon nanotubes are synthesized using thermal chemical vapor deposition. Various temperature and pressure are used to fabricate carbon nanotubes. It is found that the nanotube-diameter distribution mainly depends on the growth-temperature. With the substrate surface normal either along or against the gravity vector, different growth orientations of MWCNT are observed by scanning electron microscopy although the Raman spectra are similar for samples synthesized at different locations. The sizes of these carbon nanotubes in each sample are quite uniform and the length of the tube is up to hundreds of micrometers. These results suggest the gravitation effects in the growth of long and small diameter CNT.

### **Z3.22**

**INFLUENCE OF THE CATALYST PREPARATION ON CARBON NANOFIBERS SYNTHESIZED VIA CATALYTIC CHEMICAL VAPOUR DEPOSITION.** Thomas Schliermann, Marcus Thierley, Hartmut Pröbstle, Jochen Fricke, University of Würzburg, Physikalisches Institut, Würzburg, GERMANY; Bernd Schmidt, Gudrun Reichenauer, Bavarian Center for Applied Energy Research (ZAE), Würzburg, GERMANY; Wolfgang Braue, German Aerospace Center (DLR), Materials Research Institute, Cologne, GERMANY.

There is widespread interest in growing carbon nanofibers with defined substructure, morphology and a narrow diameter distribution in order to optimize these characteristic features for applications e.g. in the fields of hydrogen storage or battery electrodes. When synthesized via catalytic dissociation of carbon-containing gases using metal oxide powders or supported metals as catalyst, one of the key parameters for the structure of the nanofibers is the catalyst. Within the framework of this study we investigated effects of the synthesis, different pretreatment processes prior to carbon deposition as well as the preparation (supported / unsupported) of various catalysts (e.g. Ni, Ni/Cu) on the fiber characteristics. The catalysts were characterized by X-ray diffraction methods, electron microscopy, gas sorption, X-ray photoelectron spectroscopy and inductively coupled plasma spectrometry. The carbon deposit was analyzed by scanning and transmission electron microscopy to visualize the catalyst and the carbon nanofiber morphology. The crystallinity, the arrangement of the graphitic planes and the diameter distribution of the nanofibers as well as the catalyst particles embedded in or attached to the fibers were analyzed via X-ray diffraction measurements, Raman spectroscopy, thermogravimetry and high resolution transmission electron microscopy.

### **Z3.23**

**IN SITU DIAGNOSTIC-CONTROLLED CONDENSED PHASE GROWTH OF SINGLE-WALL CARBON NANOTUBES.** D.B. Geohegan, C.H. Schittenhelm, P.F. Britt, S.J. Pennycook, Oak Ridge National Laboratory, Oak Ridge, TN; A.A. Puzos, Dept of Materials Science and Engineering, Univ. of Tennessee, Knoxville, TN.

Comprehensive imaging and spectroscopy of the plume of material

generated by nanosecond laser vaporization (LV) for single wall carbon nanotube (SWNT) synthesis indicated that SWNT grow by the condensed phase conversion (CPC) of carbon clusters or nanoparticles by metal catalyst nanoparticles (diameters ; 20 nm) during the several seconds typically spent by the plume inside the hot oven. Ex situ annealing of soots prepared by time-restricted growth of SWNT using these diagnostics recently showed that growth could continue at relatively low temperatures ~1000 C outside the laser vaporization apparatus, supporting the CPC growth model. These results present opportunities for optimizing CPC growth of SWNT, both inside the LV apparatus and from annealing of nanoparticulate and cluster feedstocks (as recently reported for C<sub>60</sub>/Ni by Schlittler et al, Science **292**, 1136 (2001)).

To investigate the effect of nanoparticle density on SWNT yield and growth rates during the annealing period, the pulse width of the vaporization laser was drastically changed to 150 microseconds (~80, 200ns-pulses, free running mode of Nd:YAG laser) to evaporate the composite C/Ni/Co target. This modification results in a natural confinement, providing a tenfold increase in density over the short-pulse synthesis approach. Growth rates (estimated through in situ imaging) and material characterizations (from ex situ TEM, TGA, FESEM, Raman spectroscopy) will be presented. Material collected after incomplete conversion will be tested for continued CPC growth.

Ex situ annealing experiments will also be described using different cluster and nanoparticulate feedstocks to investigate the growth of SWNT by CPC. Rapid thermal annealing is accomplished by CO<sub>2</sub> laser irradiation with in situ pyrometry utilized to estimate the sample temperature.

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### **Z3.24**

EFFECT OF RF- AND DC-BIAS ON THE GROWTH OF CARBON NANOTUBES USING ELECTRON CYCLOTRON RESONANCE CHEMICAL VAPOR DEPOSITION. Y.S. Woo, D.Y. Jeon, Korea Advanced Institute of Science and Technology, Dept. of Materials Science and Engineering, Taejon, KOREA; I.T. Han, N.S Lee, J.E. Jung, J.M. Kim, FED Project, Samsung Advanced Institute of Technology, Suwon, KOREA.

Low temperature synthesis of carbon nanotubes (CNTs) is likely required to fabricate electronic devices such as field emitters, transistors, and microelectromechanical systems. In this aspect electron cyclotron resonance chemical vapor deposition (ECR-CVD) is one of promising routes since its plasma zone is apart from the substrate surface so that substrate temperatures are usually kept low during deposition. Moreover ECR-CVD has a high plasma density, generally giving rise to high growth rates of films. We have successfully synthesized vertically aligned CNTs on glass substrates with a methane gas at temperatures as low as 500°C using ECR-CVD. Ni, Co, Fe, and their alloy were used as a catalyst layer. Radio frequency and/or direct current bias voltage was applied to the substrate in order to study the effect of bombardment energy of ions on the growth of CNTs. It was observed by scanning electron microscopy that the changes of microwave powers, total gas pressures, and bias voltages varied the diameters and lengths of CNTs. Active chemical species in a methane gas plasma were identified using optical emission spectroscopy and mass spectroscopy. Relative ratios and total quantity of the active species were varied with microwave powers and total gas pressures. However, the RF and/or DC bias made little quantitative effect on the radical species. This is based on the fact that ECR plasma density is much higher than that of RF and/or DC plasma. From this investigation, it was shown that ion bombardment as well as the active species in the plasma also give a great influence on the synthesis of CNTs. In addition, field emission properties of CNTs were also measured.

### **Z3.25**

THERMAL AND MECHANICAL PROPERTIES OF POLY (ETHYLENE OXIDE)/CARBON NANOTUBE COMPOSITE. H. Geng<sup>1</sup>, H. Shimoda<sup>1</sup>, L. Fleming<sup>1</sup>, B. Zheng<sup>2</sup>, J. Liu<sup>2</sup> and O. Zhou<sup>1</sup>. <sup>1</sup>University of North Carolina, Chapel Hill, NC. <sup>2</sup>Duke University, Durham, NC.

Poly(ethylene oxide) (PEO) has been investigated for many years as a candidate solid electrolyte material due to its high ionic conductivity in the amorphous state. However at ambient conditions, PEO is a semi-crystalline material with a crystallization temperature of ~70°C. Formation of composite has been considered as a possible route to stabilize the amorphous phase of PEO at room temperature. Carbon nanotubes with dimensions comparable to that of the polymer chain and promising properties is an attractive filler material. We have fabricated thin films of PEO/carbon nanotube composites using both purified and chemically functionalized single-wall carbon nanotubes

(SWNTs). Differential scanning calorimetry (DSC) and x-ray diffraction results show that its crystallinity decreases with increasing nanotube concentrations. Dynamic mechanical analysis (DMA) results show an improvement of the mechanical properties of PEO by adding nanotubes.

### **Z3.26**

ENHANCED BRIGHTNESS IN M3EH-PPV BASED OLEDs USING A CARBON NANOTUBE COMPOSITE AS A CHARGE TRANSPORT LAYER. Jonathan Coleman, Marc in het Panhuis, Patrick Fournet, Diarmuid O'Brien, Martin Cadek, Werner Blau, Trinity College Dublin, Dept of Physics, Dublin, IRELAND.

Organic light emitting diodes have been fabricated, incorporating carbon nanotube based composites as charge injection layers. At moderate nanotube loading levels, charge injection into M3EH-PPV was increased by over three orders of magnitude. This was accompanied by a substantial increase in electroluminescent efficiency. This is explained by improved current balance leading to higher singlet exciton yield.

### **Z3.27**

A STUDY OF NYLON-6/CARBON NANOTUBE COMPOSITES. Zhijie Jia, Cailu Xu, Ming Zhang, Ji Liang, Dehai Wu, Tsinghua University, Dept of Mechanical Engineering, Beijing, CHINA; Bingqing Wei, Rensselaer Polytechnic Institute, Dept of Materials Science and Engineering, Troy, NY.

A new technique for fabricating nylon-6/carbon nanotube (PA6/CNT) composites was investigated. Through the use of an improved in situ process, the tensile strength of PA6/CNT composites improved significantly, although the toughness and elongation were compromised. The nucleation of cracks and the breaking of the composites happened not at the PA6/CNT interface but at the wrapping CNTs PA6 layer/PA6 matrix interface.

Keywords: Carbon nanotube, Nylon-6, composite, in-situ Process.

### **Z3.28**

TRANSPORT PROPERTIES AND PERCOLATION IN CARBON NANOTUBES/ PMMA COMPOSITES. Jean Michel Benoit, Benoit Corraze, Serge Lefrant, IMN, Univ. Nantes, FRANCE; Patrick Bernier, GDCP, Univ. Montpellier, FRANCE; Olivier Chauvet, IMN, Univ. Nantes, FRANCE.

Carbon nanotubes (CNT) possess remarkable physical properties. However, because of their size, they are difficult to handle. Making composites with them gives an alternative way to handle these objects and to make use of their properties at a macroscopic scale. Here, we present a comparative study of the transport properties of PMMA/nanotubes composites thin films with both SWNTs and MWNTs. At room temperature, the conductivity of the composites follows a pure percolation behavior when increasing the nanotube content. The universal scaling law for random site percolation with a very low percolation thresholds (0.33 weight % for SWNTs) is obeyed over two orders of magnitude in CNT content. These composite films may thus be used as semi-transparent and conducting electrodes. At low temperature, SWNTs composites and MWNTs ones behave differently. While MWNTs composites still obey the percolation law, deviations are observed for SWNTs. They are discussed in terms of tube-tube contact and charging energy of the tubes. Very high non linear response to moderate electric fields are also observed in SWNTs composites. The high field conductivity can be 6 orders of magnitude higher than the low field one. It is independent of temperature suggesting tunnelling between metallic tubes. These properties are discussed within the framework of percolation theory and transport in heterogeneous media.

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### **Z3.29**

FABRICATION AND CHARACTERIZATION OF A SERIES OF POLYMER/SINGLE-WALL CARBON NANOTUBE COMPOSITES. Thomas Gennett<sup>1</sup>, Anora K. Burwell, Department of Chemistry and Center for Materials Science, Rochester Institute of Technology, Rochester, NY; Anne C. Dillon, Jeff L. Alleman, Kim M. Jones, Michael J. Heben, National Renewable Energy Laboratory, Golden, CO.

The extraordinary mechanical properties of single wall carbon nanotubes have attracted a great deal of attention for their use in nanotube-polymer composites. Initial studies have shown the possibility of improved physical properties relative to the traditional carbon fiber-polymer composites. A key important factor is to determine the strength of the nanotube-polymer interface through the evaluation of a series of composite materials. This contribution describes ongoing work focused on understanding the nature of the nanotube-polymer matrix interactions. Highly purified (>98% by

weight) single-walled carbon nanotubes (SWNT) were obtained through a purification procedure described earlier. A series of polymers including, polyethylene, polypropylene, polyacrylonitrile, poly(vinyl butyral), poly(methyl methacrylate), poly(vinyl pyridine), polytetrafluorethylene, polyimide and Nafion were investigated. The nanotubes were incorporated into the polymer solution through a series of homogenization and folding techniques for a doping range from 0.05% to 20% by weight nanotubes. Ultrasonication was not used in order to minimize damage to the nanotube materials. The resultant solutions and solution cast thin-films were characterized by: optical adsorption spectroscopy, electron microscopy, Raman spectroscopy, thermal analysis (DSC, DTA), electroanalytical and resistivity techniques. Specifically, we have achieved dissolution of carbon nanotubes in several polymers to such an extent that the homogeneous solutions survived ultra-centrifugation without any phase separation of the nanotubes. The polymeric properties that lead to these strong interactions and the unique physical properties of the composites will be discussed.

**Z3.30**  
POLYMER-SINGLE WALL CARBON NANOTUBE COMPOSITES FOR POTENTIAL SPACECRAFT APPLICATIONS. Cheol Park\*, Zoubeida Ounaies\*, Kent A. Watson\*, Emilie J. Siochi, John W. Connell, and Joycelyn S. Harrison. \*ICASE Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton VA.

Polymer-single wall carbon nanotube (SWNT) composite films were prepared and characterized as part of an effort to develop polymeric materials with improved combinations of properties for potential use on future spacecraft. Next generation spacecraft will require ultra-lightweight materials that possess specific and unique combinations of properties such as radiation and atomic oxygen resistance, low solar absorptivity, high thermal emissivity, electrical conductivity, tear resistance, ability to be folded and seamed, and good mechanical properties. The objective of this work is to incorporate sufficient electrical conductivity into space durable polyimides to mitigate static charge build-up. The challenge is to obtain this level of conductivity ( $10^{-6}$ - $10^{-8}$  S/cm) without degrading other properties of importance, particularly solar absorptivity. Several different approaches were attempted to fully disperse the SWNTs into the polymer matrix. These included high shear mixing, sonication, and synthesizing the polymers in the presence of pre-dispersed SWNTs. In some cases, acceptable levels of conductivity were obtained at loading levels less than one weight percent SWCNTs. Characterization of the nanocomposite films and the effect of SWCNT concentration and dispersion on the conductivity, solar absorptivity and mechanical properties will be presented.

**Z3.31**  
DISPERSION AND ALIGNMENT OF CARBON NANOTUBES IN THERMOPLASTIC POLYMERS. Mike Sennett, J.B. Wright, E.A. Welsh, US Army Soldier and Biological Chemical Command, Natick Soldier Center, Materials Science Team, Natick, MA; W.Z. Li, J.G. Wen, Z.F. Ren, Boston College, Dept of Physics, Chestnut Hill, MA.

Dispersion and alignment of carbon nanotubes (CNT) in thermoplastic polymers such as polycarbonate (PC) have been studied. Dispersion was accomplished by mixing in a twin-screw extruder and orientation was carried out using a fiber spinning apparatus. The effects of mixing time and fiber draw rates on dispersion and alignment were investigated. Relatively short residence times in the extruder were required to produce uniform dispersions. Excellent alignment of CNT in nanocomposite filaments was obtained when the fiber draw rate was greater than 70 meters/min. The ability to closely control the dispersion and alignment of carbon nanotubes in polymers is expected to lead to the development of nanocomposites with desirable electronic and structural properties.

**Z3.32**  
SCANNING PROBE AND HIGH RESOLUTION ELECTRON MICROSCOPY STUDY OF SINGLE WALL CARBON NANOTUBE POLYMER COMPOSITES. Peter T. Lillehei, Cheol Park\*, Roy Crooks\*\*, and Emilie J. Siochi, Advanced Materials and Processing Branch, NASA Langley Research Center. \*ICASE. \*\*Lockheed Martin, Hampton, VA.

Single wall carbon nanotube (SWNT) reinforced polymer composites are of great interest in aerospace applications because of their potential for tremendous property improvements over conventional materials. The production of composites with optimal properties requires control over the SWNT distribution within the matrix. Evaluation of processing parameters relies on effective high-resolution characterization methods. This study correlates the results of both scanning probe microscopy (SPM) and high resolution transmission electron microscopy (HREM) examination of SWNT polymer composites. SPM methods used include magnetic force microscopy (MFM), nanoindentation and force spectroscopy. HREM study was

hindered by the weak contrast of the SWNT within the composite, and two methods were used for contrast enhancement with some success. Image math and power spectrum filtering operations are used to enhance the periodicity contrast of the SWNT vs. the polymer matrix. Electron energy loss (EELS) spectra for isolated SWNT, polyimide and the SWNT-polyimide composite are compared. The relative usefulness of electron energy loss near edge structure (ELNES) information and ionization edge peaks is shown for energy filtered mapping of SWNT distributions within the polymer matrix.

**Z3.33**  
SYNTHESIS AND CHARACTERIZATION OF SINGLE-WALL CARBON NANOTUBE/*ta*-C THIN FILM COMPOSITES. C.H. Schittenhelm, D.B. Geohegan, P.F. Britt, Oak Ridge National Laboratory, Oak Ridge, TN; A.A. Puzos, Dept of Materials Science and Engineering, Univ. of Tennessee, Knoxville, TN.

Multifunctional composites which combine the exceptional electronic, mechanical or thermal properties of single-wall carbon nanotubes (SWNT) with those of a matrix material are envisioned for a wide range of applications. Here we report the first synthesis of composites which utilize ultrahard, transparent, amorphous diamond thin films as matrices to encapsulate conducting SWNT mats. This film is intended to provide a transparent, wear-resistant coating to shield the SWNT against mechanical deformation and adsorption of many common ambient gases or liquids which have been observed to strongly modify their electronic properties. SWNT were synthesized by laser vaporization and chemically purified to > 95 wt. % SWNT as measured by TGA analysis. A dichloroethane suspension of these nanotubes was sprayed onto Si, quartz, and other substrates to form mats of varying areal densities. Pulsed laser deposition (PLD) of tetragonally-coordinated amorphous carbon was then performed in vacuum using a pyrolytic graphite target irradiated at 193-nm, generating a plume containing carbon ions with kinetic energies up to 100 eV. The interactions of these high energy ions with the SWNT are of fundamental interest for the general use of PLD to form SWNT thin film composites. The resistance of the mats was measured in situ during film deposition, while ex situ measurements before and after deposition included I-V measurements, along with FESEM, TEM and resonant Raman scattering analyses. Resonant Raman spectra from the SWNT ( $\lambda = 633$  nm) before and after deposition showed that a large fraction of SWNT survive the energetic deposition process, with the characteristic tangential and breathing modes remaining unchanged in shape and position but decreased in magnitude. An enhanced disorder band was observed, as expected. Preliminary results indicate that amorphous diamond thin films can be used as protective matrices for multifunctional SWNT composites. This research was sponsored by the Advanced Materials and Processing Branch at NASA-LaRC, the Nanotechnology CDDF at NASA-MSFC, and the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

**Z3.34**  
CARBON-NANOTUBE-BINDING PEPTIDES: BUILDING BLOCKS FOR SLUSHY NANOSTRUCTURES. R. Smith, N. Souti, D.A. Walters, Univ of Central Florida, Orlando, FL; P.A. Willis, R.E. Smalley, Rice Univ, Houston, TX.

We developed oligopeptides, short sequences of amino acids, which show binding activity to carbon nanotubes (CNTs). A random library of  $\sim 10^9$  peptides, expressed via phage display, was exposed to single-wall CNTs in multiple rounds of biopanning. In each round, peptides with weaker binding were washed away, while those with stronger binding were retained. Between rounds, the retained peptides were amplified by allowing the phage to replicate. At the end of the process, phage DNA was extracted and sequenced to determine the peptide sequence. Binding was assayed by imaging phage-CNT complexes with an atomic force microscope. The resulting peptides are general tools for manipulation and assembly of CNTs. Applications to purification, separation, lithography, and nanostructures will be discussed. The authors acknowledge the gracious assistance of Dr. Debopam Chakrabarti and his students for providing advice and access to equipment. This work was funded by the Office of Naval Research and the UCF Office of Research.

**Z3.35**  
METALLO-ORGANIC SELF-ASSEMBLY OF FUNCTIONALIZED CARBON NANOTUBES IN MONOLAYER AND MULTILAYER FOREST-LIKE ASSEMBLIES. Fotios Papadimitrakopoulos, Debjit Chattopadhyay, Izabela Galeska, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Substrate independent, normal organization of single wall carbon nanotubes (SWNTs) holds significant promise for nanoscale devices.

Herein we demonstrate that DMF dispersed SWNTs can be successfully organized in dense (up to  $1.1 \text{ g/cm}^3$ ), highly oriented regular arrays on a range of substrates by a simple self-assembly process both in monolayer and multilayer formats. This unique self-assembly is based on the acid-base interactions of the carboxyl terminated nanotubes with the Fe(III) decorated surface. Tapping mode atomic force microscopy (AFM) clearly shows that SWNTs can be directed perpendicular to the surface. Raman and spectroscopic ellipsometry investigation on these assemblies corroborate the orthogonal orientation observed by AFM. Thickness measurements on these films yield an average monolayer thickness (i.e. nanotube length) of 37.7 nm. Quartz Crystal Microbalance (QCM) along with ellipsometry studies provide additional insight into the density of these films, yielding densities up to  $1.1 \text{ g/cm}^3$ . The fast adsorption and perpendicular alignment of SWNTs assemblies open up a wide scope of possible applications ranging from optoelectronics to biological sensors.

#### SESSION Z4: NANOTUBE-POLYMER COMPOSITES

Chairs: Masako Yudasaka and Serge R. Lefrant  
Tuesday Morning, November 27, 2001  
Back Bay A (Sheraton)

##### 8:30 AM \*Z4.1

ISSUES IN THE PROCESSING AND PROPERTIES  
MULTI-WALLED CARBON NANOTUBE/POLYMER  
COMPOSITES. L.S. Schadler, E. Eitan, P.M. Ajayan, Rensselaer  
Polytechnic Institute, Troy, NY.

One of the biggest technical challenges in taking advantage of the interesting properties of carbon nanotubes in polymer nanocomposites is controlling the degree of dispersion and removing unwanted carbonaceous material. We have made considerable progress in understanding and optimizing the purification of arc-discharge based multi-walled carbon nanotubes (MWNT) and in optimizing the degree of interaction between the polymer matrix and the MWNT. For example, we have achieved transparent dispersions of MWNT in aromatic amines. This is leading to an ability to control the mechanical properties of MWNT / polycarbonate and MWNT / epoxy composites. This talk will highlight our recent advances in the processing of composites and we will report on the scratch, and wear resistance as well as tensile and compression properties of MWNT/polymer composites.

##### 9:00 AM \*Z4.2

PROCESSING AND PROPERTIES OF COMPOSITE MATERIALS  
CONTAINING MULTIWALLED CARBON NANOTUBES.  
Rodney Andrews, Terry Rantell, Univ of Kentucky, Center for  
Applied Energy Research, Lexington, KY; John Anthony, Robert G.  
Bergosh, Chad Landis, Mark S. Meier, Univ of Kentucky, Dept of  
Chemistry, Lexington, KY.

Harnessing the unique physical properties of MWNTs in materials applications is yet to be fully realized. In recent work at CAER, MWNT have been dispersed in polymer and pitch matrices by using ultrasonics to disperse MWNT into solutions. However, this approach, although providing valuable information on methods for realizing the remarkable properties of the MWNT, is not readily transferable to industrial practice. A more practical method of producing MWNT composites is by shear mixing followed by extrusion or injection molding. The dispersion of nanotubes into polymers and pitch matrices utilizing traditional polymer processing technologies will be discussed. Sufficient dispersion is found to be the key in realizing the potential of these unique nano-reinforcements. The effect of composite form, nanotube alignment, and functionalization of the nanotube surface for improved adhesion will be discussed in relation to the effect on composite properties.

##### 9:30 AM \*Z4.3

CONDUCTING POLYMER CARBON NANOTUBE COMPOSITES.  
Gordon Wallace, May Tahhan, Joseph Barisci, Geoffrey Spinks, Univ  
of Wollongong, Intelligent Polymer Research Institute, Wollongong,  
NSW, AUSTRALIA; Mei Gao, Liming Dai, CSIRO, Division of  
Molecular Science, Clayton South, VIC, AUSTRALIA.

Inherently conducting polymers (ICPs) are dynamic structures finding widespread use as sensors, molecular separation systems, electromechanical actuators and energy/conversion storage systems. The practical use of many of these systems is limited by either weak mechanical properties or inadequate electronic conductivity. The fascinating electronic and mechanical properties of carbon nanotubes (CNTs) have been the subject of many recent investigations and we now propose to combine these materials with ICPs to produce a range of new composite structures. It is envisaged that the properties of these structures will be such that the current limitations of ICPs will be alleviated. A number of approaches are under investigation. These

include: • The use of dispersed carbon nanotubes as dopants. CNTs can be dispersed in aqueous solution using anionic dispersants. The "stabilised" tubes may then be incorporated into a conducting polymer during electrosynthesis. • Electrodeposition of ICPs or CNT mats. CNT mats may be prepared using simple filtration approaches. The mats can then be used as an electrode for deposition of ICPs. • Use of soluble conducting polymers as dispersants. The water soluble sulfonated polyaniline has proven to be an effective dispersant for CNTs. Formation of composite CNT mats after filtration is possible. Each of these approaches as well as our preliminary attempts to chemically derivatise CNTs to facilitate the formation of composites will be discussed. The electrochemical and mechanical properties of these new structures have been investigated.

##### 10:30 AM \*Z4.4

ALIGNMENT AND DISPERSION OF SINGLE-WALL  
NANOTUBES IN POLYMER COMPOSITES. Karen I. Winey, Univ  
of Pennsylvania, Dept of Materials Science and Engineering,  
Philadelphia, PA.

Individual single-wall carbon nanotubes (SWNT) have demonstrated far superior mechanical, thermal and electrical properties relative to carbon fibers. Thus, an obvious direction is to produce nanotube-polymer composites in an attempt to harness these extraordinary properties. We have produced SWNT-polymer composites using melt mixing methods and a variety of processing conditions (temperature, time, torque). Subsequently, some of these composites have been subjected to melt extrusion to form SWNT-polymer composite fibers. Our early results with SWNT-poly(methyl methacrylate) composite fibers show improved mechanical properties. The elastic modulus of these fibers increases with draw ratio and the weight fraction of SWNT. More importantly, the extensional flow of melt fiber spinning was sufficient to align the SWNT within the polymer matrix. According to polarized Raman spectroscopy, the mosaic distribution of the SWNT relative to the fiber axis can be below the detection limit of the experiment. While this outstanding SWNT alignment might be an asset for mechanical properties, the alignment of one-dimensional conductors in these composites could reduce electrical conductivity. Our current efforts focus on processing methods to maximize the dispersion of SWNT within a variety of thermoplastics.

##### 11:00 AM \*Z4.5

OPTICAL AND ELECTRO-OPTIC PROPERTIES OF CARBON  
NANOTUBE MATRIX COMPOSITES. David L. Carroll, Richard  
Czerw, Scott Webster, Dept. of Physics, Clemson Univ., Clemson, SC;  
Nirupama Chakrapani, Pulickel M. Ajayan, Dept. of Materials Science  
and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Optically active composites made from single walled carbon nanotubes (SWNTs) and a laser dye (Rhodamine B. Coumarin 6), or conjugated polymer (MEH-PPV, PFO), containing matrix have been used to study the optical response of isolated nanotubes. Strong modifications to the photoluminescence behavior of dyes and photo/electro-luminescence of conjugated polymers have been observed as a function of nanotube length and loading. Specifically, enhanced luminescence yields and shifts in emission frequencies are quite pronounced in some cases. Further, extreme photo-sensitivity in electrical transport noise of the conjugated polymer - nanotube composites has been observed. A simple model of dipole coupling between the emissive species and the nanotubes can explain some, but not all of the observed phenomena. This suggests that near-field interactions within the matrix must also play a role in the behavior of "near-tube" emission of light. These results will be discussed in terms of several unique applications of the nanotube composites including: optical switching, nonlinear optical materials, organic photovoltaics, and organic light emitting diodes.

##### 11:30 AM Z4.6

PROCESSING AND MONITORING OF SINGLE WALL CARBON  
NANOTUBE COMPOSITES. Brad Files, NASA Johnson Space  
Center, Houston, TX; Olga Gorelik, Pavel Nikolaev, and Sivaram  
Arepalli, GB Tech/Lockheed Martin, Houston, TX; Victor Hadjiev,  
Institute for Space Systems Operations and Texas Center for  
Superconductivity, University of Houston, Houston, TX.

Use of the extraordinary mechanical properties of single wall nanotubes presents opportunities for designing new materials to greatly reduce the weight of structural materials. Experience with various processing methods of nanotube polymer composites shows a variety of results depending on the techniques used. Characterization methods such as Raman spectroscopy and dynamic mechanical analysis show that certain molding techniques and processing routes can produce samples with wide-ranging mechanical properties. Measurements show that flaws in most specimens drive properties, since processing of these materials is difficult. Composite production methods to be described include casting, injection molding, compression molding, and lamination. A number of mixing methods

will be discussed, including both manual and mechanical means. Data from mechanical testing will be correlated with various techniques to show those which have proven to be most reliable.

#### 11:45 AM Z4.7

CARBON-NANOTUBE/CARBON-NANOFIBRE-FILLED THERMOPLASTIC COMPOSITES. Jan Sandler, Milo Shaffer, Alan Windle, Cambridge Univ, Dept of Materials Science & Metallurgy, Cambridge, UNITED KINGDOM; Jacek Nastalczyk, Georg Broza, Karl Schulte, TU Hamburg-Harburg, Hamburg, GERMANY; Christian Keun, New-York Hamburger Gummi-Waaren AG, Hamburg, GERMANY.

Experimental and theoretical results suggest that carbon nanotubes (CNT) and carbon nanofibres (CNF) hold promise as reinforcement materials for novel polymer nanocomposites. We have investigated a range of composite systems using nanotubes and nanofibres of different structure and diameter in a number of representative thermoplastic matrices, including commodity and high performance resins. We have particularly examined the influence of the nanoscale fillers on the resulting polymer morphologies with regard to changes in the crystallinity in the vicinity of the fillers. Model thin-film nanocomposites have been examined by laser Raman spectroscopy during *in-situ* macroscopic deformation with regard to a shift of the characteristic Raman peak, which indicates an effective load transfer from the matrix to the filler. We have achieved a high degree of dispersion in all matrices, using an intensive shear mixing protocol in conventional thermoplastic processing equipment, and have fabricated macroscopic standard test samples by injection moulding. The degree of dispersion is monitored directly by electron microscopy and by analysis of the dielectric response. As with conventional composites, we have found that the critical factors influencing composite performance are the structural quality of the nanofiller and the nature of the filler dispersion.

### SESSION Z5: NANOTUBES FOR FIELD EMISSION

Chairs: Gordon G. Wallace and Karen I. Winey  
Tuesday Afternoon, November 27, 2001  
Back Bay A (Sheraton)

#### 1:30 PM \*Z5.1

RECENT DEVELOPMENTS OF CARBON NANOTUBE FIELD EMISSION DISPLAYS. J.M. Kim, FED Team, CRD, Samsung SDI and Samsung Advanced Institute of Technology, Suwon, KOREA.

Carbon nanotube emitters, prepared by screen printing, have demonstrated a great potential towards low-cost, large-area field emission displays. Carbon nanotube paste, essential to the screen printing technology, was prepared to exhibit low threshold electric fields as well as an emission uniformity over a large area. Two different types of triode structures, normal gate and undergate, have been investigated, leading us to the optimal structure designing. These carbon nanotube FEDs demonstrated color separation and high brightness over 300cd/m<sup>2</sup> at a video-speed operation of moving images. Our recent developments will be presented in details.

#### 2:00 PM Z5.2

FIELD EMISSION OF CARBON NANOTUBES WITH DIFFERENT LENGTHS. Yan Chen, Jhisook Park, Vipul Patel, Nalin Kumor and Bawa Singh, UHV Technologies, Inc., Mount Laurel, NJ.

Field emission data of well-aligned carbon nanotubes with different lengths have been obtained. The aligned carbon nanotubes were synthesized by plasma-assisted hot filament chemical vapor deposition using a gas mixture of nitrogen and methane. The field emission of the carbon nanotubes with the length of 500nm, 1 $\mu$ m, 5 $\mu$ m and 10 $\mu$ m have been measured. The lengths of the nanotubes were controlled by growth time. The results indicate that the emission capability is enhanced with the increase of the length. A theoretical model has been established to explain the experiment results.

#### 2:15 PM Z5.3

CORRELATIONS OF THE MICROSTRUCTURES OF THE CARBON NANOTUBES AND THEIR FIELD EMISSION PROPERTIES. Jun Jiao, Dave Tuggle, Lifeng Dong, Sean Foxley, Portland State Univ, Dept of Physics, Portland, OR.

Carbon nanotubes have drawn much attention as electron field emission sources because of their unique geometry and their remarkable electronic properties. In particular the emission from carbon nanotubes at low applied electric fields has been demonstrated by a number of research groups. However, the field emission behavior reported for nanotubes varies widely, and the proposed emission mechanisms are, therefore, quite different. These variations may be attributed differences in the nanotube content of measured samples.

For instance, some samples contain both single-walled and multi-walled nanotubes. Some nanotubes are well arrayed while some are randomly oriented. The uniformity of the nanotubes such as the diameter distribution and the purity of the nanotubes are also different from one sample to the other. The work reported here aimed at understanding the emission mechanisms of carbon nanotubes by systematic study of the correlation between the microstructures of different carbon nanotubes and their related field emission properties. In this study, the samples of single-walled and multi-walled carbon nanotubes with controlled diameters and aligned orientations are prepared by a chemical vapor deposition method. The field emission properties such as the field emission patterns and the I-V characteristics of each sample are measured. The effect of preparation conditions, such as the type of catalyst, the different hydrocarbon gases, reaction temperatures, and reaction duration on the formation of controlled geometric structures of carbon nanotubes will be discussed. The characteristics of the field emission behavior of each sample with respect to the microstructures of nanotubes will be analyzed.

#### 2:30 PM Z5.4

A MICROTRIODE USING CARBON NANOTUBE FIELD EMITTERS. Chris Bower, Diego Shalom, Wei Zhu, Daniel Lopez, Peter Gammel, Sungho Jin, Agere Systems, Murray Hill, NJ.

Previous studies have indicated that carbon nanotube field emitters can generate large current densities over long periods of time without decay. This ability makes carbon nanotube field emitters ideally suited for application in vacuum microelectronic devices which require current densities in excess of 1 A/cm<sup>2</sup>, such as microwave power amplifiers. Here, we will present our results on designing, fabricating, and testing microtriodes which utilize carbon nanotube cold cathodes. To date, we have observed sustainable current densities in excess of 8 A/cm<sup>2</sup>, and we have tested a microtriode with a DC power gain of 18 dB. We will compare and contrast the performance of this device against other thermionic and field emission triodes.

#### 3:15 PM \*Z5.5

FABRICATION OF CARBON NANOTUBE BASED ELECTRON FIELD EMITTERS AND THEIR POTENTIAL APPLICATIONS. G.Z. Yue, B. Gao, Y. Cheng, Q. Qiu, S.J. Oh, J. Zhang, H. Shimoda, L. Fleming, S. Chang, J.P. Lu and O. Zhou, U. of North Carolina, Chapel Hill, NC.

Carbon nanotubes have attractive electron field emission properties compared to the conventional electron emissive materials such as diamond. They have low threshold fields for emission and are relatively stable at high current densities. Motivated by potential applications in vacuum microelectronic devices, the electron field emission properties of different carbon nanotube materials have been studied in considerable detail in the last few years. In this talk we present results on incorporation of carbon nanotubes into diode and triode type cold-cathode structures. The performances of these cold cathodes will be compared and discussed. In addition, we will present some recent results obtained from carbon nanotube based vacuum microelectronic devices.

This work is supported by an ONR MURI program, Agere Systems, and Applied Nanotechnologies, Inc.

#### 3:45 PM Z5.6

UNIFORM AND SCALABLE FIELD EMISSION USING CARBON NANOTUBE THICK FILM MATERIALS. R.J. Bouchard, L.T.A. Cheng and D.H. Roach, DuPont Central R&D, Wilmington, DE.

A series of thick film materials needed for cathode fabrication of field emission displays have been developed. While any acicular conductor may be used, the preferred active emitter material is carbon nanotubes. The nanotubes can be formulated either as a conventional printable paste or as a photoimaging material. As-printed and fired these materials show poor, nonuniform emission. A scalable and simple process has been used to modify the surface which results in dramatic improvements in current density and light emission. Materials and processes will be discussed. Emission testing in diode and triode modes will also be discussed.

#### 4:00 PM Z5.7

THE ROLE OF ADSORBATES ON THE FIELD EMISSION PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES. Ramon Collazo, Raoul Schlessler, Zlatko Sitar, Dept of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Two field-emission states of single-walled carbon nanotubes were identified according to their respective emission current levels. The state yielding increased emission current was attributed to the presence of adsorbates on the nanotubes as confirmed by electron emission measurements at different background pressures. Application

of high electric fields induced large emission currents and a transition between the two states. During this transition, a current drop to 1/10 of the original value was observed. Under a constant applied electric field, the current took around 1000 s to recover its original level at a background pressure of  $10^{-10}$  Torr, while it took half that time at  $10^{-6}$  Torr. For the high current state, field-emitted electrons originated from states located 1 eV below the Fermi level, as was determined by field-emission energy distribution measurements. This suggested that adsorbates introduced a resonant state on the surface that enhanced the tunneling probability of electrons. The adsorbed states are removed at high applied electric fields, presumably due to thermal effects caused by large emission currents. This adsorption/desorption process is completely reversible.

#### 4:15 PM Z5.8

A STUDY OF FIELD EMISSION PROPERTIES OF POLAR AND NON-POLAR MOLECULE DOPED CARBON NANOTUBES. Youngsik Song, Brian C. Usner, Jaewu Choi, Louisiana State University, Center for Advanced Microstructures and Devices, Baton Rouge, LA; Young-Chul Choi, Samsung SDI, Corporate R&D Center, KOREA; Seung-Chu Lim, Jeonbuk National University, Semiconductor Physics Research Center, KOREA; Young Hee Lee, Sungkyunkwan University, Dept. of Physics, KOREA.

We have studied field emission properties of vertically aligned, multi-walled carbon nanotube films and randomly oriented single-walled carbon nanotube films by exposing both samples to polar (nitrogen dioxide) and non-polar (nitrous oxide) molecules. Because it is attributed that doping with nitrogen dioxide (polar) and nitrous oxide (non-polar) induces the electronic and physical properties of these carbon nanotubes, the turn-on voltage and emission current density were found to depend on the polarity of the doped molecules and the amount of the gas exposed. Specifically, in the case when the carbon nanotube films were doped with the polar nitrogen dioxide gas, a significant change in the turn-on voltage and emission current density was observed. Thus indicating that the polarity of the adsorbate plays an important role in the field emission properties of single-walled and multi-walled carbon nanotubes.

#### 4:30 PM Z5.9

PECVD CARBON NANOTUBES FOR FIELD EMISSION APPLICATIONS. K.B.K. Teo, M. Chhowalla, S.B. Lee, D.G. Hasko, H. Ahmed, G.A.J. Amarantunga and W.I. Milne, Cambridge University, UNITED KINGDOM; G. Pirio, P. Legagneux and D. Pribat, Thales Research and Technology, FRANCE.

PECVD is an extremely versatile technique for directly growing multiwalled carbon nanotubes onto various substrates. We will demonstrate the deposition of vertically aligned nanotube arrays, 'spaghetti' nanotubes, sparsely or densely populated nanotube forests, and precisely patterned arrays of single nanotubes. The high-aspect ratio nanotubes (~30 nm in diameter and 5 microns long) produced are metallic in nature and direct contact electrical measurements reveal that each nanotube has a current carrying capacity of ~1 million amps per square centimetre, making them excellent candidates as field emission sources. We examined the field emission characteristics of dense nanotube forests (aligned and non-aligned) as well as sparse nanotube forests and found that the sparse forests had significantly lower turn-on fields and higher emission currents. This is due to electric field shielding from adjacent nanotubes in the dense nanotube arrays. The maximum macroscopic field emission current achieved is also ~10mA per square centimetre and we believe this is limited by the substrate and the actual number of nanotubes which are emitting. We thus fabricated a uniform array of single nanotubes to attempt to overcome these issues and will present the field emission characteristics of this. The fabrication of a gated microelectronic field emission cathode utilising nanotubes will also be presented.

#### 4:45 PM Z5.10

Abstract Withdrawn.

SESSION Z6: POSTER SESSION  
CHARACTERIZATION, FIELD EMISSION AND  
ELECTRONIC DEVICES  
Tuesday Evening, November 27, 2001  
8:00 PM  
Exhibition Hall D (Hynes)

#### Z6.1

FIELD EMISSION OF CARBON NANOTUBES ON GLASS SUBSTRATE USING THERMAL CHEMICAL VAPOR DEPOSITION. C.W. Seo, J.H. Park, B.D. Min, J.H. Han, Iljin Nanotech Co., Ltd. Nano Technology R&D Center, Seoul, S. KOREA.

Field emitters for flat-panel display or vacuum microelectronic devices

are one of the most promising applications of carbon nanotubes (CNTs). For the applications of the CNTs to the field emitters sealed by soda-lime glass, it is practically important to lower the growth temperature at least 550°C. We will report here the field emission characteristics of CNTs cathode on the glass substrate, which are prepared in the two-stage heating system by the chemical vapor deposition. A Ti film with a thickness of 400 nm is deposited on the glass substrate using the DC sputtering system. Afterwards, catalytic Ni film with a thickness of 30 nm was deposited on the Ti/glass substrate. C<sub>2</sub>H<sub>2</sub> gas was pre-heated in the first zone of the reactor at 850°C and then brought into the second zone maintained at 500°C for the growth of CNTs on the Ni/Ti/glass substrate. The diameters of the CNTs are in the range of 40~60 nm, while their length can be as long as 10 μm. Field emission measurement has been made on the CNTs cathode diode-type device at room temperature and in a vacuum chamber below  $10^{-6}$  torr. The distance between the CNTs cathode and anode is 600 μm, which is kept through an insulating spacer. The dimension of field emission area was 15 mm x 15 mm. The turn-on electric field was 2-3 V/μm at an emission current of 0.1 μA/cm<sup>2</sup> and the uniform emission current of 1.2 mA/cm<sup>2</sup> are measured at 5.0 V/μm. The present results showed that CNTs have the excellent performance as field emitters in actual display devices since 0.1 mA/cm<sup>2</sup> can produce enough brightness (>1000 cd/m<sup>2</sup>) under practical operating conditions.

#### Z6.2

FABRICATION AND ELECTRON FIELD EMISSION PROPERTIES OF ADHERENT SINGLE WALL CARBON NANOTUBE FILMS BY ELECTROPHORETIC DEPOSITION. S.J. Oh, B. Gao, G.Z. Yue, H. Shimoda, L. Fleming, Y. Cheng, Q. Qiu, O. Zhou, University of North Carolina, Chapel Hill, NC.

Carbon nanotubes have been shown to have attractive electron field emission properties for potential industrial applications. Compared with the conventional electron emissive materials, they have a low threshold electrical field for emission and are capable of emitting high currents. Yet their realization in actual devices has been held back due to difficulties in processing and issues such as low emission stability. Here we show that electrophoretic deposition technique can be utilized to deposit pre-form carbon nanotubes on various surfaces and form adherent films. The results show that these films are more stable at high emission current densities than the freestanding single-wall carbon nanotube membranes. The effects of the processing conditions on the electron field emission properties will be discussed.

#### Z6.3

WORK FUNCTION AT THE TIPS OF MULTIWALLED CARBON NANOTUBES. Ruiping Gao, Natl Natural Sci Foundation and Univ of Sci and Tech, Beijing, Beijing, CHINA; Z.W. Pan and Zhong L. Wang, Ctr for Nanoscience and Nanotechnology, School of MS&E, Georgia Inst of Tech, Atlanta, GA .

The unique geometrical structure of carbon nanotubes suggests that they are likely to be an ideal field emitter for panel display application. Indeed, numerous field emission measurements show that the carbon nanotubes exhibit superior field emission performance with required electric field much lower than those of many other field emitters. For carbon nanotube emitters, most of the electrons are emitted from the tips of the tubes, and it is the local work function that matters to the properties of the tube field emission. Since the lack of suitable technical method to measure the work function of carbon nanotubes, the value of work function of carbon nanotubes used in the literatures is mainly from the well-studied carbon or graphite. Thus, it is necessary to experimentally measure the work function of carbon nanotubes. We present experimental measurements of tip work functions of individual carbon nanotubes. The experiment was done by a novel in-situ transmission electron microscopy technique [1,2]. Our results indicate that the tip work function show no significant dependence on the diameter of the nanotubes in the range of 14-55 nm. Majority of the nanotubes (~75%) have a work function of 4.6-4.8 V at the tips, which is 0.2-0.4 V lower than that of carbon. A small fraction of the tubes (~25%) have a work function of ~5.6 V, about 0.6 V higher than that of carbon. This discrepancy is suggested due to the metallic and semiconductive characteristics of the tubes. [1] P. Poncharal, Z.L. Wang, D. Ugarte and W.A. De Heer, Science, 283 (1999) 1513. [2] R.P. Gao, Z.W. Pan, Z.L. Wang, Appl. Phys. Letts., 78 (2001) 1757. [3] The research was supported by National Natural Science Foundation of China and the US NSF.

#### Z6.4

ANTI-LOCALIZATION CAUSED BY SLIGHT DOPING OF HEAVY IMPURITIES INTO ONE END OF CARBON NANOTUBES AND A C-MOS LIKE PHASE-INTERFERENCE

TRANSISTOR. Junji Haruyama, Izumi Takesue and Tetsuro Hasegawa, Aoyama Gakuin University, Tokyo, JAPAN.

Influence of impurity-doping into carbon nanotubes is currently of great interest, particularly in single walled carbon nanotubes and also Fullerenes. In contrast, characteristics of multi-walled carbon nanotubes (MWNTs) have been understood only by phase-interference effects of electron waves. None reported on the influence of impurity-doping on such effects in MWNTs. In this presentation, we report for the first time on anti-localization (AL) caused by slight doping of heavy impurities into only one end of MWNTs and propose a novel phase-interference transistor like C-MOS, based on this effect. We slightly dope impurity-atoms of electrode-materials into top end of MWNTs, standing in nanopores of nanoporous Alumina membranes [1]. Doping of the light-mass materials (Carbon and Aluminum) lead to two-dimensional weak localization (WL) in Altshuler-Aronov-Spivak (AAS) oscillation, consistent with past reports of MWNTs [2]. In contrast, we find that doping of heavy-mass materials (Gold and Platinum) at the volume-ratio of only about #5% drastically change this WL to AL [3]. Using revised Altshuler theory, it is confirmed that spin-orbit interaction in the small doping-region causes spin-flipping of electrons and introduces these electrons into the bulk of MWNTs, leading to AL. We also find that this phenomenon is observable only when electrons are injected through the doping region. This turns out that such a small doping-region acts the important role for polarized injection of spin-flipped electrons into the bulk of MWNTs. Series connection of these two-type MWNTs (i.e., with WL and AL) will promise quantum-wave transistor controllable by magnetic field, like CMOS transistors in semiconductor logic-devices, because they exhibit opposite signs in current-change to magnetic field applied (like P and N type-transistors applied a gate voltage).

[1] J. Haruyama, I. Takesue, et al., Phys.Rev.B 63, 073406 (2001), Appl.Phys.Lett. 77, 2891 (2000).

[2] A. Bachtold, C. Strunk, et al., Nature 397, 673 (1999).

[3] J. Haruyama, I. Takesue, et al., Appl.Phys.Lett. 79(2) July 9 (2001), In press on Phys.Rev.B.

#### Z6.5

FABRICATION OF NANO TRANSISTOR BY SELECTIVELY GROWN CARBON NANOTUBE. Won Bong Choi, Jae Uk Chu, Kwang Seok Jeong, Eun Ju Bae, In Kyeong Yoo, U-team, MD Lab. Samsung Advanced Institute of Technology, Suwon, KOREA; Ju Jin Kim, Jeong-O Lee, Department of Physics, Chonbuk National University.

Carbon nanotube has been proposed as an ideal quantum wire for nanoelectronics. Recent progress in carbon nanotube quantum wire has hinted at the achievement of nanoelectronics given the integration technique is supported. However, neither selective growth of carbon nanotubes nor device integration has been achieved. Here we demonstrate a novel type of carbon nanotube transistor, which would be suitable for large-scale integration. We fabricated highly ordered carbon nanotubes, which are selectively grown in the nanometer range. Each device element is formed on a vertical-carbon nanotube attached to a source and drain electrodes and a gate electrode, which is electrostatically switchable. The metal/nanotube interfaces are modified by annealing and analyzed by TEM and I-V characteristics. In this presentation fabrication technique and switching mechanism of the carbon nanotube transistor will be explained based on the experimental result.

#### Z6.6

MULTIWALLED CARBON NANOTUBES GROWTH BY CATALYTIC PYROLYSIS IN NANO-TEMPLATE AND ITS APPLICATION TO A FIELD EMITTER. Soo-Hwan Jeong, Ok-Joo Lee, Sun-Kyu Hwang and Kun-Hong Lee, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, KOREA; Kwang-Young Kim, Nam-Seok Kang, LG Electronics Inc., Seoul, KOREA.

The growth of carbon nanotubes (CNTs) in anodic aluminum oxide (AAO) template and their application to a field emitter are described. AAO templates were fabricated by anodizing bulk aluminum and sputtered thin Al film on Nb-coated Si wafer. After Co catalyst had been electrochemically deposited into the bottom of the pores in AAO template, CNTs were grown by catalytic chemical vapor deposition of  $C_2H_2$  or CO. Depending on the reaction conditions, CNTs grew up to or over the top of the pores in AAO template with different structures. The dimension and density of CNTs were controlled by reaction conditions and template geometry. The morphology and structure of CNTs were observed with a scanning electron microscope and a transmission electron microscope. The growth of CNTs strongly depended on the size of the pores in AAO template and the growing conditions. In the case of CNTs growth by  $C_2H_2$  pyrolysis, the growth of CNTs in an AAO template is significantly influenced by the presence of  $H_2$ . In all cases, CNTs growth on Co catalyst was

competitive reaction with carbon deposition on the AAO template itself. The electron field emission measurement of the samples resulted in the turn-on field of 1.9-2.2 V/ $\mu m$  and the field enhancement factor of 2450-5200. The observation of high field enhancement factors is explained in terms of low field screening effect.

#### Z6.7

SINGLE-WALL CARBON NANOTUBE ELECTRON EMITTERS PRODUCED BY ELECTROPHORESIS. E.D. Obraztsova, A.S. Pozharov, S.V. Terekhov, A.V. Osadchy, S.M. Pimenov, V.I. Konov, Natural Sciences Center of General Physics Inst., RAS, Moscow, RUSSIA; T.A. Skaballanovich, S.R. Ivanova, General Physics Inst., RAS, Moscow, RUSSIA; A.P. Volkov, A.N. Obraztsov, Physics Department of Moscow State University, RUSSIA.

Single-wall carbon nanotubes (SWNT) find one of the most promising technological applications in a vacuum electronics: the nanotube films could serve as cathodes for new light sources and flat panel displays. Nowadays the main problem here is to find a process providing a stable and homogeneous nanotube film formation. In our work a liquid electrophoresis process has been used for this purpose. SWNT were synthesized in arc. Ni:Y catalyst was used. The raw material was enriched with the tubes via a three-step chemical purification: boiling in  $HNO_3$ , rinsing and annealing at 550°C in an oxygen-containing atmosphere. As a result the nanotube content has increased from 15 to 70 weight %. Raman and HRTEM techniques were used for the material diagnostics. An electrophoretic deposition of the nanotube films has been performed in an ethanol solution of  $LaNO_3$ . An optimization of the process parameters has allowed to deposit the homogeneous thin SWNT films on different substrates: silicon, steel, nickel, metallized glass. The emission characteristics of the SWNT films have been measured. The emission threshold appeared to be quite low - about 1 V/ $\mu m$ . Under the voltage 10 V/ $\mu m$  the current was about 5 mA/cm<sup>2</sup>. A spatial distribution of the emission centers and its temporal evolution (almost negligible) were visualized on a phosphorescent screen. The deposition on a strip-patterned substrate has been performed. A prototype of the lamp with a nanotube cathode has been designed.

The work is supported by ISTC-1400 project and (in part) by grants INTAS-1700 and 7SUPJ062400.

#### Z6.8

LARGE-AREA DEPOSITION OF CARBON NANOTUBES FOR FIELD EMISSION DISPLAYS. Y.J. Park<sup>a,b</sup>, I.T. Han<sup>a,d</sup>, H.J. Kim<sup>a</sup>, Y.S. Woo<sup>a</sup>, N.S. Lee<sup>a</sup>, Y.W. Jin<sup>a,c</sup>, J.E. Jung<sup>a,c</sup>, C.Y. Park<sup>b</sup>, J.M. Kim<sup>a</sup>. <sup>a</sup>Samsung Advanced Institute of Technology, FED project, Suwon, KOREA. <sup>b</sup>Sungkyunkwan Univ., Dept. of Vacuum Science and Technology, Suwon, KOREA. <sup>c</sup>Sungkyunkwan Univ., Dept. of Materials Engineering, Suwon, KOREA. <sup>d</sup>Seoul National Univ., Dept. of Chemistry, Seoul, KOREA.

Carbon nanotubes have attracted much attention as a promising candidate for field emitters due to their superior properties such as chemical inertness as well as low threshold electric fields for electron emission. A direct synthesis of carbon nanotubes on substrates by chemical vapor deposition is one of highly probable routes to reach their application to field emission displays. Several stringent requirements are prerequisite for this purpose, including low temperature growth below 600°C to use glass substrates and large area deposition for practical use. This study carried out synthesis of carbon nanotubes by chemical vapor deposition on large area glass substrates with an A4 paper size (297 × 210 mm<sup>2</sup>) at temperatures as low as 550-600°C. Carbon nanotubes were grown by thermal decomposing of CO and H<sub>2</sub> gases at an atmospheric pressure. A Ni-Fe-Co alloy was used for a catalyst layer. Preparation of catalyst alloys had a strong effect upon the growth of carbon nanotubes. Their correlation was investigated by X-ray diffraction, field emission Auger electron spectroscopy, scanning electron microscopy, transmission electron microscopy, etc. The catalyst films with better crystallinity are suitable for the growth of carbon nanotubes. The respective role of each elemental metals of the catalyst alloys on nanotube growth morphologies, their diameters, and diffusion of carbon atoms, were studied. Their field emission characteristics are discussed in detail as well.

#### Z6.9

PRODUCTION AND CHARACTERIZATION OF MoSe<sub>2</sub> NANOTUBES BY ELECTRON IRRADIATION. D.H. Galvan, Centro de Ciencias de la Materia Condensada-UNAM, Ensenada, B.C., MEXICO; R. Rangel, Escuela de Ingenieria Quimica, Universidad Michoacana de S.N.H. Ciudad Universitaria, Morelia, Michoacan, MEXICO; E. Adem, Instituto de Fisica-UNAM, Mexico DF, MEXICO.

In this work, we report the formation of nanotube structures in MoSe<sub>2</sub> also known as Drysdallite. The initial samples were obtained from commercial powders (Alfa-Aesar 99.9% pure) of MoSe<sub>2</sub>. Afterwards,

the material was irradiated with electrons on a 2 MeV Van de Graff accelerator. The irradiation conditions were the following: 1.3 MeV voltage, 5 micro A current, dosage rate 25 Kgy/min, total dosage 1 Mgy. The dosimeter used was radiochromic films (FWT-60). X-ray analyses were performed in a Philips XRD/X'PERT system using Cu K $\alpha$  radiation at 40 KV voltage and 45 mA current. For transmission Electron Microscopy (TEM) observations, samples were ground in an agate mortar and placed on carbon coated copper grids. The microscope used was a JEOL JEM-2010 with a point to point resolution better than 0.19 nm. We found nanotubes of different sizes, onion-like structures of different sizes and shapes of MoSe<sub>2</sub> by electron irradiation.

#### Z6.10

Abstract Withdrawn.

#### Z6.11

Abstract Withdrawn.

#### Z6.12

Abstract Withdrawn.

#### Z6.13

THERMOGRAVIMETRIC ANALYSES OF C<sub>60</sub> INCORPORATED INTO SINGLE-WALL CARBON NANOTUBES (PEAPODS).

Masako Yudasaka, Minfang Zhang, Yohko Kasuya, ICORP, Japan Science and Technology Corporation, Tsukuba, JAPAN; Shunji Bandow, Meijo Univ., Nagoya, JAPAN; Sumio Iijima, Meijo Univ., Japan Science and Technology Corporation, NEC, Tsukuba, JAPAN.

Molecules of C<sub>60</sub> are easily incorporated into single-wall carbon nanotubes (SWNTs), and they are well stabilized so they do not escape even when heat treated at high temperatures in vacuum. When these so-called peapods are heat treated at 1270 K, the C<sub>60</sub> molecules coalesce, instead of escaping from the SWNT, and form another SWNT inside the sheath SWNT, resulting in double-wall carbon nanotubes. Thus it is apparent that the interaction between C<sub>60</sub> and SWNT is not weak. However, the stability of the peapods itself is not well known. To clarify the chemical stability of peapods, we performed thermogravimetric analyses (TGA) in oxygen gas. SWNTs produced by laser ablation were treated with nitric acid and oxygen gas, and C<sub>60</sub> was incorporated into SWNTs in the gas phase at 670 K. TGA showed that the burning temperature of SWNTs and peapods differed slightly. However, when SWNTs were heat treated at 670 K prior to C<sub>60</sub> incorporation, the obtained peapods burned at 1020 K, which is 100 K lower than heat-treated SWNTs did. These results suggest that C<sub>60</sub> interacted so well with SWNTs that the burning temperature was influenced strongly by defects in the SWNTs.

#### Z6.14

PROPERTIES OF RAGGED SINGLE-WALL CARBON NANOTUBES INDUCED BY ULTRASONICATION. Akira Koshio, Masako Yudasaka, Minfang Zhang, Nanotubulites Project, International Cooperative Research Project, Japan Science and Technology Corporation, Tsukuba, JAPAN; Sumio Iijima, Department of Physics, Meijo University, ICORP-JST, NEC, Nagoya, JAPAN.

Ultrasonication of single-wall carbon nanotubes (SWNTs) in organic liquids enabled us to react SWNTs with organic materials chemically. The modified SWNTs turned into ragged SWNTs (r-SWNTs) with many defects in the sidewall when burned in oxygen. The FT-IR spectra indicated that SWNTs reacted chemically with MCB and PMMA after ultrasonication. For the SWNTs/MCB reactant, three peaks were observed. The peak at 1729 cm<sup>-1</sup> corresponds to a C=C double bond or the C=O bond in carbonyl groups. The other two peaks, at 2848 and 2920 cm<sup>-1</sup>, correspond to the stretching mode of C-H bond vibration in saturated hydrocarbons. Ultrasound cut and decomposes SWNTs and organic molecules, and form defects in the sidewalls and reactive species. The reactive species reacted with SWNTs easily on the sidewalls and at the open-ends. For the SWNTs/PMMA/MCB reactant, two additional peaks were observed, at 2949 and 2989 cm<sup>-1</sup>. We think that the sonochemical reaction of SWNTs and organic materials is a simple method to functionalize SWNTs. R-SWNTs have some interesting properties, unlike normal SWNTs. They were degraded at and above 800°C in a vacuum (10<sup>-7</sup> Torr), and disappeared after heat-treatment at 1200°C for 1 h. We suggest that the holes and defects in the r-SWNTs were formed by oxidation of chemically damaged sites formed during the ultrasonication in organic liquids. We will report analysis of fragments of r-SWNTs by mass spectrometry. Shortened and disentangled r-SWNTs are well dispersed in a solution, however, they cohered as bundles due to the strong cohesion between them. The r-SWNTs were added to single-wall carbon nanohorns (SWNHs) homogeneously dispersed. As the result, they entangled and precipitated SWNHs rapidly (about one minute).

#### Z6.15

CHARGE DENSITY MODULATIONS ON CARBON NANOTUBES AT ROOM TEMPERATURE. Abdou Hassanien, Nanotech Research Institute, AIST, Tsukuba, JAPAN.

We report on the structure and electronic properties of single wall carbon nanotubes tips with atomically spatial resolution. Scanning tunneling microscopy shows topographic images of closed tips with a variety of geometrical structure; these include round, conical, as well as tips with a messy shape. Standing wave pattern of the charge density is observed at the tube cap which is formed due to constructive interference between the electronic states and its reflection on the nanotube tips. Atomically resolved images show asymmetry in the charge density that decay out within 6 nm away from the cap. These distinctive tip states do not exist elsewhere on the tube and are related to the presence of topological defects at tube ends.

#### Z6.16

MAGNETIC ANISOTROPY OF CERIUM ENDOHEDRAL METALLOFULLERENE. Masayasu Inakuma, Toshiaki Enoki, Tokyo Institute of Technology, Dept of Chemistry, Tokyo, JAPAN; Haruhito Kato, Hisanori Shinohara, Nagoya Univ, Dept of Chemistry, Nagoya, JAPAN.

The magnetic properties of Ce@C<sub>82</sub> metallofullerene have been studied. Cerium (Ce) ion, encapsulated in the metallofullerene, has a large magnetic anisotropy. Metallofullerenes have a ball-shaped spherical cage structure, the interior of which a metal atom is incorporated. The Ce@C<sub>82</sub> metallofullerene therefore has a potential to be characteristic magnetic material as a molecule magnet. The correlation of the motion with the magnetization of a molecule magnet has been attractive subject. The magnetic susceptibility of Ce@C<sub>82</sub> from 2 to 300 K was measured as the solutions with several solvents (carbon disulfide (CS<sub>2</sub>), ether, xylene, naphthalene) and the dried-up films from some solutions. The magnetization of some frozen Ce@C<sub>82</sub> solutions was found to depend on the applied field magnitude. The dependence suggests that the applied field restricts the rotational motion due to the magnetic anisotropy of Ce@C<sub>82</sub>. This result shows that the easy axis for the magnetization of Ce@C<sub>82</sub> is caused by the magnetic anisotropy of Ce ion stuck in the metallofullerene. Scanning tunneling microscopy (STM) in the magnetic field for Ce@C<sub>82</sub> evaporated on substrates is also observed. We discuss and demonstrate the correlation of the rotation with the magnetic anisotropy of Ce@C<sub>82</sub> metallofullerene.

#### Z6.17

DOUBLE RESONANT RAMAN EFFECT IN ISOLATED SINGLE-WALL CARBON NANOTUBES: SECOND-ORDER G' BAND. A.G. Souza Filho, A. Jorio, G. Dresselhaus, M.S. Dresselhaus, Massachusetts Institute of Technology, Cambridge MA; Anna K. Swan, M.S. Unlu, B.B. Goldberg, Boston University, Boston, MA; J.H. Hafner, C.M. Lieber, Harvard University, Cambridge, MA; R. Saito, University of Electro-Commun., Tokyo, JAPAN, M.A. Pimenta, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL.

We report the resonant second-order G'-band Raman spectra for isolated single-wall carbon nanotubes (SWNTs). The G' band is used to study a new kind of double resonance phenomenon observable only in SWNTs owing to the one-dimensional density of electronic states and the dispersive behavior of the second-order G'-band. By combining these two characteristics, the G' band for some SWNTs consists of two peaks that arise when both the incident and scattered photons are each resonant with different van Hove singularities in the joint density of states. We show how the G'-band profile can be used to get not only electronic but also structural (n, m) information about the SWNT in resonance with E<sub>laser</sub>. An analysis of the single nanotube spectra allows us also to gain further understanding of the second-order G'-band for SWNT bundles.

#### Z6.18

TRANSFORMATION OF MULTIWALLED CARBON NANOTUBES INTO STRINGS OF CARBON NANOSHELLS. B. Sahanadan, J. Gaillard, T. Savage, S. Bhattacharya, T.M. Tritt, A.M. Rao, Clemson Univ., Dept of Physics & Astronomy, Clemson, SC; Alan Cassell, D. Srivatsava, NASA Ames, Moffett Field, CA; Z.R. Dai, Z.L. Wang, Center for Nanoscience and Nanotechnology, School of Mat. Sci. and Eng., Georgia Inst. of Tech., Atlanta, GA; J.M. Cowley, Dept. of Physics & Astronomy, Arizona State Univ., Tempe, AZ.

Previously, we have shown that high purity multiwalled carbon nanotubes can be prepared from a mixture of xylene-ferrocene (99 at% C : 1 at% Fe) inside a quartz tube reactor at ~700 degrees C [1]. In a series of identical runs, 0.5, 1, 2, 3 and 4 grams of melamine were introduced during the growth of MWNTs from the decomposition of the xylene-ferrocene mixtures. The changes in the morphology of the MWNT products were monitored using SEM, high resolution TEM,

and EELS measurements. As increased amounts of melamine were introduced into the reactor, individual multi-walled tubes with ~50-60 walls transformed into a string of nanoshells comprising of 3-5 walls as evidenced by HRTEM studies. For all melamine concentrations used in the experiments, the purity of the products remained high. From the EELS measurements, we estimate an average nitrogen content of ~5 at% in the transformed MWNTs (or the strings of carbon nanoshells). The MWNTs with parallel graphitic walls has no detectable nitrogen content.

[1] R. Andrews et al., Chem. Phys. Lett., 303, 467 (1999).

#### Z6.19

**G-BAND RAMAN SPECTRA OF ISOLATED SINGLE WALL CARBON NANOTUBES: DIAMETER AND CHIRALITY DEPENDENCE.** Ado Jorio, Antonio G.Souza Filho, Gene Dresselhaus, Mildred S. Dresselhaus, MIT, Cambridge, MA; Anna K. Swan, M.S. Unlü, B.B. Goldberg, Boston University, Boston, MA; Marcos A. Pimenta, Univ. Federal de Minas Gerais, Belo Horizonte, MG, BRAZIL; Jason H. Hafner, Charles M. Lieber, Harvard University, Cambridge, MA; Riiichiro Saito, Univ. of Electro-Communications, Tokyo, JAPAN.

The radial breathing mode (RBM) and the tangential mode vibrations (forming the so-called *G* band) are the two main features in the Raman spectra of single wall carbon nanotubes (SWNTs), with the resonant Raman spectra of the RBM providing the (*n*, *m*) indices for an isolated SWNT [A. Jorio et al., Phys. Rev. Letters **86**, 1118 (2001)]. The *G* band is a more complex spectral feature. Due to the folding of the graphite Brillouin zone into the SWNT zone, and to the symmetry-breaking associated with the nanotube curvature, the  $E_{2g2}$  peak in the Raman spectra of graphite splits into several modes with different symmetries in the Raman spectra of SWNTs. In the case of metallic SWNTs, phonon-plasmon coupling changes the line shape of the *G*-band Raman feature. We studied the *G*-band resonant Raman spectra of isolated SWNTs prepared by the CVD method on a Si/SiO<sub>2</sub> substrate. From the radial breathing mode spectra we assign the (*n*, *m*) structural indices for the different (*n*, *m*) SWNTs, and can thus obtain the *G*-band lineshape dependence on nanotube diameter and chirality, for both semiconducting and metallic tubes. The most intense peak appears around 1591/ $\text{cm}^{-1}$  for both semiconducting and metallic SWNTs, independent of diameter and chirality. The frequency for the second most intense peak is given by  $\omega = 1591 - C/d_t^2$ , with  $C = 45.8/\text{cm}^{-1}\text{nm}^2$  for semiconducting SWNTs and  $C = 79.5/\text{cm}^{-1}\text{nm}^2$  for metallic SWNTs. Metallic SWNTs also exhibit a peak at 1580/ $\text{cm}^{-1}$ . The relative intensity of the *G*-band modes is found to be different from tube to tube, reflecting a chirality and polarization dependence. We discuss results for SWNT bundles based on isolated nanotube results.

#### Z6.20

**STRUCTURE AND PROPERTIES OF C<sub>60</sub>@SWNT.** Brian W. Smith, Richard M. Russo, B.C. Satishkumar, Ferenc Stercel, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

Our recent achievement of high-yield C<sub>60</sub>@SWNT synthesis facilitates characterization by various techniques, including selected area electron diffraction (SAD) and Raman spectroscopy. The obtained SAD patterns show that the interior C<sub>60</sub> molecules sit on a simple 1-D lattice having a parameter of 0.976 nm. Simulated SAD patterns and real-space measurements both support this determination and do not indicate a lattice with a more complex basis, e.g. a dimer basis. Some evidence is found for variable C<sub>60</sub>-C<sub>60</sub> separations. Empty and bulk-filled SWNTs (22%, 56%, and 90% yields) subjected to identical processing steps were examined by room temperature Raman spectroscopy. Systematic differences are seen between the spectra of filled and unfilled SWNTs, particularly with respect to the *G*- and RBM-bands of the nanotubes. We present a possible explanation for this behavior.

#### Z6.21

**ENCAPSULATION OF AN ISOSTRUCTURAL METALLOFULLERENE SERIES: Er<sub>x</sub>Sc<sub>3-x</sub>N@C<sub>80</sub>@SWNT (x=1-3).** Richard M. Russo, Brian W. Smith, B.C. Satishkumar, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

The future application of single-wall carbon nanotubes (SWNTs) depends on the ability to modify their intrinsic properties by manipulating their structure or microstructure. A unique advantage of nanotubular structures is the ability to modify their function through the filling of their lumens. We have encapsulated a number of fullerenes inside SWNTs including C<sub>60</sub> as well as other higher order fullerenes and metallofullerenes such as La<sub>2</sub>@C<sub>80</sub>. One of the potentially important goals of these systems is to find an isostructural series in which properties can be modified by chemical substitution. We have found such a system in Er<sub>x</sub>Sc<sub>3-x</sub>N@C<sub>80</sub> (x = 1-3). The

structural properties of this system have been studied using high resolution transmission electron microscopy and electron diffraction. It is found that the encapsulated fullerenes self-assemble into long, one-dimensional chains with the same periodic spacing. Several interesting observations indicate that the surrounding nanotubes can have a profound effect on the stability and chemistry of encapsulated molecules. For example, some of the encapsulated fullerene molecules remain stable at temperatures above the point at which they would decompose under non-confined conditions. At temperatures which chemical reactions such as molecular coalescence occur, the nanotube templates the final product through steric confinement. The thermal stability of these supramolecular assemblies are studied and large variations are found. The behavior is nominally consistent with the mass of the encapsulated metallofullerenes.

#### Z6.22

**THERMODYNAMIC ANALYSIS OF CARBON NUCLEATION ON METAL SURFACE.** Vladimir L. Kuznetsov, Anna N. Usoltseva, Andrew L. Chuvilin, Borekov Institute of Catalysis, Novosibirsk, RUSSIA; Elena D. Obraztsova, Institute of General Physics, Moscow, RUSSIA; Jean-Marc Bonard, Institut de Physique Experimentale, Lausanne, SWITZERLAND.

An understanding of the formation mechanism on nanotubes is crucial to design techniques for the controlled growth of pure nanotube material. Here we present a thermodynamic analysis of graphite-like carbon nucleation process on the metal surface. We have considered the mechanisms of catalytic formation of different carbon deposits, such as carbon fibers, multi- and single-wall carbon nanotubes. This consideration led us to conclusion that majority of these mechanisms include some common steps. The most important of them is the step of nucleation of carbon deposit on the metal surface. We suggest that the nucleation conditions and thus the critical size of carbon nucleus determine the type of forming carbon deposit. On the base of experimental and literature data we have proposed that carbon nucleus has the form of flat saucer with the edges bonded to the metal surface. The consideration of variation in Gibbs free energy provides us a functional dependence between the critical radius of the carbon nucleus and reaction parameters such as reaction temperature, carbon content in a metal-carbon particle and parameters which characterize the nature of metal catalyst. Analyzing the functional dependence of critical radius we can conclude that: a) an increase of the reaction temperature leads to the formation of smaller nuclei and finally to the formation of single-wall nanotubes; b) the use of metals, which characterized by a higher metal-carbon energy bond, yields nanotubes with smaller diameters; c) single-wall nanotubes growth is likely to proceed on liquid metal particles. d) elements that decrease the melting point of the catalyst-carbon mixture and do not form stable compounds with carbon at the reaction temperature promote also the formation of single-wall nanotubes.

This work was supported by INTAS grant 97-1700.

#### Z6.23

**FILLING SINGLE WALLED CARBON NANOTUBES WITH METAL NANOWIRES AND MOLECULAR SPECIES.** B.C. Satishkumar, Richard M. Russo, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

Single walled carbon nanotubes (SWNTs) have hollow channels of 1.4 nm diameter and can be filled with various materials like metals and metal chlorides, fullerenes and metallofullerenes, rare earth halides etc. The present exploration involves filling with crystalline and molecular systems. The nanometer dimensions of carbon nanotubes offer an ideal template to synthesize one-dimensional (1D) nanowires and study the size specific properties of various material systems. Nanowires of magnetic metals (eg. Ho, Fe, Co etc.) have been synthesized by the sealed-tube reaction and solution phase method involving the metal chlorides and SWNTs. The nanowires have been imaged using high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). The STEM imaging complements the HRTEM imaging in terms of the Z-contrast mechanism wherein the image contrast is solely decided by the scattering cross section, which is proportional to Z<sup>2</sup>. The properties of the nanowires have been studied by carrying out magnetic measurements. Several molecular species have been investigated to determine whether they fill the interior of the SWNTs by the vapor or liquid phase filling process and have been characterized using HRTEM and STEM imaging as well as electron energy loss spectroscopy (EELS). The interaction of SWNTs with molecular materials such as the porphyrins has also been studied and will be reported.

#### Z6.24

**RAMAN EXCITATION PROFILES IN CARBON NANOTUBES.** M. Canonico, J. Menéndez, Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ; H.P. van der Meulen, J.M. Calleja, J.

Rubio, Dept. de Física de Materiales, Universidad Autónoma de Madrid, SPAIN, J. Gaillard, K. McGuire, and A.M. Rao, Dept. of Physics and Astronomy, Clemson University, Clemson, SC.

Raman excitation profiles (the laser photon energy dependence of the Raman intensity) for the radial breathing mode of many carbon nanotubes have been measured using tunable dye lasers. The experiments were performed at helium and at room temperature and as function of an applied magnetic field of up to 12 T. From these measurements it is possible to determine optical transition energies in nanotubes with a precision comparable to that of the phonon frequency. The results provide the most stringent test of the predicted electronic structure of the tubes. We also discuss the effect of chirality and bundling on the Raman excitation profiles.

#### Z6.25

STUDY OF THE RAMAN D-BAND IN ISOLATED SINGLE-WALL CARBON NANOTUBES. M.A. Pimenta, Departamento de Física, Universidade Federal de Minas Gerais, BRAZIL; A. Jorio, S.D.M. Brown, A.G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, Department of Physics, MIT, Cambridge, MA; J.H. Hafner, C.M. Lieber, Department of Chemistry, Harvard University, Cambridge, MA; R. Saito, Department of Electronic-Engineering, University of Electro-Communications, Tokyo, JAPAN.

Raman D-band spectra are reported for several different isolated SWNTs using different laser energies. At a fixed laser excitation energy  $E_{laser}$ , the different isolated SWNTs actually exhibit different D-band frequencies ( $\omega_D$ ). However, the mean value of  $\omega_D$  for isolated SWNTs depends on  $E_{laser}$ , similar to the general case of  $sp^2$  carbon materials, and this mean value of  $\omega_D$  obeys the same dependence  $\bar{\omega}_D(E_{laser})$  that is observed for SWNT bundles. The observed  $E_{laser}$  dependence of  $\omega_D$  and the corresponding D-band intensity  $I_D$  for isolated tubes suggests that the associated phonons are not at the center of the 1D SWNT Brillouin zone (BZ), and each different laser energy probes different SWNTs and phonons with different wavevectors within the interior of this 1D BZ, similarly to  $sp^2$  carbons. These phonons become Raman-active due to the finite size of the SWNTs or to the presence of defects, which break the translational symmetry along the nanotube axis, explaining the fact that  $I_D$  appears to be random from one nanotube to another. By comparing the Raman spectra of the D-band with that of the tangential G-band for different SWNTs probed with a given  $E_{laser}$ , it is shown that  $\omega_D$  decreases with decreasing nanotube diameter  $d_t$  for both semiconducting and metallic tubes. Moreover, we observed that  $\omega_D$  for metallic SWNTs is in general higher than  $\omega_D$  for semiconducting SWNTs at the same  $E_{laser}$  value. Finally, we argue that the anomalous  $\omega_D(E_{laser})$  plateau behavior observed for SWNT bundles can be explained by considering the diameter dependence of  $\omega_D$  for isolated SWNTs and the resonant nature of the Raman process.

#### Z6.26

OPTICAL LIMITING CHARACTERISTICS OF PURE, B-, AND N-DOPED MULTI-WALLED CARBON NANOTUBES. J.-F. Xu, R. Czerw, D.L. Carroll, Dept. of Physics, Clemson Univ., Clemson, SC; M. Terrones, N. Grobert, M. Reyes-Reyes, Fullerene Science Center, CPES, Univ. of Sussex, Brighton, UNITED KINGDOM; H. Terrones, IPICYT, San Luis Potosí, SLP, México; P.M. Ajayan, Dept of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Optical limiting characteristics of pure, B-, and N-doped, multi-walled carbon nanotube suspensions are compared. The non-linear measurements were made with 8 ns pulses for the 532 nm and 1064 nm lines of a Nd: YAG laser using an f/65 optical system. The onset of non-linearity was observed to occur at a lower fluence in the doped carbon nanotube suspensions than in the pure carbon tubes case. Further, the doped nanotube materials exhibit a stronger overall nonlinear response with fluence than pure carbon tube suspensions, carbon black suspensions (CBS), and nanocarbon suspensions (NCS). These results suggest that the limiting mechanisms are quite sensitive to the electronic effects of the dopant on the nanotube.

#### Z6.27

A NEW CLASS OF CARBON NANO-CONES. Svetlana Dimovski, Yury Gogotsi, Drexel Univ, Dept of Materials Engineering; Joseph Libera, Northwestern Univ, Dept of Materials Science and Engineering, Evanston, IL.

A new class of low-angle conical carbon structures has been discovered. These nano-cones were first found in pores of glassy carbon along with cylindrical nanotubes and graphite polyhedral crystals (giant polyhedral nanotubes). While cylindrical nanotubes become polygonized when their diameter exceeds a certain critical value, no polygonization of the cones has been observed even for the largest diameters. Basically, the crystals are conical carbon nanotubes

with thick graphite walls and semispherical tips. Besides the perfect structure, these graphite cones differ from any carbon cones observed earlier by a much smaller apex angle, sometimes less than 3 degrees. The largest cones reach to 2-3 microns in length, although most of them are in the sub-micrometer range. Transmission electron microscopy (TEM) and selected area electron diffraction show well-ordered graphite walls. Preliminary results show a high electrical conductivity, strength, and chemical stability of these crystals. Large-scale synthesis of nano-cones and their potential application as tips for scanning probe microscopes or electron emitters are discussed.

#### Z6.28

Abstract Withdrawn.

#### SESSION Z7: CHARACTERIZATION OF NANOTUBE SYSTEMS (LIMITS AND CHALLENGES)

Chairs: Elena D. Obraztsova and Marcos A. Pimenta  
Wednesday Morning, November 28, 2001  
Back Bay A (Sheraton)

#### 8:30 AM \*Z7.1

RAMAN SPECTRA FOR ONE CARBON NANOTUBE.

M.S. Dresselhaus, MIT, MA; R. Saito, U. Electro-Comm, TOKYO; A. Jorio, MIT, MA; A.G. Souza Filho, MIT, MA; M.A. Pimenta, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL; G. Dresselhaus, MIT, MA.

A brief review is presented of the new science connected with the phonon spectra of single wall carbon nanotubes (SWNTs) as observed by Raman spectroscopy, and the information about carbon nanotubes provided by Raman spectroscopy. The very sharp one-dimensional density of electronic states in small diameter SWNTs and the strong electron-phonon coupling allow observation of the Raman spectra from one isolated SWNT when the incident and/or scattered photon is in resonance with an interband transition  $E_{ii}$  between van Hove singularities in the density of states between the nanotube valence and conduction bands. Observation of the Raman spectra of the radial breathing mode from one isolated SWNT is used to provide a definitive identification of its structure through determination of the nanotube ( $n, m$ ) indices. Variations of this basic concept for different situations for semiconducting and metallic nanotubes are discussed. This information is further used to determine to high resolution the profile of the joint density of states near a van Hove singularity. Because of the high sensitivity of the electronic, transport, vibrational and other nanotube properties to the structural ( $n, m$ ) indices, this non-destructive, readily available characterization technique is expected to have a significant impact on current basic research on carbon nanotubes. Examples of spectra and polarization effects in SWNTs are reviewed briefly.

#### 9:00 AM \*Z7.2

INTERACTIONS IN CARBON NANOTUBES AND POLYMER/NANOTUBES COMPOSITES AS EVIDENCED BY RAMAN SPECTROSCOPY. Serge Lefrant, J.-P. Buisson, O.

Chauvet, J.-M. Benoit, IMN, Univ. Nantes, FRANCE; M. Baibarac, I. Baltog, Nat. Inst. of Materials, Bucharest, ROMANIA; P. Bernier, GDPC, Univ. Montpellier II, FRANCE.

Carbon nanotubes systems have revealed large potentialities in terms of applications, especially at a nanometric scale. As a consequence, the different interactions which can take place can be of primary importance. In this paper, we report studies carried out on different carbon nanotubes systems such as SWNTs, MWNTs and polymer/nanotubes composites. By using Raman spectroscopy via the RBM and TM, apart from the expected interactions between tubes in bundles which have initiated experiments on individual entities, we put in evidence strong chemical reactions at the interface metal/nanotubes whenever Ag or Au surfaces are used to carry out SERS experiments. We show in particular that a different behavior is observed for metallic and semiconducting tubes. Also, a high state of disorder is observed, together with the transformation of nanotubes to other carbon compounds. In the case of MWNTs, theoretical calculations allow us to interpret the low frequency Raman modes by introducing interactions in concentric tubes, in rather good agreement with experiments. Finally, in polymer/nanotubes composites, an upshift of the RBM is observed and we show in this case that it originates from the dynamical stress applied by the polymer on the bundles in response to the breathing vibration.

This work has been carried out in the frame of the EEC programme COMELCAN, HPRN-CT-2000-00128.

#### 9:30 AM Z7.3

ORIENTATION DEPENDENCE RAMAN STUDY OF VERTICALLY ALIGNED CARBON NANOTUBES. D. Roy\*, M.

Chhowalla, N. Sano, T.W. Clyne\* and G.A.J. Amaratunga, University of Cambridge, Engineering Department, Cambridge, UNITED KINGDOM. \*Department of Materials Science and Metallurgy.

Aligned carbon nanotubes (ACNTs) grown by direct current plasma enhanced chemical vapor deposition (DC PECVD) using acetylene and ammonia are of technological significance for microelectronics. The advantage of PECVD is that it is a controllable and deterministic catalytic growth process. That is, the growth location of the nanotube is precisely determined by the location of the catalyst on the substrate. Raman spectroscopy was used to determine the structural characteristics of the aligned nanotubes as well as the degree of alignment. The Raman spectra obtained from ACNTs were compared with numerous other forms of carbon. In our case, the G band intensity was found to be dependent on the orientation of the tubes with reference to the polarisation of the incident light in VV configuration as reported for MWNT by Rao et al [1]. The observed variation of G band intensity for MWNT is different from that reported for SWNT. This is attributed to the difference in absorption characteristics of polarised light between MWNT and SWNT due to difference in their depolarisation effects. Also, such dependence was not observed in carbon fibers. Therefore, this technique can be used as a non-destructive 'acid' test for determining the degree of alignment as well as confirming the tubular nature of PECVD nanotubes.

Reference:

(1) Polarised Raman Study of Aligned Multiwalled Carbon Nanotubes; A.M. Rao, A. Jorio, M.A. Pimenta, M.S.S. Dantas, R. Saito, G. Dresselhaus, M.S. Dresselhaus; *Phy. Rev. Lett.* Vol. 84, No. 8 (2000).

#### 9:45 AM Z7.4

ELECTRICAL AND THERMAL PROPERTIES OF SINGLE WALL CARBON NANOTUBE FIBERS. Juraj Vavro, Marc C. Llaguno, Michael Biercuk, Alan T. Johnson, John E. Fischer, Univ of Pennsylvania, PA; Philippe Poulin, CRPP Bordeaux, FRANCE; Ray Baughman, Honeywell International, NJ.

We measured the electrical and thermal properties of single wall carbon nanotube (SWNT) fibers prepared using a recently developed technique [B. Vigolo *et al.*, *Science* 290, 1331 (2000)]. Non-metallic behavior from 1.4 to 300 K has been observed from the resistivity measurements. Heat treatment at 400°C results in a decrease of resistivity by as much as three orders of magnitude. Further studies on heat treatment will be reported. The room temperature thermal conductivity ranges from 15 to 70 W/m-K in different samples. These values lie between those of bulk unoriented mats (10 W/m-K) and magnetically-aligned SWNT films (250 W/m-K). This result indicates that some alignment of the tubes occurs during fiber formation. The thermoelectric power resembles that of SWNT mats: positive and moderately large (~40  $\mu$ V/K) at room temperature.

#### 10:30 AM Z7.5

STRUCTURAL CHANGES IN SINGLE-WALL CARBON NANOTUBES BUNDLES UNDER PRESSURE. Stéphane Rols,

Intense Pulsed Neutron Source/Spallation Neutron Source Argonne National Laboratory and Roupe de Dynamique des Phases Condensées (UMR CNRS 5581), Université Montpellier II, Montpellier Cedex 5, FRANCE; Jean-Louis Sauvajol, R. Almairac, Groupe de Dynamique des Phases Condensées (UMR CNRS 5581), Université Montpellier II, Montpellier Cedex 5, FRANCE; Igor Gontcharenko, Russian Research Center "Kurchatov Institut", Moscow, RUSSIA and Laboratoire Léon Brillouin (CEA/CNRS), CE Saclay, Gif-sur-Yvette Cedex, FRANCE; Isabelle Mirebeau, Laboratoire Léon Brillouin (CEA/CNRS), CE Saclay, Gif-sur-Yvette Cedex, FRANCE.

The pressure-induced structural changes of single-wall carbon nanotubes organised into 2D crystalline bundles are studied by neutron diffraction up to ~50 kbars. The pressure dependence of the position of the (10) Bragg peak is found to depend on the orientation of the axis of the anvil cell with respect to the diffraction plane. This behavior implies the presence of an uniaxial pressure component along the axis of the anvil cell. The pressure dependence is well described in the framework of a pressure-induced progressive deformation of the tubes section, from circular to hexagonal, in addition to the van der Waals compression.

#### 10:45 AM Z7.6

BINARY PHASE OF LAYERED NANOTUBES. Raymond Whitby,

Wen Kuang Hsu, Department of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UNITED KINGDOM; Chris Boothroyd, Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, UNITED KINGDOM; Peter Fearon, David Walton, Harold Kroto, Department of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UNITED KINGDOM.

Pyrolysis of multi-walled carbon nanotubes (MWCNs) with thin

coatings of tungsten oxide, in H<sub>2</sub>S/N<sub>2</sub>, generates a binary phase of layered nanotubes in accordance with the template effect, where tungsten disulfide coats the MWCNs.

#### 11:00 AM Z7.7

CRYSTALLIZATION OF FULLERENE IN QUASI-ONE DIMENSIONAL NANOSPACE : C<sub>60</sub> IN DOUBLE WALLED CARBON NANOTUBE. Kaori Hirahara, 'Nanotubulites' Project, Japan Science and Technology Corp., c/o Meijo Univ., JAPAN; Shunji Bandow, Dept. of MS&E, Meijo Univ., Nagoya, JAPAN; Takanori Nakahira, Kouji Itoh, Yahachi Saito, Dept. of Electronic Engineering, Mie Univ, Tsu, JAPAN; Sumio Iijima, 'Nanotubulites' Project, Japan Science and Technology Corp., Dept. of MS&E, Meijo Univ., Nagoya, JAPAN.

In the most studies of fullerene encapsulated nanotubes (so-called peapods) reported so far, the SWNTs used have a suitable inner diameter for aligning the fullerene molecules one-dimensionally in their internal space. In the present study, we used the tubes with the diameter larger enough than the diameter of fullerenes for making peapods. The fullerenes in such large diameter tubes were also packed regularly and had a certain crystal structure. The internal space for such large diameter tube with respect to the diameter of fullerene is regarded as the quasi-one dimensional nanospace for the arrangement of fullerene molecules. In one-dimensional nanospace realized in 1.4 nm tubes, the intermolecular spacings of various fullerenes were different from the values of 3D crystals due to the interactions between the fullerenes and also between the fullerene and the surrounding tube-wall. In the quasi-one dimensional nanospace, the difference of such interactions is possibly exist and come over the intermolecular spacing. Because the fullerenes should not be surrounded by the tube-wall. In the present study, we used arc derived double-wall carbon nanotubes (DWNTs) which have mean internal diameter of ca. 3 nm. Encapsulation of fullerenes were carried out by the vapor phase reaction. High-resolution electron microscope (HRTEM, JEM-2010F, 120kV) imaging and electron diffraction method were employed to characterize the crystal structure of the fullerenes. In most of TEM images observed, the fullerene chains seeing in the tubes were close packed and aligned along the tube-wall, and they formed bundle structure in the tube. The structural model for them and the diffraction pattern of the quasi-one dimensional fullerene crystal in DWNT are going to be discussed on the poster.

#### 11:15 AM Z7.8

FILLING SINGLE-WALL CARBON NANOTUBES (SWNTS) WITH METALLOCENES: A FIRST NON-FULLERENE HYBRID MOLECULAR SYSTEM. Ferenc Stercel, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA; Norbi M. Nemes, University of Pennsylvania, Department of Physics, Philadelphia, PA.

One of the unique features of carbon nanotubes is their structurally and chemically well-defined interior space. This allows for the synthesis of a range of structures in which the lumen is filled, or partially filled, with other materials; ionic compounds, alkali metals, fullerene molecules. These hybrid structures provide the possibility to modify the properties of the nanotube and/or the filling species. The only molecular-based hybrid systems created to date are fullerenes and metallofullerenes encapsulated in SWNTs. Here we report the synthesis and analysis of metallocenes (ferrocene, chromocene, vanadocene) encapsulated in SWNTs. In the case of ferrocene, efficient filling of the SWNTs was accomplished from both the liquid and the vapor phase. The other two metallocenes were filled from the vapor phase. High resolution transmission electron microscopy reveals single molecular chains of metallocenes inside SWNTs. Molecules move under the electron beam in the SWNTs indicating the absence of strong chemical bonds between each other and the SWNT wall. Their movement freezes after short illumination which is the result of irradiation damage. Energy dispersive X-ray spectrometry confirms the presence of iron, chromium and vanadium.

#### 11:30 AM Z7.9

MAGNETIC PROPERTIES OF METALLOFULLERENES ENCAPSULATING IN SINGLE-WALL CARBON NANOTUBES. Shunji Bandow, Meijo University, Dept of Materials Science and Engineering, Nagoya, JAPAN; Kaori Hirahara, Japan Science and Technology Corporation, Nagoya, JAPAN; Haruhito Kato, Toshiya Okazaki, Hisanori Shinohara, Department of Chemistry, Nagoya University, Nagoya, JAPAN; Sumio Iijima, Japan Science and Technology Corporation, NEC Corporation, Tsukuba and Meijo University, Nagoya, JAPAN.

Magnetization curves of Gd@C<sub>82</sub> encapsulated single-wall carbon nanotubes were measured by SQUID susceptometer with the magnetic field up to 7 T. According to the magnetization curve analyses, it was found that the total quantum number of Gd atom would be  $J = 7/2$  and the spin quantum number of C<sub>82</sub> cage would be  $S = 1/2$  down to

ca. 4.2 K. At 2 K, decrease of  $J$  and increase of  $S$  were observed in magnetization curve. These facts suggest that the interaction between intra-molecular spins in the Gd@C<sub>82</sub> is antiferromagnetic and the interaction between the spins on the cages is ferromagnetic. The latter interaction is probably associated with the interaction between the spins on the cage via the  $\pi$ -electrons in the SWNT. Although the intra-molecular  $J$ - $S$  and inter-molecular  $S$ - $S$  interactions detected are very small, those interactions will result the ferromagnetic superexchange interaction between the spins on Gd atoms. Temperature dependence of the magnetic susceptibility down to 2 K indicated also the small antiferromagnetic coupling between spins, which may be originated in the antiferromagnetic intra-molecular  $J$ - $S$  interaction. ESR of metallofullerene@SWNTs (metallofullerene = La@C<sub>82</sub> and Gd@C<sub>82</sub>) was not detected in the present study.

#### 11:45 AM **Z7.10**

**DYNAMICS AND ELECTRONIC STATES OF FUNCTIONAL MOLECULES CONFINED INSIDE SINGLE WALLED CARBON NANOTUBES STUDIED BY SOLID STATE NMR.** Hironori Ogata, Syouhei Takebuchi, Hosei Univ, Dept of Materials Chemistry, Tokyo, JAPAN; Yahachi Saito, Mie Univ, Dept of Electronic Engineering, Tsu, JAPAN.

Several kinds of interesting functional complexes consists of a one-dimensional array of electroactive molecules inside Single-walled Carbon Nanotubes(SWNTs) were prepared and their dynamics and local electronic states were studied by solid state NMR. <sup>13</sup>C-NMR spectra of <sup>13</sup>C-enriched C<sub>60</sub> encapsulated by SWNTs(peapod) showed a narrow peak at about 110 ppm above room temperature, which was assigned to be C<sub>60</sub> molecules inside SWNTs. This peak showed the significant broadening below room temperature, which suggests the restriction of molecular rotation. Temperature dependence of <sup>13</sup>C spin-lattice relaxation time showed different behavior from that of bulk C<sub>60</sub> crystal. We will discuss the detailed results of NMR not only for peapod but another endohedral molecules inside SWNTs.

### SESSION Z8: MODELING AND SIMULATIONS OF NANOTUBE SYSTEMS

Chairs: Susumu Saito and Ray H. Baughman  
Wednesday Afternoon, November 28, 2001  
Back Bay A (Sheraton)

#### 1:30 PM **Z8.1**

**THEORETICAL APPROACH TO NANOTUBE STABILITY, FUNCTIONALIZATION AND DEVICES.** Gotthard Seifert, Thomas Frauenheim, Thomas Köhler, Zoltan Hajnal, University of Paderborn, GERMANY; Aldo Di Carlo, University Tor Vergata, Rome, ITALY.

We present recent density-functional based investigations on functionalization of carbon nanotubes (CNT's) and the prediction of novel nanotubular structures. We show that tailoring of intrinsic electronic properties for nanoscale electronics may be achieved by side-wall functionalization of CNT's with Fluorine. In establishing metallic and semiconducting C<sub>2</sub>F-tubes 1-dimensional quantum heterostructures are demonstrated. Furthermore, our calculations address the stability, mechanical and electronic properties of various inorganic nanotubes, some of which already have been successfully produced. Whereas experimental evidence is given for metal-dichalcogenide NT's, other tubular structures formed by silicides, siloxenes and germynes still have to be confirmed and should stimulate effort on their synthesis. We also describe the possible formation of SiO-C composite NT's using carbon NT's as template.

#### 1:45 PM **\*Z8.2**

**QUANTUM TRANSPORT IN NANOTUBE-BASED STRUCTURES.** Marco Buongiorno Nardelli<sup>1</sup>, J.-L. Fattebert<sup>1,2</sup> and J. Bernholc<sup>1</sup>.

<sup>1</sup>Department of Physics, North Carolina State University, Raleigh, NC. <sup>2</sup>Center for Applied Scientific Computing, Lawrence Livermore National Laboratory, CA.

Although the field of carbon nanotubes has seen an explosive growth due to the substantial promise of these molecular structures in novel nanoscale electronic devices, fundamental questions about their electrical transport properties remain to be answered. In particular, the processing and positioning of individual nanotubes as specific device components is likely to introduce large mechanical deformations in nanotube geometry, which will modify the electronic and transport behavior of the system. Using state of the art quantum calculations, we have studied the electronic and transport properties of a variety of nanotube-based structures relevant for the design of nanoscale electronic devices. In particular, we have examined the influence of mechanical deformations and/or disordering in carbon nanotubes and discovered several classes of behavior. Our results show that bent armchair tubes keep their metallic character for most

practical purposes, while metallic chiral nanotubes undergo a bending-induced metal-semiconductor transition that manifests itself in the occurrence of effective barriers for transmission. We have demonstrated the possibility of forming intra-tube junctions and conducting electrical contacts via the rebonding of open-ended NT's that are put in close proximity to each other. Finally, we will examine the behavior of nanotube-metal contacts and explain the anomalously large contact resistance observed in nanotube devices as due to the spatial separation of their conductance eigenchannels. The results for various contact geometries and strategies for improving device performance will be discussed.

#### 2:15 PM **\*Z8.3**

**WATER CONDUCTION THROUGH CARBON NANOTUBES.** G. Hummer, National Institutes of Health, Laboratory of Chemical Physics, NIDDK, Bethesda, MD; Jayendran C. Rasaiah, Jerzy P. Noworyta, University of Maine, Department of Chemistry, Orono, ME.

The interactions of small, un-capped carbon nanotubes with water are studied by long molecular dynamics simulations. Water is found to penetrate the nanotube interior, forming well-ordered hydrogen-bonded water chains. Water penetration is sensitive to details of thermodynamic conditions and interaction potentials, resulting in sharp, first-order like transitions between filled and empty states. Under wetting conditions, water molecules are transported efficiently through nanotubes. Implications on the design of nanotube channels for small molecules and protons will be discussed.

#### 2:45 PM **Z8.4**

**CHARGING CARBON NANOTUBES.** P. Keblinski, P.M. Ajayan, Material Science and Engineering Department, S. Nayak, Physics Department, Rensselaer Polytechnic Institute, Troy, NY, and P. Zapol, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Ab-initio calculations of charge distribution on negatively and positively charged carbon nanotubes result in charge distribution profiles with a significant increase of charge density at tube ends, in quantitative agreement with classical electrostatic analysis, even for tubes with a single electron total charge. Using density-functional-based tight-binding simulations with self-consistent charge scheme we study structural response of the tube to the charge and identify the maximum value of charge at which the tube is stable. This result in combination with classical electrostatic analysis allows us to determine a simple analytical dependence of the stability criterion on the tube length. We also calculate related critical value of the electrostatic potential and discuss differences between closed and open ended carbon nanotubes.

This research was supported by Phillip Morris USA. P.Z. acknowledges support by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

#### 3:15 PM **\*Z8.5**

**NANOMECHANICS OF NANOTUBES AND NANOTUBE-POLYMER COMPOSITES.** Deepak Srivastava, Computational Nanotechnology, NASA Ames Research Center, CA; Chengyu Wei and Kyeongjae Cho, Department of Mechanical Engineering, Stanford University, CA.

Recently carbon nanotubes are considered as nanoscale fibers that can strengthen polymer composite materials. Nanotube-polymer composite materials can be used for micron scale devices with designed mechanical properties and smart polymer coating to protect materials under extreme physical conditions. To explore these possibilities it is important to develop a detailed atomic scale understanding of the mechanical coupling between polymer matrix and embedded nanotubes. In this talk we will describe the physical, mechanical and chemical properties of polymer matrix and carbon nanotube interfaces using molecular dynamics. The density of the CNT/nanotube composite, as a function of cooling rate, is found to change significantly above glass transition temperature indicating the formation of a high thermal expansion coefficient material above glass transition temperature. The thermal conductivity of polymer-nanotube matrix also depends significantly on thermal conductivity of nanotubes and of polymer matrix. The mechanical load transfer for very small strains lead to up to 30% increase in the value of the Young's modulus of the composite, it is found that limiting strain for non-bonded interactions can be increased by mechanical strain-relaxation cycle of the composite. The load transfer is studied as a function of the angle of inclination of the nanotube within the matrix fibers, and processing of the composite through strain-relaxation cycles lead to alignment of the polymer molecules with the nanotubes. Study shows that the bonding between polyethylene and CNT is energetically favorable. Chemical bonds can be formed at multiple sites, which makes the mechanical load transfer from the polymer chain to the tube more favorable. Detailed results and analysis will be described to study the effect of mechanical and

chemical coupling between CNTs and polymer matrix on the mechanical properties of the composite and the tubes.

### 3:45 PM \*Z8.6

INTERACTION OF SMALL MOLECULES AND RADICALS WITH CARBON NANOTUBES. Saroj K. Nayak, Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, NY.

We have studied the interaction of small molecules like O<sub>2</sub>, NO<sub>x</sub>, CO and radical like SiH<sub>3</sub> with perfect as well as defect induced carbon nanotubes using first principle density functional calculation. We find that the interaction of atoms and molecules are substantially modified due the presence of vacancy and other types of defects. For example, while the interaction of O<sub>2</sub> with a defect free nanotube results a weak binding (~ 0.1 eV) presence of defect in nanotubes result in dissociating the molecule on the nanotube surface. We will also discuss the effect of vacancy induced interaction on transport properties of carbon nanotubes. Finally, our results will be compared with recent related experiments.

Work done in collaboration with P. Ajayan, Rensselaer Polytechnic Institute, Troy; A. Rubio, Spain, R. Car, Princeton University.

### 4:15 PM Z8.7

SELECTIVE PARTITIONING OF HYDROPHOBIC SOLUTES INTO CARBON NANOTUBES. Amrit Kalra<sup>1</sup>, Tuhin Ghosh<sup>1</sup>, Gerhard Hummer<sup>2</sup>, and Shekhar Garde<sup>1</sup>. <sup>1</sup>Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY. <sup>2</sup>Laboratory of Chemical Physics, National Institutes of Health, Bethesda MD.

Much of the interest in carbon nanotube research stems from their unique mechanical and geometrical characteristics and resulting mechanical, structural, and electronic properties. Open ended single walled carbon nanotubes are ideal model systems that resemble in shape and size to the pores in biological macromolecules, such as transmembrane ion channel proteins. Recent molecular simulation studies by Hummer et al. (submitted) show that studies of hydrogen bonded water wires formed in short segments of carbon nanotubes can provide important insights into functions of their biological analogs. Here we present results from simulations of carbon nanotubes in aqueous solutions of hydrophobic solutes. We find that the interior of carbon nanotubes is highly selective to partitioning of hydrophobic solutes. The partitioning process is fast and occurs over time scale of 1 to 2 nanoseconds. Kinetics of selective partitioning process are obtained by performing several tens of simulations started from different initial conditions. These studies point to future applications of functionalized carbon nanotubes as sensing and/or separation devices that are highly selective to specific molecules of interest.

### 4:30 PM Z8.8

LARGE SCALE *AB INITIO* INVESTIGATION OF LITHIUM DIFFUSION IN CARBON NANOTUBES. Vincent Meunier, Christopher Roland, Jerry Bernholc, North Carolina State University, Department of Physics, Raleigh, NC.

It is well known that the performance of Li-ion batteries depends directly on its intrinsic capacity (e.g. the Li/C uptake ratio) which for Li-graphite systems is ideally 372mAh/g (LiC<sub>6</sub>). Recently, there has been considerable interest in carbon nanotube systems as providing a suitable alternative to graphite as an intercalation material. Because of their unique structure, nanotubes may provide for an increased Li uptake ratio of 1:2. This is the ideal case in which, in addition to the interstitial space available between nanotubes, the interior regions of the nanotubes may be accessed. With large-scale *ab initio* simulations we have therefore investigated Li adsorption both on, and into, isolated carbon nanotubes and nanotubes ropes. Specific issues addressed include the effect of metallicity on Li adsorption, charge transfer effects, dynamics of Li motion, and different pathways for the ions to enter nanotubes interiors. Our calculations show that only in the presence of open nanotubes, or nanotubes with topological defects with 9-(or higher) membered rings can the ions enter readily. These results are consistent with recent experiments which show that Li uptake is greatly enhanced if the nanotubes are initially processed via ball-milling. To complement these static calculations, we have also directly simulated the long-time motion of Li ions in nanotube systems using a frozen charge density molecular dynamics approximation.

### 4:45 PM Z8.9

DETAILED GEOMETRIES AND THEIR IMPORTANCE TO THE ELECTRONIC PROPERTIES OF CARBON NANOTUBES. Kenjiro Kanamitsu, Susumu Saito, Tokyo Institute of Technology, Dept of Physics, Tokyo, JAPAN.

In the framework of the density-functional theory (DFT), we study geometries and the electronic structure of so-called zig-zag carbon nanotubes with various diameters. From the total-energy calculation their structural parameters are completely optimized. Interestingly, there are two kinds of bonds which are found to be considerably

different from each other, with strong tube-diameter dependences. Also the two kinds of bond angles show different diameter dependences. The electronic band structure of these optimized carbon nanotubes are found to show sizable changes from that of initial "ideal-geometry" nanotubes with uniform bond lengths. This indicates the importance of the detailed geometries in discussing the electronic properties of carbon nanotubes. We also show an interesting difference of the energy gap values between the present DFT results and the previous tight-binding results.

SESSION Z9: POSTER SESSION  
MODELING, ENERGY STORAGE, ELECTRODE  
APPLICATIONS, AND CHEMICAL  
MODIFICATIONS  
Wednesday Evening, November 28, 2001  
8:00 PM  
Exhibition Hall D (Hynes)

### Z9.1

MECHANICAL BEHAVIOR OF CARBON NANOTUBES FILLED WITH METAL NANOWIRES BY ATOMISTIC SIMULATIONS. D. Danailov, P. Koblinski, P.M. Ajayan, MS&E Department and S. Nayak, Physics, Applied Physics and Astronomy Department, Rensselaer Polytechnic Institute, Troy, NY.

Using molecular dynamics simulations we studied mechanical behavior of (10,10) carbon nanotubes filled with a crystalline fcc metal wires. The interatomic interactions were described by a combination of Tersoff's bond-order potential for carbon, embedded atom method (EAM) potential for metal and pair potential for carbon-metal interactions. The elastic properties, as well as failure mechanism were determined by simulating three point bending test, by pressing the center of relatively long tube with a moving hard repulsive cylinder crossed at 90° with respect to the tube, while supporting the tube ends with fixed cylinders. We observed that following elastic response, at larger deformation, the metal wire yields well before the carbon bonding is affected. The behavior of filled tubes was compared with that of hollow tubes. We also simulated indentation of filled tubes residing on a hard flat surface. Similarly as in the bending test, metal wire yields first, is cut in half along its cleavage plane and pushed away from under the indenter. Upon further increase of the indentation force, carbon tube is broken and forms two open ends that are rapidly zipped around the cut metal wire. Remarkably, the shape of the zipped tube ends is similar to a sharply cut cylinder at about 45° angle and appear to be determined by the shape of the metal wire cleavage. This result imply a possibility of designing tubes with various closed end shapes using nanoscale manipulation procedures. This research was support by Phillip Morris USA.

### Z9.2

MODEL NARROW NANOTUBES RELATED TO C<sub>36</sub>, C<sub>32</sub> AND C<sub>20</sub>: COMPUTATIONAL INSIGHT. Zdeněk Šlanina, Filip Uhlík, Toyohashi Univ of Technology, Dept of Knowledge-Based Info. Engn., Toyohashi, JAPAN; Charles Univ, Dept of Phys. and Macromol. Chem., Prague, CZECH REPUBLIC.

Very recently, narrow nanotubes have been observed with a diameter of 5 Å (Sun *et al.*, Nature **403** (2000) 384) and even with a diameter of 4 Å (Qin *et al.*, Nature **408** (2000) 50). It has been supposed that the narrow nanotubes are closed by fragments of C<sub>36</sub> and C<sub>20</sub> fullerenes. The contribution reports computations on related model nanotubes with stoichiometries like C<sub>84</sub>, C<sub>96</sub> or C<sub>80</sub>. Computations are carried out at the PM3, SAM1, and B3LYP/6-31G\* levels. Two C<sub>36</sub> fullerenes are considered, D<sub>6h</sub> and D<sub>2d</sub>, and, for example, at the PM3 level and with the C<sub>84</sub> nanotube stoichiometry the D<sub>2d</sub> cage closure gives a lower energy (by 185 kcal/mol and diameter of 5.42 Å). There is another possible candidate, C<sub>32</sub> cage with a D<sub>4d</sub> symmetry. At the PM3 level and with the C<sub>96</sub> nanotube stoichiometry the D<sub>4d</sub> closure has the nanotube energy lower by 210 kcal/mol (with the nanotube diameter of 5.43 Å) compared to the D<sub>6h</sub> nanotube closure. On the other hand, four-membered rings should not play a significant role in the narrow nanotubes with the diameter of 4 Å, where the dodecahedron-related closure should be exclusive. The findings are also supported by the B3LYP/6-31G\* calculations.

### Z9.3

LOCALIZED ELECTRONIC AND PHONON STATES AROUND DEFECTS OF A CARBON NANOTUBE. Riichiro Saito<sup>a</sup>, A. Gruneis<sup>a</sup>, Tadamas Kimura<sup>a</sup>, Gene Dresselhaus<sup>b</sup>, Mildred S. Dresselhaus<sup>c</sup>, A. Jorio, A.G. Souza Filho, and M.A. Pimenta, <sup>a</sup>Dept of Electronics-Engr, Univ of Electro-Communications, Tokyo, JAPAN; <sup>b</sup>Francis Bitter Magnet Laboratory, and <sup>c</sup>Dept of Physics and Dept of Electrical Engr and Computer Sci, MIT, Cambridge, MA; Dept of Physics, Cambridge; <sup>d</sup>Dept de Fisica, Univ Federal de Minas Gerais, Belo Horizonte.

Symmetry breaking in the electronic and phonon structures of carbon nanotubes is considered theoretically, especially for the possible functionalities introduced by the defects in nanotubes. Edges at an open cap, 5-7 membered ring pairs, and point defects have been proposed as topological defects. Such defects are relevant to the functionality of nanotubes or to their solid state physics, such as defects effects on the deformation of the nanotube, the D-band Raman spectra, the absence of back scattering, and chemical reactions. A key idea for such defects is that the eigenstates of the electrons or phonons become localized by collecting a range of  $k$  vectors near the Fermi energy. As a result, the amplitude of the eigenvectors would be locally large and give a better sensitivity to various quantum physical properties. The localization phenomena should depend on the geometrical shape of the defect. Here we present recent calculated results for the physical origin of the D-band Raman spectra in a single wall carbon nanotube and compared them with observations on single nanotube Raman spectra of the D-band and  $G'$ -band. Electron-phonon coupling around the defect becomes strong since both the electron and phonon wavefunctions have a large amplitude. Another key issue for such a defect is that the defect may be essential for scattering since it affects the transport properties of both electrons and phonons. We propose to characterize the size and the depth of the scattering as a function of the defect shape. We have previously shown the absence of back scattering by electrons. We here apply the effects of defects on phonon scattering. An anomalous thermal conductivity, which affects single nanotube spectroscopy, might be relevant to this scattering. We gratefully acknowledge the support of NSF grant DMR-98-04734, and the grant of Ministry of Education (No.13440091).

#### **Z9.4** ENERGETICS OF FINITE, OPEN ENDED, SINGLE WALLED BORON-NITRIDE AND CARBON NANOTUBES.

Marian W. Radny, Philip V. Smith, School of Mathematical and Physical Sciences, The University of Newcastle, Callaghan, NSW, AUSTRALIA; Yoshiyuki Kawazoe, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Determination of the optimum, energetically favourable atomic structure of nanotubes (NT) is essential for any "smart" application of NTs. This includes the knowledge of the diameter variation of NTs, capping features, shell chirality, structure of kinks and other possible defects. Despite the large number of experimental and theoretical studies performed for Carbon NTs (C NTs) the collected data indicate that while the atomic structure of C NTs is relatively simple and easy to describe, it is, however, purely understood. Among the successfully synthesised non-carbon tubes, the BN nanotubes (BN NT) are usually considered to be structural analog of C NTs. Recent studies have suggested, however, that this relationship is as complicated as intriguing. It has been discovered, for instance, that the "zig-zag" shell helicity of BN NTs is a favourable shell structure of BN NT assemblies. This domination has been observed in the tube assemblies produced by different methods (laser heating at high pressure, thermochemical processes), and indicates on some kind of universal behaviour of BN NTs. This experimental fact is, however, in sharp contrast to C NT for which the structure analysis of the C NT assemblies indicates on no preferred shell helicity of the formed tubes. It is easy to show that the shell chirality is directly related to the topology of edge of the open ends of the ideal, finite tubes. In this paper we want to report on our Tight Binding total energy calculations for clean, ideal, open-ended BN tubes where the relationship - chemistry of the open edges of the BN NT with different chirality vs mechanics (strain energy) of the infinite tubes with the same chirality - has been explored. The analog calculations performed for C NTs will also be discussed.

#### **Z9.5** A COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY OF ION BEAM MODIFICATION OF CARBON NANOTUBE BUNDLES.

Boris Ni, The University of Florida, Dept. of Materials Science and Engineering, Gainesville, FL; Rodney Andrews, David Jacques, Dali Qian, Center for Applied Energy Sciences, The University of Kentucky, Lexington, KY; Muthu Wijesundara, Yongsoo Choi, Luke Hanley, The University of Illinois at Chicago, Department of Chemistry, Chicago, IL; Susan B. Sinnott, The University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

The modification of bundled singlewalled and multiwalled carbon nanotubes are examined using a combination of computational and experimental methods. The computational approach is classical molecular dynamics simulations using the many-body reactive empirical bond-order potential parameterized by Brenner. The simulations consider the deposition of methyl ions at incident energies of 10, 45 and 80 eV. They predict the chemical functionalization of the nanotubes, the formation of defects on the nanotube walls, and the formation of cross-links between neighboring nanotubes or

between the walls of a single nanotube. They also illustrate the manner in which the number of walls in the nanotube and incident energy affect the results. In the experiments multiwalled nanotubes with about 40 shells (average diameter of 25 nm) are synthesized by chemical vapor deposition.  $CF_3^+$  ions are deposited at incident energies of 10 and 45 eV and then the nanotubes are examined with x-ray photoelectron spectroscopy and scanning electron microscopy. These experiments find strong evidence of chemical functionalization, in agreement with the simulation results.

#### **Z9.6** BAND FILLING AND CORRELATION EFFECTS IN ALKALI METAL DOPED CARBON NANOTUBES.

Jaewu Choi, Iran Amildo Samayoa, Louisiana State University, Center for Advanced Microstructures and Devices, LA; Seung-Chu Lim, Jeonbuk National University, Semiconductor Physics Research Center, KOREA; Young Chul Choi, Samsung SDI, Corporate R&D Center, KOREA; Chulsu Jo, Young Hee Lee, Sungkyunkwan University, Dept. of Physics, Korea; P.A. Dowben, University of Nebraska-Lincoln, Dept. of Physics and Astronomy, NE.

We have investigated modification of the electronic structure of the vertically aligned multiwalled carbon nanotubes (MWCNTs) as a function of sodium doping. The changes in band structure can be largely associated with shifts of the Fermi level position relative to the multiwalled carbon nanotube band structure. The changes in the apparent density of states in the vicinity of the Fermi level suggest effects associated with the repulsive on-site Coulomb interaction (the correlation energy) although the intrinsic poor screening in the quasi-one dimensional carbon nanotubes, particularly near the tube termination, cannot be neglected entirely. The results are compared with "unaligned" single walled and multiwalled carbon nanotube films (or mats).

#### **Z9.7** ATOMISTIC STUDY OF MECHANICAL PROPERTIES OF CARBON NANOTUBES.

T. Narita, K. Shintani, Univ of Electro-Communications, Dept of Mechanical Engineering and Intelligent Systems, Tokyo, JAPAN.

The mechanical properties of single-walled carbon nanotubes are investigated by means of molecular dynamics simulations. The Tersoff-Brenner potential is used for the calculation of the interatomic forces. Two kinds of simulation cells are considered; one adopts the periodic boundary condition along the tube axis and the other corresponds to tube clusters. The atoms at the ends of a simulation cell are translated along its axis, and the Young's modulus and Poisson's ratio are estimated. How these mechanical properties of carbon nanotubes depend on their temperature and chiral vectors is discussed.

#### **Z9.8** CARBON NANOTUBES UNDER BENDING STRAIN.

M. Huhtala, A. Kuronen, K. Kaski, Research Centre for Computational Engineering, Helsinki University of Technology, Helsinki, FINLAND.

Carbon nanotubes are highly elastic semiconducting or metallic all-carbon molecules. Single walled nanotubes can be visualized as a graphite layer rolled seamlessly into a tubular form. The tubes are considered to be an extremely promising novel material both for nanoelectronics components and for structural properties based applications. From the applications point of view no structure is perfect and defects, strain, and the resulting deformations play a significant role on the properties of a structure. This is especially true for carbon nanotubes, in which small changes in the structure can change the properties considerably. We study the effects of strain and strain induced defects and deformations by computer simulations. The structural effects are first looked into by employing a Molecular Dynamics scheme based on Brenner's carbon potential energy model. For critical parts of the structure, Tight Binding calculations are then performed in order to obtain more precise information. Here we report the results on carbon nanotube junctions. Carbon nanotube junctions are considered to be one of the key structures in future applications because of the interface formed between the tubes of different conductivity. In this work we present the results of a comparative computational study of single walled carbon nanotube junctions and uniform carbon nanotubes under bending strain.

#### **Z9.9** FULLERENES INSIDE CARBON NANOTUBES: HOW LARGE CAN THEY BE?

Miroslav Hodak, L.A. Girifalco, Dept. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

The potential energies of interaction between carbon nanotubes and internal fullerenes of spherical and ellipsoidal shape, as well as between nanotubes in multi-walled nanotubes were calculated using

the Lennard-Jones potential for carbon-carbon interactions. The distribution of carbon atoms was assumed to be continuous on all considered surfaces. The optimum and maximum size of internal fullerenes and multi-walled nanotubes are determined as a function of the external nanotube radius. It was found that at the potential energy minimum, the van der Waals distance is close to that in graphite for all studied cases. For the maximum size of internal fullerene, the van der Waals distance can be decreased by up to 0.8 Å, depending on the fullerene shape. The calculated results are in accord with available experimental observations and can be used as a guide for future experiments.

#### Z9.10

**MECHANICAL PROPERTIES OF STACKED LAMPSHADE NANOTUBE.** Takuya Hayashi, Morinobu Endo, Shinshu Univ, Dept of Electrical and Electronic Engineering, Nagano, JAPAN; Humberto Terrones, IPICYT, San Luis Potosi, MEXICO.

Stacked lampshade nanotube is a different form of nanotube having sidewalls not parallel to the longitudinal tube axis, meaning that each layers have their edge exposed at the surface of the tube. Considering the structure, we can easily imagine that the mechanical properties can be completely different from the conventional nanotubes. Lampshade tube might be weaker compared to the conventional tube on the tensile strength basis, but under the compressive stress, the stacked structure will act as a damping mechanism which could suppress the physical impact, vibrations and sonic waves when applied to composite materials. In this presentation, we will deal with the study on mechanical properties of this nanotube via computational simulations, and the results of various modes of deformations, such as bend, stretch and twist will be presented.

#### Z9.11

**PRESSURE ISOTHERMS OF HYDROGEN ABSORPTION IN CARBON NANOSTRUCTURES.** Xiaohong Chen, Urszula Dettlaff-Weglikowska, Miro Haluska, Martin Hulman, Siegmund Roth, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY; Michael Hirscher, Marion Becher, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

The hydrogen absorption capacity of various carbon nanostructures (single walled carbon nanotubes, activated carbons) is measured as a function of pressure (up to 80 bar) at different temperatures (77K, 200K, room temperature) using volumetric method. At room temperature and 80 bar the hydrogen storage capacity is less than 1 wt% for all samples investigated. The storage capacity depends roughly linear on hydrogen pressure. Upon cooling the hydrogen storage capacity increases and the best result of hydrogen absorption for single walled carbon nanotubes reaches about 2.7 wt% at 77K and 80 bar. The correlation between hydrogen storage capacity and surface area (BET) will be discussed.

#### Z9.12

**ELECTROCHEMICAL INSERTION OF LITHIUM IN MULTI-WALLED CARBON NANOTUBE FILMS AND THEIR APPLICATION AS ANODE IN LITHIUM ION BATTERIES.** Hunjoon Jung, Lim Hyuck, Jong-Hyuk Park, Min Park, Byoung-Dong Kim, and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

Vertically aligned multiwalled carbon nanotubes (CNT) films have been obtained by DC plasma-assisted hot filament chemical vapor deposition (CVD) over Ni/Cr/SiO<sub>2</sub>. About 3 micrometer thick as grown film was electrochemically characterized for applications as anode in lithium ion batteries. Cyclic voltammograms of CNT/1M LiClO<sub>4</sub>, PC/Li half cell show that CNT films can reversibly intercalate Li mainly under 0.5V. Reversible capacity (1mAh/cm<sup>2</sup>) has been estimated from galvanostatic charge-discharge characteristics under constant current density of 1mA/cm<sup>2</sup>. Kinetic studies on the lithium intercalation reaction also have been carried out using electrochemical impedance spectroscopy (EIS). Reversible capacity was quantitatively analyzed using Electrochemical voltage spectroscopy (EVS). We employed 10µm thick LiMn<sub>2</sub>O<sub>4</sub> screen printed on stainless steel mesh as cathode to characterize the full cell of LiMn<sub>2</sub>O<sub>4</sub> / 1M LiClO<sub>4</sub>, PC/ CNT system, for the first time. Twenty charge-discharge cycles have been performed and, no noticeable performance degradation was found compared with LiMn<sub>2</sub>O<sub>4</sub> / 1M LiClO<sub>4</sub>, PC/ Li cell.

#### Z9.13

Abstract Withdrawn.

#### Z9.14

Abstract Withdrawn.

#### Z9.15

**NANODISK FIBERS FOR ELECTRODE WITH LARGE CAPACITANCE.** J.G. Wen, Y. Tu, W.Z. Li, J.H. Chen, and Z.F. Ren, Department of Physics, Boston College, Chestnut Hill, MA.

Due to the nanometer size, high surface area, good conductivity and chemical stability, carbon nanotubes are potentially superior electrode materials with large capacitance. Compared to nanotubes, the accessible surface area of nanodisks is much larger because of the large amount of dangling bonds at the edge of nanodisk fiber. Carbon nanodisk fibers have been directly grown on graphite foil as a binder-free electrode. Electrochemical characterization shows that this kind of carbon nanodisk electrode has several advantages: sufficient mechanical strength, binder-free, and minimum contact resistance between carbon nanodisk and the current collector. Transmission electron microscopic studies showed that surface structures of nanodisk fibers could be modified by annealing as-grown nanodisk fibers in air. The large accessible surface area was confirmed by the high specific capacitance and featureless rectangular-shaped cyclic voltammograms over a wide range of scan rates.

#### Z9.16

**RAMAN INVESTIGATIONS OF H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O ADSORPTION IN NANOTUBES AND ACTIVATED CARBON.** Keith A. Williams, U.-J. Kim, B.K. Pradhan, M.K. Kostov, M.W. Cole, P.C. Eklund, Pennsylvania State University, University Park, PA; T. Enoki, Tokyo Institute of Technology, Tokyo, JAPAN.

We report Raman spectroscopic studies of H<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub> adsorbed on single-walled carbon nanotubes and activated carbon at several temperatures and pressures. Shifts in the stretching-mode frequencies of these adsorbates are correlated with the strengths of the surface interactions. Also, the rotational spectra of these adsorbates are used to examine the effect of confinement within the nanopores on the freezing transitions.

This work was supported by NSF MRSEC (PSU).

#### Z9.17

**<sup>13</sup>C AND <sup>1</sup>H NMR INVESTIGATION OF GAS ADSORPTION ON SWNTs.** A.R. Harutyunyan, A. Loper, B.K. Pradhan, G.U. Sumanasekera, P.C. Eklund, Dept. of Physics, The Pennsylvania State University, University Park, PA; A. Benesi, Dept. of Chem., The Pennsylvania State University, University Park, PA.

<sup>13</sup>C NMR studies were carried out in purified bundles of SWNTs. Degassed and purified SWNTs exhibit 2 groups of relaxation times: "fast" ~ 10 sec and "slow" ~ 40 sec. The origin of these different relaxation times is not clear, although they might be assigned to metallic and semiconducting tubes, as reported previously [1]. Admission of O<sub>2</sub> gas (1atm at room temperature) to the system affects these relaxation times. The slow relaxation time decreases significantly, while the fast relaxation time is found to be only slightly changed. The data therefore suggest that the semiconducting tubes are involved in a weak chemisorption (weak charge transfer), whereas the metallic tubes are not. Also the effect of hydrogen on the relaxation times has been studied and will be reported. The NMR observations are supported by thermoelectric power and gravimetric studies on SWNTs under similar conditions. This work was supported by ONR (ONR N00014-99-1-0619).  
1. X.-P.Tang, et.al., Science, v288, 492, 2000.

#### Z9.18

**CHEMICAL MODIFICATION OF SINGLE-WALL CARBON NANOTUBES USING MONOCHLOROBENZENE.** Minfang Zhang, Masako Yudasaka, Akira Koshio, ICORP, Japan Science and Technology Corporation, Tsukuba, JAPAN; Sumio Iijima, Meiji Univ., ICORP-JST, NEC, Tsukuba, JAPAN.

Our recent studies have shown that it is possible to modify single-wall carbon nanotubes (SWNTs) chemically by using monochlorobenzene (MCB) with ultrasonic treatment. We will describe their properties in this presentation. Thermogravimetric analysis (TGA) results showed that the burning process of the modified SWNTs was separated into two or more steps, indicating that there are at least two types of the modified SWNTs. TEM images showed SWNTs were modified at their outside- and inside-walls. Raman spectra of modified SWNTs had a new peak at about 1350 cm<sup>-1</sup>, and their tangential mode shifted slightly to the higher energy side compared with the spectra of the original SWNTs. This reflects the MCB-treatment changing the chemical structure of SWNTs and influencing their optical properties. We analyzed the electrical resistance of the modified SWNTs from room temperature to 50 K. The resistance versus temperature curve of original purified SWNTs was parabolic with a minimum at about 170 K, indicating that metallic behavior became semiconductor-like below 170 K. The resistance of the modified SWNTs increased as the temperature decreased, indicating that the modified SWNTs had the characteristics of a semiconductor. These results show that chemical

modification of SWNTs by MCB changed their structure and chemical and electrical properties.

#### **Z9.19**

##### **INFRARED SPECTROSCOPY STUDY OF PRISTINE AND FUNCTIONALIZED CARBON NANOTUBES.**

Jean-Louis Bantignies, David Maurin, Jean-louis Sauvajol, Groupe de Dynamique des Phases Condensées (UMR CNRS 5581), Université Montpellier II, Montpellier, FRANCE; C.L Huillier, Francois Beuneu, Laboratoire des solides irradiés, Ecole Polytechnique, Palaiseau, FRANCE.

Resonant Raman scattering is widely used to study single-Walled Nanotubes (SWNT). On the other hand, experimental infrared studies remains very sparse due very small signal available. We present here an experimental Fourier Transform mid-InfraRed (FTIR) transmission study of both single and multiwall carbon nanotubes. Tangential and radial infrared modes are identified. The sensitivity of infrared measurement to the structure is pointed out. The results are in good agreement with our calculations of active infrared modes. FTIR is one of the most powerful technique available to study organic fingerprints. Chemical processes and functionalization of SWNT lead to organic groups located at the surface of the tubes. On the basis of FTIR results obtained on pristine samples, we discuss here spectroscopic studies of functionalized samples modified by : (1) electrons produced by Van de Graaf accelerator, interaction with electrons leading to the presence of localized defects. (2) By chemical reactions with organic mixtures that induce various defects.

#### **Z9.20**

##### **DONOR-ACCEPTOR COMPLEXES OF CARBON NANOTUBES WITH ORGANIC CHROMOPHORES: EXPERIMENT AND THEORY.** Kristopher E. Wise, NRC/NASA-LaRC, Hampton, VA; Cheol Park, ICASE/NASA-LaRC, Hampton, VA.

The lack of an adequate method for manipulating and dispersing carbon nanotubes is a key obstacle to their widespread use in composite materials. Recent experimental work [1,2] suggests that carbon nanotubes can form thermodynamically stable intermolecular (noncovalent) complexes with certain conjugated organic molecules. These findings are significant because they provide a chemical handle for nanotubes that does not significantly perturb the extended pi electron system, which is responsible for many of their impressive properties. This contribution describes a combined experimental and theoretical study aimed at understanding the nature of the interaction and identifying new complexes with improved properties.

[1] R.J. Chen, et al. J. Am. Chem. Soc. 2001, 123, 3838-39.

[2] A. Star, et al. Angew. Chem. Int. Ed. 2001, 40, 1721-25.

#### **Z9.21**

##### **IN-SITU CHEMICAL EXPERIMENTS IN CARBON NANOTUBES.**

Nevin Naguib, Yury Gogotsi, Drexel Univ, Dept of Materials Engineering, Philadelphia, PA; Joseph Libera, Northwestern Univ, Dept of Materials Science and Engineering, Evanston, IL.

Nanotubes are considered for nanofluidic applications, such as drug delivery to a single cell or interconnects in nano-fluidic chips. We developed a new method for making nanotubes, which is hydrothermal synthesis (Y.Gogotsi et. al., J. Mater. Res., Vol. 15, No. 12, 2591-2594, 2000). Graphitic carbon nanotubes were synthesized in high temperature autoclaves by using an equilibrated C-H-O fluid. TEM and electron diffraction analysis show that these carbon nanotubes are characterized by high perfection of graphite layers, long and wide internal channels and internal liquid inclusions trapped during the synthesis. Hydrothermal nanotubes typically have 20-70 layers in their walls (wall thickness 7-25 nm) and an outer diameter of about 100 nm. Closed hydrothermal nanotubes, unlike conventional nanotubes produced in vacuum or at ambient pressure, contain water and gases encapsulated under pressure. During the growth, the synthesis fluid exists inside the tube. After closure of the tube, aqueous liquid and gases are trapped inside. H<sub>2</sub>O, CO and CH<sub>4</sub> are expected to dominate from thermodynamic calculations. The liquid inclusions were studied by using TEM, where apparent condensation and evaporation of liquid as well as a strong interaction between the liquid and the nanotube walls, including wall dissolution, were observed. These processes were studied for the first time in-situ with the lattice fringe resolution. The presented work demonstrates the possibility of surface modification and chemical nanomodeling of nanotubes using entrapped aqueous fluids.

#### **Z9.22**

##### **PNEUMATIC ACTUATION MECHANISM IN CARBON**

**NANOTUBE SHEETS.** Geoffrey M. Spinks, Gordon G. Wallace, University of Wollongong, Intelligent Polymer Research Institute, Wollongong, AUSTRALIA; Leonard S. Fifield, Larry R. Dalton, University of Washington, Dept of Chemistry, Seattle, WA; Alberto Mazzoldi, Danilo De Rossi, University of Pisa, School of Engineering,

Pisa, ITALY; Ilyas I. Khayrullin, Ray H. Baughman, Honeywell Int., Honeywell Technology Center, Morristown, NJ.

A new mechanism for electromechanical actuation giving giant strains is demonstrated for sheets of carbon single-wall nanotubes (SWNTs) used as artificial muscles. An electrochemically reorganized network of self-assembled nanotube bundles provides microscopic gas pressure containers in which actuation is pneumatically driven. The carbon nanotube array acts as a strain amplifier, so a 3% actuator stroke in the in-plane direction is amplified to over 300% in the thickness direction. This thickness-direction actuator strain is ten times higher than previously reported for a low-voltage actuator material providing a fast response. Strain amplification results from Poisson's ratio's that exceed 100, which are ~300 times larger than for most solids. This Faradaic actuation mechanism provides a "high-gear" response for non-Faradaic actuators, associated shape memory and hydrogen storage effects, and a means for switching volume dependent properties.

#### **Z9.23**

Abstract Withdrawn.

#### **Z9.24**

**HIGH RESOLUTION MAGNETIC FORCE MICROSCOPY SUPERTIPS PRODUCED BY FOCUSED ELECTRON BEAM INDUCED DEPOSITION.** I. Utke, P. Hoffmann, Institute of Applied Optics, Department of Microtechnique, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND; R. Berger, IBM SSD GmbH, Mainz, GERMANY; L. Scandella, Nansosurf AG, Liestal.

Tip apexes of commercial pyramidal Si scanning probes were magnetically functionalized by means of focused electron beam (FEB) induced deposition. It is experimentally shown for the first time that deposits obtained from local electron beam decomposition of a magnetic metal containing carbonyl precursor result in high-resolution magnetic force microscopy images. Furthermore, thus produced tips were used directly in magnetically actuated atomic force microscopes. Depending on exposure time, beam current, and scan mode, high aspect ratio supertips and local tip coatings with varying apex diameters can be produced. The magnetic resolution is shown to be directly related to the deposit apex diameter. Using magnetic force microscopy at ambient conditions, magnetic bit periods of 81nm could be readily resolved on storage harddisks. As precursor cobaltcarbonyl Co<sub>2</sub>(CO)<sub>8</sub> was used. The FEB-deposit composition was determined by Auger Electron Spectroscopy: 14-39at% Co, 70-46at% C, and 10-24at% O depending on deposition parameters. With regard to the precursor stoichiometry 11at% Co and 44at% for C and O, the metal and carbon content in the deposit is higher (factor 1.3-3.5 for Co, 1.03-1.6) whereas the oxygen content is lower (factor 0.22-0.54). The chemical reactions taking place are not completely understood. An attempt to explain the product formation is carried out considering the electron beam assisted Co catalyzed thermodynamic equilibrium formation of the Boudouard reaction describing the equilibrium of the metastable carbon monoxide (CO) and the reaction products carbon (C) and carbon dioxide (CO<sub>2</sub>). The deposits show no aging or loss of functionality with storage time. The deposit nanostructure revealed by transmission electron microscopy consists of cobalt nanocrystals with cubic phase and 2-8nm in diameter dispersed in a carbonaceous matrix. Currently, FEB deposition experiments are being carried out to achieve the final resolution limit given by the above nanocrystal size.

#### **Z9.25**

**NANOSCALE SENSORY DEVICES.** A.I. Minett, Media Lab Europe, Dublin, IRELAND; R.L. Shepherd, National Centre for Sensor Research, Dublin City University, Dublin, IRELAND; M. in het Panhuis, Media Lab Europe, Dublin, IRELAND.

Biological molecules and systems have a number of attributes that make them highly suitable for the development of sensing devices. Both macro-, and to an increasing extent micro-scale biosensing devices have been extensively researched over the past decade. Proteins fold into precisely defined shapes, nucleic acids assemble according to well-understood rules and antibodies and enzymes are highly specific in recognising their respective ligands. These attributes are governed by molecular behaviour at the nanoscale, where chemistry, physics, biology and increasingly, computer simulation are now converging in nanotechnology. Although very promising, the bio-related aspects of nano-particles, -systems and -devices are less developed than their non-biological cousins. It has become increasingly obvious that nanoscale technology exhibits novel behaviour that is not necessarily predictable from that observed at macroscale levels. Carbon nanotubes have been shown to exhibit phenomenal physical properties; hence it is our aim to devise a range of biological sensors on a nanoscale, using carbon nanotubes as the transducer in biosensor devices. Utilising a range of biological recognition entities (antibodies, enzymes or DNA), nanoscale sensory

systems can be made specific to a range of biological analytes of interest to the medical industry. For instance, to not only distinguish one analyte of interest but also to distinguish the electronic signature of a mixture, such as glucose and protein levels in blood. Development of such devices on a small scale could lead to truly in-situ physiological sensing. For instance, sensory systems that detect physiological conditions or emerging disease in the body could lead to a shift in focus of medical research from disease treatment towards earlier detection and prevention.

#### **Z9.26**

**THE PREPARATION AND OPTIMIZATION OF CARBON NANOTUBE SHEETS FOR ELECTROMECHANICAL ACTUATOR APPLICATIONS.** Edgar Munoz, Ray H. Baughman, Mikhail Kozlov, Alexander Lobovsky, Alan B. Dalton, James Matrunich, Han Hui, Honeywell Int., Morristown, NJ; Robert Morris, Morris Associates, NJ; Andrew G. Rinzler, University of Florida, Gainesville, FL.

Methods are described for the preparation of carbon nanotube sheets having increased surface area and mechanical properties for electromechanical actuator applications. The processes used exploit highly purified single-wall nanotubes, methods for debundling carbon nanotubes, processes for achieving chain orientation, and mechanical homogenizers to achieve dispersions with uniform aggregate size. Modulus increases of about an order of magnitude (to 7 GPa) resulted for nanotubes that had no preferred direction of orientation within the sheet plane. Partial tube orientation within the sheet plane was achieved both by post-fabrication and pre-fabrication processes (in a flow field during sheet formation). Since the actuator strain is independent of load level, the product of actuator strain (0.5%) and observed failure stress (55 MPa) can be used to calculate the maximum gravimetric work per cycle in the absence of creep. While this work per cycle (260 J/kg) is about three times higher than for hard ferroelectrics, creep processes must be eliminated in order to make practical actuator devices.

#### **Z9.27**

**INTRINSIC THERMOELECTRIC POWER OF CARBON NANOTUBES.** H.E. Romero, G.U. Sumanasekera, C.A.W. Adu, B.K. Pradhan, and P.C. Eklund, Pennsylvania State University, University Park, PA.

The electronic and transport properties of single-walled carbon nanotubes (SWNT) have been shown to be sensitive to the presence of oxygen. At ambient temperature, large positive thermopower values,  $S > 40 \mu\text{V/K}$ , are observed in mat samples when tubes are  $\text{O}_2$ -doped, and large negative thermopower values,  $S < -40 \mu\text{V/K}$ , are found after samples are degassed in vacuum at 200 °C for 10 hours. We re-examined the effects of oxygen doping on the thermopower and resistivity of purified SWNT mats. We find that, metallic tubes dominate the large negative thermopower with a small, low-T nonlinearity introduced by phonon drag. We show that the data for de-oxygenated tubes are in agreement with a two-band, mirror symmetry model where the Fermi level is upshifted by wall defect states. New experimental studies also reveal that, via oxygen doping, the thermopower can be reliably "tuned" to select intermediate values (such as zero) between that found for a fully oxygenated and oxygen-depleted states. This work was supported by ONR (ONR N00014-99-1-0619).

#### **Z9.28**

**UTILIZING ANCIENT EGYPTIAN WISDOM FOR CONTROLLING THE INTERFACIAL BEHAVIOR OF CARBON NANOTUBES.** Rajdip Bandyopadhyaya, Einat Nativ-Rot, Oren Regev, Rachel Yerushalmi-Rozen, Department of Chemical Engineering and The Ilse Katz Center for Meso and Nano-Scale Science and Technology, The Ben-Gurion University of the Negev, Beer-Sheva, ISRAEL.

Single-Wall Nanotubes tend to pack into crystalline ropes that further aggregate into tangled networks, due to strong inter-tub van der Waals attraction. Aggregation acts as an obstacle to most applications, and attenuates the special properties of the individual tubes. We describe a simple procedure for dispersing as-produced nanotubes powder into individual, isolated tubes: A two-step process of dispersing in aqueous solutions of Gum Arabic, a natural polysaccharide, and re-dispersing leads to the formation of highly concentrated (up to 50%) stable, dispersion of isolated tubes. The method is inspired by the ancient Egyptian recipe used for preparation of carbon-black ink. The use of GA for stabilization of SWNT dispersions offers a few advantages: Disruption of the inter-ropes packing, leading to dispersion of isolated tubes enables the testing of isolated tube properties, and comparison to theoretical predictions. From the practical point of view, the ability to prepare a dry powder of isolated tubes, well separated by a polymeric spacer, offers a by-pass to the tedious efforts involved in pulling-out single tubes from an as-synthesized powder. The adsorbed polymer is

expected to act as a compatibilizer leading to marked strengthening of the nanotube-matrix interface. We envisage that polymer coated tubes will open the way for mass production of "instant" nanotube powder, to be used in the field of reinforced elastomers and of nano-electronics.

#### **Z9.29**

**A STUDY IN THE DISPERSION OF CARBON NANOTUBES.** Matthew Bratcher, Bonnie Gersten, Wendy Kosik, U.S. Army Research Laboratory, AMSRL-WM-M, Aberdeen Proving Ground, MD; Helen Ji, Jimmy Mays, Department of Chemistry, University of Alabama, Birmingham, AL.

In the past, the dispersion of carbon nanotubes (CNTs) in both liquids and solids has been difficult due to the high surface interactions between the tubes. Dispersion of polymer CNT composites is important for such benefits as structural reinforcement of composites, the percolation threshold of CNT based conducting materials, and the thermal properties with the exploitation of the high surface area of CNTs. In this paper we discuss two approaches towards addressing dispersion of multiwalled nanotubes (MWNTs). One approach is the use of surfactant chemicals selected on the basis that they interact with CNT chemical groups. The second approach is the functionalization through covalent bonding of the CNTs with various polymers including polyethyleneimine (PEI), polyethylene oxide (PEO), and polymethylmethacrylate (PMMA). The two approaches were evaluated to determine whether covalent functionalization was more beneficial than the use of surfactants. Characterization of the dispersion was performed using various microscopy techniques and surface analysis was performed using x-ray photoelectron spectroscopy (XPS).

#### **Z9.30**

**SINGLE WALL CARBON NANOTUBES: A CHEMICAL SENSOR.** G.U. Sumanasekera, B.K. Pradhan, C.A.W. Adu, H.E. Romero, and P.C. Eklund, Pennsylvania State University, University Park, PA.

The thermoelectric response of a mat of a carbon nanotubes is shown to be sensitive to the details of the molecule-SWNT interaction. In this presentation, we consider the effects of the vapor adsorption of a series of six-membered-ring hydrocarbon molecules with varying degrees of  $\pi$  electron population, heteroatoms (N), and adducts, etc. A wide variety of the thermoelectric response to these similar molecules is observed. For example, no response, or a complete reversal of the thermopower sign at 300 K is observed, depending on the structure of the adsorbed molecule. A heterogeneous model is proposed to explain the experimental data. This work was supported by NSF MRSEC (PSU).

#### **Z9.31**

Abstract Withdrawn.

#### **Z9.32**

**CARBON NANOSTRUCTURES PREPARED BY LASER ABLATION OF TRANSITION METAL-CONTAINING GRAPHITE IN OXYGEN ATMOSPHERE.** K. Nakajima, T. Yamamoto, J. Tashiro, A. Sasaki, M. Yoshimoto, Tokyo Inst. of Tech., Yokohama, JAPAN; P. Ahmet, T. Chikyow, Nanomaterial Lab.-COMET, Tsukuba, JAPAN; Y. Takagi, Teikyo Univ. of Sci. & Tech., Yamanashi, JAPAN.

Carbon nanostructures, such as C60 fullerenes, carbon nanotubes (CNTs) and carbon nanofibers are very promising materials for superconductors, scanning probes, hydrogen storages or field emitters. Growth of CNTs or carbon nanofibers reported are performed through arc discharge, chemical vapor deposition and laser ablation method, usually through the metal catalyst. On the other hand, we recently have succeeded in growth of diamond films by laser ablation of pure graphite target in an oxygen atmosphere, and diamond crystals are grown epitaxially on sapphire (single-crystal aluminum oxide) substrates [Nature, vol. 399 (1999) 340]. In our laser ablation process, films are deposited in oxygen atmosphere and grown on the substrate which is placed parallel to the target and about 2cm away from the target surface. In this experiment, we employed the laser ablation of transition metal-containing graphite for synthesis of carbon nanomaterials. Resultant carbon materials were characterized by FESEM, TEM, XRD and Raman Scattering Spectroscopy. By using a graphite target containing the transition metal oxide such as NiO or  $\text{Fe}_2\text{O}_3$ , highly oriented carbon nanofibers of 10-50nm in diameter were grown toward the target from the substrate surface. During the depositions, the oxygen pressure was kept at 50-200 mTorr, and the substrate was heated at 200-700C. Nanofibers could be grown at temperatures above 250C, and diameter of nanofibers increased as the substrate temperatures. The relationship between the structures of these nanofibers and the laser ablation parameters are discussed in this talk.

### Z9.33

ALUMINA COATED GRAPHITE NANOFIBERS AS CATALYST SUPPORTS. C.L. Marotta, Northeastern Univ, Dept of Chemistry, Boston, MA; R.T.K. Baker, Catalytic Materials Ltd, Holliston, MA.

There has been considerable interest in developing ceramic composites in the nanometer size range, since they exhibit unusual properties when reduced to this dimension. These materials have potential applications as novel catalyst support media, humidity sensors, reinforcement materials, and electronic devices. Very small ceramic particles have also been found to lower mobility temperatures and improve the quality of sintered materials. Baker and coworkers have shown that graphite nanofibers (GNF) possess excellent crystalline characteristics at a synthesis temperature of 600°C. These materials have properties rivaling those of artificial pyrolytic graphite produced at 2800°C. The surfaces of GNF are comprised primarily of prismatic faces (the armchair and zig-zag planes) in contrast to traditional graphite structures that expose mainly basal plane regions. Metals deposited on the surfaces of GNF exhibited extraordinary wetting and spreading behavior when compared to that on other supports. This action resulted in a strong metal-support interaction that was claimed to be responsible for the superior catalytic activity and resistance to deactivation exhibited by such systems. In this study chemical vapor deposition (CVD) was used to coat the nanofibers with a thin film of aluminum oxide, exploiting the unique structure of GNF as a template. The alumina-coated nanofibers were employed as a catalyst support onto which iron was deposited by incipient wetness. Iron catalyzed nanofiber growth from the decomposition of CO was then used as a probe reaction to compare differences in the gas and solid product distributions with those obtained from the same metal loading on other support media. The alumina coated GNF, industrial alumina powder (Degussa), and pristine GNF were utilized as catalyst supports with a CO/H<sub>2</sub> feed at a temperature 600°C. Gas chromatography/mass spectrometry was used to monitor the effluent product gases from the reaction. High-resolution transmission electron microscopy (HRTEM) and temperature programmed reduction techniques were used to examine the nature of the metal/support interactions and nanofiber morphologies. Significant differences in the nanofiber characteristics and the reaction products were attributed to a modification of the alumina structure generated by the underlying nanofiber template.

#### SESSION Z10: ENERGY STORAGE, ELECTRODE APPLICATIONS AND CHEMICAL MODIFICATION OF NANOTUBES

Chairs: Patrick Bernier and Yoshi Iwasa  
Thursday Morning, November 29, 2001  
Back Bay A (Sheraton)

### 8:30 AM \*Z10.1

HYDROGEN STORAGE IN SINGLE WALLED CARBON NANOTUBES. Michael Hirscher, Marion Becher, Miro Haluska, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY; Urszula Dettlaff-Weglikowska, Martin Hulman, Xiaohong Chen, Siegmund Roth, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY.

The hydrogen storage in single walled carbon nanotubes (SWNTs) from various suppliers has been investigated after different treatments for purification and opening. The SWNTs were characterized by X-ray diffraction, transmission electron microscopy, and Raman spectroscopy. The hydrogen absorption was measured using a volumetric method with hydrogen pressures up to 8 MPa. Furthermore, after loading at room temperature and ambient pressure, the hydrogen storage was determined by thermal desorption spectroscopy utilizing a mass spectrometer. For opening the SWNTs an ultra-sonic treatment was performed. Using a stainless steel tip no hydrogen storage was found, whereas, using a Ti-alloy tip the storage capacity increases with sonication time. The sonication treatment introduces particles of the tip material into the samples. All of the hydrogen uptake can be explained by the assumption that the hydrogen is only stored in the Ti-alloy particles (1). Summarizing all results, at room temperature the hydrogen storage capacity of the investigated SWNTs is below 2 wt%.

(1) M. Hirscher et al., Appl. Phys. A 72 (2001) 129-132.  
We thank the German BMB F for financial support.

### 9:00 AM \*Z10.2

THE MECHANISM OF HYDROGEN STORAGE ON SINGLE-WALL CARBON NANOTUBES. M.J. Heben, A.C. Dillon, J.L. Alleman, K.E.H. Gilbert, K.M. Jones, P.A. Parilla National Renewable Energy Laboratory, Golden, CO; T. Gennett, Rochester Institute of Technology, Rochester, NY; L. Grigorian, Honda R&D Americas, Detroit, MI.

Carbon single-wall nanotubes (SWNTs) are capable of adsorbing hydrogen at room temperatures and pressures [1-4]. Although early experiments were performed on highly impure samples, hydrogen storage densities were estimated to be between 5 and 10 wt% on a SWNT weight basis. Since that time we have developed methods for obtaining SWNTs in purities as high as 98 wt% [5], and developed methods to activate these materials for hydrogen storage. The activation process involves exposing the pure SWNTs to high-intensity ultrasonic energy, which cuts the tubes into shorter lengths. An impurity metal alloy is also introduced into the SWNTs during the process. Detailed analyses with carefully calibrated equipment shows that the SWNT fraction of the composite material can adsorb up to 7 wt% hydrogen. The role of the impurity metal alloy introduced during processing will be discussed. Two-color Raman spectroscopy shows that variation in material synthesis can lead to the formation of tube samples of differing chirality. Adsorption measurements on these samples reveal a link between SWNT chirality and hydrogen capacity. This data will be discussed with respect to the mechanism of the hydrogen stabilization interaction and the relationship between electronic and structural factors.

1. A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, and M.J. Heben, Nature 386, 377, 1997.
2. A.C. Dillon, T. Gennett, J.L. Alleman, K.M. Jones, P.A. Parilla, and M.J. Heben, Proceedings of the 2000 U.S. D.O.E. Hydrogen Program Review (2000).
3. M.J. Heben, A.C. Dillon, T. Gennett, J.L. Alleman, P.A. Parilla, K.M. Jones, and G.L. Hornyak, Proc. Mat. Res. Soc. Fall, 2000.
4. A.C. Dillon and M.J. Heben, Appl. Phys. A 72, 133-142 (2001).
5. A.C. Dillon, T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla and M.J. Heben, Advanced Mat. 11, 1354, 1999.

### 9:30 AM Z10.3

LARGE CRYOGENIC STORAGE OF HYDROGEN IN CARBON NANOTUBES. B.K. Pradhan, A. Harutyunyan, D. Stojkovic, J. Grossman, P. Zhang, M.W. Cole, V. Crespi, and P.C. Eklund, Dept. of Physics, The Pennsylvania State University, University Park, PA; T. Tokune, H. Goto, Y. Fujiwara, Honda R&D Co., Ltd., Wako Research Center, JAPAN.

We report (6 wt%) storage of H<sub>2</sub> at T=77 K in aggressively processed bundles of single-walled carbon nanotubes at p ~ 2 atmospheres. The hydrogen storage isotherms are completely reversible. D<sub>2</sub> isotherms confirm the high storage values for H<sub>2</sub> and further reveal the effects of quantum mechanical zero point motion. We propose that the post-synthesis treatment of the sample not only improves access of the hydrogen to the central pore within an individual nanotube, but also may create a roughened tube surface (via 5-7 wall defects) with an enhanced binding energy for hydrogen. This enhancement is needed to understand the strong adsorption at low pressure. We obtain an experimental value for the isosteric of 130 meV near liquid N<sub>2</sub> temperature.

### 9:45 AM Z10.4

THERMOELECTRIC STUDY OF HYDROGEN STORAGE IN CARBON NANOTUBES. G.U. Sumanasekera, C.A.W. Adu, B.K. Pradhan, H.E. Romero, and P.C. Eklund, Pennsylvania State University, University Park, PA.

In situ resistivity ( $\rho$ ) and thermoelectric power (S) have been used to study the nature of the adsorption of hydrogen into bundles of single-walled carbon nanotubes (SWNT) for pressure  $p < 1$  atm and temperatures 77 K < T < 500 K. Isothermal plots of S vs.  $1/\rho$  are found to exhibit linear behavior as a function of gas coverage, consistent with a physisorption process. Studies of S,  $\rho$  at T = 500 K as a function of pressure exhibit a plateau at a pressure  $p \sim 30$  Torr, the same pressure where the H<sub>2</sub> wt % measurements suggest the highest binding energy sites are being saturated. The data have been interpreted to indicate that H<sub>2</sub> is physisorbed in SWNTs for  $p < 1$  atm and T < 500 K.

This work was supported by HONDA R&D.

### 10:30 AM Z10.5

CARBON NANOTUBE ANODES FOR LITHIUM ION BATTERIES. Ryne P. Raffaele, Thomas Gennett, Laboratory for Micropower Research, Rochester Institute of Technology, Rochester, NY; Jeff Maranchi, Prashant Kumta, Carnegie Mellon University, Pittsburgh, PA; Alosius F. Hepp, NASA Glenn Research Center, Cleveland, OH; Michael J. Heben, Anne C. Dillon, Kim C. Jones, National Renewable Energy Laboratory, Golden, CO.

This presentation outlines the evaluation of carbon nanotubes for use in thin film lithium ion batteries. Highly purified single-walled carbon nanotubes (SWNT) were obtained through chemical refinement of soot generated by pulsed laser ablation. The purity of the nanotubes was determined via thermogravimetric analysis, two wavelength Raman spectroscopy and transmission electron microscopy. The specific surface area and lithium capacity of the SWNTs was

compared to that of other conventional anode materials (i.e., carbon black, graphite, and multi-walled carbon nanotubes). The Brunauer, Emmett, and Teller technique based on nitrogen adsorption was used to measure the specific surface area of the various anode materials. The SWNTs exhibited a specific surface area on the order of 915 m<sup>2</sup>/g, much higher than the other carbonaceous materials. The lithium-ion capacity of the materials was measured using a standard 3-electrode cell. The electrochemical discharge capacity of the purified single walled carbon nanotubes was in excess of 1300 mAh/g after 30 charge/discharge cycles when tested using a current density of 20 μA/cm<sup>2</sup>. The preparation of Li ion battery anodes via direct chemical vapor deposition of carbon nanotubes and by the incorporation of the carbon nanotubes into ionically conductive polymer films will be discussed. Finally, results on the in-situ performance of carbon nanotube anodes in thin-film Li ion batteries will also be presented.

#### 10:45 AM \*Z10.6

##### ARTIFICIAL MUSCLES BASED ON CARBON NANOTUBES.

R.H. Baughman, M. Kozlov, E. Munoz, H. Hui, A.A. Zakhidov, I. Udod, Honeywell Int., Morristown, NJ; J.N. Barisci, G.M. Spinks, L. Fifield, G.G. Wallace, University of Wollongong, Wollongong, AUSTRALIA; R. Morris, Morris Associates; Z.V. Vardeny, C.P. An, Univ. of Utah, UT; M. Kertesz, G. Sun, Georgetown Univ, Washington, DC.; R. Raj, S.R. Shaw, Univ. of Colorado, CO.

We have previously described a promising new type of electromechanical actuator, which is based on electrochemical double-layer charging of carbon nanotubes. Realized performance was limited by the low modulus and low strength of nanotube sheets. We here describe methods for obtaining carbon nanotube sheets and fibers having order-of-magnitude higher mechanical properties and show that these property improvements lead to nanotube actuators providing an actuation force of 26 MPa (which is two orders of magnitude higher than for natural muscle) and an isometric gravimetric work/cycle that is 3X higher than for the best hard ferroelectric. Theoretical analysis of actuator strain versus charge agree with experiment and indicate that charge transfer is uniformly distributed on outer nanotubes in a bundle, electrostatic charges in bond length dominates over band-structure effects at large changing levels, and that reversible slip occurs between inner and outer tubes in a nanotube bundle when strain is large. This agreement between theory and experiment, and the increase in actuator performance with modulus increase, support our arguments that carbon nanotubes will eventually provide order-of-magnitude higher work/cycle and stress generation than any prior art technology.

#### 11:15 AM Z10.7

ELECTROCHEMICAL CHARACTERIZATION OF CARBON NANOTUBE ELECTRODES AND THE OPTIMIZATION FOR SENSOR DEVELOPMENT. Jun Li, Alan Cassell, Cattien Ngyyen, and Jie Han, ELORET Corp., NASA AMES Research Center, Moffett Field, CA; Lance Delzeit, and Meyya Meyyappan, NASA Ames Research Center, Moffett Field, CA.

Carbon nanotubes have unique electronic properties as well as extraordinary adsorption properties due to the large surface area. Many studies have indicated that carbon nanotubes can be used as ultrasensitive sensors for gas molecules as well as good storage media for hydrogen and lithium ions. But little is known about the fundamental issues of carbon nanotubes as electrodes in aqueous electrolyte solutions. We report here our studies on the electrochemical characterization of nanotube electrodes with different configurations including single walled nanotube (SWNT) paper, multi-walled nanotube (MWNT) powder, and aligned MWNT arrays on solid substrates. These nanotubes were grown under different conditions and thus present quite different electrochemical properties. Our results have shown that the electrochemical behavior strongly depends on the density, structure, and purity of the carbon nanotube. Purification and functionalization appear to be essential in defining the active surface area, charge transfer rate, and electrolyte adsorption/desorption on the electrode surface. Several methods have been investigated to purify the nanotube surface including strong acid treatment, high temperature thermal treatment, and high temperature steam treatment. Our results have shown dramatic effects of these treatments. We will also report our recent results on functionalizing carbon nanotube electrodes with biomolecules for the purpose to develop ultrasensitive electrochemical biosensors.

#### 11:30 AM Z10.8

3D MEMS DEVICES WITH FUNCTIONALIZED CARBON NANOTUBES. Vijay K. Varadan, Vasundara V. Varadan, Pennsylvania State University, Center for the Engineering of Electronic and Acoustic Materials and Devices, University Park, PA.

Carbon Nano Tubes(CNT) with their unique structure, have already proven to be valuable in their application as tips for scanning probe

microscopy, field emission devices, nanoelectronics, H<sub>2</sub>- storage, electromagnetic absorbers, ESD, EMI films and coatings and structural composites. For many of these applications, highly purified and functionalized CNT which are compatible with many host polymers are needed. A novel microwave CVD processing technique to meet these requirements has been developed at Penn State Center for the Engineering of Electronic and Acoustic Materials and Devices (CEEAMD). This method enables the production of highly purified carbon nano tubes with variable size (from 5-40 nm) at low cost (per gram) and high yield. Whereas, carbon nano tubes synthesized using the laser ablation or arc discharge evaporation method always include impurity due to catalyst or catalyst support. The Penn State research is based on the use of zeolites over other metal/metal oxides in the microwave field for a high production and uniformity of the product. An extended conventional purification method has been employed to purify our products in order to remove left over impurity. A novel composite structure can be tailored by functionalizing carbon nano tubes and chemically bonding them with the polymer matrix e.g. block or graft copolymer, or even cross-linked copolymer, to impart exceptional structural, electronic and surface properties. Bio- and Mechanical-MEMS devices derived from this hybrid composites will be presented.

#### 11:45 AM Z10.9

##### CHEMICAL FUNCTIONALIZATION OF CARBON NANOTUBES.

Rodney Andrews, David N. Jacques, Center for Applied Energy Research and Advanced Carbon Materials Center, Univ. of Kentucky, Lexington, KY; John Anthony, Robert G. Bergosh, Monica Ho, Chad Landis, Fiona McKenzie, Mark S. Meier, Grant J. Palmer, John P. Selegue, Department of Chemistry and Advanced Carbon Materials Center, University of Kentucky, Lexington, KY; Eric Grulke, Monika Kannadagali, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY; Robert C. Haddon, Hui Hu, Department of Chemistry, Univ. of California-Riverside, Advanced Carbon Materials Center, Univ. of Kentucky, Lexington, KY.

We have chemically modified SWNTs and MWNTs with a variety of different reagents to produce halogenated, alkylated, and otherwise modified nanotubes. The resulting nanotubes have been characterized by techniques that include FTIR, NAA, and SEM. In this talk we will report the types of chemical changes that have been induced in the nanotubes.

#### SESSION Z11: NANOTUBE-BASED DEVICES

Chairs: Pulickel M. Ajayan and Yahachi Saito

Thursday Afternoon, November 29, 2001

Back Bay A (Sheraton)

#### 1:30 PM \*Z11.1

NANOENGINEERING OF CARBON NANOTUBES AND THE STATUS OF ITS APPLICATIONS. Yoshikazu Nakayama, Seiji Akita, Osaka Prefecture Univ, Dept of Physics & Electronics, Osaka, JAPAN; Takashi Okawa, Daiken Chemical Co. Ltd, Osaka, JAPAN; Sigenori Yamanaka, Unisoku Co. Ltd, Osaka, JAPAN; Toshikazu Nosaka, Technology Research Institute of Osaka Prefecture, Osaka, JAPAN.

Recently, we have developed a well-controlled method for manipulating carbon nanotubes. The first crucial process involved is to prepare a nanotube array, named nanotube cartridge. We have found the ac electrophoresis of nanotubes by which nanotubes are aligned at the knife-edge. The nanotubes used were multiwalled and prepared by an arc discharge with a relatively high gas temperature. The second important process is to transfer a nanotube from the nanotube cartridge onto a substrate in a scanning electron microscope. Using this method, we have developed nanotube tips and nanotube tweezers that operate in a scanning probe microscope. For the nanotube tips, the advantage of their high aspect ratio has been revealed by imaging the 1-micrometer pitch line-and-spaces prepared on a Si wafer, the pits in DVD media, the local solvation shell in water and the bio-cells such as human erythrocytes and proteins. Their high resolution has been confirmed for imaging DNA and a Si (111) 7 x 7 structure. The cyclic observation of the surface roughness of Si wafers has proved the nanotube tips to have longer lifetime than conventional Si tips. The nanotube tips have also successfully been applied to magnetic force microscopy, Kelvin force probe microscopy, nanoindentation and nanolithography. For the nanotube tweezers, two nanotubes were attached parallel each other on the metal electrodes patterned on a conventional Si tip and their fixations were made by carbon deposition. The application of a dc voltage to the two nanotube-arms narrows the spacing between the tips of the nanotube-arms and it is fully closed when the applied voltage is beyond a certain value (pull-in voltage) which is less than 10 V. Furthermore, returning the applied voltage to zero opens it fully. Utilizing these nanotweezers, a scanning probe microscope has been developed that enables nano-sized substances to be carried.

**2:00 PM Z11.2**

**CARBON NANOTUBE SPM PROBES: FUNDAMENTALS AND APPLICATIONS.** Liwei Chen, Chin-Li Cheung, Karl Haushalter, Gregory Verdine, Charles M. Lieber Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA.

The contrast of SFM is based on additive interactions between the surface and probe; therefore, the resolution of SFM imaging greatly depends on the geometrical and mechanical properties of the probes. Carbon nanotubes make potentially ideal tips for SFM due to its small diameter, high aspect ratio, mechanical robustness, electrical conductance and chemical functionality at the open end. Here we report the preparation of carbon nanotube probes by individual assembly or direct chemical vapor deposition. The fundamental resolution limit of nanotube probes was investigated. The nanotube probes showed complex tip-induced broadening behavior in AFM imaging depending on the interaction between the probe and the surface. When imaging soft biomolecules in fluid, the resolution of these nanotube probes could be predicted based on the tube geometry. As an example of the applications, nanotube probes were utilized in high-resolution imaging to study the search mechanism of the DNA repair glycosylase hOgg1. The question is biologically crucial in DNA repair and ill suited for conventional structural method. Single molecule imaging of hOgg1-DNA complexes in air with carbon nanotube probes revealed drastic kinks at non-damaged DNA sites, which were previously believed to be induced by the protein only at damaged bases. These results suggest that hOGG1 causes substantial structural rearrangements in DNA while searching for damaged bases and a two-intermediate mechanism by which hOgg1 searches for damaged bases in the genome was proposed.

**2:15 PM Z11.3**

**IMPROVED RESOLUTION IN MAGNETIC FORCE MICROSCOPY WITH CARBON NANOTUBE TIPS.** Pete Eames, Dan Dahlberg, Univ. of Minnesota, MN; Katerina Moloni, Max Lagally, PIEZOMAX Technologies, Middleton, WI.

Carbon nanotube Magnetic Force Microscopy (MFM) tips have been fabricated using commercially available Silicon probes and bundles of or single multiwall carbon nanotubes. These tips have been directionally coated with Cr/Co multilayers to produce either an effective magnetic monopole or magnetic dipole coating as the imaging measure of the samples stray fields. Ex situ transmission electron microscopy was used to characterize the carbon nanotubes and these multilayer coatings. MFM images were acquired using a Digital Instruments Dimension 3000 in intermittent tapping mode. A comparison between our monopole/dipole carbon nanotube MFM tips and commercially available MFM tips has been made using test tracks written into a perpendicular recording media with a bit transition period of 130 nm (330 KFCI). These carbon nanotube tips demonstrate exceptional durability while achieving resolution improvements of a factor of 3 over conventional MFM techniques.

**3:00 PM Z11.4**

**THERMAL AND ELECTRONIC PROPERTIES OF A CARBON NANOTUBE-EPOXY COMPOSITE.** Michael J. Biercuk, M.C. Llaguno, M. Radosavljevic, A.T. Johnson Jr., University of Pennsylvania, Dept of Physics and Astronomy, Philadelphia, PA; J.K. Hyun, University of Pennsylvania, LRSM, Philadelphia, PA; J.E. Fischer, University of Pennsylvania, Dept of Matls Sci and Engr, LRSM, Philadelphia, PA.

We exploit the high thermal conductivity of single-wall carbon nanotubes (SWNTs) to augment the thermal transport properties of a widely utilized industrial epoxy. Preliminary results show significant enhancement of the composite thermal conductivity at all temperatures with low weight percent nanotube loading. Samples loaded with 1.0wt% SWNT material show a temperature independent increase in thermal conductivity of nearly 50 percent, providing evidence that thermal conductivity is largely limited by tube-matrix interactions. Electrical conductivity measurements provide evidence for the onset of a percolation effect between 0.2 and 0.5 wt% loading, indicated by an increase in conductivity of approximately four orders of magnitude. Results from samples of higher loading, various production techniques and samples incorporating different SWNT materials will be presented.

**3:15 PM Z11.5**

**ENERGY DISSIPATION IN CURRENT-CARRYING CARBON NANOTUBES.** Philip Kim, Paul L. McEuen, Dept of Physics, Univ. of California, Berkeley, CA; Li Shi, Arun Majumdar, Dept of Mechanical Engineering, Univ. of California, Berkeley, CA.

The temperature distributions in electrically-heated multi-walled nanotube (MWNT), metallic, and semiconducting single-walled nanotube (SWNT) have been measured with a scanning thermal microscope. The temperature profiles along the tube axis in MWNT

and semiconducting SWNT indicate the bulk dissipation of electronic energy to phonons, which suggests diffusive electronic transport. At low bias regime, metallic SWNTs exhibit dissipation only near the contacts between the tubes and the electrodes, while bulk heat dissipation has been observed at high bias voltages. This change, from non-dissipative to dissipative, in metallic SWNT suggests that the electron transport in these nanotubes is ballistic at a low electrical field regime and it becomes diffusive at a high field regime, possibly due to optical phonon coupling.

**3:30 PM Z11.6**

**DESIGN AND QUANTIFICATION OF A NANOSCALE FIELD EFFECT TRANSISTOR.** Marc in het Panhuis, Media Lab Europe, Dublin, IRELAND; Jonathan Coleman, Department of Physics, Trinity College, Dublin, IRELAND; Brian Foley, Department of Electrical and Electronic Engineering, Trinity College, Dublin, IRELAND; Paul Popelier, Robert Munn, Department of Chemistry, UMIST, Manchester, UNITED KINGDOM; Werner Blau, Department of Physics, Trinity College, Dublin, IRELAND.

A new design for a field effect transistor able to push back the physical limits of Moore's Law is described. The ON state of the device is characterized using ab initio computer simulation. An electron introduced on one side of conjugated molecular switching element can move across to the other side of molecule in an electric field in the absence of a gate voltage, a process analogous to conduction. The presence of a gate voltage effectively interrupts conjugation and suppresses conduction. A molecular-based processor of this type could demonstrate transistor density of up to  $2 \times 10^{12}$  transistors per  $\text{cm}^2$  and run at up to 12 THz.

**3:45 PM Z11.7**

**CARBON NANOTUBE LOGIC GATES.** V. Derycke, R. Martel, J. Appenzeller, Ph. Avouris, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Single carbon nanotubes can be used as the active channel in field effect transistors (FETs). Without any special treatment, the obtained FETs are always P-type: the current carriers are holes and the devices are off for positive gate bias. Here we show that this transistor behavior is due to the pinning of the Fermi level at the valence band of the semiconducting nanotubes and the presence of a large Schottky barrier for electron injection into the device. The fabrication of N-type FETs has recently been achieved by doping the device with an electron donor such as potassium. We introduce a novel approach of converting SWNT-based P-FETs into N-FETs without the use of dopants. The technique relies on the control of the electrostatic barriers and the modification of the contacts. In this way, we can position the Fermi level at any position within the band gap in a controlled manner and therefore modify the character of the device. When the Fermi level lies in the middle of the band gap, the device shows both hole and electron conduction at negative and positive gate biases respectively. When the Fermi level lies close the conduction band edge, the resulting FET is fully N-type. Using our ability to prepare both P- and N-type transistors we were able to fabricate the first nanotube-based integrated logic circuit, a NOT gate (voltage inverter). Inverters using K-doped tubes were also fabricated. We will compare the voltage inverters made by the two techniques.

**4:00 PM Z11.8**

**CONTROLLED CREATION OF A CARBON NANOTUBE DIODE BY A SCANNED GATE.** Marcus Freitag and A.T. Johnson, University of Pennsylvania, Department of Physics and Astronomy, Philadelphia, PA.

We use Scanning Gate Microscopy to precisely locate the gating response in field-effect transistors made of individual semiconducting single wall carbon nanotubes. In all samples, a dramatic increase in transport current occurs when the device is electrostatically doped with holes near the positively biased electrode. We explain this behavior with the turning on of a reverse biased Schottky barrier formed at the interface between the p-doped nanotube and the metal electrode. By positioning the gate near one of the contacts, we induce rectifying behavior in the previously symmetric device. These experiments indicate a strategy for diode fabrication based on controlled placement of acceptor impurities near a contact.

**4:15 PM Z11.9**

**STRUCTURE AND ELECTRONIC PROPERTIES OF STRAIGHT CARBON NANOTUBE Y-JUNCTIONS.** W.Z. Li, J.G. Wen, Z.F. Ren, Department of Physics, Boston College, Chestnut Hill, MA.

Carbon nanotubes are one of the most promising elements for the fabrication of nanoelectronic devices (1). However, connection of two or more CNTs together to form an ideal junction is very challenging. Alumina membrane with splitting nanochannels has been attempted to grow Y-junctions of one big stem and two small branches oriented

nearly in the same direction confined by the shape and size of the channels (2). Pyrolysis of organometallic precursor such as nickelocene along with thiophene has also been reported to result in Y-shaped junctions with angles between the arms vary in the range of  $90^\circ$  -  $150^\circ$  from junction to junction (3). Single wall Y-junctions have also been observed by scanning tunneling microscopy in the residue of the thermally decomposed C60 in the presence of transition metals (4). For electronic property measurement and practical application, large amount of high quality and identical-structured Y-junctions are required. We have successfully synthesized the very straight carbon nanotube Y-junctions by pyrolysis of methane over cobalt supported on magnesium oxide. The Y-junctions have neat smooth surfaces and uniform diameters, and the angles between the three arms are close to  $120^\circ$ . The Y-junctions carbon nanotubes grow in a similar way which is very important in the development of nanoelectronic devices. With the straight truly Y-junctions, the structure characterization and electronic property measurement are going to be reported.

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3. Satishkumar, B.C. et al. Appl. Phys. Lett. 77, 2530-2532 (2000).

4. Nagy, P. et al. Appl. Phys. A 70, 481-483 (2000).

#### **4:30 PM Z11.10**

**AFM-BASED SURFACE POTENTIAL MEASUREMENTS ON CARBON NANOTUBES.** Sandra B. Schujman, Dept. of Physics, Applied Physics and Astronomy; Robert Vajtai, Dept. of Materials Science and Engineering; Yuriy Shusterman, Sujit Biswas, Brian Dewhirst, Leo J. Schowalter, Dept. of Physics, Applied Physics and Astronomy; P. Ajayan, Dept. of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

In order to build electrical devices based on carbon nanotubes, it is crucial to understand the effects of the substrate, electrical contacts, defects and junctions on the transport properties of both multi-wall and single-wall nanotubes (MWNT and SWNT). In the present study, carbon nanotubes were deposited onto an insulating oxide layer over a conducting substrate and platinum electrical contacts were prepared via a Focused Ion Beam (FIB) deposition method. To investigate transport properties, we used an atomic force microscope (AFM) to determine the surface potential of MWNT. The technique employed applies a dc-voltage to the tip that equilibrates the local electrostatic potential on the sample so as to eliminate forces on the AFM tip caused by electric repulsion or attraction between tip and sample. The advantage of this method compared to other AFM-based techniques to measure electrical properties is that there is no alteration of the sample potential caused by the tip. An ohmic contact to the substrate allowed us to polarize it at a different potential than the nanotubes themselves. Surface potential measurements show that the potential drops along the MWNT with a slope that varies with the bias applied across the nanotube but also that slope changes near the electrical contacts. With this method, we are also able to determine configurations of charges trapped on the substrate near the nanotubes and contacts, and their effect on the electrical properties of the nanotubes. We will present results of measurements for different bias configurations of both nanotubes, nanotube networks and substrates.