

**SYMPOSIUM A**  
**Nanotubes and Related Materials**

November 27 – 30, 2000

**Chairs**

**Otto Zhou**

Physics & Astronomy Dept  
Univ of North Carolina  
CB 3255 Phillips Hall  
Chapel Hill, NC 27599-3255  
919-962-3297

**Patrick Bernier**

USTL-GDPC  
Univ of Montpellier II  
CC-26  
Montpellier, F-34095 FRANCE  
33-46-7143538

**Daniel T. Colbert**

Dept of Chemistry  
Rice Univ  
MS 100  
Houston, TX 77005  
713-348-4688

**John Fischer**

Dept of MS&E  
Univ of Pennsylvania  
Philadelphia, PA 19104-6272  
215-898-6324

**Sumio Iijima**

NEC R&D Group  
Meijo Univ  
Ibaraki, 305-8501 JAPAN  
81-298-501117

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\* Invited paper

SESSION A1: SYNTHESIS I  
Chair: Sumio Iijima  
Monday Morning, November 27, 2000  
Grand Ballroom (Sheraton)

**8:30 AM \*A1.1**

**GROWING SINGLE-WALLED CARBON NANOTUBES IN THE GAS PHASE.** Peter Willis, Michael J. Bronikowski, R. Kelley Bradley, Dan T. Colbert, Robert H. Hauge, Ken A. Smith, and Richard E. Smalley, Center for Nanoscale Science and Technology, Rice University, Houston, TX.

Large-scale production of high-purity carbon single-walled nanotubes (SWNT's) has been achieved via the High Pressure Carbon Monoxide (HiPCO) Process. This gas-phase process utilizes a continuously recirculating flow of highly pressurized (10-100 atm) carbon monoxide as the feedstock gas for nanotube production. Into a precisely designed region at the heart of the apparatus, an approximately room temperature gas mixture containing ppm concentrations of metal carbonyls is rapidly mixed into a flow of hot (700-1100 @degrees C) CO gas. Following thermal decomposition of the organometallic precursors, metal atoms condense into clusters entrained in the flowing gas. These clusters act as catalyst particles upon which SWNT nucleate and grow via CO disproportionation:  $CO + CO \rightarrow CO_2 + C(SWNT)$ . The resulting nanotubes are swept downstream of the mixing region and are collected on a series of filters. In this fashion, SWNT material of up to 99 mole-% purity has been produced at rates of up to 350 mg/hr on a prototype laboratory reactor designed and fabricated at Rice. The dependence of the quantity and quality of SWNT material produced on system parameters such as temperature, pressure, and catalyst concentration/composition will be discussed, along with recent technical advances in the HiPCO experimental apparatus.

**9:00 AM A1.2**

**PERFECTLY ALIGNED SINGLE WALL CARBON NANOTUBE CRYSTALS.** Jin Won Seo<sup>1,2</sup>, James K. Gimzewski<sup>2</sup>, Reto R. Schlittler<sup>2</sup>; <sup>1</sup>Institut de Physique, Université de Neuchâtel, Neuchâtel, SWITZERLAND; <sup>2</sup>IBM Research Division, Zurich Research Laboratory, Rüschlikon, SWITZERLAND; Mark E. Welland, Engineering Department, University of Cambridge, Cambridge, UNITED KINGDOM.

Since the discovery of carbon nanotubes in 1991 [1], new methods of synthesizing multi-walled and single-walled carbon nanotubes (MWCNT's and SWCNT's respectively) have been developed from the initial use of electric arc discharges, to laser ablation and more recently catalytic chemical vapor deposition and solid-state chemical reactions. SWCNT's are currently the subject of much research because they represent an ideal 1-D nanostructure with unique physical properties. Nevertheless, only limited success has been achieved in the preparation of ordered bundles [2,3], which are thought to be held together by weak Van der Waals forces. Here we demonstrate a new breakthrough where perfect single crystals made of well-ordered SWCNT bundles are directly fabricated using a nano-patterned solid-state reaction in vacuum. Transmission electron microscopy (TEM), Atomic Force Microscopy and Electron Energy Loss Spectroscopy were used to elucidate the structure and unique ordering of the tubes. Single walled tubes within a single crystal were found to be completely straight and have uniform diameters of approx.1.5 nm, which provides them with the unique capability to order in the micron scale. The bundles were found to terminate abruptly and they exhibit faceting, particularly in larger crystallites. Video sequences of aspects of the growth process using in-situ heating in the TEM will also be used to illustrate the basic growth mechanism. [1] Iijima, Nature 354 (1991) 56. [2] A. Thess et al., Science 273 (1996) 483. [3] Y. Zhang et al., Science 285 (1999) 1719.

**9:15 AM A1.3**

**VECTORIAL GROWTH OF CARBON NANOTUBES.** Ernesto Joselevich, Thomas Rueckes, Kyoung-ha Kim, Charles M. Lieber, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA.

Carbon nanotubes have been proposed as ideal interconnects for molecular electronics. Recently, for instance, a novel approach for carbon nanotube based random access memory has been presented. In order to realize these concepts, new methods are required for the production of ordered arrays of nanotubes on surfaces. Here we demonstrate a novel concept whereby the growth of carbon nanotubes on the surface is geometrically defined as a vector. Single-wall carbon nanotubes are produced by chemical vapor deposition on silicon wafers under the action of a local electric field parallel to the surface. The origin of the vectorial growth is defined by patterning the catalyst nanoparticles, while the direction of growth is determined by the electric field. The mechanism of growth and field-alignment, and its implications are discussed.

**9:30 AM A1.4**

**FORMING ALIGNED NANOTUBE INTERCONNECTIONS BETWEEN THIN Ni LAYERS AND Si(001).** Bingqing Wei, Z.J. Zhang, P.M. Ajayan and G. Ramanath, Department of MS&E, Rensselaer Polytechnic Institute, Troy, NY.

There is widespread interest in growing networks of aligned carbon nanotubes for creating new nano-scale device architectures on planar substrates such as Si. It is crucial to evolve strategies to interconnect nanotubes with each other, with catalyst metal films, and with the substrate, for realizing such architectures. Here, we demonstrate a way of growing vertically aligned nanotubes, which connect patterned metal lines and the Si substrate. Thin Ni layers were lithographically patterned on Si(001) substrates and exposed to xylene-metalloocene mixtures. Electron microscopy of the exposed samples show that vertically aligned multiwalled nanotubes grow only underneath the Ni layers, and result in the lifting-off of the Ni patterns from the substrate. Thus, a forest of nanotubes links the Ni layer and Si(001). In some areas, the delaminated Ni film flips over, without detaching from the nanotubes, indicating a strong bonding between Ni and the nanotubes. The mechanisms of metal film lift-off and nanotube alignment are discussed in the context of the nanotube growth behavior on patterns of other metal alloys.

**9:45 AM A1.5**

**SINGLE-WALL CARBON NANOTUBE SYNTHESIS BY THE ROOM TEMPERATURE IRRADIATION OF MILLISECOND CO<sub>2</sub> LASER PULSES.** Fumio Kokai, Kunimitsu Takahashi, Institute and Research and Innovation, JAPAN; Daisuke Kasuya, Meijo Univ, JAPAN; Masako Yudasaka, JST-ICORP, JAPAN; and Sumio Iijima, JST-ICORP, NEC, Meijo Univ., JAPAN.

Single-wall carbon nanotubes (SWNTs) were synthesized by the irradiation of CO<sub>2</sub> laser pulses (1-20 ms pulse widths and 1 kW peak power) onto graphite-Co/Ni composite target at room temperature in an Ar gas environment. In the Raman spectra of carbonaceous deposits obtained on a quartz tube wall in front of the target, the intensity of a band at about 180 cm<sup>-1</sup>, due to the radial breathing mode of SWNTs, relative to that of a broad band at 1350 cm<sup>-1</sup>, due to non-SWNT carbon materials, was found to change significantly depending on the width of the CO<sub>2</sub> laser pulse. TEM micrographs of the SWNTs synthesized by room-temperature CO<sub>2</sub> laser irradiation showed thinner bundle structures, compared to the SWNTs synthesized with the help of a furnace (1200°C). In pole-like laser plumes produced by CO<sub>2</sub> laser pulses with 1-20 ms pulse widths, emissions of C<sub>2</sub> (Swan bands) and C<sub>3</sub> and blackbody radiation was observed. The C<sub>2</sub> and C<sub>3</sub> emissions were distributed only near the target (<1cm from the target). However, the blackbody radiation were observed up to about 5 cm from the target. Based on the temperature distribution of the plume (C<sub>2</sub> vibrational temperature and the temperature of clusters and particles estimated using Planck blackbody radiation function) and shadowgraphic images indicating the formation of mushroom and turbulent clouds of growing carbonaceous materials through the interaction of Ar gas, we discuss SWNT growth from a molten carbon-metal particle via super-saturation and segregation during the time of milliseconds.

SESSION A2: SYNTHESIS II

Chair: Daniel T. Colbert  
Monday Morning, November 27, 2000  
Grand Ballroom (Sheraton)

**10:30 AM \*A2.1**

**NANOTUBE CATALYST OPTIMIZATION USING COMBINATORIAL APPROACHES.** Alan M. Cassell, Sunita Verma, Goldwyn Parker II, Ramsey Stevens, Cattien Nguyen, Lance Delzeit, Meyya Meyyappan, Jie Han, NASA Ames Research Center, Moffett Field, CA.

Libraries of liquid-phase catalyst precursor solutions were printed onto various substrates and evaluated for their effectiveness in catalyzing the growth of carbon nanotubes by chemical vapor deposition (CVD). The catalyst precursors were composed of inorganic salt solutions of Al, Si, Fe, Co, Ni, Mo and a removable tri-block copolymer structure-directing agent. Scanning electron microscopy (SEM) was used to rapidly screen the catalyst libraries for activity. Parameters such as catalyst composition (stoichiometry, concentration) and reaction conditions (temperature, gas flow rate) were varied to quickly identify high yielding nanotube catalysts. As many as 100 different catalysts can be screened at one time, making the discovery process much less time-consuming. Catalyst compositions were identified that afforded aligned multi-walled carbon nanotube arrays as well as high yielding, single-walled carbon

nanotube arrays. The optimized catalysts were then employed in a variety of applications such as the growth of scanning probe microscope tips and nanoelectronic components.

#### 11:00 AM A2.2

CONDENSED PHASE CONVERSION GROWTH OF CARBON NANOTUBES. D.B. Geohegan, X. Fan, M.C. Guillorn, R.D. Seals, S.J. Pennycook, Oak Ridge National Laboratory, Oak Ridge, TN; A.A. Puzos, Department of Materials Science and Engineering, Univ. of Tennessee, Knoxville, TN.

Single-wall carbon nanotubes (SWNT) are efficiently grown by laser vaporization of composite carbon and metal catalyst targets inside a hot oven environment. From time-resolved, in situ imaging and laser spectroscopy of the plume of vaporized material, along with TEM analysis of deposits collected under direct diagnostic monitoring, we conclude that the majority of SWNT growth occurs over seconds of time from a feedstock of carbon clusters and nanoparticles. Ex situ annealing of short, SWNT "seeds" results in continued growth of SWNT, supporting a condensed phase conversion of particulate carbon feedstock by activated metal catalyst nanoparticles or SWNT "seeds" as a viable mechanism for growth of carbon nanotubes during laser vaporization. These measurements have been broadened and extended to include the growth of multiwall carbon nanotubes by condensed phase conversion (CPC) of various feedstocks. The processing conditions resulting in optimal nanotube growth were monitored using in situ diagnostics and ex situ FESEM and TEM analyses of the resulting carbon nanotube-based carbon composites.

#### 11:15 AM A2.3

SYNTHESIS OF HOMOGENEOUS DIAMETER SINGLE-WALL CARBON NANOTUBES BY HIGH TEMPERATURE INDUCTION HEATING. Thomas Gennett, Rochester Institute of Technology, Department of Chemistry and Center for Materials Science, Rochester, NY; Anne C. Dillon, Jeff L. Alleman, Kim M. Jones, Phillip A. Parilla and Michael J. Heben, National Renewable Energy Laboratory, Golden, CO.

Over the past several years a large number of synthetic procedures for the production of Carbon Single-Wall Nanotubes (SWNTs) have been developed. The resultant SWNT materials, regardless of the specific synthetic technique, are a mixture of various diameters and types of SWNTs. The polydispersity in tube diameter and type makes it difficult to observe the physical, electrical and mechanical properties of specific nanotubes. Monodisperse or "diameter-pure" nanotubes are required in order for a more detailed understanding of SWNT materials. This presentation will describe a set of experimental conditions utilizing induction heating of a graphite target that reproducibly results in the synthesis of a very narrow diameter distribution of SWNTs. Our typical synthesis technique is similar to the pulsed laser vaporization technique described by Guo et al [1] Under a 100 sccm argon flow the susceptor is heated by inductively-coupled RF to a maximum of 1650°C as measured by a two color pyrometer. The maximum temperature is limited by the coupling of the induction heating supply to the susceptor. The rest of the reaction vessel is not externally heated. The resultant web-like material is collected and subsequently analyzed by Raman and optical spectroscopy as well as TEM. A very narrow diameter distribution corresponding to a Raman line centered at 182  $\text{cm}^{-1}$  is observed. The SWNTs also form unusually small bundles containing as few as 1-5 tubes. The results indicate that the high temperature of the target material coupled with the low temperature of the immediate surroundings greatly reduce the reaction plume region as the laser strikes the target. This rapid quenching produces an SWNT raw soot with a very narrow diameter distribution and small bundle sizes. These results will be discussed in greater detail. (1) T. Guo, P. Nikolaev, A. Thess, D.T. Colbert and R.E. Smalley, Chem. Phys. Lett. 1995, 243, 49.

#### 11:30 AM A2.4

CONDENSED PHASE NUCLEATION AND CONTINUING GROWTH THEORY FOR SINGLE WALL CARBON NANOTUBES. X. Fan, R. Buczko, Solid State Div, Oak Ridge National Laboratory, Oak Ridge, TN; A.A. Puzos, Dept of Materials Science and Engineering, Univ of Tennessee, Knoxville, TN; D.B. Geohegan, Solid State Div, Oak Ridge National Laboratory, Oak Ridge, TN; S.T. Pantelides, Dept of Physics and Astronomy, Vanderbilt Univ., Nashville, TN; S.J. Pennycook, Solid State Div, Oak Ridge National Laboratory, Oak Ridge, TN.

Previous experimental results by in-situ diagnostic in pulsed laser ablation found atomic species or small clusters (C<sub>2</sub>, C<sub>3</sub>, Co) disappear during most of the single wall carbon nanotube (SWNT) growth period. Also the Z-contrast imaging and electron energy loss spectroscopy does not find any metallic atoms incorporated in the carbon nanotube bundles, and no catalyst particles smaller than 2 nm in diameters. Furthermore, continuation of growth was achieved

outside the laser ablation chamber indicating a condensed phase growth mechanism. Therefore we propose a new atomic level nucleation and continuing growth theory for catalyst assisted SWNT growth. In this model, both carbon and catalyst are vaporized initially. On cooling, carbon vapor were condensed first forming small clusters followed by the metal catalyst condense on to the carbon clusters. The well established equilibrium bulk carbon/metal phase diagram suggests that they form either liquid or liquid/solid eutectics nano-particles/droplet at high temperature. The further cooling leads to the phase separation in carbon/catalyst nano-particle. With sufficient low carbon concentration and small particle size, the carbon atoms can diffuse fast enough to one side of the particle and form solid carbon phase. Theoretical studies show that carbon clusters are more favorable to form caps than flakes when atom number  $n > 40$ . Although cage is more favorable for free carbon clusters, cap is more likely in this case because the presence of catalyst. The interaction between catalyst and carbon at the interface will determine the optimal diameter of the cap. Once the cap is formed, further carbon segregation is naturally crystallized at the root of the carbon cap which eventually leads to a cylindrical tube. Since no vapor phase carbon/catalyst is needed in this growth model, condensed phase continuing growth is readily achieved with right temperature and supplies of carbon atoms.

#### 11:45 AM A2.5

FORMATION OF CARBON NANOTUBES AND SILICON NANOWIRES BY RAPID THERMAL PROCESSING FROM ION-BEAM SPUTTERED FILMS. T.S. Wong, K.H. Chen, Academia Sinica, Institute of Atomic and Molecular Sciences, Taipei, TAIWAN; L.C. Chen, National Taiwan University, Center for Condensed Matter Sciences, Taipei, TAIWAN; C.T. Wang and K.J. Ma, Chung Cheng Institute of Technology, Dept. of Mechanical Engineering, Long-Tan, TAIWAN.

We report here an efficient method to produce carbon nanotubes (CNT) and silicon nanowires (SiNW) using rapid thermal process (RTP) of thin films deposited by ion beam sputtering (IBS). Both RTP and IBS are convenient and robust techniques suitable for large-area wafer process and are well established in the industry. For CNT, iron-containing amorphous carbon film was first prepared by IBS from graphite-Fe mixed target, then subjected to RTP for different duration times at temperatures of 800-1200°C. For SiNW, iron-containing amorphous Si film was first prepared by IBS from Si-Fe mixed target and followed by RTP treatment. The RTP treatment was carried out in either argon or nitrogen ambient at atmospheric pressure. The latter gas was found to be most efficient for transforming amorphous carbon into CNT. For instance, high density of multi-wall CNTs with a diameter of about 15-30 nm and a length of micron were found to cover the entire substrate after RTP for 15 sec at 1200°C in nitrogen ambient. The IBS-RTP approach offers an unprecedented opportunity for studying the kinetics of CNT growth in that the dimension changes of CNT can be monitored as a function of time and temperature in a controllable manner.

### SESSION A3: ELECTRONIC PROPERTIES I

Chair: Luc Henrard

Monday Afternoon, November 27, 2000

Grand Ballroom (Sheraton)

#### 1:30 PM \*A3.1

FUNDAMENTAL PROPERTIES AND APPLICATIONS OF SINGLE-WALLED CARBON NANOTUBES. Charles M. Lieber, Harvard University, Department of Chemistry and Chemical Biology, Division of Engineering and Applied Sciences, Cambridge, MA.

Single-walled carbon nanotubes (SWNTs) represent unique systems both for testing our fundamental understanding of the physics of low-dimensional materials and for building new nanoscale tools and devices. This presentation will overview selected studies addressing both areas. First, atomically-resolved scanning tunneling microscopy and spectroscopy studies of the interaction of magnetic atoms and clusters with extended and finite size SWNTs, and the structure and electronic properties of intramolecular nanotube junctions will be described. Second, a new concept for a carbon nanotube based molecular scale computer, which is based on a suspended SWNT crossbar array, will be discussed together with proof of concept experiments. Third, critical tools for imaging, sensing and manipulation at the nanometer to molecular scales, which are based on the unique mechanical and electromechanical properties of nanotubes, will be presented. Future directions and challenges for the field will be discussed.

#### 2:00 PM A3.2

NEGATIVE DIFFERENTIAL RESISTANCE IN NANOTUBE DEVICES. F. Léonard, J. Tersoff, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

We present results of quantum transport calculations of the device properties of degenerately doped nanotube p-n junctions and undoped metal-nanotube-metal junctions. We show that both of these devices exhibit negative differential resistance, with very high peak-to-valley current ratios even at room temperature. The undoped junctions rely on the quasi-one-dimensional geometry of nanotubes and have no analog in bulk devices.

### 2:15 PM **A3.3**

QUANTUM TRANSPORT THROUGH INTERMOLECULAR NANOTUBE JUNCTIONS. Alper Buldum, Jijun Zhao, Calin Buia, Jie Han and Jianping Lu, Dept. of Physics and Astronomy, University of North Carolina at Chapel Hill, NC.

Quantum transport properties of intermolecular nanotube junctions are investigated. Intermolecular conductance is found to depend sensitively on atomic scale registry of contacts and nanotube chirality. Contact resistance can vary several orders of magnitude with atomic scale movement. In optimal configurations the intermolecular conductance approaches that of perfect nanotubes. Novel phenomena such as negative differential resistance, resonance conductance, and nonlinear variation of resistance with contact area are found. These unusual properties may lead to novel device applications.

### 2:30 PM **A3.4**

DYNAMIC CONDUCTANCE OF CARBON NANOTUBES.

C. Roland<sup>1</sup>, M. Buongiorno Nardelli<sup>1</sup>, J. Wang<sup>2</sup> and H. Guo<sup>3</sup>.

<sup>1</sup>Department of Physics, NC State University, Raleigh, NC;

<sup>2</sup>Department of Physics, The University of Hong Kong, Hong Kong, CHINA;

<sup>3</sup>Department of Physics, McGill University, Montreal, PQ CANADA.

The dynamic conductance of carbon nanotubes was investigated using a nonequilibrium Green's function formalism within the context of a tight-binding model. Specifically, the AC response through "infinite" and finite-sized nanotubes will be discussed for tubes of different helicities, heterojunctions and defects. Because of the induced displacement currents, the dynamic conductance of nanotubes differs significantly from the DC conductance displaying both capacitive and inductive responses. The important role of photon assisted transport through nanotubes is revealed, and its implications for experiments discussed.

## SESSION A4: ELECTRONIC PROPERTIES II

Chair: Ray H. Baughman

Monday Afternoon, November 27, 2000

Grand Ballroom (Sheraton)

### 3:15 PM **\*A4.1**

NMR STUDIES OF SINGLE WALLED CARBON NANOTUBES.

Alfred Kleinhammes, X.-P. Tang, C.L. Liu, H. Shimoda, L. Fleming, K.Y. Bennoune, S. Sinha, C. Bower, O. Zhou, and Y. Wu, Department of Physics and Astronomy, University of North Carolina at Chapel Hill, NC.

In previous work we studied the electronic properties of single walled carbon nanotubes (SWNTs) by measuring the <sup>13</sup>C spin lattice relaxation times (T<sub>1</sub>) to determine the density of states at the Fermi Level. Since NMR measures the local density of states, different types of SWNTs with different local density of states can be resolved. Indeed, two types of SWNTs are observed. In some samples, one-third of SWNTs relaxes about 10 times faster than the other two-thirds of SWNTs. The fast-relaxing component is attributed to metallic SWNTs and the slow-relaxing component is attributed to semiconducting SWNTs. The spin-lattice relaxation rate of the fast-relaxing component is proportional to the temperature as expected for metallic systems. From the T<sub>1</sub> data the density of states at the Fermi level can be estimated. The determined value agrees well with theoretical predictions. The electronic properties of SWNTs might change with exposure of the sample to molecules which adsorb on to the tubes or intercalate into the bundles. The molecules can be introduced in gas form (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, He, air) or through solid state reaction (Li). We studied the effect of the adsorbed molecules on the relaxation behavior of the <sup>13</sup>C spins and find significant decreases in T<sub>1</sub> for Li, O<sub>2</sub> and air. A smaller decrease in T<sub>1</sub> was observed for He and no change was observed upon exposure to H<sub>2</sub> and N<sub>2</sub>. The properties of adsorbed gases were studied using <sup>1</sup>H, <sup>7</sup>Li NMR.

### 3:45 PM **A4.2**

ELECTRONIC STATES OF ALKALI METAL DOPED SINGLE WALL CARBON NANOTUBE AGGREGATES STUDIED BY LOW TEMPERATURE NMR. Hironori Ogata, Kyuya Yakushi, Institute for Molecular Science, Okazaki, JAPAN; Syunji Bandow, ICORP-JST, JAPAN; Syogo Kuno, Yahachi Saito; Dept of Electrical and Electronic Engineering, Mie University, Tsu, JAPAN.

Electronic states of alkali metal doped Single Wall Carbon Nanotube aggregates (SWNTs) below 100 K were studied by <sup>13</sup>C-NMR. The starting SWNTs samples used in this study were synthesized by the dc arc discharge method using non-ferromagnetic Pt-Rh mixed catalyst. Amorphous carbon contained in the raw soots were removed by using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Doping of alkali metals were performed by so-called two-bulb method. Recovery of <sup>13</sup>C-magnetization for undoped SWNTs was found not to obey the single exponential law. This fact suggests the existence of two kinds of nuclear spin components below 100 K, i.e. fast-relaxing spins which may be attributed to metallic tubes and slow-relaxing spins to semiconducting tubes. On the other hand, we found that single exponential curve fitting can reproduce the data points of <sup>13</sup>C-magnetization curve for K-doped SWNTs sample. The value of <sup>13</sup>C-T<sub>1</sub> was found to become smaller by K-doping. Moreover, we found that the value of <sup>13</sup>C-T<sub>1</sub> become much smaller by using SWNTs samples after appropriate heat treatment as a starting sample. Changes in the electronic states by K-doping and results for the other kinds of alkali-doped samples will be discussed in this presentation.

### 4:00 PM **A4.3**

STM IMAGING OF CHIRAL METALLIC CARBON NANOTUBES.

A. Maarouf, N. Wilson and C.L. Kane, University of Pennsylvania, Department of Physics, Laboratory for Research on the Structure of Matter, Philadelphia, PA.

Energy resolved STM imaging of short carbon nanotubes offers a unique opportunity for probing the wavefunctions of the discrete electronic states. However, interpretation of such images will be complicated for two reasons: (1) Since the electronic states of the nanotube have two bands, the structure of the wavefunctions (and thus the image) is determined by the 2 by 2 reflection matrices characterizing each end. In all but non-chiral tubes with high symmetry caps, reflection will mix the bands in a non-universal way. (2) Asymmetry of the STM tip is known to severely modify the images of nanotubes and graphite: the STM image is *not* simply a picture of the wavefunction. We have developed a framework for calculating the STM tunneling density of states for chiral nanotubes, taking into account both the tube-ends and tip effects. By focusing on the longest wavelength Fourier components of the STM image we show that it is possible to "calibrate" the STM tip with three parameters. Since there are two bands there are two distinct classes of wavefunctions on the tubes. The images of the two wavefunctions contain enough information to determine the tip calibration, and the orthogonality between the two states leads to a nontrivial pair of constraints on the images. In this way, the wavefunctions of the eigenstates *can* be measured.

### 4:15 PM **A4.4**

WORK FUNCTION OF CARBON NANOTUBES. Masashi Shiraishi, Masafumi Ata, SONY Corporation, Frontier Science Laboratories, Yokohama, JAPAN.

Carbon nanotubes (CNTs) is recognized as a fascinating material for nano scale electronic device<sup>(1)</sup> for the variety of electronic structure and one-dimensional geometry. The work function (W.F.) is one of the basic physical quantities to determine the electronic structure of the CNT/metal interface and it is essential to know the precise value for device fabrication. There is a room for discussion on the W.F. of CNTs and there have been many reports by various methods. We studied the W.F. of CNTs by open-counter photoelectron emission (PEE) system. While there is a difficulty in the measurement of air-exposed materials by ultraviolet photoemission spectroscopy (UPS), the PEE method makes us easy and precise work function measurements possible.

We found that the W.F. of multi-walled CNTs is 4.95eV and that of single-walled CNTs is 5.05eV. For single-walled CNTs, this value is not significantly different from the previously reported value of 4.8eV as measured by UPS method<sup>(2)</sup>. For comparison, we measured the W.F. of highly oriented pyrolytic graphite (HOPG) that has an orthogonal  $\pi$ - $\sigma$  valence state. The measured value was 4.85eV, slightly smaller than that of CNTs. Because CNTs has a non-orthogonal  $\pi$ - $\sigma$  valence state, the experimental results can be interpreted as a reflection of different valence states between HOPG and CNTs. First principle *ab-initio* calculation was carried out and the experimental data were well reproduced in this calculation.

References:

(1) Z. Yao et. al., Nature 402 (1999), 273.

(2) S. Suzuki et. al., submitted in Appl. Phys. Lett.

### 4:30 PM **A4.5**

EFFECT OF TRANSITION METAL IMPURITY ON TRANSPORT PROPERTIES OF SWNTS. B.K. Pradhan, G.U. Sumanasekera, C. Adu, P.C. Eklund, Department of Physics, Penn State University, University Park, PA.

Electrical transport properties in as-synthesized SWNTs are now

known to be sensitive to oxygen doping under ambient conditions[1,2]. Degassing samples in vacuum at 500 K drives the thermopower negative, indicating degassed metallic tubes are n-type. But the origin of the anomalously large value of thermopower is still not clear. Recently, the coupling of the conduction electrons in SWNTs with localized magnetic moments of residual transition metal catalyst impurity (Kondo effect) has been shown to account for some of these anomalies[3]. We present results of thermopower and resistivity as a function of residual catalyst concentration (as determined by TGA analysis) through a series of purification steps which successively remove the Ni impurity in the samples. We have found the suppression of the size of the Kondo peak in the thermopower of O<sub>2</sub> doped and degassed SWNT mats correlates with the amount of Ni in the samples. Temperature dependence of the resistivity shows almost no change with the amount of Ni suggesting low temperature upturn in resistivity has different origin other than the Kondo effect. This work was supported by Grants NSF DMR 98-09686 and DOD DAAB07-97-C-J036. [1] P.G. Collins et al., Science, **287**, 622 (2000) [2] G.U. Sumanasekera et al., accepted for Phys. Rev. Lett. [3] L. Grigorian et al., Phys. Rev. B, **60**, R11309 (1999)

#### 4:45 PM A4.6

SPIN-POLARIZED ELECTRON TRANSPORT IN CARBON NANOTUBES. Dirk Orgassa, Gary J. Mankey, Hideo Fujiwara, Univ of Alabama, MINT Center, Tuscaloosa, AL.

Electronic transport measurements in multiwall carbon nanotubes indicate the possibility for ballistic (Frank *et al.*, Science **280**, 1744) and spin-coherent (Tsukagoshi *et al.*, Nature **401**, 572) electron transport. We present spin-polarized transport measurements on carbon nanotubes contacted by ferromagnetic electrodes. The electrodes are prepared by electron-beam evaporation through a shadow mask. In contrast to previous measurements the gap between the electrodes is as wide as a micrometer. The observed magneto-resistance effect is consistent with a mean free path for spin-flip scattering of at least 400 nm.

### SESSION A5: PROCESSING AND PURIFICATION

Chair: Zhifeng Ren

Tuesday Morning, November 28, 2000  
Grand Ballroom (Sheraton)

#### 8:30 AM \*A5.1

MAGNETICALLY ALIGNED MEMBRANES OF SINGLE-WALL CARBON NANOTUBES. D.A. Walters, Univ of Central Florida, Dept of Physics, Orlando, FL; M.J. Casavant, X.C. Qin, J.J. Schmidt, C.B. Huffman, K. Smith, D.T. Colbert, R.E. Smalley, Rice Univ, Ctr for Nanoscale Science and Technology, Houston, TX.

Nanotubes have exceptionally anisotropic properties: mechanical, optical, thermal, electronic, and magnetic. In order to measure and apply these properties, we prepared an aligned bulk solid of single-wall carbon nanotubes. Nanotubes were sonicated extensively to produce a stable colloidal suspension containing mostly individual nanotubes and small ropes. Such a well-dispersed suspension was demonstrated to align in a magnetic field; the average alignment energy was 28 times thermal energy at room temperature. Under similar conditions, a suspension was filtered in the presence of a magnetic field parallel to the filter, producing an aligned solid membrane of nanotubes. The magnetically aligned membrane displays anisotropic mechanical, optical, thermal, and electronic properties. Its density is over half of the theoretical bulk density of close-packed nanotubes. This is an order of magnitude greater than the density of unoriented membranes ("buckypaper"); however, SEM and TEM results indicate that the aligned membranes are microfibrillar rather than crystalline, with frustration in the packing of nanotubes into ropes. Nevertheless, this represents a starting point for the experimental study of anisotropy in a wide variety of nanotube properties, the latest results of which will be discussed.

#### 9:00 AM A5.2

SIMPLE AND COMPLETE PURIFICATION OF SINGLE-WALL CARBON NANOTUBES. A.C. Dillon, J.L. Alleman, K.M. Jones, P.A. Parilla, M.J. Heben, National Renewable Energy Laboratory, Golden, CO; T. Gennett, Department of Chemistry and Center for Materials Science, Rochester Institute of Technology, Rochester, NY.

Carbon single-wall nanotubes (SWNTs) have a variety of unique physical, electronic and mechanical properties. However, the SWNTs must be thoroughly purified if they are to be used in a variety of projected applications and basic studies. We employ a laser synthesis technique similar to that described by Guo *et al.*<sup>1</sup> that yields crude soots containing 10-25 wt% SWNTs. When care is taken to avoid both forming graphite-encapsulated metal particles and incorporating sputtered target material into the collected soot, the non-destructive, scalable, 3-step purification scheme described here produces materials

with > 98 wt% pure SWNTs. A dilute nitric acid reflux digests, functionalizes, and redistributes non-nanotube carbon fractions in the soots to form a uniform and reactive coating on the SWNTs. This coating is selectively removed by oxidation in air. Raman and inductively coupled plasma spectroscopies (ICPS), and thermogravimetric analysis (TGA) are used to evaluate the purity of the material at each step of the process, and illustrate that very few tubes are consumed. Such a simple purification technique is not currently available and the use of TGA and ICPS defines a technique by which the components in raw and processed materials may be accurately determined on a weight percent basis. Infrared (IR) and UV-vis spectra of these highly pure materials are also compared to spectra of crude nanotube soots. By employing multiple internal reflectance infrared spectroscopy on our highly pure SWNT samples, we for the first time clearly observe IR active SWNT modes at 862 and 1545 cm<sup>-1</sup>. (1) T. Guo, P. Nikolaev, A. Thess, D.T. Colbert and R.E. Smalley, Chem. Phys. Lett. (1995) 243, 49.

#### 9:15 AM A5.3

SOLUBILITY OF SINGLE WALLED CARBON NANOTUBES.

Marc in het Panhuis, Department of Physics, Trinity College, Dublin, IRELAND; W.J. Briels, Department of Chemical Engineering, Twente University, Enchede, THE NETHERLANDS; R.W. Munn, Department of Chemistry, UMIST, Manchester, UNITED KINGDOM; and W.J. Blau, Department of Physics, Trinity College, IRELAND.

It has been experimentally established that single walled nanotubes (SWNT) are soluble in a toluene/PPV (oligo-polyphenylenevinylene) solution, but not in a toluene/DOC (dioctoxy naphthalene) solution. Although both molecules have similar chemical characteristics. Molecular dynamics simulations have been carried out to investigate the difference in absorption between PPV and DOC solutions. Toluene, SWNT, PPV and DOC are modelled using the united atom (UA) approach. Each UA is the centre of a Lennard-Jones potential. The free energy profile was calculated using extended ensemble dynamics. The calculated free energy suggests that the free energy difference for PPV onto SWNT is much smaller compared to DOC onto SWNT, hence the difference in adsorption behaviour.

#### 9:30 AM A5.4

THE EFFECTS OF ANNEALING ON THE PHYSICAL AND ELECTRONIC STRUCTURE OF CARBON NANOTUBES INVESTIGATED WITH TEM/EELS. B.W. Reed, M. Sarikaya, University of Washington, Dept of Materials Science and Engineering, Seattle, WA; L.R. Dalton, University of Washington, Dept of Chemistry, Seattle, WA; G.F. Bertsch, University of Washington, Dept of Physics, Seattle, WA.

Samples of carbon nanotube material with various growth and annealing histories were investigated with high-resolution transmission electron microscopy and electron energy loss spectroscopy. We demonstrate significant differences in both the physical structure and the electronic properties of samples which differ only in the conditions under which they were annealed. The carbon K-edge structure, which is sensitive to the relative proportions of sp<sup>2</sup> and sp<sup>3</sup> hybridization, shows a significant increase in the  $\pi^*$  density of states under annealing at 1100°C, for a sample consisting mostly of single-walled nanotubes. This suggests that defects in the bonding of the nanotubes are healed at this temperature, resulting in a material that more closely approximates the ideal purely sp<sup>2</sup>-hybridized structure. This low-temperature anneal produced no apparent change in the physical structure, as viewed in high-resolution electron microscopy. Upon annealing at a higher temperature of 2150°C, the single-wall tubes gave way to multi-layer structures, including multi-wall nanotubes and spherical "bucky onions", mixed with amorphous carbon. The multi-layered structures produced an energy loss profile essentially identical to that of randomly oriented graphite.

#### 9:45 AM A5.5

THERMAL STABILITY OF SINGLE-WALLED CARBON NANOTUBES. Lu-Chang Qin<sup>1</sup>, Masako Yudasaka<sup>1</sup> and Sumio Iijima<sup>1,2,3</sup>. <sup>1</sup>JST Nanotubulite Project, c/o NEC Corp., Tsukuba, JAPAN; <sup>2</sup>R&D Group, NEC Corporation, Tsukuba, JAPAN; <sup>3</sup>Dept. of MS&E., Meijo Univ., Nagoya, JAPAN.

Single-walled carbon nanotubes, produced by laser evaporation, have been subject to heat treatment at high temperatures up to 2200°C and the structural changes have been studied by high-resolution electron microscopy. Carbon nanotubes are found to undergo noticeable morphological changes when they are treated at high temperatures. At temperature below 2000°C, an increase of the average nanotube diameters was observed as demonstrated by a shift of the center of distribution in the histogram of diameter distribution. This is attributed to the fact that smaller nanotubes, due to their higher structural instability compared with larger ones, would collapse first before larger ones were destroyed. When the nanotubes were heated to temperatures higher than 2000°C, strong graphitization was

found to have occurred and single-walled carbon nanotubes could no longer be observed. The graphitized structure contains a lot of cage-like structures, indicating that single-walled carbon nanotubes can be regarded as non-graphitizing carbon.

SESSION A6: SYNTHESIS AND CHARACTERIZATION  
Chair: Michael J. Heben  
Tuesday Morning, November 28, 2000  
Grand Ballroom (Sheraton)

**10:30 AM A6.1**

RECENT PROGRESS ON GROWTH OF MULTIWALL CARBON NANOTUBES. Z.F. Ren, Z.P. Huang, W.Z. Li, D.Z. Wang, J.H. Chen, Y. Tu, S.X. Yang, J.G. Wen, J. Moser, M.J. Naughton, Boston College, Department of Physics, MA.

Following our success of aligned growth of large arrays of multiwall carbon nanotubes, we have extended this technique to grow carbon nanotubes on a variety of useful substrates such as tungsten coil, conventional STM tip, quartz fiber, etc. for applications such as lamp element, high resolution STM tip, scanning metrological tip, etc. respectively. SEM and TEM are used to examine the microstructure. In addition, we also discovered a new technique that can yield kilograms of multiwall carbon nanotubes at extremely low cost. Using the carbon nanotubes produced by this new technique, we have improved conductivity by 250 times in the electrospun polymer fiber mat. We have also succeeded to synthesize electrodes with capacity above 200 F/g which is very much desired for Li battery applications and energy storage.

**10:45 AM A6.2**

WELL-ALIGNED CARBON NANOTUBES SYNTHESIZED BY ELECTRON CYCLOTRON RESONANCE CHEMICAL VAPOR DEPOSITION. F. Hoshi, T. Ishikura, FCT Research Dept, Japan Fine Ceramics Center, Tsukuba, JAPAN; S. Yamashita, Frontier Technology Research Institute, Tokyo Gas Co., Ltd, Yokohama, JAPAN; K. Tsugawa, A. Goto, FCT Research Dept, Japan Fine Ceramics Center, Tsukuba, JAPAN; M. Yumura, National Institute of Materials Chemical Research, Tsukuba, JAPAN; T. Hirao, Osaka University, Osaka, JAPAN; S. Fujiwara, Y. Koga, National Institute of Materials Chemical Research, Tsukuba, JAPAN.

Well-aligned high density carbon nanotubes (CNTs) perpendicular to metal thin films deposited on n-type Si (100) substrate have been synthesized successfully by electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-CVD). The metal thin films were coated on the Si substrate using vacuum evaporation method. The metal of Pd, Fe, Co, and Ni was utilized. CNTs were grown at 550-800°C. Methane is used as the carbon source for the growth of the CNTs with the mixture of hydrogen and argon. The applied microwave power and the pressure during the growth of CNTs were 800 W and  $1.8 \times 10^{-1}$  Pa, respectively. The growth time of the CNTs was maintained for 30 min. The morphology of the CNTs was examined by scanning electron microscopy. The CNTs with diameter in the range of 50-80 nm were obtained in this study. The length and the density of CNTs range from 1.5 to 2  $\mu\text{m}$  and from  $10^9$  to  $10^{10}$  /  $\text{cm}^2$ , respectively. Transmission electron microscope images reveal the CNTs to be multiwalled tubes. We examined the diameter and uniformity of the CNTs as a parameter with plasma intensity and methane, hydrogen and argon gas ratio, and their flow rates. The ECR-CVD process has characteristics of high plasma density at low temperature, less ionic damage, contamination-free and high deposition rate. Thus the ECR-CVD process is a suitable method to synthesize the CNTs of large area. Moreover their electron field emission characteristics have been measured. Using this method, devices requiring freestanding vertical CNTs such as scanning probe microscopy, field emission flat panel displays, etc. can be fabricated without difficulty.

**11:00 AM A6.3**

UNUSUAL RESONANCE RAMAN SCATTERING FROM HIPCO-DERIVED SWNTS. A.A. Sirenko, P.C. Eklund, Dept. of Physics, Pennsylvania State University, University Park, PA; M.J. Bronikowski and R.E. Smalley, Rice University.

We have carried out resonant Raman scattering studies of mat samples obtained from different batches of SWNT material made at Rice University by catalytic growth in high pressures of CO with Ni-carbonyl (HIPCO). The Raman spectra using visible excitation is similar to that of bundles of SWNTs produced by the arc discharge and pulsed laser vaporization methods. That is, the spectra exhibit characteristic radial breathing and tangential C-atom displacement modes. However, the resonance curve (i.e., Raman cross section vs. laser excitation energy) is strongly sensitive to the HIPCO synthesis

conditions, with the maxima in the cross section shifting by about  $\sim 0.5$  eV from one HIPCO sample to the other. Careful electron microscopy and transport properties measurements are proceeding to explain the sensitivity of these resonance curves to the physical properties of the SWNTs.

**11:15 AM A6.4**

EFFECT OF THE INTERTUBE INTERACTIONS ON VIBRATIONAL PROPERTIES OF FINITE AND INFINITE BUNDLES OF SINGLE-WALL NANOTUBES. Luc Henrard, Lab Phys Sol, Fac. Univ. ND de la Paix, Namur, BELGIUM; Valentin N. Popov, Fac Physics, Univ Sofia, Sofia, BULGARIA; Angel Rubio, Dept Phys. Theor., Univ. Valladolid, Valladolid, SPAIN; Philippe Lambin, Lab Phys Sol, Fac. Univ. ND de la Paix, Namur, BELGIUM.

Carbon single-wall nanotubes are routinely produced by various methods and they are most often collected as two-dimension microcrystals of tens of individuals. In order to investigate the effect of the tube-tube interaction on vibrational properties of these ropes, we use a pair-potential approach for the evaluation of van der Waals bounding. In a continuum limit, we show that the inter-tubes mode range from  $5 \text{ cm}^{-1}$  to  $60 \text{ cm}^{-1}$  [1], depending on the number of tubes in the bundle and on the tube diameters. We also present dispersion curves of infinite arrays of nanotubes and have found that the sound velocity are 1226 m/s and 806 m/s for the two acoustic phonon branches [2]. On another hand, we focus on the so-called 'radial breathing mode' (RBM). Indeed, this low frequency fully symmetric Raman active mode is one of the more popular nanotube signature for the characterization of samples. From both rigid cylinder approach [1,2] and valence force field [3], we have found that the van der Waals interaction upshifts the resonant frequency by 10% for (10,10) infinite bundles and that this value is already reached for a bundle of 20 tubes. For smaller bundles, the more intense breathing mode appears at intermediate frequency and a complex excitation scheme occurs that depends on the symmetry of the bundle. Moreover, from a Valence Force Field calculation, we found that large tubes (larger than (10,10) tubes), can hardly be considered as rigid 'breathing' cylinders and that the smaller upshift and the splitting of modes that are observed in that case can be explain by this softening. We also investigate the RBM of irregular bundles, that is for bundles made of various kinds of tubes. The RBM signature of such bundles is found to be different from the superposition of individual nanotube excitations. [1] L. Henrard, E. Hernandez, P. Bernier, A. Rubio. Phys. Rev. B 60 (1999) R8521 [2] L. Henrard, Ph. Lambin, A. Rubio. Proceedings of the IWEPNM 2000 - Kirchberg, In Press [3] V.N. Popov, V.E. Van Doren, M. Balkanski. Phys. Rev. B 59 (1999) 8355

**11:30 AM A6.5**

POLARIZED RAMAN SPECTRA OF CARBON NANOTUBES. Ado Jorio, Sandra D.M. Brown, Gene Dresselhaus, Mildred S. Dresselhaus, Massachusetts Institute of Technology, Cambridge, MA; Marcos A. Pimenta, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL; Riichiro Saito, Dept. of Electronics-Engineering, Univ. of Electro-Communications, Tokyo, JAPAN; Apparao M. Rao, Center for Applied Energy Research, Dept. of Physics and Astronomy, Univ. of Kentucky, Lexington, KY; Katrin Kneipp, Dept. of Physics, Technical University of Berlin, Berlin, GERMANY.

We performed polarized resonant Raman spectroscopy (RRS) of single wall nanotube (SWNT) samples with different diameter distributions. Resonant Raman spectra from metallic or semiconducting SWNTs were selected by using different incident laser excitations. We discuss the dependence of the G-band on polarization geometry for the different nanotube samples, focusing on the polarized Raman spectra of metallic SWNTs, where the depolarization effect is strong. We compare the results with polarization Raman studies on semi-conducting SWNTs and multi-walled carbon nanotubes. We also performed polarized surface-enhanced Raman studies (SERS) on SWNTs, and we compare the polarized SERS and RRS results.

**11:45 AM A6.6**

TEM STUDIES ON MULTIWALL CARBON NANOTUBES GROWN BY CHEMICAL VAPOR DEPOSITION. Jianguo Wen, Zhongping Huang, Wenzhi Li, Yi Tu, Dezhi Wang, Jinhua Chen, Shaoxian Yang, Zhifeng Ren, Department of Physics, Boston College, Chestnut Hill, MA.

An array of single freestanding multiwall carbon nanotubes (MWNTs) grown on nanonickel on Si substrates by plasma-enhanced chemical vapor deposition (CVD) are characterized by cross-sectional TEM to understand the microstructures of the tip, middle part, and the interface between substrate and nanotube. All single freestanding MWNTs we have imaged are hollow and capped by a graphite dome with a diameter of the curvature of about 2 nm. At each tip, one can always find an encapsulated single crystalline Ni cylinder. Micro-

structures at interface show that the outer diameter of multiwall carbon nanotubes is determined by the size of nanonickel. The growth mechanism at initial stage of the growth will be discussed based on these microstructures. Our characterization indicates that arrays of freestanding MWNTs with sharp tip (2 nm radius), controlled diameter, length, and site spacing (1 and 2 micrometer) have been achieved by plasma-enhanced CVD. Microstructure of MWNTs grown on silica AND graphite foil by CVD have also been studied by high-resolution TEM (HRTEM) and image analysis. With this technique, we found that the chirality of MWNTs can be determined quickly by the HRTEM image and diffraction pattern. Zigzag, mixture of armchair and zigzag, and other chiral MWNTs have been observed. Furthermore, we found that any one of the three  $\{10\bar{1}0\}$  lattice fringes in the center of carbon nanotube is enough to determine the chirality of a MWNT, which is of great importance to rapidly establishing the relationship among the properties, structure, and growth conditions of carbon nanotubes. The broken microstructures of MWNTs with different chiralities under tensile strength will be also presented.

#### SESSION A7: MECHANICAL PROPERTIES

Chair: Taner Yildirim  
 Tuesday Afternoon, November 28, 2000  
 Grand Ballroom (Sheraton)

##### 1:30 PM **\*A7.1**

**NANOTUBE MECHANICS.** Min-Feng Yu, Oleg Lourie, Richard Piner, Henry Rohrs, Kevin Ausman, Hui Huang, Rodney S. Ruoff, Dept of Physics, Washington University, St. Louis, MO.

We have designed, built, and used new tools that operate inside of electron microscopes (SEM and separately, TEM) to pick up, attach, and mechanically load nanotubes. Stress and strain are determined from direct EM imaging of the operating nanostressing stages. Results from such experiments will be presented.

##### 2:00 PM **A7.2**

**C2F, BN AND C NANO-SHELL ELASTICITY BY AB INITIO COMPUTATIONS.** Konstantin N. Kudin, G.E. Scuseria, Dept of Chemistry, and B.I. Yakobson, Dept of Mechanical Engineering and Materials Science, and Center for Nanoscale Science and Technology, Rice Univ, Houston, TX.

The concept of a continuum elastic shell provides a useful reduced description for quasi-two-dimensional objects, as soon as their parameters are well determined. We have computed the in-plane stiffness, flexural rigidity, shear modulus and Poisson ratio for the monoatomic layers and tubules of carbon, boron nitride and the novel forms of fluorinated carbon. Using the same gradient corrected PBE density functional together with the periodic boundary conditions [1] has allowed to test the limits of linear elasticity and to consistently compare the properties of these materials. A noticeable equilibrium curvature of the C2F has been predicted, in contrast to the naturally flat BN and C sheets. We further apply these parameters to estimate the elastic axial stiffness, lateral compressibility, and the bending (compressive) strength of multiwall nanotubes [2], where the interlayer van der Waals forces begin to play significant role. [1] K.N. Kudin and G.E. Scuseria, Phys. Rev. B 61, 16440 (2000). [2] R.E. Smalley and B.I. Yakobson, Solid State Comm. 107, 597 (1998).

##### 2:15 PM **A7.3**

**MECHANICAL PROPERTIES OF CHARGED CARBON NANOTUBE.** Jianwei Che, Xin Xu, Tahir Cagin, and William A. Goddard III, Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA.

Over the past decade, both theory and experiment have shown that carbon nanotubes have both unique electronic properties (e.g. it may be semiconducting or metallic depending on the chirality) and extreme mechanical strength (e.g. tensile modulus  $\sim 1000$  GPa). Consequently, there is considerable interest in designing and manufacturing functional devices and novel composite materials based on carbon nanotubes. In particular we have considered how introducing and controlling charges in various locations might modify the mechanical properties of carbon nanotubes. In agreement with experiments by Baughman et al.<sup>1</sup>, we find that introducing excess charges into nanotubes can lead to mechanical deformations that do mechanical work. We have studied the relation between tube deformation and stress and the charge distribution using tight-binding electronic structure theory. In addition, we have determined how the vibrational modes are affected by charge injection and the implications for the stability of carbon nanotubes. These results suggest a wide range of practical implications, including the design of nano-electronic-mechanical systems (NEMS) and nano-actuators. Reference: 1. R.H. Baughman, C. Cui, A.A. Zakhidov, et. al., Science, **284**, 1340, 1999.

##### 2:30 PM **A7.4**

**IN-SITU NANOFLUIDIC EXPERIMENTS IN A CARBON NANOTUBE.** Yury Gogotsi, Drexel University, Department of Materials Engineering, Philadelphia, PA; Joseph Libera, Constantine Megaridis, University of Illinois at Chicago, Department of Mechanical Engineering, Chicago, IL.

The behavior of liquids in nanotubes can be different from that in macroscopic pipes or even micro-capillaries. Already in micron-thick channels, interaction with walls and surface tension make movement of liquid difficult. However, capillary forces can facilitate filling of thin channels in case of good wettability of the internal wall surface by the liquid. These are critical issues in growing nanofluidic industry. However, there is hardly any information available on the behavior of water in nanosize channels. A recently suggested hydrothermal method of nanotube synthesis produced multiwall carbon nanotubes with encapsulated water and gas inclusions. These nanotubes allow for in-situ nanofluidic studies in TEM, as well as for investigation of chemical interactions between water and carbon. Hydrothermal nanotubes have a large internal diameter (up to 90% of the outer diameter) and graphitic walls with minimal or no disorder and high continuity of graphene plains. These nanotubes are leak-tight by virtue of holding water at high vacuum in TEM and allow for unique study of water chemistry and physics in TEM. They can be used as miniature pressure vessels or chemical reactors forming an experimental apparatus orders of magnitude smaller compared to the smallest capillaries used in fluidic experiments. A single nanotube can be used as a nanometer-sized laboratory for chemical and physical (nanofluidic) experiments. Evaporation, condensation, and expansion of the liquid, as well as chemical interaction of the supercritical fluid with tube walls upon heating have been monitored in-situ using TEM and dynamics of these process will be demonstrated and analyzed.

##### 2:45 PM **A7.5**

**EFFECT OF COMMENSURATE CONTACT ON ELECTRONIC TRANSPORT ACROSS THE CNT/HOPG INTERFACE.**

Scott Paulson, University of North Carolina, Dept. of Physics and Astronomy, Chapel Hill, NC; Michael R. Falvo, University of North Carolina, Dept. of Physics and Astronomy, Chapel Hill, NC; Adam Seeger, University of North Carolina, Dept. of Computer Science, Chapel Hill, NC; Russell M. Taylor II, University of North Carolina, Dept. of Computer Science, Chapel Hill, NC; Richard Superfine, University of North Carolina, Dept. of Physics and Astronomy, Chapel Hill, NC; Sean Washburn, University of North Carolina, Dept. of Physics and Astronomy, Chapel Hill, NC.

We report measurements of the effect of atomic interlocking on the mechanical behavior and electrical conduction between bodies. We have manipulated carbon nanotubes on an HOPG substrate with a conducting AFM tip as an electrical probe. Along with our lateral force evidence of commensurate contact, we present the first data measuring the change in contact resistance between two atomically smooth surfaces as they go between the commensurate and incommensurate states. The conducting AFM tip contacts the CNT from the top and current is collected in the HOPG substrate, therefore our measurement of resistance is across the CNT diameter as opposed to its length. We find very low resistance for this circumferential current as compared to longitudinal currents that have been reported. Our results will be interpreted in light of models of coupling between the tip and the various electrical modes in the CNT. This work was supported by the National Science Foundation (HPCC, ECS), the Office of Naval Research (MURI), and National Institutes of Health (NCR).

#### SESSION A8: PROBES AND SENSORS

Chair: James Hone  
 Tuesday Afternoon, November 28, 2000  
 Grand Ballroom (Sheraton)

##### 3:30 PM **A8.1**

**STRAIN-INDUCED ELECTRONIC PROPERTY HETEROGENEITY OF A CARBON NANOTUBE.** D. Tekleab, D.L. Carroll, Clemson University, Department of Physics and Astronomy, Clemson, SC; G.G. Samsonidze, B.I. Yakobson, Rice University, Mechanical Engineering and Materials Science Department, Houston, TX.

We have studied the effect of strain on the electronic properties of multiwall carbon nanotubes using scanning tunneling microscopy and spectroscopy. Small elastic strain causes no change of the electronic structure of the nanotubes. In contrast, the tube largely strained by what is believed to be an inter-grain boundary in the substrate shows drastic heterogeneity in the electronic properties. Band gap widening as well as density of states enhancement are observed within a short tube segment, forming a S-M-S junction. Local compression of the outer most layer can cause mechanical relaxation through Stone-Wales

bond rotations. Molecular dynamics allows to generate an atomic configuration of the junction (20,19)-(20,20)-(20,19) which matches well the observed geometry, the "force history", and the resulting electronic property sequence observed in the experiment. It provides first evidence of the effect of mechanical modification on the local electronic structure of CNT.

#### 3:45 PM **A8.2**

**MANIPULATION AND CHEMICAL MODIFICATION OF INDIVIDUAL CARBON NANOTUBES AS PROBES FOR TOPOGRAPHICAL AND CHEMICAL AFMS.** Nami Choi, Takayuki Uchihashi, Tetsuo Shimizu, Suzanne P. Jarvis, Wataru Mizutani, Hiroshi Tokumoto, JRCAT, Tsukuba, Ibaraki, JAPAN; Seiji Akita, Yoshikazu Nakayama, Osaka Prefecture University, Sakai, Osaka, JAPAN; Atsushi Ando, Electrotechnical Laboratory, Tsukuba, Ibaraki, JAPAN.

Carbon Nanotubes (CNT) are of great interest from the viewpoint of their unique electronic and mechanical properties, chemical stability, and potential application in molecular devices as well as probe tips for atomic force microscopy (AFM). To prepare CNT-tips, two techniques have previously been demonstrated. One is to attach CNT onto a commercial tip either by using adhesive carbon tape under an optical microscope or by depositing amorphous carbon in a scanning electron microscope (SEM). The second is to grow a CNT at the apex of the tip by a chemical vapor deposition technique. With these techniques, it can be difficult to control important parameters such as the length of CNT tip (except for shortening by cutting which produces an open end), the direction of the CNT tip, and the formation of good mechanical and electrical interfaces between CNT and tip. To overcome these problems, we have developed a new manipulator system installed in the SEM. This consists of two sets of piezoelectric stages with which we can adjust accurately both the position and orientation of CNT on the tip. In this talk, we will explain how this system manipulates CNT, and show several SPM applications (observation of individual single wall CNT, double stranded DNA, the solvation effect by water molecules, I/V characteristics, etc). Chemical force microscopy is very important for molecular recognition with the AFM technique. For this application, it is crucial to manipulate and control individual CNT before attaching it to the tip. To manipulate a large number of individual CNT, it is essential to disentangle the bundles of CNT and to prepare well-dispersed individual CNT in solvent. We will explain how individual CNTs are prepared and are chemically modified, and show clear AFM images of CNT covalently attached to a gold colloid.

#### 4:00 PM **A8.3**

**THE FABRICATION OF CARBON NANOTUBES FOR NANO-DEVICES AND BIOSENSORS.** Jun Li<sup>1</sup>, Hou Tee Ng<sup>2</sup>, Mawlin Foo<sup>2</sup>, Aiping Fang<sup>2</sup>, Roderick Y.H. Ljm<sup>1</sup>, Weide Zhang<sup>1</sup>, Yafeng Xing<sup>2</sup>, Guoqin Xu<sup>2</sup>, Stephan Jaenicke<sup>2</sup> and Sam F.Y. Li<sup>1,2</sup>. <sup>1</sup>Institute of Materials Research & Engineering, SINGAPORE; <sup>2</sup>National Univ of Singapore, Dept of Chemistry, SINGAPORE.

Carbon nanotubes (CNTs) have shown delicate macromolecular structure and extraordinary materials properties. This class of materials has provided great application potential in the uprising nanotechnologies. We will report on our studies on the following issues: (1) mass production, (2) directly growth of CNTs into nanodevices, and (3) application of CNTs in chemical and biological sensors.

Recently, chemical vapor deposition (CVD) has been recognized as an attractive method due to many advantages. The selection of catalysts and the control of the size of catalyst particles have been known to play an important role. We have developed a method to synthesize CNTs by CVD using catalysts impregnated in a mesoporous support. This mesoporous catalyst support has an ordered hexagonal array of uniform, one-dimensional channels with pore sizes tunable from about 2 nm to 30 nm, which is exactly in the range of the outer diameters of carbon nanotubes. It is anticipated that the growth of carbon nanotubes can be controlled by this substrate.

Many applications of carbon nanotubes rely on the ability to control the growth of carbon nanotubes into regular microarrays or deliberately architected structures. Here, we demonstrate a non-photolithographic approach to pattern solution-based organo-metallic precursors onto novel flexible substrates. Highly ordered and uniform arrays of CNTs could be directly grown on these templates by CVD methods with controlled alignment and configuration, which may be useful for future device fabrication such as field emission displays and sensors. By making use of the physical shrinking properties of polymer templates at high temperature, we extended this approach to the fabrication of a freestanding complex network of CNT 'membranes'. We will show that this membrane can be used in electrochemical sensors and gas sensors.

#### 4:15 PM **A8.4**

**PROPERTIES OF CARBON NANOTUBE PROBES FOR ATOMIC**

**FORCE MICROSCOPY.** Katerina Moloni, Max Lagally, PIEZOMAX Technologies, Madison, WI.

We have investigated a number of properties of multiwall C nanotube tips used as probes for atomic force microscopy (AFM). We mount multiwall nanotubes bundles on conventional cantilever tips and shape their ends. The advantages of C nanotubes for surface profiling are, of course, the high aspect ratio and the compliancy of the probe. So that high resolution is not sacrificed for the sake of high aspect ratio, the bundles are 'sharpened' using a method we developed.(1) We have profiled a variety of high-aspect ratio nanomorphologies in Si, including 200nm wide and 650 nm deep trenches as well as 2-3 micron deep features. We demonstrate that our tips are capable of imaging deep and narrow trenches (side wall angles of ~88 degrees). We have made comparative studies of tip-sample interactions with C nanotube probes and conventional Si or Si nitride AFM tips to determine the lifetime of the tips and sample degradation with both hard and soft samples. Whereas conventional tips cause significant sample damage, C nanotube probes do not. Similarly, conventional tips wear rapidly, losing resolution, whereas C nanotube probes maintain their resolution and thus have a minimum useable lifetime at least an order of magnitude greater than conventional tips. We will also present preliminary but very positive results using C nanotubes coated with magnetic material for obtaining magnetic force microscopy (MFM) images. Finally, we show a variety of C nanotube AFM imaging applications in a wide range of materials. Supported by DARPA SBIR program. (1) patent applied for

#### 4:30 PM **A8.5**

**INDIVIDUAL SINGLE-WALLED NANOTUBE TIPS FOR ATOMIC FORCE MICROSCOPY.** Jason H. Hafner, Chin-Li Cheung, Charles M. Lieber, Harvard University, Dept. of Chemistry and Chemical Biology, Cambridge, MA.

The unique properties of carbon nanotubes make them ideal atomic force microscopy (AFM) probe tips. Previously, the fabrication of carbon nanotube tips has been limited to laborious assembly or catalytic tip preparation procedures and only produced multi-walled nanotubes or bundles of single-walled nanotubes, which limited the imaging resolution. A new chemical vapor deposition based synthesis approach will be described which allows simple and reproducible fabrication of individual single-walled nanotube tips. These tips have ca. 1 nm radii, yet are mechanically rigid due to the high Young's modulus of carbon nanotubes. Images of spherical gold nanoparticle standards demonstrate the expected high resolution based on the nanotube tip structure. Force spectroscopy with the nanotube tips demonstrates that they elastically buckle rather than fracture under large loads, making them highly robust probes. The nanotube tip length is critical as it strongly affects the buckling force, lateral stiffness, and thermal vibration amplitude of the tip. An etching technique will be described which allows control over the nanotube tip length with 2-nanometer precision. The unique combination of high resolution and high aspect ratio of the nanotube tips allows structural studies of large, isolated protein assemblies difficult to assess by other methods. Recent results in this area will be presented.

#### 4:45 PM **A8.6**

**USE OF MULTI-WALLED CARBON NANOTUBES FOR CONDUCTIVE PROBE SCANNING FORCE MICROSCOPY (CP-SFM).** Kevin B. Stavens and Ronald P. Andres, Purdue Univ, Dept of Chemical Engineering, W. Lafayette, IN.

Multi-Walled Carbon Nanotubes (MWNTs) mounted on commercial SFM cantilevers have proven to be excellent probes for high resolution Tapping Mode Scanning Force Microscopy (TM-SFM)[1]. Because of their robust nature and relatively high electrical conductance, MWNTs are also attractive for use in Conductive Probe Scanning Force Microscopy (CP-SFM). To be used in this application, however, the MWNT must be mounted via a high conductance contact to a conductive cantilever. The technique employs a spatially selective electro-deposition of gold to mechanically and electrically secure a MWNT to the tip of a gold plated silicon cantilever. The thin gold adlayer provides good electrical contact between the cantilever and the MWNT allowing the MWNT to be used as a conductive probe. Preliminary measurements indicate this probe behaves in an ohmic manner. The superior mechanical adhesion provided by this technique also produces an extremely robust probe for both TM-SFM and CP-SFM studies. [1] Moloni K., Buss M.R., Andres R.P., *ULTRAMICROSCOPY* 80:(4) 237-246 DEC 1999

SESSION A9: HYDROGEN STORAGE IN CARBON NANOTUBES

Chair: John E. Fischer

Wednesday Morning, November 29, 2000

Grand Ballroom (Sheraton)

## NOTE EARLY START

### 8:15 AM \*A9.1

RAPID, ROOM TEMPERATURE, ATMOSPHERIC PRESSURE STORAGE OF HYDROGEN IN SWNTs. Michael J. Heben, Anne C. Dillon, Jeffrey L. Alleman, Kim M. Jones, and Philip A. Parilla, National Renewable Energy Laboratory, Golden, CO; Thomas Gennett, on sabbatical from Department of Chemistry and Center for Materials Science, Rochester Institute of Technology, Rochester, NY.

As we demonstrated in 1997 [1], single wall carbon nanotubes are capable of adsorbing hydrogen at room temperatures and pressures. Early experiments were performed on highly impure samples. Although hydrogen storage densities were estimated to be between 5 and 10 wt% on a SWNT weight basis, the amount of hydrogen stored on the total sample was only  $\sim 0.01$  wt%. Since that time we have developed methods for obtaining SWNTs in purities as high as 98 wt% [2], and also developed methods to activate these materials for hydrogen storage. Hydrogen can be stored on these materials at 6.5 - 7 wt%. The activated SWNT material can be charged in a matter of minutes at room temperature and normal atmospheric pressure. Temperature programmed desorption spectroscopy shows that there are two distinct sites for hydrogen adsorption. Approximately  $2/5^{th}$ s of the total hydrogen is in a low temperature site that can easily be removed at room temperature. The remaining  $3/5^{th}$ s of the hydrogen is more stable and is not removed until temperatures greater than  $300^\circ\text{C}$ . Since the hydrogen-charged samples are fairly stable in air they can be investigated with a variety of *ex situ* techniques. In particular, Raman spectroscopy has been used to observe that charge transfer from the SWNT backbone accompanies hydrogen uptake. We will discuss these results in detail with particular attention to the relationship between electronic and structural factors. The hydrogen storage activation process will also be discussed. 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, K.M. Jones, J.L. Alleman, P.A. Parilla and M.J. Heben, Advanced Mat. 11, 1354, 1999.

### 8:45 AM \*A9.2

HYDROGEN STORAGE IN CARBON NANOTUBE-BASED MATERIALS. Ping Chen, Jianyi Lin, Kuang Lee Tan, Dept of Physics, National University of Singapore, Singapore, SINGAPORE.

Much attention has been paid to the hydrogen storage by carbon nanotubes. Unlike single-wall carbon nanotubes, the multi-wall carbon nanotubes absorb substantial hydrogen only after being treated with alkali metals. Several techniques have been applied to measure and confirm the amount of hydrogen uptake by the material. It was found that the conditions in preparation and pre-treatment of alkali metal-doped carbon nanotubes strongly affected the capability of hydrogen storage. Characteristic studies show that a new phase of alkali and carbon is formed, and the tubular structure is somewhat destroyed. The electronic and structural changes in carbon nanotubes will favour the chemical absorption of hydrogen. The behaviour of contaminants, such as moisture and oxygen, in the hydrogen absorption process was also investigated.

### 9:15 AM \*A9.3

HYDROGEN DESORPTION MEASUREMENTS ON CARBON NANOSTRUCTURES. Michael Hirscher, Marion Becher, Ursula Detlaff-Weglikowska, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY; Andrea Quintel, Viera Skakalova, Young-Moon Choi, Miro Haluska, Siegmund Roth, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY; Ingrid Stepanek, Patrick Bernier, University of Montpellier II, Montpellier, FRANCE.

Measurements of the hydrogen storage on single-walled carbon nanotubes (SWNTs) and graphite will be presented. SWNTs have been purified, opened and surface cleaned by various methods, such as boiling in different acids, oxidation, ultra-sonication, mechanical grinding, and ball milling. The specimens have been well characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. The hydrogen content is investigated by thermal desorption spectroscopy utilizing a mass spectrometer. The effects of the different treatments on the hydrogen storage capacity will be discussed. These investigations indicate that an opening of the SWNTs is essential to reach high storage capacities. We thank the BMBF for financial support.

## SESSION A10: HYDROGEN STORAGE AND INTERCALATION

Chair: Peter C. Eklund  
Wednesday Morning, November 29, 2000  
Grand Ballroom (Sheraton)

### 10:15 AM A10.1

DEEP INELASTIC NEUTRON SCATTERING STUDIES OF  $\text{H}_2$  IN

CARBON NANOTUBES. David Narehood, Paul Sokol, Peter Eklund, Dept. of Physics, The Pennsylvania State University, University Park.

Deep Inelastic Neutron Scattering (DINS) provides a unique microscopic perspective of the state of adsorbed molecules on nanotubes. We report DINS studies of  $n\text{-H}_2$  ( $J=1$  concentration of 75%) gas adsorbed on bundles of SWNTs at 15K. We find that the  $J = 1 \rightarrow J = 0$  conversion rate for the adsorbed nanotubes is anomalously high. This rate is too fast to measure in our studies. We can, however, set a lower limit on the rate of 400%/hr - an enhancement of 200 over the rate in liquid  $\text{H}_2$ . DINS studies yielded spectra consisting of multiple peaks, due to rotational transitions, with widths determined by the translational momentum distribution  $n(p)$ . The average kinetic energy, obtained from the width of  $n(p)$ , is  $100 \pm 30\text{K}$ , slightly lower than observed on planar graphite surfaces. These values are much lower than theoretical predictions for  $\text{H}_2$  adsorbed in the interstices between tube, indicating that  $\text{H}_2$  may adsorb either on the outer surface of the bundles or in the core of the tubes. The measured rotational energy levels are consistent with those of bulk  $\text{H}_2$ . However, the rotational form factors associated with the transitions are much different than the bulk values indicating a significant modification of the rotational wave function of the molecule. The modification of the rotational wave function, which is not observed for  $\text{H}_2$  on planar graphite, may indicate the primary adsorption sites are in the core of the tube. This work was supported by the NSF DMR 9970126 (MERSEC) and Honda.

### 10:30 AM A10.2

ADSORPTION AND QUANTUM ROTATION OF HYDROGEN IN SINGLE-WALL CARBON NANOTUBES. C.M. Brown<sup>a,b</sup>, T. Yildirim<sup>b</sup>, D.A. Neumann<sup>b</sup>, J.E. Fischer<sup>c</sup>, M.J. Heben<sup>d</sup>; <sup>a</sup>University of Maryland, College Park, MD; <sup>b</sup>National Institute of Standards and Technology, Gaithersburg, MD; <sup>c</sup>Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA; <sup>d</sup>Center for Basic Science, National Renewable Energy Laboratory, Golden, CO.

Adsorption of atoms or molecules in nanopore materials has considerable fundamental interest because of two main reasons; the reduced dimensionality and technological importance, such as gas separation and hydrogen storage. We report hydrogen absorption isotherms in single-wall carbon nanotubes as a function of pressure, temperature, and various sample treatment. The loading isotherms are compared with various model calculations based on Monte Carlo simulation in the grand canonical ensemble. Neutron scattering techniques are used to characterize the SWNT samples and to probe the dynamics of hydrogen molecules trapped in nanotubes. The inelastic neutron scattering measurements clearly shows the *ortho* to *para* conversion of physisorbed hydrogen in a nanotube-containing soot loaded with hydrogen. Unlike  $\text{H}_2$  adsorbed in solid  $\text{C}_{60}$ , the conversion rate is very fast, which is attributed to the paramagnetic metal impurities in the sample. From the rotational  $J = 0 \rightarrow 1$  transition, no indication of a significant barrier to quantum rotation seen. Details of the temperature evolution of the  $J = 0 \rightarrow 1$  transition will be discussed and compared to those observed in graphite and solid  $\text{C}_{60}$ .

### 10:45 AM \*A10.3

DOPING PROPERTIES OF POTASSIUM INTO SINGLE-WALL CARBON NANOTUBES BY VAPOR PHASE REACTION. Shunji Bandow, Morio Takizawa, Japan Science and Technology Corporation, Dept. Materials Science and Engineering, Meijo University, Nagoya, JAPAN; Sumio Iijima, Japan Science and Technology Corporation, NEC Corporation Tsukuba and Meijo University, Nagoya, JAPAN.

The doping of K to the interstitial site of (10,10) single-wall carbon nanotube (SWNT) bundles is a candidate for the superconductor [1: S. Saito, MRS 1999 Fall Meeting Proceedings]. The stoichiometry of this material is  $\text{K}_2\text{C}_{80}$  [1]. In order to increase the density of state at the Fermi level, the doping into the interior site of SWNT is more favorable. When the K is fully doped to both the interior and interstitial sites of SWNT bundle, the stoichiometry will be represented by  $\text{K}_{12}\text{C}_{80}$ . Recently, we have found a method for doping the various fullerenes into the interior site of SWNT with high yield (poster presentation by K. Hirahara *et al*). The samples used in the present study were synthesized by using this technique and prepared two types of K-doped SWNTs: one is considered to correspond with  $\text{K}_2\text{C}_{80}$  (interstitial doped SWNTs) and the other is  $\text{K}_{12}\text{C}_{80}$  (interior and interstitial doped SWNTs). However, the stoichiometric ratios have not yet been confirmed by experiment. Therefore, in the present study, we temporary call the samples as  $\text{K}_2\text{C}_{80}$  for interstitial doped SWNTs and as  $\text{K}_{12}\text{C}_{80}$  for interior and interstitial doped SWNTs. Characterization of two types of K-doped SWNT samples was carried out by electron spin resonance (ESR) and Raman scattering. From ESR, magnitude of the Pauli paramagnetic susceptibility for  $\text{K}_2\text{C}_{80}$  sample indicated smaller value by  $\sim 1/3$  (average) than that for

K<sub>12</sub>C<sub>80</sub> sample around room temperature. Reaction time dependences on the Raman scattering taken for two types of samples showed the evidence for passing through the different transition stages before reaching the final stage corresponding to K<sub>2</sub>C<sub>80</sub> or K<sub>12</sub>C<sub>80</sub>. The low field signals recorded by ESR for K<sub>2</sub>C<sub>80</sub> and K<sub>12</sub>C<sub>80</sub> materials did not show the evidence for superconducting feature down to 2 K.

#### 11:15 AM A10.4

##### INTERMEDIATE INTERCALATION STAGES IN RUBIDIUM DOPED SINGLE WALL CARBON NANOTUBES MATS.

Philippe Poncharal, Laurent Spina, Nejma Ben-Diab, Christian Marliere, Jean-Louis Sauvajol and Ahmed Zahab, GDPC, Université Montpellier II, Montpellier, FRANCE.

We present new results on the electrical conductivity of purified single wall carbon nanotubes (SWNT) mats doped with rubidium. Recent studies of I, K, Cs and Rb intercalation into SWNT bundles have indicated that intercalant reside in the interstitial channels between the tubes and a charge transfer from the  $\pi$  orbital of tubes to the intercalant occurs (from tube to intercalant in a p-type doping and from intercalant to tube in a n-type doping) [1-3]. After a preliminary annealing to remove water and gas from the sample [4-6], its resistance have been monitored during all stages of the Rb vapor phase doping. In the saturated phase, the sample resistance was divided by a factor  $\sim 20$  compared to his initial resistance, which is in good agreement with several previous works [1-3]. The very slow doping rate (doping time around 30 hours), allowed the observation of new details in the sample resistance behavior versus time. An additional and very important experimental investigation have been simultaneously done during the doping: a small differential heating have been used to determine the electrical conductivity type and its activation energy during the different phases. A semiconductor to metallic transition of the sample conductivity type occurs during the first hour. Two other transitions seem to be observed: after 5 hours of doping (metallic-to-semiconductor) and after  $\sim 8$  hours (semiconductor-to-metallic). These observations are closely correlated with important changes in the Raman response of the sample (in-situ Raman measurement). [1] R.S. Lee, et al. Nature 388, 255 (1997) [2] A.M. Rao, et al. Nature 388, 257 (1997) [3] L. Grigorian, et al. Phys. Rev. B 58, R4195 (1998) [4] C. Marliere, et al. in MRS Proceeding, 1999, Boston [5] J. Kong, et al. science 287, 622 (2000) [6] P.G. Collins, et al. Science 287, 1801 (2000)

#### 11:30 AM A10.5

##### INTERCALATION PROCESSES OF SINGLE WALLED CARBON NANOTUBE ROPES AS INVESTIGATED BY SPECTROSCOPIC PROBES. Y. Iwasa, H. Fudou, Y. Yatsu, T. Mitani, JAIST, JAPAN; H. Kataura and Y. Achiba, Tokyo Metropolitan University, JAPAN.

Intercalation processes and evolution of electronic states of single walled carbon nanotubes have been investigated by means of several spectroscopic techniques. Alkali metals, K or Rb, were intercalated in vapor phase into carbon nanotube films fabricated by a spray technique. The Raman peak of the  $E_{2g}$  mode first shows a hardening to about  $1600\text{cm}^{-1}$ , followed by a downshift to  $1550\text{cm}^{-1}$  depending on the K concentration. The XPS analysis revealed that the K/C atomic ratio of the newly found intermediate state, showing the upshifted  $E_{2g}$  mode, is KC<sub>27</sub>, where a calculation predicts that alkali metals are inserted between two tubes rather than in the hollow channel between three tubes. The hardening of the  $E_{2g}$  mode in this concentration is consistent with this structural model in view of the Raman spectra of graphite intercalation compounds. The infrared absorption spectra ( $20\text{cm}^{-1}$  -  $30,000\text{cm}^{-1}$ ) for the KC<sub>27</sub> state consist of a low energy Drude-like band and a series of peaks above  $5000\text{cm}^{-1}$ . The former is attributed to the free carrier absorption of doped semiconducting tube. The quantitative analysis of the Drude band gave a small plasma frequency, being also consistent with the drastic lattice expansion which results from the insertion of alkali metals between two tubes. The effect of tube radii on the doping processes will be also discussed.

#### 11:45 AM A10.6

##### ALKALI-DOPING OF SINGLE WALL CARBON NANOTUBES PROBED BY *IN SITU* RAMAN EXPERIMENTS. N. Bendiab, L. Spina, A. Zahab, E. Anglaret, J.L Sauvajol, GDPC-UMR CNRS 5581, Université Montpellier II, Montpellier, FRANCE; P. Petit, Institut Charles Sadron, Strasbourg, FRANCE.

All-carbon lattices can form intercalating synthetic metals by chemical doping. This has been extensively investigated for graphite and fullerene compounds. This has also been recently demonstrated for multiwall and singlewall carbon nanotubes. The resistivity of SWNT compounds was especially shown to be considerably affected by alkali-metal doping. The alkalin atoms are likely inserted in the ropes channels in between the tubes. However, the short and long-range order of the alkalin lattice is still controversial. On the other hand, electron transfer and a concomitant ionic character of

alkali-doped samples were evidenced by drastic changes in the resonant Raman spectra [1]. Here, we probe the mechanisms of alkalin intercalation and charge transfer by *in situ* Raman investigations coupled with conductivity measurements performed during a gas phase doping experiment. We measure different characteristic spectra which we assign to different stoichiometries and degrees of charge transfers [2]. Our conclusions are supported by further Raman investigations on Li-doped SWNT samples. The Li-doped SWNT are prepared via redox reactions between SWNT and solutions of organic radical-anions, using Li as counter ion which allows to control the charge carrier concentration per carbon atom for each sample [3]. Different Raman responses are measured and associated to different levels of doping. [1] A.M. Rao et al, Nature 388, 257 (1997). [2] N. Bendiab et al, to be published. [3] E. Jouguelet, C. Mathis and P. Petit, Chem. Phys. Lett. 318, 561 (2000).

#### SESSION A11: CHEMICAL MODIFICATION

Chair: Anne C. Dillon

Wednesday Afternoon, November 29, 2000

Grand Ballroom (Sheraton)

#### 1:30 PM \*A11.1

##### FIXATION AND ORGANIZATION OF PROTEINS AROUND CARBON NANOTUBES. F. Balavoine, C. Richard, P. Schultz, C. Mioskowski, CEA Saclay and U. Strasbourg, Gif sur Yvette, FRANCE.

Carbon nanotubes have been used as supports for the fixation and crystallization of proteins. The linkage between the nanotubes and the proteins was realized *via* bifunctional molecules. One end of these molecules binds strongly to nanotubes in water solutions. Lipidic long chains give strong hydrophobic interactions, or polyaromatic structures leading to tight  $\pi$ - $\pi$  interactions with carbon surfaces have been used. The other end of these bifunctional molecules is highly hydrophilic in order to bring the nanotubes in suspension in the water solutions and to insure efficient protein / nanotube interactions. Nickel / NTA (nitriloacetic) complex, which binds to polyhistidine-tagged proteins was found to be efficient. Thus, nanotubes covered with proteins are easily obtained by treating carbon nanotubes with these bifunctional tools in water solutions, followed by the addition of polyhistidine-tagged proteins. In some cases, crystallization of the proteins around the nanotubes has been observed. Applications toward the development of nano-biosensors are under way.

#### 2:00 PM \*A11.2

##### NMR STUDY OF PURIFIED AND FUNCTIONALISED SWNTS. C. Goze<sup>1</sup>, M. Holzinger<sup>2</sup>, S. Latil<sup>1</sup>, A. Rubio<sup>3</sup>, P. Bernier<sup>1</sup> and A. Hirsch<sup>2</sup>, <sup>1</sup>CNRS GDPC Uni. Montpellier, FRANCE; <sup>2</sup>IOC, Uni. Erlangen, GERMANY; <sup>3</sup>DPT, Uni. Valladolid, SPAIN.

Dynamical properties of the SWNTs were investigated using solid state NMR on purified SWNTs. The temperature dependence study reveals a maximum at 170K in the relaxation rate that we attribute to molecular dynamics of small amplitude of the tubules inside the ropes. An important question arises concerning the modification of the electronic properties by the purification procedure. On the functionalised SWNTs using cross polarization and decoupling NMR techniques we identify the chemical modifications induced by acid treatment, in particular carboxylic groups could be observed. These functional groups on the tubule surface can be regarded as defects which may modify the SWNTs' properties. NMR and ESR investigations providing evidence for such modifications will be presented.

#### 2:30 PM A11.3

##### COMPARATIVE ADSORPTION OF SIMPLE MOLECULES ON SINGLE WALL CARBON NANOTUBES. M. Bienfait, K. Muris, J.P. Palmari, CRM2-CNRS, Marseille, FRANCE; N. Dupont-Pavlovsky, Laboratoire Chimie du Solide Minéral, Vandoeuvre-lès-Nancy, FRANCE; P. Zeppenfeld, Johannes-Kepler University, Linz, AUSTRIA; N. Dufau, Y. Grillet, CTM-CNRS, Marseille, FRANCE; B. Asmussen, University, Kiel, GERMANY; M. Johnson, ILL, Grenoble, FRANCE.

Methane, krypton, xenon and SF<sub>6</sub> adsorption on single wall carbon nanotubes {SWCN} associated in bundles produced by the Montpellier group have been studied by adsorption isotherm measurements, calorimetry, quasi-elastic neutron scattering and neutron diffraction. Methane, krypton and xenon adsorption isotherms exhibit two steps corresponding to the adsorption on two types of comparatively uniform patches during the first stages of the adsorbate condensation. The values of the methane isosteric heat of adsorption on these two adsorption sites have been determined. They are in very good agreement with those measured by means of isothermal micro-calorimetry. In contrast with methane, krypton and

xenon, SF<sub>6</sub> adsorption isotherms exhibit only one step corresponding to the less attractive adsorption sites. These results are consistent with the adsorption - for the first step, inside the interstitial channels between the nanotubes forming a bundle, except for the biggest molecule SF<sub>6</sub> which cannot penetrate them, - for the second step, on the external surface of the bundles. The quasi-elastic neutron scattering experiment was performed on CH<sub>4</sub> adsorbed on the same SWCN's in order to characterize the diffusivity of these molecules. It was shown that the two sites of adsorption, previously observed by adsorption volumetry and calorimetry measurements, correspond to a solid-like phase for the more strongly bound site at T < 120 K and to a viscous liquid-like component for the more weakly bound site at 70 < T < 120 K. Neutron diffraction experiments were carried out on CD<sub>4</sub>/SWCN's to complete this study and determine the packing of the adsorbed solid. It was shown that the methane molecules are aligned along the interstitial channels of the bundles and form a unidirectional solid with a short range order.

#### 2:45 PM **A11.4**

**CHEMICAL EFFECTS OBSERVED IN THE SERS SPECTRA OF SINGLE WALL NANOTUBES.** M. Baibarac, I. Baltog, Natl. Inst. of Materials Physics, Bucharest, ROMANIA; S. Lefrant, O. Chauvet, J.Y. Mevellec, IMN, Univ. Nantes, FRANCE; L. Vaccarini, P. Bernier, GDPC, Univ. Montpellier II, FRANCE.

The SERS technique is very successful in the case of SWNT's to amplify the Raman response leading to interesting results such as the asymmetry observed in the Stokes/anti-Stokes spectra of metallic tubes (1). In our study, we have focused on the strong chemical effects arising at the interface between the nanotube layer and the metallic support. Strong modifications are observed on the Raman spectra, which depend on different parameters such as the nature of the metallic surface, the type of solvent used to disperse the nanotubes and the thickness of the nanotube layer. These results will be discussed in terms of interfacial compounds which induced a strong disorder or defects on the nanotubes. 1. S.D.M. Brown et al, PRB 61, R5137 (2000)

### SESSION A12: COMPOSITES

Chair: Alan M. Cassell  
Wednesday Afternoon, November 29, 2000  
Grand Ballroom (Sheraton)

#### 3:30 PM **\*A12.1**

**DISPERSIONS AND FIBERS OF CARBON NANOTUBES.** B. Vigolo, A. Pénicaud, C. Coulon, P. Poulin, CRPP-CNRS, Pessac, FRANCE; C. Journet, P. Bernier, GDPC, Montpellier, FRANCE; C. Sauder, R. Pailler, LCTS, Pessac, FRANCE.

We have studied the phase diagram of single wall carbon nanotubes stabilized in water by surfactant molecules. Homogeneous dispersions, compact clusters or ramified gels are observed. The phase behavior can be understood by considering surfactant adsorption and depletion interactions induced by the surfactant micelles. When extruded through a capillary tube in the co-flowing stream of a polymer solution, homogeneous dispersions can be transformed into long ribbons of nanotubes. As shown by electron and optical microscopy, the carbon nanotubes exhibit a preferential orientation arising from flow induced alignment. When the ribbons are extracted from water, capillary collapse and water evaporation lead to dense carbon fibers made of entangled nanotubes. The diameter of the fibers can be varied from 10 to 100 microns and their elastic modulus is about 15 GPa, an order of magnitude greater than the modulus of bucky paper. By contrast to more classical carbon fibers, nanotube fibers are highly flexible and do not break even when tightly knotted. This simple and versatile processing may serve in the future for making new fibers with potentially useful mechanical, electrical and electromechanical properties.

#### 4:00 PM **A12.2**

**MULTIFUNCTIONAL CARBON NANOTUBE CHARGE-TRANSFER COMPLEXES: STRUCTURAL, ACTUATOR, ENERGY STORAGE, AND ENERGY HARVESTING FUNCTIONS.** Ray Baughman, Changxing Cui, Anvar Zakhidov, Ilyas Khayrullin, Mikhail Kozlov, Honeywell Int., Morristown, NJ; Norm Barisci, Geoff Spinks, Gordon Wallace; University of Wollongong, Wollongong, AUSTRALIA; Miklos Kertesz, Georgetown University, Washington, DC; Leo Fifield and Larry Dalton, Univ. Washington, Seattle, WA.

The ultimate goal of this work is to provide carbon nanotube composites that provide a structural function together with one or more other key functions, such as electrical energy storage, mechanical and thermal energy harvesting, mechanical actuation, mechanical damping, and sensing. Most of these functions utilize

electrochemical double-layer charging injection between ultra-strong nanotube electrodes in an ionically conducting matrix. We describe our efforts to demonstrate and optimize each of these functions. The functions that we have experimentally demonstrated are electro-mechanical actuation, energy storage, electro-chemical thermal energy harvesting, and sensing. These functions will provide the focus of the talk. However, theoretical analysis of other functionalities, and initial experimental work towards their experimental realization, will also be described.

#### 4:15 PM **A12.3**

**RAMAN SPECTROSCOPY OF NANOCOMPOSITES: TEST OF LOAD TRANSFER, INTERFACES, RESIDUAL STRESSES.** V.G. Hadjiev, Institute for Space Systems Operations and Texas Center for Superconductivity, University of Houston, Houston, TX; M.N. Iliev, Texas Center for Superconductivity, University of Houston, Houston, TX; S. Arepalli, P. Nikolaev, G.B. Tech/Lockheed Martin, Houston TX; B.S. Files, C.D. Scott, NASA Johnson Space Center, Houston, TX.

We report on a Raman scattering test that is used to infer elastic properties of single-wall carbon nanotubes (SWNTs) in composites. The test exploits the strain-induced frequency shift of Raman active modes of SWNTs embedded in epoxy resin subjected to bending. It takes advantage of polarization selectivity of the Raman response: it is dominated by the signal from nanotubes aligned along the laser polarization direction. Polarized Raman spectra are used to distinguish between strain due to pressure effects and that due to direct coupling of SWNTs to the matrix. Epoxy curing and tensile stress to failure of the composite are found to create residual stresses on the SWNT ropes. This data is used to estimate load transfer between SWNTs and the matrix.

#### 4:30 PM **A12.4**

**DIELECTRIC SPECTROSCOPY OF CARBON NANOTUBE COMPOSITES.** B.H. Fishbine, T.W. Hardek, D.Q. Li, L.S. Li and L.E. Rohlev, Los Alamos National Laboratory, Los Alamos NM; Z.K. Tang and G. Li, Physics Department, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR CHINA.

Theoretical studies and experimental measurements of the electronic properties of individual carbon nanotubes suggest that they can be used to make interesting dielectric composites for use in capacitors, filters, phase shifters, microwave lenses, electromagnetic shields, and electromagnetic absorbers. However, the processes used to produce these composites—such as sonication—could also change the nanotube conductivity and other properties required for good composite performance. In addition, the local environment of a nanotube can change its conductivity dramatically, as has been seen in recent experiments with oxygen adsorption onto nanotube surfaces. Similar effects could occur when nanotubes are suspended in liquid or solid matrix material. Also, room-temperature ballistic electron transport could affect the dielectric properties of composites made with either multiwall or single-wall carbon nanotubes. (Although thus far, room-temperature ballistic electron transport has been seen only in freely suspended multiwall carbon nanotubes.) By fitting the parameters of a Maxwell-Garnett calculation of a composite's complex dielectric constant to frequency-dependent measurements of this quantity, we can determine the average conductivity of a large number of nanotubes that have been processed to produce a macroscopic volume of composite material. The technique could also allow us to see the effects of ballistic electron transport, if they are present. In our calculations we can use either a classical Drude free-electron model or quantum mechanical models of the nanotube's complex dielectric constant. The technique has allowed us to measure the in situ conductivity of nanotubes suspended in various types of matrix material.

#### 4:45 PM **A12.5**

**FABRICATION AND CHARACTERIZATION OF CARBON NANOTUBE-REINFORCED POLYMER COMPOSITES BY ELECTROSPINNING AND SPIN COATING.** Yi Tu, Wenzhi Li, Jinhua Chen, Jianguo Wen, Zhifeng Ren, Boston College, Dept of Physics, Chestnut Hill, MA; Heidi Schreuder-Gibson, Michael Sennett, Natick Soldier Center, US Army Soldier Biological & Chemical Command, Natick, MA.

Different concentration of carbon nanotubes were added into polymer solution (PEO, PVP, etc.) to form the carbon nanotube-reinforced composites by electrospinning and spin coating. The electrical conductivity and mechanical properties of the composites have been studied. An improvement of at least two orders of electrical conductivity has been observed so far. Carbon nanotubes used in this study has been synthesized by conventional chemical vapor deposition

in a tube furnace. In order to establish the relationship between the concentration, diameter, length of carbon nanotubes, and the properties of the end composites, we have synthesized carbon nanotubes with different diameters and length.

SESSION A13: POSTER SESSION  
SYNTHESIS  
Wednesday Evening, November 29, 2000  
8:00 PM  
Exhibition Hall D (Hynes)

**A13.1**  
SYNTHESIS, CHARACTERIZATION AND APPLICATION OF THIN FILM CARBON NANOTUBE MATERIAL. A.N. Obratsov, A.P. Volkov, Faculty of Physics, Moscow State University, Moscow, RUSSIA.

Thin film carbon material consisting of multiwall carbon nanotubes and nanosized graphite crystallites was synthesized using non-catalytic chemical vapor deposition (CVD) process in direct current discharge plasma activated of methane-hydrogen gas mixture. A low-threshold field of 1.5 V/ $\mu\text{m}$ , high-emission current and site densities of 100 mA/cm<sup>2</sup> and 10<sup>7</sup> cm<sup>-2</sup>, correspondingly, for an applied field of 5 V/ $\mu\text{m}$  were achieved. It was established by using high-resolution electron microscopy that graphite sheets composing these nanotubes and graphite crystallites have predominant orientation along a normal to the film surface. X-ray and UV-photoelectron spectroscopy exhibit in the films carbon clusters characterized by low work function. Cathodoluminescence at around 4 eV and 2 eV was found for the CVD films. This combination of experimental observations are explained by specific structure of obtained graphite-like material with curved atomic layers having modification of electronic properties due to rehybridization of atomic bonds. Applicability of the CVD films are demonstrated by fabrication of flat panel display prototypes with diode and triode configurations.

**A13.2**  
DECORATED NANO-TUBULAR STRUCTURES DEPOSITED BY HF-CVD. Ralph Kurt, Ayatollah Karimi, Swiss Federal Institute of Technology (EPFL), Dept of Physics, Lausanne, SWITZERLAND.

A hot filament chemical vapour deposition (HF-CVD) process was used to synthesise a new type of nitrogenated carbon tubes. The structure and the chemical composition of the deposits grown onto pure Si wafer were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS). Spherical agglomerates, twisted nitrogenated carbon fibres, chains of nanobeads, and coiled nanotubes were produced in a controlled way which shape, diameter and length depend on the lateral distance from the filament. All these tubular structures show an interesting feathered surface. A possibly interpretation of the observed growth perpendicular to the tube axis regarding to the influence of Nitrogen in the structure will be given. The crystallinity of the structure is derived from the electron diffraction pattern and the lattice planes clearly seen in high resolution (HR) TEM. The nanotubes seem to be hollow. The question, if the tubular structures growth auto-catalytically or a possibly influence of any tungsten carbide acting as catalyst will be discussed. The optical vibrational properties were analysed by Raman spectroscopy showing the typical disordered graphitic bands. Additionally an unidentified peak at 1080 cm<sup>-1</sup> was observed and the G-Peak was decomposed into two sharp but overlapping peaks. This might be interpreted in terms of two different growth mechanisms resulting in the decorated tubular structures. The large surface area might make the material interesting for any catalytic application or for mechanical composite materials.

**A13.3**  
ON THE ROLE OF THE PRECURSORS IN THE EARLY STAGES OF NANOTUBE NUCLEATION. Dario Narducci, Istituto Nazionale per la Fisica della Materia and Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY; Barbara Marangon, Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY; Paolo Milani, Istituto Nazionale per la Fisica della Materia and Dept. of Physics, University of Milano, Milano, ITALY.

A study will be presented on the role of chemicals in Aerosol-Assisted Chemical Vapor Deposition (AACVD) of carbon nanotube (NT) films. Attention has been paid to the effect of different precursors on the growth rate and on the graphite/nanotube ratio. NTs were nucleated onto oxidized Si (001) substrates between 500 and 650 K by co-depositing NiO and C from a solution containing Ni acetate and different organic chemicals. Films were eventually annealed up to 800 K in Ar. Micro- and macro-Raman spectra were used to identify the presence and the relative abundance of NT structures. It will be

shown how the choice of proper organic precursors must be optimized accounting for the interplay between the organics catalytic decomposition temperature (which is generally different from the standard thermodynamic decomposition point) and the critical temperature separating the thermodynamically-controlled and the catalytically-controlled growth regimes. High temperature decomposing chemicals will display a stronger tendency to nucleate graphite, inhibiting the possibility of successfully growing NT films at low temperatures. At the same time we will show how no memory of the chemical structure of the precursor is kept even at low temperatures, the way C is supplied to the heteronucleation centers being that of small fragments (C<sub>n</sub> units with n < 3). Specifically, we will present evidence of the possibility of nucleating NT's at temperatures lower than 500 K by using phenol as precursor, while it will be shown how different organic precursors cannot be used under the same deposition conditions to obtain NT films.

**A13.4**  
ENERGY BARRIERS AND NORMAL MODES IN ROLLING OF GRAPHENE FRAGMENTS INTO CARBON NANOTUBES. Manuela Volpe, ENEA, Divisione Materiali, Centro Ricerche Casaccia, and Dip. Scienze e Tecnologie Chimiche, Università Tor Vergata, Roma, ITALY; Fabrizio Cleri and Gregorio D'Agostino, ENEA, Divisione Materiali, Centro Ricerche Casaccia, and INFN, Roma, ITALY; Vittorio Rosato, ENEA, High-Performance Computing Project, Centro Ricerche Casaccia, and INFN, Roma, ITALY.

We present a theoretical study of the nucleation mechanism of carbon nanotubes based on the hypothesis that the starting nanotube seed can be nucleated by rolling a small fragment of a graphite sheet (graphene) under thermal fluctuations. The energy barriers for rolling a graphene along different crystallographic directions are calculated from a tight-binding model, and are plotted as a function of the curvature radius of the nanotube. This allows to establish a universal energy scale for each family (n,m) of carbon nanotubes. The effect of introducing an increasing number of pentagonal rings in the flat, hexagonal graphene structure is investigated. We then estimate the amplitude of the fluctuations and the vibrational modes of graphene sheets of increasing size by means of tight-binding molecular dynamics simulations at very high temperatures. Such a model can be representative, e.g., of the high-temperature ablation of graphite fragments during arc discharge experiments. We discuss the combined effects due to: (a) the decrease of the energy barriers against rolling with increasing nanotube radius, and (b) the increase of random fluctuations with increasing size of the graphene sheet. The superposition of such effects may lead to a preferential range of nanotube diameters which could nucleate more abundantly than others. Work performed under the Project RDR500110 "Innovative Materials Based on Carbon Nanostructures" of the Italian Space Agency (ASI).

**A13.5**  
SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CARBON NANOTUBES PREPARED BY ARC DISCHARGE UNDER LIQUID NITROGEN. Marco Vittori Antisari, Renzo Marazzi, Francesco Cardellini, Vittoria Contini, Fabrizio Cleri, Manuela Volpe, Roberto Conversano, ENEA, Centro Ricerche Casaccia, Roma, ITALY.

Carbon nanotubes prepared by arc discharge performed under liquid nitrogen have been characterized by x-Ray diffraction, transmission electron microscopy and electron energy loss spectroscopy. Both XRD and EELS spectra were also simulated by means of tight binding molecular dynamics simulations. The effect of the processing conditions and particularly the DC voltage across the discharge, on the quality of the resulting carbon nanostructures has been assessed. The raw material has been purified following the classical route of selective oxidation in nitric acid. Multiwall nanotubes with very clean and sharp surfaces, was observed for a applied voltage of the order of 22 V. On carbon rods 5mm in diameter the DC current resulted of the order of 20 A. The method is very simple, stable over long times and shows a high yield with productivities of the order of grams/hour of raw material; furthermore it can be scaled to even larger size without any conceptual difficulty. By contrast when the voltage was raised to about 30 V, with a current of about 25 A, the rough material shows a diffraction pattern with a very reduced intensity of the 002 graphite peak, suggesting the presence of nanostructures based on graphite monolayers; the relative TEM image shows a complex and heavily convoluted microstructure whose identification requires further work currently in progress.

**A13.6**  
CALCULATION OF NANOTUBE CONTENT IN ARC PRODUCED CARBON POWDER USING ELECTRON PARAMAGNETIC RESONANCE. J.N. Coleman, D.F. O'Brien, R.C. Barklie, W.J. Blau, Department of Physics, University of Dublin, Trinity College, Dublin, IRELAND.

We have described a method that maximises the phase separation of turbostratic graphite (TSG) and multi walled carbon nanotubes (MWNT) in solutions of various organic polymeric hosts. This involves the formation of sediment and a solute. These components were characterized for MWNT and TSG content using electron paramagnetic resonance (EPR) measurements. All EPR signals could be deconvoluted into nanotube and TSG components. When normalized these components are representative of the mass of MWNT and TSG present. This allows us to make quantitative measurements of nanotube and TSG content in different environments. The most successful polymer host was poly (m-phenylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV). Using thermogravimetric analysis to calculate the mass of nanotubes in a host film we could calculate an EPR signal intensity per unit mass. By comparing this to the signal intensity of the nanotube component in the crude powder we could calculate for the first time the nanotube content or purity of arc produced nanotube powder.

**A13.7**  
CONTROLLED GROWTH OF CARBON NANOTUBES BY CHEMICAL VAPOR DEPOSITION. W.Z. Li, D.Z. Wang, S.X. Yang, J.G. Wen, Z.F. Ren, Department of Physics, Boston College, Chestnut Hill, MA.

Carbon nanotubes have been synthesized directly on graphite foil coated with stainless steel film with thickness ranging from 2 to 100 nm by chemical vapor deposition. The catalyst particle size increases with the thickness of the stainless steel film. The diameter, the number of walls and the purity of the carbon nanotubes were controlled by the catalyst particle size. Transmission electron microscopic examination reveals that the carbon nanotubes are well graphitized and consist of 3 to 20 graphitic layers depending on the catalyst particle size. This result indicates that it is possible to synthesize required carbon nanotubes by tuning the size and distribution of the catalyst particles in the chemical vapor deposition process.

**A13.8**  
DIRECTED GROWTH OF NANOTUBES USING MICRO-CONTACT PRINTING OF CATALYSTS. Jin-Koog Shin, Young-Soo Han, Sung-Tae Kim, LG Electronics Institute of Technology, Innovation Center, Seoul, KOREA.

The directed growth of suspended nanotube is essential for CNT device applications. It is well known that soft lithography is very useful technique in many applications. In the present work, selective growth of carbon nanotube in orientation parallel to substrate, was attempted by microcontact printing. Synthesis of structurally perfect nanotube has been demonstrated by an acetylene CVD method. We observed that the morphology and growth rate were strongly dependent on the acetylene gas flow rate, the fraction in diluted reaction gas and temperature. These results will be discussed in terms of reaction kinetics of CVD process.

**A13.9**  
PURIFICATION OF SINGLE-WALL CARBON NANOTUBES FOR FIELD EMISSION APPLICATIONS. H.Y. Kim, S.J. Lee, W.B. Choi, Y.W. Jin, Y.J. Lee, N.S. Lee, J.E. Jung, K.M. Kim, J.H. You, M.H. Moon; The National Creative Research Initiatives Center for Electron Emission Source, Display Lab., Samsung Advanced Institute of Technology., Suwon, KOREA.

Single-walled carbon nanotubes (SWNTs) have recently been considered as a new class of electronic materials because of their ultra narrow tube diameters and unique electrical properties, which are strongly dependent on their diameters and chirality. The SWNTs are easily produced by a arc discharge method which results in extremely long, highly tangled nanotubes. They also contain large amounts of impurities such as amorphous carbon and catalytic metal particles, which should be removed for their advanced applications. Thus, the development of a suitable method for purification and separation of SWNTs is crucial for further progress on nanotubes. SWNTs were reacted with typical oxidizing acids such as nitric and sulfuric acid and were cured in an ambient of H<sub>2</sub>O<sub>2</sub> to minimize damage on the tips of acid-treated SWNTs. By such chemical oxidation, raw SWNTs were purified and cut into short lengths, which was confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive spectrum analysis (EDS). The purified SWNTs were classified into different sizes by the Field Flow-Fractionation (FFF) method. The sizes of SWNTs are more uniformly distributed after acid treatment and it is estimated that SWNTs are cut into short lengths of less than 2  $\mu$ m. Moreover, field emission characteristics of purified SWNTs were investigated to study the effect of purification on the field emission. The purified SWNTs were uniformly deposited onto patterned ITO electrodes by electrophoresis. A turn-on electric field was 6-7 V/ $\mu$ m, where an

emission current was uniformly maintained to be 10-6A/cm<sup>2</sup> as long as 800 min. In this study, the effects of purification and size distribution on the field emission will be discussed.

**A13.10**  
EFFECT OF ULTRAFINE GOLD PARTICLES AND CATIONIC SURFACTANT ON BURNING OF AS-GROWN SINGLE-WALL CARBON NANOTUBES. Minfang Zhang, Masako Yudasaka, Fumihiko Nihey, Sumio Iijima, ICORP-JST, NEC, Tuskuba, JAPAN; Meijo Univ., Dept. of Physics, Nagoya, JAPAN.

A simple method of purifying single-wall carbon nanotubes (SWNTs) proposed so far is gas-phase oxidation; but amorphous carbon (a-C) and graphite are difficult to remove because their burning temperatures are close to that of SWNT. Other purification methods using strong acids can remove a-C, but the acid is thought to damage the SWNTs. Recently, Mizoguchi et al. [1] have shown that a-C in as-grown SWNTs can be removed by oxidation at lower temperature by using ultrafine gold particles and the cationic surfactant of benzalkonium chloride (BKC). In this purification, SWNTs remain less damaged than in the former two purification methods. In this study, we used thermogravimetric analysis (TGA) to investigate the effect of ultrafine gold particles and the cationic surfactant on the burning of the various carbonaceous materials contained in as-grown SWNTs. We found that the ultrafine gold particles catalyzed the oxidation of carbonaceous materials leading to a decrease in its burning temperatures, and BKC played the role of homogenizing the a-C aggregation states, which resulted in a-C burning in a narrow temperature range.

**A13.11**  
ELECTROPHORETIC DEPOSITION OF CARBON NANOTUBES FOR FIELD EMISSION DISPLAYS. S.J. Lee, H.Y. Kim, W.B. Choi, Y.W. Jin, Y.J. Lee, Y.S. Choi, N.S. Lee, J.E. Jung, J.H. You, and J.M. Kim The National Creative Research Initiatives Center for Electron Emission Source, Samsung Advanced Institute of Technology, Suwon, KOREA.

Carbon nanotubes have been deposited by electrophoresis for field emission display (FED) devices. Single-walled carbon nanotubes (SWNTs) were used after purification. A solution for the electrophoresis was prepared by mixing SWNTs, surfactant, chargers, water, and so on. Carbon nanotubes (CNTs) were selectively deposited on 5.2-inch patterned ITO glass substrates. The deposition was optimized by computer simulations for different line and space widths, which agreed well with experimental results. Better deposition behavior was observed at smaller line widths for a given line pitch due to concentration of higher electric fields at the line edges. In case of the 60  $\mu$ m wide line and 98  $\mu$ m wide space, the electrophoresis was optimally carried out at 20-40 V for 5-20 sec for the electrode distance of 5 mm. A turn-on electric field was approximately 0.6-0.7 V/ $\mu$ m and uniform emission of 10-4 A/cm<sup>2</sup> for an extended time of 800 min was achieved at 2V/ $\mu$ m. The CNT cathode deposited by electrophoresis showed lower outgassing than that of the screen-printed CNT cathode after vacuum packaging. The electrophoresis of CNTs showed its simplicity of fabrication processing and excellent field emission characteristics for the application to FEDs. We successfully fabricated a triode type field emission display using the cathode plates with CNTs deposited by electrophoresis. Main factors to control electrophoresis of CNTs, its optimal process conditions, and fabrication processes for FED applications will be discussed in detail.

**A13.12**  
FORMATION OF CARBON NANOTUBES BY USING RF PLASMA CVD EQUIPMENT FROM METHANE, ACETYLENE AND HYDROGEN GASES. Yoshiyuki Show, Toshikazu Matsukawa, Mitsuo Iwase and Tomio Izumi, Department of Electronics, Tokai University, Hiratsuka, Kanagawa, JAPAN.

Carbon nanotubes (CNTs) are promising material for cold cathode in the field emission display. The CNT is formed by the thermal and the microwave-plasma CVD methods. However, these synthetic methods are difficult to form the CNTs on large substrates. In this presentation, we will report the synthesis of the CNTs on the SiO<sub>2</sub> film by the radio frequency (RF) plasma CVD method at temperatures below 100°C. This CVD method has the advantage of formation of the CNTs on large substrates. The SiO<sub>2</sub> film (thickness of 100 nm), formed on the Si substrate, was used for the substrate. The round Ni particles with the size of 50 nm were deposited on the SiO<sub>2</sub> film for the nucleation of the CNTs. The CNTs were synthesized by the RF-plasma CVD method from the methane (CH<sub>4</sub>), the acetylene (C<sub>2</sub>H<sub>4</sub>) and the hydrogen (H<sub>2</sub>) gases. Typical condition of the gas flow was 0.6 and 10 sccm for the CH<sub>4</sub> and H<sub>2</sub> gases, respectively. The chamber pressure and the RF power during the deposition were kept at 1x10<sup>-2</sup> torr and 50 W, respectively. The deposition time was varied from 10 to 30 min. The substrate temperature during the deposition of the CNTs was kept below 100°C. The SEM observation

showed that the CNTs with average diameter of 10 nm were synthesized on the Ni-particle-coated SiO<sub>2</sub> films at the above mentioned deposition condition. The CNTs were uniformly formed on the large area of 50x50 mm. The density and length of the CNTs were increased with the deposition time. The average length of the CNTs, which were synthesized for 30 min., was 500 nm.

#### **A13.13**

**NATURE OF A FIELD-EMISSION FROM CARBON NANOTUBE FILMS.** Zoia Kosakovskaya, Yurii Gulyaev, Tat'yana Mshenskaya, Ann Kosakovskaya, Inst of Radio Engineering and Electronics of RAS, Moscow, RUSSIAN FEDERATION.

Now carbon nanotube structure are considered as an extremely perspective material for cold cathodes of flat displays. This interest is caused by high field emission from nanotube structures [1,2]. It's known, the stability of field emission is very important characteristic for practical application of nanotube in flat display, but till now this problem haven't full decision. The reason of this is absence of understanding of the mechanism of occurrence of high field emission from these structures. In our work we studied the features of emission properties of carbon nanotube films. The object of our researches were a well-oriented carbon nanotube films on substrates of silicon, quartz and nickel, which were synthesized by electron beam method [3]. The analysis of current-voltage characteristics of field emission (VAX) has shown impossibility of the full description this phenomenon by Fowler-Nordheim tunneling mechanism. Fowler-Nordheim tunneling mechanism does not give answers to the following questions: Why density current of field emission from nanotube films is higher than we have by calculation? Why have not a threshold of saturation? The threshold of saturation is extremely important characteristic for practical applications nanotube films in flat display. Why at critical current we observed a destruction of nanotubes without substantial increase of temperature of substrate? What is mechanism? In this work we offer a new mechanism of field emission which takes into account as a geometry of nanopipe, as well as particularities of carrying a charge in them. This work was supported by RFBR under Grant #98-02-17130. 1. Gulyaev Yu.V. et al. Revue 'LE Vide, les Couches Minces' Supplement an N271 - Mars-Avril 1994 (7th Int. Vacuum conf, 94, Grenoble, France) P.322-326. 2. W.A.S. de Heer et al. Science, 1995, 270 1179 3. Kosakovskaya Z.Ya. JETP Lett. 1992, v.56, No.1, pp.26

#### **A13.14**

**SELF-SELECTIVE GROWTH OF ALIGNED CARBON NANOTUBES ON SiO<sub>2</sub>/Si PATTERNS FROM XYLENE-METALLOCENE MIXTURES.** Z.J. Zhang, B.Q. Wei, G. Ramanath, P.M. Ajayan, Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, Troy, NY.

Growing 3D networks of aligned carbon nanotubes on flat substrates by a bottoms-up approach is important to harness the unique electronic properties of carbon nanotubes for device applications. Simultaneous control over nucleation sites and growth direction-essential to realize such nanotube architectures-remains a big challenge. Here, we report a new method for growing aligned carbon nanotubes selectively on SiO<sub>2</sub> surfaces by chemical vapor deposition from xylene-metalloocene mixtures. This approach obviates the use of metal-catalyst films, thus providing an easier way of selectively growing nanotubes on Si substrates through standard device processing methods. SiO<sub>2</sub> patterns on Si, obtained by lithographic patterning and etching of thermally oxidized Si (001) substrates, were exposed to xylene-metalloocene mixtures at 800°C. Scanning and transmission electron microscopy (SEM and TEM) of SiO<sub>2</sub>/Si patterns after deposition reveal the selective growth of vertically-aligned multi-walled carbon nanotubes on SiO<sub>2</sub> surfaces. There is no observable nanotube growth on the Si surfaces. This interesting growth behavior maybe used to realize 3D architectures of carbon nanotubes for applications into nanodevices. Based upon the above, and the segregation of metalloocene particles on and around the SiO<sub>2</sub> patterns, we proposed a phenomenological model to explain the mechanism of selective growth and alignment of nanotubes.

#### **A13.15**

**1D P-BLOCK HALIDE CRYSTALS CONFINED INTO SINGLE WALLED CARBON NANOTUBES.** E. Flahaut, J. Sloan, K. Coleman, V.C. Williams, S. Friedrichs, N. Hanson and M.L.H. Green.

The preparation of highly anisotropic 1D structures confined into single walled carbon nanotubes is one of the key objectives in carbon research, as the introduction of these materials into the hollow nanotubes cavities could result in interesting effects on their physical and electronic properties. We report here the filling of single and double walled carbon nanotubes by two different p-block halides, TlCl and PbI<sub>2</sub>. The nanotubes were produced either by the arc synthesis [1] or by a CVD method [2], based on the reduction of a Mg<sub>0.9</sub>C<sub>0.1</sub>O solid solution by a Hydrogen-Methane mixture. In the case of TlCl,

the structure of the crystals observed inside the tubes were all found to be derived from the rocksalt form and bi- and trilayer crystals were observed which exhibited reduced or partially reduced coordination relative to the fcc structure, as determined from HRTEM. In contrast, the crystal structure of bulk TlCl is a CsCl type structure. These results are consistent with the recently reported reduced coordination KI crystals formed within SWNTs [3]. In the case of PbI<sub>2</sub> (CdCl<sub>2</sub> crystal structure), the use of HRTEM image simulations will be combined to the characterisation by Pb Solid State NMR, to confirm the modification of the coordination of Pb atoms in the 1D confined structure. The confined structure forms a 1D array of reduced coordination polyhedra formed within the SWNT capillaries. [1] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. de la Chapelle, S. Lefrant, P. Darnier and J.E. Fisher, Nature 388 (1997) 756. [2] E. Flahaut, A. Peigney, Ch. Laurent, A. Rousset, J. Mater. Chem., 10, 2000, 249 [3] J. Sloan, M.C. Novotny, S.R. Bailey, G. Brown, C. Xu, V.C. Williams, S. Friedrichs, E. Flahaut, R.L. Callendar, A.P.E. York, K.S. Coleman, M.L.H. Green, R.E. Dunin-Borkowski and J.L. Hutchison, Chem. Phys. Lett., in press.

#### **A13.16**

**SYNTHESIS OF SINGLE WALL CARBON NANOTUBES UNDER HIGH MAGNETIC FIELD BY ARC DISCHARGE.** Haruo Yokomichi, Toyama Prefectural Univ, Dept of Electronics and Informatics, Toyama, JAPAN; Masaaki Ichihara, Fumiko Sakai, Univ of Tokyo, Inst for Solid State Physics, Chiba, JAPAN; Kikuo Itoh, Naoki Kishimoto, National Research Inst for Metals, Tsukuba, JAPAN.

Morphology control of carbon nanotubes as well as the bundle arrangement is important in application of the nanotubes to actual devices. Recently, we have reported the synthesis of multi wall carbon nanotubes under high magnetic field up to 10 T in order to achieve morphology control of nanotubes [1]. In the present study, synthesis of single wall carbon nanotubes was attempted under high magnetic field by arc discharge. The arc discharge was carried out under a current of 40 A in a He gas atmosphere using the graphite composite rod for the anode. The composite rods were prepared by boring a 3 mm diameter hole at the end of a 5 mm diameter carbon rod and the hole was filled with a mixture of graphite, Fe and Ni powder with 95:2.5:2.5 (at.%). The rod was annealed in a vacuum of approximately 0.01 mTorr at 950°C for 1 hour. Synthesized cathode deposit and soot were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From TEM images, it was confirmed for the first time that single-wall carbon nanotubes form in the cathode deposit under a magnetic field of 10 T. This result corresponds to the fact that the cathode deposits synthesized under 10 T contain Fe and Ni catalytic metals, whereas these synthesized without magnetic field do not contain these metals. The radius of nanotubes synthesized under 10 T is larger than that without magnetic field. Furthermore, the yield of the former nanotubes seems to be larger than that of the latter nanotubes. Based on these results, effects of magnetic field on synthesis of nanotubes are discussed. [1] H. Yokomichi, H. Sakima, M. Ichihara, F. Sakai, K. Itoh and N. Kishimoto, Appl. Phys. Lett. 74, 1827 (1999).

#### **A13.17**

**COMPUTATIONS OF NANOTUBES RELATED TO C<sub>36</sub>.** Zdeněk Slanina, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi, JAPAN; Filip Uhlik, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, CZECH REPUBLIC; Eiji Ōsawa, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi, JAPAN.

Recently, Sun et al. (Nature 403, 384, 2000) reported the narrowest carbon nanotubes so far and suggested that it could be closed by a half of a C<sub>36</sub> cage. The present paper reports computations on related model systems. There is a symmetric cut of D<sub>6h</sub> C<sub>36</sub> cage with six pentagons and model nanotubes with such cap are derived. One can also cut the D<sub>2d</sub> C<sub>36</sub> cage and thus create another cap and D<sub>2d</sub>-related model nanotubes (this patch can also be obtained from the D<sub>6h</sub> cage). There is a clear difference in the energies of the two model nanotubes. For example, at the PM3 computational level in a reduced C<sub>84</sub> representation, the D<sub>2d</sub>-related model nanotube is lower in energy by some 775 kJ/mol and has in its middle a diameter of about 5.42 Å (the D<sub>6h</sub>-related model nanotube about 4.81 Å). This computed model geometry corresponds well with the observed value of 5 Å reported by Sun et al. (Nature 403, 384, 2000). Various modelling approaches are to be discussed in the paper.

#### **A13.18**

**COLLOIDAL SOLUTION OF METAL NANOPARTICLES AS A CATALYST FOR CARBON NANOTUBE GROWTH.** Hiroki Ago, Satoshi Ohshima, Toshiki Komatsu, Yasunori Kuriki, Motoo Yumura, National Institute of Materials and Chemical Research (NIMC), Tsukuba, JAPAN; Japan Fine Ceramics Center (JFCC), Tokyo, JAPAN.

As a method to synthesize carbon nanotubes, chemical vapor deposition (CVD) in the presence of a transition metal catalyst has attracted a great interest, because the CVD proceeds at relatively lower temperature with less carbon impurities and gives much larger quantities compared with other methods. In the CVD method, metal nanoparticles are essential for the growth of carbon nanotubes, because they act as a catalyst of the nanotube growth; the size and chemical composition of the metal nanoparticle determines diameter and structural perfection of the nanotube. Metal nanoparticles employed in the CVD reaction have been realized mainly by using nanoporous substrates or by etching metal substrates. For future development, a more simple synthetic method applicable to plane and large area substrates is very important. In this paper, we show that metal nanoparticles (an average diameter of 4 nm) chemically synthesized by a reverse micelle method catalyzes the growth of multi-wall carbon nanotubes (MWNTs). The surface of the nanoparticles is covered with surfactants so that the nanoparticles can be dispersed in organic solvent and, thus, highly processible. Thermal CVD reaction of acetylene in the presence of the cast film of the dispersion on a plane Si substrate resulted in the MWNT array aligned perpendicular to the substrate. This array of the MWNTs has potential applications, especially to field emission displays, because the density of the present MNWT array is relatively low and the array can be developed to large area. We also show that the colloidal dispersion of the metal nanoparticles can be applied to the vapor-phase reaction in a hydrogen flow, which produced a large quantity of nanotubes. Through the control over the diameter and chemical composition of the nanoparticles, we may be able to control the diameter and chirality of the nanotube in the near future.

#### **A13.19**

**SYNTHESIS OF CARBON NANOSTRUCTURE BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF FE-PHTHALOCYANINE.** Takashi Ikuno, Shin-ichi Honda, Takuji Oyama, Yang-Gyu Baek, Shigeharu Okura, Mitsuhiro Katayama, Kenjiro Oura, Department of Electronic Engineering, Graduate School of Engineering, Osaka University, Osaka, JAPAN; Jeong-Tak Ryu, Department of Computer and Communication Engineering, Taegu University, Kyungbook, KOREA; Masahiko Kitagawa, Shinko-seiki Corp., Kobe, JAPAN.

Recently, carbon films with nanostructure have been attracted due to their property of cold cathode materials for flat panel display applications. The low temperature process for display has been required because glass materials would be used as the substrate. We have established low temperature synthesis a carbon nanostructure. The carbon nanostructure was formed using plasma enhanced chemical vapor deposition on Si(100) and glass substrate at 400°C. Plasma was generated between W filament and anode electrode at  $7.8 \times 10^{-3}$  Torr of Ar atmosphere. Fe phthalocyanine (FePc:  $\text{FeC}_{32}\text{H}_{16}\text{N}_8$ ) was used as a source material, which can supply Fe, C, H and N. FePc was positioned on anode electrode, which was sublimated by plasma and formed carbon nanostructure on substrate. The formed carbon nanostructure was analyzed its surface morphology, internal structure, and crystalline structure by scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), and x-ray diffraction (XRD), respectively. The general feature of the nanostructure has fiber like shape with 10-100nm diameter and 1-10 $\mu\text{m}$  length. The fibers were oriented randomly but were grown with high density. This nanostructure was crystalline graphite determined by x-ray diffraction measurement. High vacuum chamber was used to measure the field electron emission from these carbon nanostructure. The density of emission current J reached a value of 0.1mA/cm<sup>2</sup> at a turn-on field of about 3V/ $\mu\text{m}$  which was remarkably efficient electron emission current at a low field in comparison with other carbon related field emitters. More detail results of structural analysis and emission properties for the nanostructure will be reported.

#### **A13.20**

**GROWTH OF CARBON NANOTUBES ON CARBON CLOTH.** W.Z. Li, J.G. Wen, Z.F. Ren, Department of Physics, Boston College, MA.

Up to now, carbon nanotubes can be easily prepared on many kinds of substrates, such as silicon and glass, by different methods. However, it is still a main challenge to synthesize large area of carbon nanotubes on flexible and conducting substrates. In this contribution, a significant advancement has been developed to synthesize large area of carbon nanotubes on iron nitrate silica gel coated carbon cloth using chemical vapor deposition. The carbon nanotubes have uniform diameter and high purity. The density and uniformity of the carbon nanotubes are dominated by the substrate preparation and growth condition. Carbon nanotube film grown on the carbon cloth can be easily tailored to meet different applications.

#### **A13.21**

**LITHIUM INTERCALATED SINGLE-WALL CARBON NANOTUBES.** Hideo Shimoda, Xiaoping Tang, Bo Gao, Alfred Kleinhammes, Leslie Fleming, Yue Wu, Otto Zhou, Univ. of North Carolina at Chapel Hill, Dept of Physics and Astronomy, Chapel Hill, NC.

SWNTs fabricated by the laser ablation method were purified and reacted with lithium via solid state and electrochemical methods. <sup>13</sup>C-NMR measurements show that the spin-lattice relaxation times ( $T_1$ ) of both the metallic and semiconducting SWNTs become shorter after reaction with Li, indicating increase of the electronic density of state at Fermi level due to charge transfer. Crystalline X-ray diffraction pattern similar to that of the pristine materials was observed from Li-reacted SWNTs. Purified SWNTs were also cut into short bundles by the oxidation method. The effects of nanotube structure/morphology on the intercalation kinetics will be discussed.

#### **A13.22**

**FABRICATION OF FREESTANDING CARBON NANOTUBE ARRAYS IN LARGE SCALE.** Z.P. Huang, J. Moser, M. Sennett, H. Gibson, M.J. Naughton, and Z.F. Ren, Boston College, Dept. of Physics, Boston, MA.

We have successfully fabricated many freestanding carbon nanotube arrays on a silicon substrate. Different sizes of dot arrays have been made by E-beam lithography. It has been found that the size of the carbon nanotubes is closely related to the size of the dot. Compared with our previous report on diameters of about 300 - 400 nm, much thinner carbon nanotubes of 100 - 150 nm have been made. With even smaller dot, it would be expected that even thinner nanotubes of 10 - 20 nm can be possibly made. The nanotube height was controlled by the growth time. Height uniformity has been greatly improved.

#### **A13.23**

**THE ACCURATE CONTROL OF THE DIAMETERS OF CARBON NANOTUBES WITH TRI-LAYER CATALYSTS.** Tong-Ryung Choi, Hyuck Ihm, Byoung-Dong Kim, Woen-Chul Chung, Yong-Chul Kim and Seung-Ki Joo, Seoul National Univ, School of Material Science and Engineering, Seoul, KOREA.

Recently, Carbon nanotubes are in the center of intense interests due to their promising physical properties. These carbon nanotubes can be used in many applications. In each application, different properties and sizes are required. It is well known that the diameters of nanotubes are controlled by surface roughness or morphology of catalytic islands. So many attempts have been made to control diameter by various kinds of methods. However, such efforts have been unsatisfactory because conventional methods can provide only the tendency of changes, not the means of an accurate control. We propose here that a novel accurate method to control the size of carbon nanotubes by means of annealing temperature, time and thickness of layers. When the sandwich-typed tri-layer structure of Ag/NiFe/Ag or Ag/Ni/Ag is used as a catalyst and annealed, NiFe or Ni layer can be transformed to the island of expected size depending on the thickness of each layer and the heat treatment condition. In this method, we can change the spacing of catalytic islands as well as the size of them. After the formation of catalytic islands, carbon nanotubes are produced by Hot-filament CVD method. SEM, TEM and Raman spectroscopy are adopted as analytical tools. In addition to the detailed discussion on the results, the synthesis procedure of carbon nanotubes will be also described.

#### **A13.24**

**STUDIES OF COMPATIBILIZATION OF POLYSTYRENE AND POLY(METHYL METHACRYLATE) WITH MoS<sub>2</sub> NANO TUBE.** W. Zhang, Y. Wang, H. White, M. Rafailovich, J. Sokolov, State University of New York at Stony Brook, Dept of Mat Sci & Eng, Stony Brook, NY; R. Tenne, Weizmann, Institute Rehovith, ISRAEL; A. Ulman, M. Shafi, Chemistry Dept, Polytechnic University, Brooklyn, NY; A. Winesett, H. Ade, Dept Physics, North Carolina State University, Raleigh, NC.

MoS<sub>2</sub> nanotubes were functionalized with thiols and dispersed in polystyrene and poly(methyl methacrylate) toluene solution. The mixture was spun cast onto Si Surface and the film were examined with Scanning Transmission X-ray Microscopy and Scanning Force Microscopy as a function of annealing time at 170°C. The results show that addition of nanotubes decreased the domain size and the contact angle between the polymer. This indicate that the nanotube are effective at decreasing the interfacial tensions between the component, and can serve as potential compatibilizers. Funded in part by NSF-MRSEC Program and the Procter & Gamble Co.

### **A13.25**

**SELF-ASSEMBLED ORGANIC NANOTUBES.** Hicham Fenniri, Purdue University, H.C. Brown Chemistry Laboratories, West Lafayette, IN.

The universal importance of non-covalent forces in the assembly and stabilization of biological systems provides a compelling motivation to consider a new type of organic synthesis based on these interactions. The challenge lies both in the chemical design and synthesis. The conceptualization of an organized state of matter is intimately linked with the chemical information embedded in the molecules in the form of charges, dipoles, and other functional elements necessary to translate chemical information into substances. Much of the research endeavor has been devoted to the use of the hydrogen bond as the alphabet for chemical information encoding, and the structures expressed have spanned the range of dimensions and shapes, from discrete to infinite networks. The starting point of this research theme is a DNA mimetic in which the hydrogen bonding array of the bases as well as the deoxyribose backbone were synthetically modified so that the structural outcome of this bio-inspired material is a six-stranded rather than a double-helical assembly. The specific molecular recognition between six alternating triaminopyrimidine (TAP) and barbituric acid (BA) molecules, through a set of six hydrogen bonds per unit, can be chemically encoded so that structural outcome is a six-membered supermacrocycle. Over the past two years we have developed a synthetic strategy to incorporate TAP and BA into oligomeric strands. As a result, their propensity to self-assemble and self-organize into well-defined hydrogen bonded supermacrocycles was conferred upon the oligomers to which they were attached. The resulting tubular 6-stranded framework may be compared to the DNA double helix except that it has a different backbone, six strands instead of two, and defines a built-in channel with predetermined dimensions. Each level of the sextuple helix involves six self-assembling units (3 TAP's, 3 BA's, eighteen hydrogen bonds) and is engaged in stacking interactions with one or two neighboring plateaus.

### **A13.26**

**STRUCTURE-TUNABLE CARBON MATERIALS FROM GRAPHITE COMPOUNDS.** Gong Kecheng, Wang Weixing, Polymer Structure & Modification Research Lab, South China University of Technology, Guangzhou, CHINA.

The discovery of carbon nanotube, nanorod, nanosphere, nanowire etc. has stimulated intensive scientific investigations because of their special properties and potential applications. But, how to achieve such nanomaterials in large quantity by some simple and inexpensive fabrication method is challenging. Here we report a novel method of preparing structure-tunable carbon materials from graphite compounds. Graphite compounds such as graphite intercalation compounds, graphite oxide etc. are subjected to heat treatment at various temperature to obtain structure-tunable carbon materials. The intercalation guests and catalyst have great influence on the morphologies of result materials. Such carbon materials can be used to prepare (not limited to) electrode materials for supercapacitors.

### **A13.27**

**SELECTIVE FORMATION OF CARBON NANOMATERIALS BY CO<sub>2</sub> LASER VAPORIZATION AT ROOM TEMPERATURE.** Daisuke Kasuya, Faculty of Science and Technology, Meijo University, Nagoya, Aichi, JAPAN; Kunimitsu Takahashi, Fumio Kokai, Institute of Research and Innovation, Kashiwa, Chiba, JAPAN; Masako Yudasaka, "Nanotubulites" Project, Japan Science and Technology, c/o NEC, Tsukuba, Ibaraki, JAPAN; Sumio Iijima, Faculty of Science and Technology, Meijo University, Nagoya, Aichi, JAPAN, "Nanotubulites" Project, Japan Science and Technology, c/o NEC, Tsukuba, Ibaraki, JAPAN.

Single-wall carbon nanohorns (SWNHs) [1] can be produced with a yield of about 90% by CO<sub>2</sub> laser ablation of graphite at room temperature. An SWNH is a horn-shaped sheath of single-walled graphene sheets with a diameter of 2-3 nm, and they form an aggregate shaped like the flower of a dahlia having a diameter of about 100 nm. The ethanol adsorption capacity of the dahlia-shaped aggregates was considerably larger than that of the commercially available activated carbon [2]. Besides the dahlia shaped aggregate, there are two more types that are called bud-like and seed-like SWNH aggregates. So far we have been unable to study their adsorption capacities because of their low yields. Recently we have found that the type and pressure of the buffer gas could control the aggregate structure. When 760 Torr of Ar gas was used, dahlia-shaped aggregates with diameters of about 120 nm were formed. When 760 Torr of He gas or N<sub>2</sub> gas was used bud-like ones with diameters of 70 to 100 nm were formed. Seed-like aggregates with diameters of 60 to 70 nm were produced with Ar gas pressure of 300 Torr. To elucidate the mechanism of the effect of buffer gas on the SWNH aggregate structure, we clarified the yields of C<sub>60</sub> contained in the SWNH. The

C<sub>60</sub> yield was large in He and low in Ar and N<sub>2</sub>, and it decreased with increasing buffer gas pressure. These results do not correspond to the conventional explanation of C<sub>60</sub> formation depending on the buffer gas, so our results require a new model. References [1] S. Iijima *et al.*, Chem. Phys. Lett., 309 (1999) 165. [2] J.A. Nisha *et al.*, Chem. Phys. Lett., in press.

### **A13.28**

**GROWTH OF CARBON NANOTUBE FROM VAPOR PHASE.** Y.M. Chen and Jyh-Ming Ting, Department of MS&E, National Cheng University Tainan, TAIWAN.

Multi-wall carbon nanotube (MWCNT) was prepared via a chemical vapor process. This process not only allows the growth MWCNT with less "thermal carbon" but also bares the potential of low cost production of MWCNT. In the study, we investigated effect of substrate preparation, vapor phase composition, and temperature on the characteristics of MWCNT. The microstructure was determined using transmission electron microscopy (TEM) and the surface morphology was examined using scanning electron microscopy (SEM). The growth kinetics and the variation of microstructure along the tube radial direction were investigated. The substrate preparation was found to be critical to the successful growth of MWCNT. The growth rate of MWCNT increased and then decreased with the gaseous concentration at lower flow rates, while increased with hydrocarbon concentration at high flow rates. It was also found that the temperature has a great impact on the morphology of CNT. A very unusual carbon structure, i.e., CNT with beaded carbon, was found. The formation of the unusual carbon structure was discussed.

### **A13.29**

Abstract Withdrawn.

### **A13.30**

**EFFECT OF TEMPERATURE GRADIENT NEAR THE TARGET AND GAS FLOW RATE ON THE DIAMETER DISTRIBUTION OF SINGLE-WALLED CARBON NANOTUBES GROWN BY THE LASER ABLATION TECHNIQUE.** Rahul Sen, Tokyo Metropolitan Univ. Dept of Chemistry, Tokyo, JAPAN; Hiromichi Kataura, Tokyo Metropolitan Univ., Dept of Physics, Tokyo, JAPAN; Yohsuke Ohtsuka, Toshinobu Ishigaki, Shinzo Suzuki and Yohji Achiba, Tokyo Metropolitan Univ., Dept of Chemistry, Tokyo, JAPAN.

Electronic properties of Single-walled carbon nanotubes (SWNTs) depend very crucially on their diameter and chirality. Thus, diameter control during the growth of SWNTs is very important, not only to grow nanotubes having a desired property, but also to understand their growth mechanism. We have studied the effect of temperature gradient near the target and gas flow rate on the diameter distribution of the SWNTs grown by the laser ablation of Ni/Co catalyzed graphite targets. Our results indicate that when the temperature is almost uniform near the target, the gas flow rate has a small effect on the diameter distribution of the SWNTs. However, when the thermal gradient around the target is large then the gas flow rate affects the diameter distribution strongly. We have also studied the spontaneous emission as well as the scattering images from the laser ablated species at different gas flow rates by using a high speed video camera. We find that the velocities of these species are dependent on the gas flow rate but this dependence is evident only 30-90 msec after the laser ablation. Since the gas flow rate affects the final diameter distribution of the SWNTs (especially when there is large thermal gradient near the target), we can deduce that the growth rates of the SWNTs are much slower than that of fullerene formation.

### **A13.31**

**TIME AND SPACE EVOLUTION OF EMITTING CARBON NANO PARTICLES - CORRELATION WITH THE FORMATION OF FULLERENES AND CARBON NANOTUBES.** Shinzo Suzuki, Rahul Sen, Hiroshi Yamaguchi, Toshinobu Ishigaki, Yohsuke Ohtsuka, Yohji Achiba, Dept of Chemistry, Tokyo Metropolitan Univ, Tokyo, JAPAN; Hiromichi Kataura, Dept of Physics, Tokyo Metropolitan Univ, Tokyo, JAPAN.

Time and space evolution of emitting carbon nano particles were investigated using a laser furnace apparatus combined with a high speed video camera or that with an ICCD system. It was confirmed that an apparent increase in the blackbody emission intensity at longer wavelength correlated with the increase in the yield of fullerenes obtained with the same condition. Also, it was found that in our typical experimental condition for making fullerenes and carbon nanotubes, emitting carbon nano particles proceeded in the upstream direction within c.a.10 msec, then spent another a few hundred micro sec inside the furnace, going back to the downstream direction. These findings are used for the discussion on the formation of fullerenes and carbon nanotubes.

### **A13.32**

#### **MULTIWALL CARBON NANOTUBES AND HOLLOW NANOPARTICLES BY HYDROTHERMAL TREATMENT.**

Jose Calderon-Moreno, Masahiro Yoshimura, Materials and Structures Laboratory, Tokyo Institute of Technology, Tokyo, JAPAN.

The nanostructure evolution of purified single wall carbon nanotubes under hydrothermal conditions, at temperatures below 800°C and pressure of 100 MPa, has been studied by high-resolution microscopy (HRTEM) and selected area electro-diffraction. New layers of rolled graphene sheets form during hydrothermal treatment at this mild temperature without the presence of any catalyst, resulting in the formation of multiwall nanotubes and hollow nanoparticles with a well-ordered layered structure, never observed in mild hydrothermal conditions. In both cases each layer correspond to a rolled graphene sheet. The nanoparticles associated with the multiwall nanotubes formation were found to be hollow multishell polyhedral nanocages of concentric bended graphene sheets, with the same graphitic interlayer spacing than in multiwalled nanotubes. The mechanism for the evolution is discussed at the light of the nanostructure evidence.

### **A13.33**

#### **THE CRYSTALLIZATION OF CARBON NANOFIBRES ON UNIAXIAL ORIENTED POLYBUTENE-1.** G. Broza, J. Sandler, K. Schulte, Polymer Composites Section, Technical University Hamburg-Harburg, Hamburg, GERMANY.

Nanoscale carbon fibres (CNF, supplied by Applied Sciences Inc., USA) with a diameter 200-300 nm, are a new class of material with the potential to reinforce polymers. The combination of CNF's with polymer matrices can be considered as a step forward in composites technology. A fundamental understanding of the CNF / polymer interaction will further enhance the exchange of materials for high performance fibre-reinforced semi-crystalline polymers. Ultra-thin films of polybutene-1 with nanoscale carbon fibres were prepared either by solution casting techniques or by a special thin film drawing technique. The dispersion process developed in this project for CNF's leads to well-separated carbon nanofibres in an uniaxially oriented semi-crystalline polybutene-1 film. It is the purpose of this paper to investigate whether the lattice orientation and spacing of the carbon nanofibres influence the uniaxially oriented polybutene-1 matrix. Additionally, the influence of the polymeric matrix and their lattice structure upon the occurrence of dispersion of the CNF is investigated different solution temperatures during drawing of the uniaxially oriented polybutene-1 matrix. The mechanical properties of these nanocomposites will be investigated. Furthermore, the electrical properties are studied by AC impedance spectroscopy. Due to the high aspect ratio of the tube-like filler the filler weight fraction necessary to form a conductive path through the matrix should be determined and how it influences the anisotropy in conductivity.

### **A13.34**

#### **A THEORETICAL APPROACH TO NANOTUBE FUNCTIONALIZATION AND TECHNOLOGY.** Thomas Frauenheim Gotthard Seifert, Thomas Köhler, Marcus Elstner, Gerd Jungnickel, University of Paderborn, GERMANY; Efthimios Kaxiras, Ickjin Park, Harvard University, MA; Young-Hee Lee, Seung-Mi Lee, Jeonbuk National University, Jeonju, KOREA.

We present recent density-functional based investigations on functionalization of carbon nanotubes (CNT's). Potential problems and applications that will be addressed include: (i) Chemical force imaging by interaction of open-end functionalized CNT's with self-assembled monolayers; (ii) Tailoring of intrinsic electronic properties for nanoscale electronics by side-wall functionalization of CNT's with Fluorine; and (iii) Electrochemically based mechanisms for Hydrogen storage. We further describe in detail the structure, stability and electronic properties of recently produced metall-dichalcogenide NT's,  $MS_2$  (M=Mo,W,Nb) and predict the structure, stability and properties of Silicon- and Siloxene-based tubular structures.

### **A13.35**

#### **SINGLE WALL NANOTUBE POLYMER FORMS: TYPES AND MECHANISMS OF POLYMERIZATION, MOLECULAR AND ELECTRONIC STRUCTURE MODELLING.** Leonid A. Chernozatonskii, Dept of Material Researches, Inst of Biochemical Physics, Moscow, RUSSIA; Madhu Menon, Dept of Physics and Astronomy, Univ Kentucky, Lexington, KY.

We draw attention to a number of high-pressure-high-temperature structures which retain the SWNT ropes, but in which all the tubes are connected by means of cycloaddition process. We consider different known for C60 polymers types of the SWNT cycloaddition: (2 2), (2 4), (6 6), and common 4-sided ring fragments. Mechanism of polymerization both two crossed (n,m) nanotubes and two parallel (n,n) and (n,0) SWNT's is discussed. Coupling of two neighbor

nanotubes is energetically favorably under scheme of 'zipper': quick pair atom coupling along two parallel tubes after movement of 2 2 cycloaddition of some two atom pairs, disposed one opposite other on these neighbor nanotubes. Role of hydrogenation in the process of coupling and depolymerization of SWNT is discussed. The 'zipper' mechanism permits to explain the following: 1) formation of zeolite structures<sup>1</sup>, 2) transformation of molecular coupled nanotube rope into graphite needle under high pressure treatment<sup>2</sup>; 3) formation of double diameter nanotubes under high temperature and light atom flow treatment.<sup>3</sup> We have modeled some examples of polymer SWNT rope transformations using (n,n) and (n,0) carbon nanotubes with  $n = 5 - 12$ . New nanotube polymer crystal structures are computed by using of molecular mechanics and generalized tight-binding molecular-dynamic methods<sup>4</sup>: energetic characteristics show high stability of all these structures; computed energy band structures of such SWNT polymers show possibility of changing their electronic properties - from metallic ((12,12) structure) to high dielectric ((6, 6) structure of 'porous diamond' with all sp<sup>3</sup> atoms). This work was supported by the NSF (No. OSR 99-07463) and partially RFFI (No. 99-02-17578).

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### **A13.36**

#### **BROMINE DOPED CARBON NANOTUBES.** Bingbing Liu, Jan Carlsten, Bertil Sundqvist, Dept of Experimental Physics, Umea University, Umea, SWEDEN.

Carbon nanotubes can be doped by both donors and acceptors, and in both cases doping leads to charge transfer between dopant and nanotubes. We present here the results of an experiment in which we have doped single wall carbon nanotubes, obtained from three different sources, with bromine. The properties of the doped samples have been studied using surfaced enhanced Raman spectroscopy under ambient conditions and, in one case, under high pressure. In the low frequency range we observe Raman signals from intercalated bromine molecules. For large diameter tubes the observed radial breathing mode frequencies are 10% higher for tubes in bundles than for "free" tubes. This result is consistent with theoretical predictions. Doping also leads to a small shift in the high-frequency modes because of charge transfer. When the doped samples are heated in a dynamic vacuum most of the bromine deintercalates from the samples.

### **A13.37**

#### **INSULATED MOLECULAR WIRE FORMED BY MOLECULAR NANOTUBE AND CONDUCTING POLYMER.** Takeshi Shimomura, Tomonori Akai, Takumi Abe, Kohzo Ito, Univ of Tokyo, Graduate School of Frontier Sciences, Tokyo, JAPAN.

Recently, a new series of nanotubes has been synthesized from  $\alpha$ -cyclodextrin ( $\alpha$ -CD) by Harada et al. This molecular nanotube is soluble in several kinds of solvents including water and has a small inside diameter of 0.45nm. Further, this molecular nanotube can include a linear polymer chain with the size matching the inside cavity of nanotube. In this study, we formed the insulated molecular wire from the molecular nanotube and a conducting polymer, polyaniline (PAN), and observed the conformation of the insulated molecular wire by atomic force microscopy (AFM). As a result, we observed the rod-like insulated molecular wires with the length about 300nm clearly by the AFM measurement. This length agrees with the contour length of PAN evaluated from the molecular weight. Further, the thickness of this molecular is equal to the outside diameter of the molecular nanotube. In this insulated molecular wire, the nanotubes shield the interaction between conducting polymer chains to isolate a single chain and increase the solubility greatly. In addition, since the nanotube confines the conformation of the polymer chain to a rodlike one (all trans configuration) owing to very small cavities, it is possible that the defects of the  $\pi$ -conjugated system (gauche configuration) are eliminated from the polymer chain.

### **A13.38**

#### **SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE-CARBON NANOTUBE COMPOSITES.** J.H. Chen, W.Z. Li, Z.F. Ren, Boston College, Department of Physics, Chestnut Hill, MA.

Carbon nanotubes can improve both the strength and conductivity of organic polymer. Polypyrrole-carbon nanotube composites were obtained by cycling the potential of a platinum electrode in an aqueous solution containing pyrrole monomer and multiwalled carbon nanotube suspension. It is shown that the rate of polymerization is enhanced by the presence of carbon nanotubes. The composite was

characterized by cyclic voltammetry, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

#### **A13.39**

**CARBON NANOTUBE/POLYELECTROLYTE COMPOSITES AS NOVEL ACTUATOR MATERIALS.** Debjit Chattopadhyay, Fotios Papadimitrakopoulos, Department of Chemistry, Polymer Program, Nanomaterials Optoelectronic Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT; Ray Baughman, Anvar Zakhidov, Ilyas Khyrulin, Honeywell Co, Morristown, NJ.

Present state-of-the-art carbon nanotube actuators use highly porous, paper-like sheets of nanotubes, which are fabricated via filtration from an aqueous suspension of single-walled carbon nanotubes (SWNTs). This technique mostly yields largely bundled nanotubes, which decreases the net surface area available for double layer charging and also limits the number of cross-nanotube junctions that ultimately control mechanical properties. The use of polymeric surfactants, such as Nafion and other electrolytes is presently being investigated to help unbundle the SWNT and increase the net surface area available for charge injection. Films of these composites, consisting of percolated nanotubes in an ionically conducting polymer matrix, are easily fabricated by solution casting. These composites have shown to exhibit improved mechanical properties (modulus of 2GPa) and strains of about (0.25% in a 5M NaCl solution (vs Ag/AgCl)). These composite also display very strong adhesion to a variety of substrates, which is expected to be a useful characteristic for micro-actuator applications. The effect of the incorporation of these polyelectrolytes on morphology, surface area and mechanical properties will be also presented.

#### **A13.40**

**DIAMOND CLUSTERS STRUCTURED WITH NANOTUBES: ATOMISTIC SIMULATION RESULTS.** O.A. Shenderova, D. Areshkin, B.L. Lawson, V. Zhirnov, D.W. Brenner.

The emerging field of nanoengineering requires the design of nanoscale structures that have controllable physical and chemical properties, and that can be constructed from readily accessible building blocks. Nanodiamonds and carbon nanotubes, for example, are unique structures that can be produced in bulk quantities that have diverse electronic properties depending on their size and morphology. The feasibility of designing composites composed of nanodiamond clusters and carbon nanotubes as well as their electronic properties will be discussed. Depending on nanotube size and morphology, some types of open nanotubes can be chemically connected with different diamond surfaces, atom to atom. So far, the following nanotube/nanodiamond combinations have been designed: (12,0) and (6,0) nanotubes with cubo-octahedron particles, and a (5,5) nanotube with a pentaparticle. All structures are mechanically stable with all bonds saturated. Fabrication of these structures could potentially be achieved using self-assembly of the components in microemulsions or by laser irradiation. Different types of heterojunctions useful for nanodevices can be designed by combining semiconducting or metallic nanotubes with diamond clusters. Nanotube/nanodiamond composites could also find application in field emitting displays. Currently nanotubes have potential as a field emitting material and the above design of a nanotube capped with nanodiamond may, in principle, reduce tube erosion and increase device lifetimes. Electronic and optical properties of nanostructures consisting of carbon nanocones will be also discussed.

#### **A13.41**

**STABILITY INVESTIGATION AND THERMAL BEHAVIOR OF MULTI-WALLED CARBON AND SILICON NANOTUBES.** Solange B. Fagan, Daniela S. Sartor, Suzana B. Peripolli, R. Mota, Depto. de Física, Universidade Federal de Santa Maria, Santa Maria, RS, BRAZIL; R.J. Baierle, Centro Universitário Franciscano, Santa Maria, RS, Brazil; Antônio J.R. da Silva, A. Fazzio, Instituto de Física, Universidade de São Paulo, São Paulo, SP, BRAZIL.

A systematic study about the stability and thermal behavior of multi-walled carbon and silicon nanotubes is presented through two alternative approaches: Monte Carlo simulations using Tersoff empirical potential and first-principles calculations based on density functional theory. Even considering that silicon nanotubes have never been observed and despite the known difficulties for Si in having an  $sp^2$ -like structure [1], it is worth to explore the fact that both elements have the same valence electron number and a similar distribution of the outermost electrons for the free atoms. As expected, we show that the two nanotubes disintegrate at different temperatures, much smaller for the silicon, reflecting the fact that the  $sp^2$  hybridization is more stable in carbon. Also they disintegrate differently, with the Si tending to form more compact 3D-like clusters. At low temperatures, to avoid initial structural deformations, carbon and silicon tubes are assumed to be coaxially apart at least 1.4 times the C-C distance and 1.65 times the Si-Si distance, respectively. In

particular, for the double-walled and triple-walled Si nanotubes, we observe that the energy per atom presents a minimum around the temperature where silicon partially recovers the  $sp^3$ -type structure. The same behavior is not observed for the carbon nanotubes. [1] Solange B. Fagan et al., Phys. Rev. B **61**, 9994(2000).

#### **A13.42**

**SYNTHESIS OF CARBON, SILICON, AND BORON-NITRIDE NANOSTRUCTURES VIA MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION.** Hongtao Cui, Brian R. Stoner, Curriculum in Applied and Materials Sciences, Univ of North Carolina, Chapel Hill, NC; Wei Liu, Dept of Materials Science and Engineering, North Carolina State Univ, Raleigh, NC.

Carbon, silicon and boron-nitride nanostructures were synthesized using microwave plasma enhanced chemical vapor deposition. Both scanning and transmission electron microscopies were used to observe the morphology and structures while a combination of micro-Raman and electron energy loss spectroscopies were used to determine the composition of the nanostructured materials. Predominantly hollow carbon nanotubes were observed while the Si and BN exhibited a solid, nanowire structure. All materials were deposited using a thin film iron catalyst seeded on either silicon or boron-nitride substrates with reactive plasma gases containing either methane, ammonia or a mixture of the two. A general discussion of the nucleation and growth mechanisms for the various materials will also be included.

#### **A13.43**

**CARBON NANOTUBE / PMMA COMPOSITES.** Nachiket R. Ravavikar, Bingqing Wei, Linda S. Schadler, Pulickel M. Ajayan, Rensselaer Polytechnic Institute, Dept of Materials Science and Engineering, Troy, NY.

Carbon nanotube based composites, as one of the potential application areas of nanotubes, have attracted wide attention in recent years. In this paper, we report the processing and properties of single walled carbon nanotube / poly methyl methacrylate (PMMA) nanocomposites. They were prepared by polymerizing the PMMA in the presence of nanotubes thereby increasing the interaction between nanotubes and PMMA. Tensile tests, DMA, DSC, RAMAN and four-point probe electrical measurements were employed to characterize the properties of composites. Nanocomposites with 5wt% carbon nanotubes were found to be electrically conducting. Our results indicate that the interfacial bonding between nanotubes and matrix and resulting mechanical properties depend strongly on the processing conditions. New procedures, involving surfactant-assisted dispersion of nanotubes will be described as a viable route to preparing well-dispersed nanotube composite.

#### **A13.44**

**HOLLOW FIBERS CONTAINING CARBON NANOTUBES FOR STRUCTURAL APPLICATIONS.** Carolyn Dry, School of Architecture, University of Illinois, Champaign, IL; Natural Process Design, Champaign, IL.

Filled hollow fibers containing carbon nanotubes and other chemicals have enhanced material strength, electrical, and thermal properties. The issues in nanotechnology usage are how to increase to engineering scale from nanoscale and how to reduce the cost. Therefore we use hybrid fibers, hollow fibers containing nanotubes and other components as the main fiber in designs for materials for infrastructure and device applications. Translation of nanotube properties to the outside wall of the hollow fiber is accomplished by the other chemical constituents. These other constituents allow for reduction in the number of nanotubes required. Also the nanotubes can be configured in a variety of architectural arrays within the hollow fiber, among the other constituents of fibers and chemicals surrounding the tubes. The placement of these hybrid hollow fibers filled with carbon nanotubes at critical regions in the matrix should exert added compressive strength to close fractures when stressed, as fibers they can bridge across cracks and they can be interrogated as to their state of stress. In this paper the properties of matrices made with hollow fibers containing carbon nanotubes and chemical constituents will be compared to matrices containing empty hollow fibers, or hollow fibers containing the chemicals without the nanotubes, or hollow fibers containing other chemicals.

#### **A13.45**

**YIELD OPTIMIZATION IN THE SYNTHESIS OF C<sub>60</sub>@SWNT.** Brian W. Smith, David E. Luzzi, Univ of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA.

We have previously shown that single wall carbon nanotubes (SWNTs) can be filled with C<sub>60</sub> molecules by annealing a sample infused with exterior C<sub>60</sub> crystallites. A C<sub>60</sub> vapor is produced, and the fullerenes enter the SWNTs through defects by vapor phase transport or surface diffusion [1]. In this work, we explore the

parameters required to synthesize these C<sub>60</sub>@SWNT assemblies. The imposition of defects by acid oxidation, the amount of infused C<sub>60</sub>, and the annealing time and temperature are varied for different samples. Samples are subsequently treated to allow any interior C<sub>60</sub> that has formed to leach into toluene solution. Each solution is examined using UV-VIS spectroscopy in order to quantify the filling fraction for the corresponding sample. By correlating the measured filling fraction to the varied parameters, we determine the kinetics of the synthesis process, the efficiency of the filling process, and the synthesis condition that maximizes the production of C<sub>60</sub>@SWNT. The results of this study may enable the bulk synthesis of these so-called bucky peapods, affording the opportunity to measure their properties. The application of our synthesis method for producing hybrid materials using other types of molecules will be discussed. [1] B.W. Smith, D.E. Luzzi, Chem. Phys. Lett. 321 (2000) 169.

#### **A13.46**

EFFECTS OF SYNTHESIS CONDITIONS ON SWNT STRUCTURE AND MORPHOLOGY. L. Fleming, S. Sinha, H. Shimoda, C. Bower, K. Horton, X.-P. Tang, A. Kleinhammes, Y. Wu, O. Zhou, University of North Carolina at Chapel Hill, NC.

Pulsed-laser vaporization remains an important research technique for the production of single-walled carbon nanotubes because it allows the greatest amount of control over the nanotube growth conditions, and hence offers the best possibility for gaining control over SWNT structure and morphology. Our work examines structural changes in PLV-grown SWNTs as a function of the growth parameters but especially emphasizes the effects of target composition. Both the catalyst type and concentration are varied and shown to alter the diameter distribution of the resulting nanotubes. An interesting effect will also be shown in which the material changes from carbon nanoparticles to "bamboo" structured MWNTs and finally to SWNTs with increasing catalyst concentration. Nanotube materials are characterized with TEM, Raman spectroscopy, and x-ray diffraction. The results of these will be shown with supporting NMR data, which offers a way to measure the percentages of metallic and semiconducting tubes in a sample.

#### **A13.47**

SIMULATING THE IN-PLANE PHOSPHORUS DOPED NANOTUBE. Takuya Hayashi, Morinobu Endo, Shinshu Univ, Dept of Electrical and Electronic Eng, Nagano, JAPAN.

Doping Boron and Nitrogen into nanotubes has been intensively studied both experimentally and theoretically. The results were interesting in the way that the modification of the electronic properties have occurred, opening possibilities to novel electronic devices. In the world of semiconductors, phosphorus is also playing an interesting role for the effect on the electronic structure. Here, we present the computer simulated results of the phosphorus doped carbon nanotubes. Local structure and electronic properties will be shown.

#### **A13.48**

INTERCALATION AND FUNCTIONALIZATION OF CARBON NANOTUBES. Jijun Zhao, Alper Buldum, Jianping Lu, Dept. of Physics and Astronomy, University of North Carolina at Chapel Hill; Jie Han, NASA Ames Research Center.

Electronic properties of nanotubes can be dramatically altered with intercalation and chemical functionalization. Using first principles methods we studied the Li intercalation of nanotubes for battery application and functionalization of nanotubes by absorption of molecules. We find that both the interstitial sites of nanotube rope and the hollow interior of nanotubes are susceptible for Li intercalation. By utilizing both spaces large intercalation density up to LiC<sub>2</sub> can be achieved with intercalation potential compatible to Li intercalated graphite. The adsorption of gap molecules, such as O<sub>2</sub>, H<sub>2</sub>O, NO<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>, and He, has profound impact on electronic properties of nanotubes. The electronic structure calculations shows that SWNT can be either charge donor or acceptor depending on the molecule. Thus, the conductive properties of SWNTs can be dramatically changed by exposing to gases, leading to potential application in sensors and devices.

#### **A13.49**

ELECTROSPINNING OF CONTINUOUS FIBERS OF CARBON NANOTUBE AND POLYMER COMPOSITE. W. Han, F. Ko, Drexel Uni., Philadelphia, PA; R. Rosen and O. Zhou, Uni. of North Carolina, Chapel Hill, NC.

Electrospinning is an electrostatic induced self-assembly process wherein ultrafine fibers are produced. In this process, a high voltage electric field is generated between an oppositely charged polymer fluid contained in a glass syringe with a capillary tip and a metallic collection screen. As the voltage is increased, the charged polymer

solution is attracted to the screen. Once the voltage reaches a critical value, the charge overcomes the surface tension of the suspended polymer with cone formed on the capillary tip of the syringe and a jet of ultrafine fibers is produced. As the charged fibers are sprayed, the solvent quickly evaporates and the fibers are accumulated on the surface of the collecting screen. This results in a nonwoven mesh of nano to micron scale fibers. We have used the electrospinning method to fabricate fibers of carbon nanotubes and polyethylene oxide using different solvents. Electron microscopy studies show that fibers are continuous and 2-5micron in diameter. The structure, morphology and properties of these fibers will be discussed.

#### **A13.50**

A STUDY OF GROWTH MECHANISM OF CARBON NANOTUBES. Frank Tsui and Paul Ryan, University of North Carolina, Dept of Physics and Astronomy, Chapel Hill, NC.

Nucleation and growth mechanism of carbon nanotubes synthesized by molecular beam epitaxy have been studied using real-time reflection high energy electron diffraction, mass-spectrometry, and in-situ scanning tunneling microscopy. Three-dimensional transition metal epitaxial films grown on oxide substrates were used as the catalytic templates. Various metals, including Mo, Y, Co, Ni, and Fe, grown along various crystallographic orientations, e.g. (001) and (111), were used to probe the catalytic effects of different elements and surfaces. During initial deposition of carbon in the temperature range between 200 and 1200°C, carbon clusters are first broken down by the catalysts leading to the incorporation of atomic carbon into the films thus forming superlattices of metal/carbon nanoparticles. This is followed by kinetic coarsening of the nanoparticle superlattice and the corresponding carbon saturation process of the film. Subsequently, carbon nanotubes nucleate from the metal/carbon nanoparticle 'seeds', forming "sea urchin" structures. The diameters of the nanotubes appear to correlate with those of the 'seeds', rather than the size of the metal islands, which are much larger in this study. The competition between the coarsening of the nanoparticle 'seeds' and precipitation of nanotubes appears to play a key role in determining the size and uniformity of the nanotubes.

#### **A13.51**

ANODIZED ALUMINUM OXIDE FILMS AS NANOSTRUCTURED TEMPLATES FOR GROWING CARBON NANOTUBES. Y.C. Sui<sup>1</sup>, D. Acosta<sup>2</sup>, A. González-León<sup>1</sup>, A. Bermúdez<sup>1</sup>, J. Feuchtwanger<sup>2</sup>, B.Z. Cui<sup>2</sup>, J.M. Saniger<sup>2</sup>. <sup>1</sup>Laboratorio de Materiales y Sensores, Centro de Instrumentos, Universidad Nacional Autónoma de México; <sup>2</sup>Instituto de Física, Universidad Nacional Autónoma de México.

Anodic aluminum oxide (AAO) films grown in acid electrolyte possess regular and highly anisotropic porous structure. The range of pore density (10<sup>9</sup>-10<sup>11</sup>/cm<sup>2</sup>) may be tailored as a function of the anodization voltage and acid electrolyte, while a wide pore diameter range (5-100 nm) could be obtained by control the post-anodization chemical etching. These characteristics allow the use of AAO as microfilters, templates for the growth of metal or semiconductor nanowires, carbon or carbon nitride nanotubes, etc. Additionally, semiconductor or metal deposited on AAO templates often possess unique electronic, optical and magnetic properties. In this work a summary of our experiences in growing of AAO films and their use as template for carbon nanotubes (CNTs) ropes from the pyrolysis of acetylene is presented. A discussion about the straight or multi-branched shape of the AAO pores and the experimental conditions favoring the formation of each kind of pore arrays will be presented. The possibility of grow CNTs by acetylene pyrolysis with or without the presence of Co deposited on the bottom of the pores and its implication on the catalytic role of the alumina pore internal walls and on the CNTs formation mechanism will be discussed. Contrary to the multiwall carbon nanotubes made by arc-discharge which consist of long and straight coaxial cylindrical units, the walls of AAO grown CNTs consist of numerous stacked flakes or chips of carbon atomic layer. Finally, in view of the former considerations the possibility that the AAO grown CNTs could be considered as a carbon nanotube-like structure with specific physico-chemical properties will be evaluated.

#### SESSION A14: POSTER SESSION PROPERTIES

Wednesday Evening, November 29, 2000  
8:00 PM

Exhibition Hall D (Hynes)

#### **A14.1**

FORMATION OF NbSe<sub>2</sub> NANOTUBES BY ELECTRON IRRADIATION. D.H. Galvan, Jun-Ho Kim, M.B. Maple, Institute of Pure and Applied Physical Sciences, University of California-San Diego, La Jolla, CA; M. Avalos-Borja, Centro de Ciencias de la Materia Condensada-UNAM, Ensenada, MEXICO; E. Adem,

We report the production of NbSe<sub>2</sub>, (niobium diselenide) nanotubes by high doses of Electron irradiation. The apparatus used for irradiation was a 2 MeV Van de Graaf Accelerator, while the irradiation conditions were the following: voltage 13 MeV, current 5  $\mu$ A, dose rate 25kGy/min, and total dosage 1000kGy. Samples were analyzed with high-resolution transmission electron microscope. The main characteristics observed were huge and very well defined nanotubes of several nm long and few nm wide, which are presumably hollow, although they are capped at one end. At this level of irradiation, we were able to find neither onion-like structure nor particles throughout other areas, as it is usual in similar hexagonal structures of the dichalcogenide family.

#### **A14.2**

##### **HYDROGEN STORAGE IN CARBON NANOTUBES: QUANTUM CHEMISTRY AND MOLECULAR SIMULATION STUDIES.**

Richard L. Jaffe, Deepak Srivastava, NASA Ames Research Center, Moffett Field, CA.

Recent publications have proposed the use of carbon nanotubes as a hydrogen storage medium. To evaluate the feasibility of these proposals, we have undertaken quantum chemistry and molecular simulation studies to probe the mechanism of hydrogen physisorption and chemisorption in single wall carbon nanotube (SWNT) materials. Quantum chemistry calculations are used to determine the interaction energies for the chemisorption of atomic hydrogen and physisorption of molecular hydrogen on SWNT and graphene surfaces. In this work, sections of the substrates are represented by model molecules with varying curvature and chirality and the effect of electron correlation and basis set incompleteness are included in the calculations. In addition, the possibility of enhancement of the hydrogen-nanotube interaction due to alkali metal doping is explored. Molecular simulation studies include molecular dynamics calculations of molecular hydrogen inside capped nanotubes and interstitial hydrogen storage in SWNT ropes. Modeling of atomic hydrogen migration on curved graphene surfaces is achieved using a semiclassical wavepacket method. The results indicate that neither the curvature of the SWNT surface nor alkali metal doping provides significant enhancement in the binding energy of physisorbed hydrogen. MD simulations at moderate temperatures and pressures are consistent with < 2 wt% storage capacity for ropes of small diameter SWNT and ~5 wt% for individual nanotubes with diameters of 2 nm.

#### **A14.3**

##### **CHARACTERIZATION AND NONLINEAR OPTICAL LIMITING PROPERTIES OF A POLY (ACRYLIC ACID)-SURFACTANT-MULTI-WALLED CARBON NANOTUBE COMPLEX. Zhaoxia Jin, Suat Hong Goh, Guoqin Xu, National University of Singapore, Dept of Chemistry, Singapore, SINGAPORE; Lei Huang, Wei Ji, National University of Singapore, Dept of Physics, Singapore, SINGAPORE.**

A poly (acrylic acid) (PAA)-surfactant-multi-walled carbon nanotube (MWNT) complex was synthesized and characterized using TEM, SEM, WAXD, and SAXD. The complex was found to retain a lamellar structure by SAXD, SEM and TEM. SEM showed that MWNTs were trapped and covered by the PAA-hexadecyltrimethylammonium (C<sub>16</sub>TAB) complex. The nanotube trapped inside the complex showed deformable property. TEM micrograph of the PAA-C<sub>16</sub>TAB-MWNT complex showed that the nanotube in the complex is nearly 1  $\mu$ m in length with a diameter of 20-30 nm. NLO measurements were made to evaluate the potential application of the PAA-C<sub>16</sub>TAB-MWNT complex. Z-scan results showed that the complex showed the same NLO properties as the MWNT suspended in CHCl<sub>3</sub>. By fitting the standard Z-scan theory, the effective nonlinear refractive index and nonlinear absorption index are found to be about  $6.8 \times 10^{-18}$  m<sup>2</sup>/W and  $4.5 \times 10^{-9}$  m/W, respectively. The complex could be a potential candidate for solid NLO devices because of its ease to prepare cast film.

#### **A14.4**

##### **DEFORMATION ANALYSIS OF SINGLE-WALL CARBON NANO-TUBES BY THE VIRTUAL-INTERNAL-BOND (VIB) CONTINUUM THEORY. P. Zhang, Y. Huang, University of Illinois, Dept of Mechanical Engineering, Urbana, IL; H. Gao, Stanford University, Dept of Mechanical Engineering, Palo Alto, CA; K.C. Hwang, Tsinghua University, Dept of Engineering Mechanics, Beijing, CHINA.**

Carbon nano-tubes have exhibited superior mechanical properties over their bulk counterparts. This has attracted significant efforts to study the mechanical behavior of nano-tubes, including the deformation pattern and bifurcation mode. These studies, however, have all been limited to the molecular dynamics simulations since the single-wall carbon nano-tubes contain only a layer of carbon atoms in the wall thickness direction. It is commonly believed that the continuum

mechanics theories are not applicable at this level. The virtual-internal-bond (VIB) model is a new continuum theory that is capable of incorporating the atomistic information into the continuum analysis. We have used the VIB continuum model that builds on the atomistic potential of carbon to study the deformation mode of single-wall carbon nano-tubes. The predictions of the VIB continuum model agree very well with the molecular dynamics simulations.

#### **A14.5**

##### **CARBON NANOTUBES, BUCKYBALLS, ROPES AND A UNIVERSAL GRAPHITIC POTENTIAL. L.A. Girifalco, Miroslav Hodak and Roland S. Lee, Department of Materials Science, University of Pennsylvania, Philadelphia, PA.**

The potential energies of interaction between two parallel, infinitely long carbon nanotubes of the same diameter, and between C<sub>60</sub> and a nanotube in various arrangements, were computed by assuming a continuous distribution of atoms on the tube and ball surfaces and using a Lennard-Jones carbon-carbon potential. The constants in the L-J potential are different for graphene-graphene and C<sub>60</sub>-C<sub>60</sub> interactions. From these, the constants for tube-C<sub>60</sub> interactions were estimated using averaging rules from the theory of dispersion forces. For tubes in ropes, the cohesive energy per unit length, the compressibility and the equilibrium separation distance were computed as a function of tube radius. For a C<sub>60</sub> molecule interacting with tubes, the binding energy inside a tube was much higher than on a tube or at the tube mouth. Within a tube, the binding energy was highest at a spherically capped end. The potential energies for tubes of all radii, as well as for interactions between C<sub>60</sub> molecules, for a C<sub>60</sub> molecule outside of a nanotube, between a C<sub>60</sub> molecule and a graphene sheet and between graphene sheets, all fell on the same curve when plotted in terms of certain reduced parameters. Because of this, all the potentials can be represented by a simple analytical form, thereby greatly simplifying all computations of van der Waals interactions in graphitic systems.

#### **A14.6**

##### **RESONANT TUNNELING IN CARBON NANOTUBE DEVICES: FINITE-TUBES AND MAGNETIC TUNNEL JUNCTIONS. H. Mehrez<sup>1</sup>, J. Taylor<sup>1</sup>, H. Guo<sup>1</sup>, J. Wang<sup>2</sup>, and C. Roland<sup>3</sup>.**

<sup>1</sup>Department of Physics, McGill University, Montreal, PQ, CANADA; <sup>2</sup>Department of Physics, The University of Hong Kong, Hong Kong, CHINA; <sup>3</sup>Department of Physics, NC State University, Raleigh, NC.

We have investigated theoretically transport through metal-carbon nanotube-metal devices, showing that transport is dominated by length-dependent resonant transmission. Specifically, distinct on- and off-resonance behavior is predicted for armchair tubes commensurate with a 3N, N integer role. Other aspects of resonant tunneling such as peak distributions as a function of nanotube length, helicity and defects will also be discussed. For the case of ferromagnetic leads such as Co, a clear spin-valve effect is predicted for armchair nanotubes with a magnetoconductance ratio of up to 20%. The implications of these results for the fabrications of nanotube devices will be discussed.

#### **A14.7**

##### **COMMENSURABILITY AND WETTING PROPERTIES OF KRYPTON ADSORBED ON MULTI-WALLED CARBON NANOTUBES. DEPENDENCE ON THE NANOTUBE MORPHOLOGY. D. Billaud, A. Bougrine, N. Dupont-Pavlovsky, J. Ghanbaja, Laboratoire de Chimie du Solide Minéral, Vandoeuvre-lès-Nancy, FRANCE; F. Beguin, CRMD, Orléans, FRANCE.**

Krypton adsorption has been investigated on multiwalled carbon nanotubes prepared at the Orleans Laboratory by catalytic decomposition of acetylene. The isotherms measured from the first stages of adsorption to the adsorbate saturation vapour pressure are compared to those obtained in the same conditions on graphite. The results are discussed in the light of the nanotube morphology, as determined by transmission electron microscopy and electron energy loss spectrometry. Krypton adsorption on the external nanotube walls proceeds, as on graphite, by successive monomolecular layer condensations. The first adsorbed layer is commensurate with the substrate. At its completion, it undergoes a transition towards an incommensurate two-dimensional solid of higher density. The curvature of the graphene sheets, with respect to those of graphite, produces a stabilization of the commensurate film. Moreover, the monolayer condensation pressures are higher than those observed with graphite, which probably limits their number before krypton bulk condensation.

#### **A14.8**

##### **DEFECTS ENERGETICS, MECHANICAL INSTABILITY AND LOCALIZED ELECTRONIC STATES IN CARBON NANOTUBES. Roberto Conversano and Vittorio Rosato, ENEA, High-Performance Computing Project, Centro Ricerche Casaccia, and INFN, Roma, ITALY; Fabrizio Cleri, Manuela Volpe and Gregorio D'Agostino,**

ENE, Divisione Materiali, Centro Ricerche Casaccia, and INFM, Roma, ITALY.

We report the result of a theoretical study, based on Tight Binding Molecular Dynamics (TBMD), of the thermodynamic properties of different prototypes of chiral and armchair carbon nanotubes. We characterized both the perfect and the defective structures, i.e. in presence of point (vacancies) and topological (5-7 rings) defects. Simulations are carried out at different temperatures up to the onset of the mechanical instability. The origin of such an instability is investigated by calculating a topological order parameter (order of connectivity). The nanotubes mechanical instability is compared to that observed in other forms of  $sp^2$ -bonded carbon structures (e.g. fcc-( $C_{36}$ )<sub>2</sub> schwarzite). In this latter case, a closed (connected) topological structure unfolds to give origin to disordered graphene sheets. The effect of the different types of defects on the carbon nanotubes physical properties is ascertained by evaluating: (a) the change in the instability temperature, (b) the electronic and vibrational density of states, (c) the elastic response. Work performed under the Project "Innovative Materials Based on Carbon Nanostructures" of the Italian Space Agency (ASI).

#### **A14.9**

LARGE FIELD EMISSION FROM WELL-ALIGNED CARBON NANOTUBE ARRAYS. Jung Inn Sohn, Seonghoon Lee, Kwangju Institute of Science and Technology, Dept. of MS&E, Kwangju, KOREA; Yoon-Ho Song, Sung-Yool Choi, Kee-Soo Nam, Micro-Electronics Tech. Labs., ETRI, Taejon, KOREA.

We have grown well-aligned carbon nanotube arrays by thermal chemical vapor deposition at temperatures below 800°C on Fe nanoparticles deposited by a pulsed laser on a porous Si substrate. Porous Si substrates were prepared by the electrochemical etching of p-Si(100) wafers with resistivities of 3 to 6  $\Omega\text{cm}$ . These well-aligned carbon nanotube field emitter arrays are suitable for electron emission applications such as cold-cathode flat panel displays and vacuum microelectronic devices like microwave power amplifier tubes. Field emission characterization has been performed on the cold cathode diode device. The anode is maintained at a distance of 60  $\mu\text{m}$  away from the carbon nanotube cathode arrays through an insulating spacer of polyvinyl film. The measured field emitting area is  $4.0 \times 10^{-5} \text{cm}^2$ . We made a field emission measurement at room temperature. Our carbon nanotube field emitter arrays start to emit  $1 \text{mA}/\text{cm}^2$  at the turn-on electric field,  $2 \text{V}/\mu\text{m}$ . Even at  $3 \text{V}/\mu\text{m}$ , they emit a large current density as high as  $80 \text{mA}/\text{cm}^2$  which is orders of magnitude higher than any other results reported so far. The field emitter arrays in our diode device are vertically well-aligned carbon nanotubes on the Si-wafer substrate.

#### **A14.10**

BREIT-WIGNER-FANO LINESHAPE ANALYSIS OF THE TANGENTIAL G-BAND OF METALLIC NANOTUBES. S.D.M. Brown<sup>a</sup>, A. Jorio<sup>a</sup>, P. Corio<sup>a</sup>, M.S. Dresselhaus<sup>a,b</sup>, G. Dresselhaus<sup>c</sup>, K. Kneipp<sup>d</sup>. <sup>a</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, MA; <sup>b</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA; <sup>c</sup>Francis Bitter National Magnet Laboratories, Massachusetts Institute of Technology, Cambridge, MA; <sup>d</sup>Technical University of Berlin, Berlin, GERMANY; G.R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, MA.

A method for distinguishing between metallic and semiconducting single-walled carbon nanotubes (SWNT) in any given sample could be based on the distinct differences in the tangential  $G$ -band ( $\sim 1600 \text{cm}^{-1}$ ) feature in their Raman spectra. The  $G$ -band of semiconducting nanotubes has been extensively studied, and is well accounted for using Lorentzian oscillators, and recent polarization studies have identified the symmetries of the various lineshape components. A detailed Breit-Wigner-Fano lineshape analysis of the tangential  $G$ -band features attributable to *metallic* carbon nanotubes is presented. Only two components are needed to account for the entire  $G$ -band for metallic nanotubes, both with predominantly  $A$  ( $A_{1g}$ ) symmetry, and the nanotube curvature causes the differences in their frequencies and the Breit-Wigner-Fano coupling. Surface-enhanced Raman spectroscopy studies show that the coupling mechanism involves the coupling of the  $G$ -band tangential phonons (associated with the circumferential displacements) to a surface-plasmon based electronic continuum. Evidence in support of this mechanism is presented, providing a basis for future theoretical calculations.

#### **A14.11**

SIMULATION AND HREM OF  $\text{MoS}_2$  CONCENTRIC NANOSTRUCTURES. J.A. Ascencio, M. Perez, and M. Jose-Yacamán.

$\text{MoS}_2$  nanostructures have been observed in different configurations since the named fullerene like onions to the single and multiple walls nanotubes. Also their corresponding applications are very rich, because of the  $\text{MoS}_2$  particular characteristics that have been used in tribology, catalyst, etc. The High Resolution Electron Microscopy (HREM) techniques have allowed to analyze the structure and local configuration, mainly in basis of the corresponding contrast. Besides the application of molecular simulation in nanostructure materials has helped a lot in the HREM image interpretation and in the properties prediction or the atomistic and electronic distribution involved. This simulation are based in approximations of Molecular Dynamics and Quantum Mechanics theories. In the present work we applied both molecular simulation approaches in order to determine the minimal energy configuration for these structures that implies the geometry optimization for the randomly proposed atomic positions for each one of the models. By using these models we calculated the corresponding HREM image to confirm their existence by comparison with experimental results. Quantum mechanics analysis is also presented to predict optimal configuration to the proposed application for this kind of materials. Experimental images were obtained from irradiated samples produced by P. Santiago in ININ for the nanotubes and onion like nanostructured systems facilitated by Prof. Reshef Tenne.

#### **A14.12**

SURROUNDING EFFECTS IN SINGLE-WALLED AND MULTI-WALLED CARBON NANOTUBES. J.P. Buisson, O. Chauvet, Serge Lefrant, C. Stéphan, J.M. Benoit<sup>a</sup>, IMN, Univ. Nantes, FRANCE. <sup>a</sup>Also at TC, Dublin, IRELAND.

The low frequency RBM observed in SWNT's has been proved to probe efficiently their diameter distribution. We have made a model to estimate interaction between individual nanotubes when arranged in bundles and shown that an upshift of 6 to  $10 \text{cm}^{-1}$  can be calculated. In a PMMA-SWNT's composite, our model shows that an upshift can be also predicted, as due to the hydrostatic pressure applied by the polymer to the bundles. Finally in multiwalled carbon nanotubes, the interaction between concentric layers can lead to low frequency modes, as observed experimentally.

#### **A14.13**

NMR CHEMICAL SHIFT OF SINGLE-WALL CARBON NANOTUBES. Sylvain Latil, Christophe Goze, Patrick Bernier, Groupe de Dynamique des Phases Condensées, Montpellier, FRANCE; Luc Henrard, Lab. de Physique des Solides, Namur, BELGIUM; Angel Rubio, Dept de Física Teórica, Valladolid, SPAIN.

We report calculation of the NMR chemical shift anisotropy (CSA) tensor of single-wall carbon nanotubes, within the London approximation (ring-currents contribution). Our results clearly indicate that the CSA isotropic line as measured by high-resolution NMR experiments is able to distinguish between metallic and semiconducting tubes (because we predict that the separation of the lines is 11 ppm). We carefully check that this result remains valid and observable when disorder, bends, functionalization and bundle packing are taken into account. Finite size effects are usually small but show interesting 3 periods oscillations (magic numbers) in the magnetic response. Packing effect broadening is 20 ppm, but shrink onto a sharp lorentzian ( $< 1$  ppm) when averaging (High resolution NMR).

#### **A14.14**

SIMULATION OF THE DIFFRACTION PATTERN OF SINGLE-WALLED CARBON NANOTUBE BUNDLES IN GAS ENVIRONMENT. R. Almairac, S. Rols, J.L. Sauvajol, E. Anglaret, J.L. Bantignies, Groupe de Dynamique des Phases Condensées-UMR 5581, Univ. Montpellier II, Montpellier, FRANCE.

Simulations of the diffraction spectra of single-walled carbon nanotube (SWNT) bundles in the presence of gas are presented in the following cases: i) bundle without gas, ii) tubes filled with gas, iii) gas in the channels between the tubes and iv) gas everywhere in the bundle. We show that the difference curves (empty bundle - gas) are characteristic of each case considered. The measured diffraction patterns of a raw SWNT mat in different environment conditions (in air, in vacuum and after injection of a small amount of water in the sample chamber) are compared to the model predictions. It gives the following results: i) at the beginning of the experiment the air molecules are everywhere in the bundle, ii) after vacuum the water molecules enter preferentially in the tubes core. These results are briefly discussed.

#### **A14.15**

MAGNETIC MEMORY OF WELL-ORIENTED CARBON NANOTUBE FILMS. Zoia Kosakovskaya, Vyacheslav Vdovenkov, Yurii Gulyaev, Aleksandr Korovin, Tat'yana Kolesnikova, Ann Kosakovskaya, Inst of Radio Engineering and Electronics of RAS, Moscow, RUSSIA.

In our work we studied magnetic properties of well-oriented

multi-walled carbon nanotube films on silicon substrates, which were synthesized by electron-beam method [1]. It was shown, that the nanotube films have diamagnetic nature similar graphite (nanotube film was pushed out by magnetic field). Magnetoresistance of nanotube films at different orientation nanotube concerning a direction of magnetic field was investigated. It was obtained, that the magnetoresistance of multi-wall nanotube film depends on orientation nanotube in magnetic field was changed very much. At the orientations nanotube along and across the direction of a magnetic field the magnetoresistance was negative. But for intermediate orientations nanotube in magnetic field we observed the change of sign magnetoresistance. We observed that the nanotube films has the memory to initial magnetic influences After presence nanotube films in a magnetic field (0.2 Ts) during long time the magnetoresistance has increase and may achieve the large significance ( $\Delta R/R \sim 0.2$ ). The relaxation time of magnetoresistance was very big (more than month). Observably anomalies of magnetic behaviour of nanotube films we attribute the one-dimensional character of nanotube structure and the manifestation of quantum effects of transport a charge. The study of magnetic properties of carbon nanotube films is shown the perspective this material for sensors of magnetic field. This work was supported by grant RFBR #98-02-17130 1. Kosakovskaya Z.Ya. JETP Lett. 1992, v.56, N1, pp. 26

**A14.16**  
ACOUSTOELECTRON PROPERTIES OF CARBON NANOTUBE FILMS. Georgii Mansfeld, Sergeii Alekseev, Yurii Gulyaev, Zoia Kosakovskaya, Vladimir Saraykin, Inst of Radio Engr & Electronics, Moscow, RUSSIA.

Many properties of carbon nanotubes materials were investigated both theoretically and experimentally but the elastic and acoustoelectron properties of the carbon nanotubes are at the initial stage of the investigation. In this work two methods are used for the experimental acoustic characterization of the thin-film carbon nanotubes. The first one is High Overtone BAW Resonator (HBAR) spectroscopy on microwaves. It was applied to obtain data on material densities, sound velocities and the attenuation in the carbon nanotube films. In this series of experiments the influence of the carbon film on resonant peaks frequencies and widths was used as a source of the information. The second method is based on the measurements of SAW propagation characteristics and acoustoelectron effects in layered structures containing the carbon nanotube films. The experiments were carried out using nanotubes synthesized by original method - electron-beam evaporation of pure graphite in vacuum. In HBAR experiments the carbon nanotube films were evaporated onto the surface of YAG or quartz substrates. The numerical data on mass density, elastic constants and attenuation were obtained. The new previously unknown effect of selfdoping of the nanotubes with time by the elements that are forming the substrate was found and explained. The special investigation in SAW experiments the carbon nanotube films were evaporated onto the surface of  $yz\text{-LiNbO}_3$ . Acoustic attenuation of SAW on 140MHz and acoustoelectric current were observed and studied as a function of transverse magnetic field direction and intensity. The correlation between electric and acoustoelectron phenomena that were observed and some peculiarities of the effect are discussed. This work was supported by grant RFBR #98-02-17130

**A14.17**  
REINFORCEMENT MECHANISMS IN POLYMER NANOTUBE COMPOSITES. S.J.V. Frankland, D.W. Brenner, North Carolina State University, Dept of Materials Science and Engineering, Raleigh, NC; A. Caglar, M. Griebel, University of Bonn, Dept. of Applied Mathematics, Division of Scientific Computing and Numerical Simulation, Bonn, GERMANY.

Carbon nanotubes have been proposed as fibers to mechanically reinforce polymers. The load transfer mechanism between the polymer and nanotube has been investigated with classical simulation methods in model polyethylene matrices. From molecular dynamics simulation we have estimated that the shear strength of carbon nanotubes in polyethylene is very weak yielding critical lengths (>mm) much longer than is normally physically reasonable for carbon nanotubes. Shear strengths in epoxy matrices are estimated relative to polyethylene. To allow a more direct examination of the mechanical properties, very large-scale simulations of these composite materials (> 1 million atoms) will be reported where the modeled carbon nanotubes approach an experimentally comparable size. These simulations implement a parallel version of the Brenner potential capable of achieving O(N) complexity with good scaling behavior of up to 512 processors at parallel efficiency of 99% on a CRAY-T3E. A new technique is used to apply tensile stress which varies box shape and size. In addition other reinforcement mechanisms will be considered including the effect of bending the nanotube in the polymer and chemically functionalizing the polymer to the nanotube.

**A14.18**  
APPLICATION OF FLUORINATED CARBON NANOTUBES AND NANOFIBERS AS AN ENERGY STORAGE MATERIAL. Morinobu Endo, Takuya Hayashi, Y.A. Kim, Shinshu Univ, Dept of Electrical and Electronic Eng, Nagano, JAPAN.

Carbon nanotubes and nanofibers are promising as an electrode material for the Li-ion batteries and capacitors. The market demands for a higher storage capacity because the mobile information technology devices are so widespread and people ask for a longer battery life for such devices. Many materials have been tested for high energy storage capacity, and carbon nanotubes and nanofibers survived the competition. In the past, we have showed that boron-doped nanotubes and fibers' energy storing capacity is very high, and we have related this to the microstructure of the doped fibers which is different from the non-doped fibers. In the present work, according to the knowledge that we have obtained in the previous studies, microstructural study using energy-filtered transmission electron microscopy and Raman spectroscopy and application of the fluorinated carbon nanotubes and nanofibers as an energy storage materials will be shown. Obtained results will be compared with the microstructure and energy storage capacity of boron-doped nanofibers.

**A14.19**  
PRESSURE DEPENDENCE OF THE RAMAN MODES IN IODINE DOPED SINGLE WALL CARBON NANOTUBE BUNDLES. Uma D. Venkateswaran, E.A. Brandson, Department of Physics, Oakland University, Rochester, MI; A. Harutyunyan and P.C. Eklund, Department of Physics, Pennsylvania State University, State College, PA.

Successful doping of single wall carbon nanotube (SWNT) bundles with molten iodine has been shown to produce a charge transfer compound which is stable at ambient conditions.[1] The Raman spectrum of the iodine doped SWNT (I-SWNT) contains the radial breathing (R) and tangential (T) vibrational modes of SWNT as well as modes due to polyiodide chains.[1] In this paper, we report the hydrostatic pressure dependence of the  $(I_5)^-$  Raman modes of I-SWNT. With the 514.5 nm excitation, the strongly resonant  $(I_5)^-$  mode, which is at  $179\text{ cm}^{-1}$  at ambient pressure, softens gradually by about  $3\text{ cm}^{-1}$  until 3 GPa and then gradually hardens by the same amount up to 5.5 GPa. This pressure-induced shift is very weak compared to the shift of  $\sim 6\text{ cm}^{-1}/\text{GPa}$  observed for the T-modes in the same pressure run and also as reported earlier for the T-modes in undoped SWNT.[2] The intensity of the  $(I_5)^-$  mode is found to decrease smoothly with increasing pressure. The ratio, S, of the peak intensity of the  $(I_5)^-$  mode to that of the T-mode, shows an initial increase, an abrupt increase near 2 GPa, and it remains more or less a constant between 2 and 5.5 GPa. The discontinuity in S is due to an abrupt decrease in the T (and R) mode intensity at 2 GPa, which has been attributed to a hexagonal distortion in the cross-section of the SWNT bundle.[2] The weak pressure shift of the  $(I_5)^-$  mode frequency observed in this study, is consistent with the recently reported Z-contrast transmission electron microscope images showing that the polyiodide chains reside inside the SWNTs.[3] [1] L. Grigorian et al., Phys. Rev.Lett. 80, 5560 (1998). [2] U.D. Venkateswaran et al., Phys. Rev. B 59, 10 928 (1999). [3] X. Fan et al., Phys. Rev. Lett. 84, 4621 (2000).

**A14.20**  
EFFECT OF GAS ADSORPTION AND COLLISIONS ON TRANSPORT PROPERTIES OF SWNTS. G.U. Sumanasekera, C. Adu, K.A. Williams, P.C. Eklund, Department of Physics, Pennsylvania State University, University Park, PA.

The effects of gas adsorption and collisions on the thermoelectric power and resistivity of tangled bundles of single-walled carbon nanotubes (SWNT) are investigated. Degassing samples in vacuum at 500 K drives the thermopower strongly negative, indicating that the degassed metallic tubes in a bundle are n-type. The magnitude of the negative thermopower indicates important asymmetry in the electronic carbon  $\pi$  bands exist near the Fermi Energy.  $O_2$  doping through exposure to ambient conditions leads to a strongly positive thermopower, suggestive of weak charge transfer between the  $O_2$  and the nanotube wall. A very surprising outcome from this study is the easily measurable increase in the thermopower ( $\sim 5 - 10\ \mu\text{V}/\text{K}$ ) and resistivity (2 - 10%) observed at 500 K upon exposure of the mats of SWNTs to  $N_2$  and He, suggesting that even gas collisions with the nanotube wall can contribute significantly to the transport properties at elevated temperatures. This work was supported by Grants NSF DMR 98-09686 and DOD DAAB07-97-C-JG36.

**A14.21**  
EFFECT OF GAS ADSORPTION ON TRANSPORT PROPERTIES OF SWNTS. C. Adu, G. Sumanasekera, P.C. Eklund, Department of Physics, Penn State University, University Park, PA.

The effects of H<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub> adsorption on the thermoelectric power (TEP) and resistivity of tangled bundles of single-walled carbon nanotubes (SWNT) are investigated. Degassing samples in vacuum at 500 K drives the thermopower strongly negative, indicating that the degassed metallic tubes in a bundle are n-type. By a systematic study of TEP and resistivity of degassed SWNTs when exposed to oxygen at 500 K with varying partial pressure, we found that for smaller partial pressures ( $P < 100$  Torr) TEP becomes positive with increasing resistance in a reversible manner. But for larger partial pressures ( $P > 100$  Torr), the TEP becomes strongly positive and in sharp contrast to the  $P < 100$  Torr results, the resistance decreases. Admission of H<sub>2</sub> and NH<sub>3</sub> drives the thermopower further negative (below the values obtained from "degassed" tubes) while the resistivity is still increasing. For H<sub>2</sub>, adsorption/desorption is fully reversible, but only partially reversible for NH<sub>3</sub>. Results of H<sub>2</sub> partial pressure dependence on electrical transport properties at 500 K, 300 K and 77 K are also presented. This work was supported by Grants NSF DMR 98-09686 and DOD DAAB07-97-C-3036.

#### **A14.22**

##### **FIRST-PRINCIPLES CALCULATIONS OF IODINE ATOMS INSIDE SINGLE-WALLED CARBON NANOTUBES.**

Sung-Yool Choi, Kee Soo Nam, Kyung-Ik Cho, Micro-Electronics Technology Laboratory, ETRI, Taejeon, SOUTH KOREA.

Recent experiments and calculations by Grigorian et al. [Phys. Rev. Lett. **80**, 5560 (1998)] and Fan et al. [Phys. Rev. Lett. **84**, 4621 (2000)] show that iodine atoms inside single-walled carbon nanotubes arrange in the form of helical chains and increase prominently electrical conductivity by orders of magnitude, but the structure and properties are not completely explained. In this work we investigate structural and electronic properties of iodine-intercalated single-walled carbon nanotubes and explore the effect of charge transfer on the physical properties of these novel systems from first-principles calculations. Our calculations are based on the density functional method with local density approximation of exchange-correlation functionals, norm-conserving pseudopotentials and supercells.

#### **A14.23**

Transferred to A12.3

#### **A14.24**

**COMPRESSIBILITY OF FULLERENE-FILLED CARBON NANOTUBES.** Jie Tang<sup>1</sup>, Lu-Chang Qin<sup>2</sup>, Shunji Bandow<sup>3</sup>, Masako Yudasaka<sup>2</sup>, Taizo Sasaki<sup>1</sup>, Akiyuki Matsushita<sup>1</sup> and Sumio Iijima<sup>2,3,4,5</sup>. <sup>1</sup>National Research Institute for Metals, Tsukuba, JAPAN; <sup>2</sup>JST Nanotubulite Project, c/o NEC Corp., Tsukuba, JAPAN; <sup>3</sup>JST Nanotubulite Project, c/o Meijo Univ., Nagoya, JAPAN; <sup>4</sup>R&D Group, NEC Corporation, Tsukuba, JAPAN; <sup>5</sup>Dept. of Mat. Sci. & Engg., Meijo Univ., Nagoya, JAPAN.

Though carbon nanotubes are very strong in their axial direction with an axial Young's modulus of about 2 TPa, they are soft in their radial directions due to largely the hollow cores. When such carbon nanotubes are filled with fullerenes to form the peapod structures, it is expected that their radial modulus will be increased. We have carried a measurement of the radial compressibility of such peapod structures using a diamond-anvil press cell combined with in situ synchrotron X-ray diffraction. It is shown that the radial stiffness of the C60 fullerene-filled carbon nanotubes has been greatly strengthened compared with the unfilled nanotubes. The volume compressibility of the C60 fullerene-filled peapod nanotubes has been reduced by about 30% from the unfilled starting single-walled carbon nanotubes. Details and implications will also be presented and discussed.

#### **A14.25**

**EXTRACTION OF CARBON NANOTUBES BY AN AFM TIP.** Sébastien Decossas<sup>1</sup>, F. Schmithüsen<sup>1</sup>, Giovanni Cappello<sup>1,2</sup>, Guillaume Poignant<sup>1</sup>, Lionel Patrone<sup>3,4</sup>, Anne Marie Bonnot<sup>3</sup>, Irina Snigireva<sup>1</sup> and Joël Chevrier<sup>1,3,4</sup>. <sup>1</sup>ESRF, Grenoble, FRANCE; <sup>2</sup>Institut Curie, Laboratoire Physico-Chimie-Curie, Paris, FRANCE; <sup>3</sup>LEPES-CNRS, Grenoble, FRANCE; <sup>4</sup>Université Joseph Fourier, Grenoble, FRANCE.

Micrometer thick layers of multiwall carbon nanotubes (nanotube carpet) have been produced by Hot Filament Chemical Vapor Deposition. Atomic Force Microscopy (AFM) in the phase detection mode and Scanning Electron Microscopy reveal that the nanotubes, typically 20 nanometers in diameter and more than 1 micrometer long, are entangled. AFM force-distance curves are used to investigate the interaction of the tip with the nanotube carpet. This provides information on the adhesive properties between the nanotubes and the silicon nitride tip and on the deformation properties of this nanotube carpet. If the AFM tip is strongly pressed against the layer, force-distance curves clearly reveal that many nanotubes are

interacting with the AFM tip. In the case of a soft contact, we demonstrate that just a few nanotubes interact with the tip (presumably down to a single nanotube). A non-linear behavior is observed in force curves. This is an evidence for a non-elastic response of the stuck nanotubes due both to their bending and stretching. A simple numerical simulation based on the Van der Waals interaction between a set of nanotubes and the AFM tip reproduces the experimental characteristic features of the adhesion and the friction. Transport of nanotubes extracted from the nanotube carpet using the AFM tip, their deposition onto a clean silicon wafer and their observation with AFM notably in friction mode with a clean tip are also demonstrated.

#### **A14.26**

Abstract Withdrawn.

#### **A14.27**

**MOLECULAR MECHANICS OF BINDING IN CARBON NANOTUBE-POLYMER COMPOSITES.** Vincenzo Lordi, Nan Yao, Princeton Materials Institute, Princeton University, Princeton, NJ.

Nanoscale composites have been a technological dream for many years. Recently, increased interest has arisen in using carbon nanotubes as filler for polymer composites, owing to their very small diameters on the order of 1 nm, very high aspect ratios of 1000 or more, and exceptional strength with Young's modulus of ~1TPa. A key issue for realizing these composites is obtaining good interfacial adhesion between the phases. In this work, we use force-field based molecular mechanics calculations to determine binding energies and sliding frictional stresses between pristine carbon nanotubes and a range of polymer substrates, in an effort to understand the factors governing interfacial adhesion. The particular polymers studied were chosen to correspond to reported composites in the literature. We also examine polymer morphologies by performing energy-minimizations in vacuum. Hydrogen bond interactions with the p-bond network of pristine carbon nanotubes are found to bond most strongly to the surface, in the absence of chemically altered nanotubes. Surprisingly, we find that binding energies and frictional forces play only a minor role in determining the strength of the interface, but that helical polymer conformations are essential.

#### **A14.28**

**SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY OF MULTIWALL CARBON NANOTUBES.** Abdou Hassanien, Madoka Tokumoto, Electrotechnical Laboratory, Tsukuba Ibaraki, JAPAN; X. Zhao, and Y. Ando, Department of Physics, Meijo University, Shiogamaguchi, Tempaku-ku, Nagoya, JAPAN.

We report on the structural analysis of multiwall carbon nanotubes (MWNTs), produced by DC arc discharge in hydrogen gas, using a scanning tunneling microscope operated at ambient conditions. On a microscopic scale the images show tubes condensed in ropes as well as individual tubes which are separated from each other. Individual nanotubes exhibit various diameters (2.5-6 nm) and chiralities (0-30°). For MWNTs rope, the outer portion is composed of highly oriented nanotubes with nearly uniform diameter (4-5 nm) and chirality. Strong correlation is found between the structural parameters and the electronic properties in which the MWNTs span the metallic-semiconductor regime. True atomic-resolution topographic STM images of the outer shell show hexagonal arrangements of carbon atoms that are equally visible by STM tip. This suggests that the stacking nature of MWNTs has no detectable effects on the electronic band structure of the tube shells. Unlike other MWNTs produced by arc discharge in helium gas, the length of the tubes are rather short (80-500 nm), which make it feasible to use them as a components for molecular electronic devices.

#### **A14.29**

**TORSION AND BENDING OF CARBON NANOTUBES.** Laetitia Vaccarini, Christophe Goze, Patrick Bernier, GDPC, UMR 5581, Montpellier II Univ, Montpellier, FRANCE; Angel Rubio, DFT, Valladolid Univ, Valladolid, SPAIN.

We report on a theoretical investigation of the elastic properties of single walled carbon nanotubes. The nanotube response is examined under axial, torsional and bending strains using a non-orthogonal tight binding method. The Young's modulus, Poisson ratio, torsional and bending modulus were calculated for several nanotubes with various diameters and chiralities. The results demonstrate that single walled carbon nanotubes are both extremely stiff in the axial direction and flexible. The torsional and bending modulus are almost insensitive to the helicity of the tube but depend strongly on its diameter. These modulus are also estimated with the continuum theory of elasticity and compared to the available experimental values.

#### **A14.30**

**NANOMANIPULATION AS A PATHWAY TO NANOTUBE-BASED**

DEVICES. Oliver Jaschinski, Patrick Bernier, Universite Montpellier II, GDCP, Montpellier, FRANCE; Pascal Falgayrettes, Universite Montpellier II, CEM2, Montpellier, FRANCE; Jörg Muster, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY.

Carbon nanotubes are promising materials for nanoscaled devices due to their unique electrical and mechanical properties. Nanotube-based devices need specific configurations of nanotubes. Using the tip of an atomic force microscope (AFM) as a manipulation tool one can overcome the problem of the randomly distributed arrangement of nanotubes adsorbed onto a surface. By shifting the nanotubes with an AFM tip specific layouts of nanotubes are created. Here we demonstrate how a commercial AFM without any technical changes can be used for this purpose. We developed a protocol which allows us to perform multi-step manipulations of single-walled nanotubes (SWNTs) or SWNT bundles in a very reliable and controlled manner. Simultaneous measurements of the normal and lateral forces during the manipulation give an insight into the mechanism of the nanoscaled movement of objects (bending, sliding, unraveling of bundles).

**A14.31**  
THE CRYSTALLOGRAPHY OF METAL HALIDES FORMED WITHIN SINGLE WALLED CARBON NANOTUBES. Jeremy Sloan, Gareth Brown, Sam Bailey, Karl Coleman, Steffi Friedrichs, Cigang Xu, Malcolm Green, Inorganic Chemistry Laboratory, University of Oxford, UNITED KINGDOM; Rafal Dunin-Borkowski, John Hutchison, Dept. Materials, University of Oxford, Angus Kirkland, Rüdiger Meyer, Dept. Materials, University of Cambridge, UNITED KINGDOM.

The crystal growth behaviour and crystallography of a variety of metal halides incorporated within single walled carbon nanotubes (SWNTs) as determined by high resolution electron microscopy (HREM) is described. Simple packed structures, such as the alkali halides form related structures within SWNTs that are integral atomic layers in terms of their thickness. An enhanced HREM image restoration technique reveals precise data concerning lattice distortions present in these crystals. More complex structures formed within SWNTs, such as those derived from 3D complex, layered and chain halides form related crystal structures within SWNTs. In narrow (i.e. >1.6nm diameter) SWNTs, these halides form structures that consist of individual 1D polyhedral chains (1D-PHCs) derived from the corresponding bulk halides within SWNTs. In the case of the 3D complex and layered halide structures, the polyhedral chains form with lower co-ordination than in the bulk. Molecular halides also form within SWNTs but these are frequently disordered and do not readily form organised structures within SWNTs.

**A14.32**  
MICRO-RAMAN INVESTIGATION OF ALIGNED SINGLE-WALL CARBON NANOTUBES. M.A. Pimenta, C.F. Leite, M.S.S. Dantas, UFMG, Belo Horizonte, BRAZIL; D. Ugarte, LNLS, Campinas, BRAZIL; H.M. Cheng, Institute of Metal Research, Shenyang, CHINA; A.M. Rao, University of Kentucky, Lexington, KY; A. Jorio, G. Dresselhaus, M.S. Dresselhaus, MIT, Cambridge, MA.

Aligned single-wall carbon nanotubes (SWNTs) were prepared using the hydrogen and argon electric arc method, and the sample shows a good nanoscale alignment. Polarized micro-Raman experiments, allowing a spatial resolution of 1  $\mu\text{m}$ , were performed in samples prepared in special substrates and previously characterized by TEM, using different laser excitation lines. The majority of nanotubes in the sample exhibits diameters in the range  $d_t = 1.85 \pm 0.25$  nm, giving rise to a broad band in the Raman spectra around  $120$   $\text{cm}^{-1}$ , associated with the radial breathing mode (RBM) of the tubes. However, very sharp Raman peaks are sometimes found superimposed on the broad RBM band, indicating also the presence of small diameter SWNTs in the sample. The frequencies of these sharp peaks depends on the position of the laser spot on the sample, revealing the presence of isolated small diameter SWNTs of different types. By analysing the different shapes of the tangential band, between  $1500$  and  $1600$   $\text{cm}^{-1}$ , when the position of the laser beam changes from spot to spot on the sample, and by comparing the associated changes in the RBM and tangential bands, it is possible to differentiate the Raman spectra coming from isolated semiconducting and metallic SWNTs.

**A14.33**  
ELECTRONIC AND STRUCTURAL PROPERTIES OF METAL-SEMICONDUCTING JUNCTIONS IN CARBON NANOTUBES. M.P. Machado, P. Piquini, R. Mota, Depto. de Física, Universidade Federal de Santa Maria, Santa Maria, RS, BRAZIL; A. Fazzio, Instituto de Física, Universidade de São Paulo, São Paulo, SP, BRAZIL.

The electronic and structural properties at the Fermi level of junctions produced by connecting two or more nanotubes with different helicities are investigated using two different approaches. The first is

based on Monte Carlo simulation with empirical Tersoff potential and the second is an electronic calculation through self-consistent field Hartree-Fock-Roothaan method. One main target of our study is a  $(10,0)/(6,6)$  junction which connects a semiconductor tube with a metallic one by introduction of a pentagon-heptagon pair defects diametrically opposed in the structure. In this case, the optimized structure implies in a knee that forms an angle of approximately  $36^\circ$  on the junction between the two tubes. In particular, we have assumed a previously optimized structure using a simplified molecular mechanics model. Using an empirical Tersoff potential we discuss the energy of the junction and the energy gain is calculated for the bent nanotube compared with a hypothetical straight one. Using self-consistent field Hartree-Fock-Roothaan method, the character of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are determined for the  $(10,0)$  and  $(6,6)$  nanotubes and for the junction. For the pure  $(10,0)$  and  $(6,6)$  nanotubes, the  $\pi$  is the dominant character for both HOMOs. The local electronic states of the metallic-semiconducting junction region present a mixture of characters and the corresponding HOMO is displaced for the semiconducting region, creating the condition to build electronic logical devices at the nanometer scale. We also determine how these properties change from the metallic to semiconducting side of a nanotube junction. Also, preliminary results for the semiconducting-metallic-semiconducting  $((10,0)/(6,6)/(10,0))$  heterojunction permit the discussion about the properties of the associated single-electron transistor.

**A14.34**  
PROGRESS ON CNT NANO-ELECTROMECHANICAL DEVICES. Phillip Williams, Neal Snider, Scott Paulson, Michael R. Falvo, Sean Washburn, Richard Superfine; The University of North Carolina, Dept. of Physics and Astronomy, Chapel Hill, NC.

Using e-beam lithographic techniques, substrate etching, and AFM manipulation, we have created a variety of integrated nanotube device structures that include suspended and cantilevered tubes, and CNT/CNT contacts. In a system directly relevant to CNT/CNT contacts, we have found that the resistance of the CNT/HOPG contact depends on the relative angle of the contacting graphene lattices and have also explored the locality of these circumferential transport modes. We have manipulated CNT/CNT contacts through AFM or electrostatic actuation in order to probe the effect of relative lattice translation and rotational orientation on contact resistance. Progress on an integrated electromechanical resonator, CNT/CNT transport measurements, and atomic scale effects of tube-on-tube contacts will be presented. This work was supported by the National Science Foundation (HPCC, ECS), the Office of Naval Research (MURI), and National Institutes of Health (NCRIR).

**A14.35**  
ELECTRONIC BAND STRUCTURE STUDY ON CARBON NANOTUBES USING ANGLE RESOLVED ULTRAVIOLET AND X-RAY PHOTOEMISSION SPECTROSCOPY. Jaewu Choi, Louisiana State University, Center for Advanced Microstructures and Devices, Baton Rouge, LA; Young Hee Lee, Jeonbuk National University, Jeonju, KOREA; Hyeong Seok Yoo, Exxon Mobil Process Research, Baton Rouge, LA.

Electronic band structure of the vertically aligned multiwall carbon nanotubes has been experimentally studied using angle resolved ultraviolet photoemission spectroscopy and core level photoemission spectroscopy. The finite density of states near the Fermi level is observed. The valence band dispersion of the multiwall carbon nanotubes was small unlike the calculated band dispersion of the single wall carbon nanotube. There are two main peaks which are at  $3.04$  eV and  $7.66$  eV. These valence band structures indicates the electronic structure of the polycrystalline graphite than fullerenes. The carbon 1s core level spectra support that there are strong SP<sub>2</sub> hybridization character rather than SP<sub>3</sub> character. With increasing the amount of Ar ion sputtering, the electronic structure of the carbon nanotubes resembles to the amorphous carbon.

**A14.36**  
ABSORPTION OF HYDROGEN ON CARBON SINGLE-WALLED NANOTUBES AS MEASURED BY THE VOLUMETRIC TECHNIQUE. Philip A. Parilla, Anne C. Dillon, Jeffery L. Alleman, Kim M. Jones, and Michael J. Heben, National Renewable Energy Laboratory, Golden CO; Thomas Gennett, Department of Chemistry and Center for Materials Science, Rochester Institute of Technology, Rochester, NY.

Of the many possible applications for carbon single-walled nanotubes (SWNTs), one of the most intriguing is for the storage of hydrogen. As previously reported, [1] hydrogen absorption onto samples containing SWNTs have gravimetric storage density per SWNT estimated between 5 and 10 wt %. This would provide high energy

storage efficiencies for applications requiring lightweight storage capabilities such as for vehicles. Since this original report, much effort has been applied toward developing the growth and purification of SWNTs as well as understanding the nature of their hydrogen absorption. This has resulted in highly pure samples capable of absorbing up to  $\sim 7$  wt % hydrogen as measured by temperature programmed desorption (TPD). While we have gone to great efforts to ensure that the calibration of the TPD results are accurate, it is important to verify these exciting results using another measurement technique. Here, we report on hydrogen absorption onto SWNTs as measured by the volumetric technique. This method determines the amount absorbed by monitoring the pressure in a known volume at a known temperature with a given number of moles of hydrogen introduced. The raw material for the samples is produced through pulsed laser vaporization of a graphite target containing Ni (0.6 at %) and Co (0.6 at %) dopants. This is followed by a purification procedure and then by a cutting procedure. Finally, the sample is degassed before the hydrogen absorption is measured. A description of the apparatus will be given that has allowed us to measure these small samples (a few milligrams) and we will discuss crucial experimental procedures needed to activate the SWNT samples for hydrogen absorption. [1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, *Nature* **386**, 377 (1997)

**A14.37**  
**TOPOLOGY AND ENERGETICS OF THE MECHANICALLY-SIGNIFICANT DEFECTS IN BN NANOTUBES.** H.F. Bettinger<sup>1,2</sup>, G.E. Scuseria<sup>1,2</sup>, and B.I. Yakobson<sup>1,3</sup>. <sup>1</sup>Center for Nanoscale Science and Technology; <sup>2</sup>Department of Chemistry; <sup>3</sup>Department of Mechanical Engineering and Materials Science Rice University, Houston, TX.

The alternating chemical order in the boron nitride lattice makes the atomic relaxation mechanisms different than in a similar hexagonal carbon lattice. We analyze the topology and energy of the defects responsible for the mechanical relaxation and strength of BN nanotubes and small clusters using the semiempirical AM1 Hamiltonian and density functional theory in combination with the polarized all-electron 6-31G(d) basis set. The analogue of the Stone-Wales transformation in BN produces a dislocation dipole of  $b = -(0,1)$  represented by a 5/7/7/5 ring defect containing B-B and N-N bonds. It corresponds to a local potential energy minimum and is thus metastable. Another important defect with the preserved alternating B-N bonding pattern is proposed, a 4/8/8/4 dipole of Burgers vector  $b = -(1,-2)$ . Whereas for the "free" defects in clusters both alternatives are similar in energy, the B-B-N-N structures are significantly more favorable energetically by  $\sim 4$  eV for the defects incorporated into a finite unstrained BN tube or sheet. The comparison with the analogous all-carbon structures indicates that the formation of the 5/7/7/5 defect requires more energy for BN structures. We analyze the strain dependencies of the energies and discuss the consequences for the relative mechanical stability of these materials.

**A14.38**  
**PROPERTIES OF GAS ADSORPTION ON SINGLE WALL CARBON NANOTUBES.** Hironori Ogata, Institute for Molecular Science, Okazaki, JAPAN; Syogo Kuno, Yahachi Saito; Dept of Electrical and Electronic Engineering, Mie University, Tsu, JAPAN.

We present the results of the  $N_2$ ,  $O_2$  or several kinds of inert gas adsorption isotherm of both end-closed and end-opened Single Wall Carbon Nanotubes (SWNTs). The samples used in this study were synthesized by the dc arc discharge method using Pt-Rh mixed catalyst. Amorphous carbon contained in the raw soots were removed by using hydrogen peroxide ( $H_2O_2$ ). The end-opened samples were synthesized by doing appropriate heat treatment in air. The  $\alpha_s$ -plot analysis of  $N_2$  adsorption isotherms at 77K revealed that heat treatment increase the intensity of two upward swings (filling- and condensation-swing) below  $\alpha_s = 1.0$ . This fact suggest that the heat treatment lead to the micropore filling and capillary-like condensation inside the tube space. Analysis of the other gas adsorptions will be discussed in this presentation.

**A14.39**  
**EVIDENCE FOR LUTTINGER LIQUID BEHAVIOR IN MULTI-WALLED CARBON NANOTUBES.** E. Graugnard, R. Reifenberger, Purdue Univ, Dept of Physics, W. Lafayette, IN; B. Walsh, A.W. Ghosh, S. Datta, Purdue Univ, Dept of Electrical and Computer Engineering, W. Lafayette, IN; P.J. de Pablo, Universidad Autónoma de Madrid, Dept. Física de la Materia Condensada, Madrid, SPAIN.

We report on the conductance of multi-walled carbon nanotubes as a function of voltage and temperature between room temperature and 4.2K. The data show a monotonic decrease in conductance as the temperature is lowered. At temperatures below  $\sim 20$ K, a non-linearity

develops in the V(I) data, corresponding to a pronounced dip in the conductance near zero bias. The size of the dip increases as the temperature is lowered. The data are explained in terms of the Luttinger liquid model for transport.

**A14.40**  
**PROPERTIES OF XENON GAS ADSORBED INSIDE OF SINGLE WALL CARBON NANOTUBES.** Hironori Ogata, Institute for Molecular Science, Okazaki, JAPAN; Syogo Kuno, Yahachi Saito; Dept of Electrical and Electronic Engineering, Mie University, Tsu, JAPAN.

Pressure and temperature dependences of  $^{129}\text{Xe}$ -NMR were performed by xenon gas adsorbed single wall carbon nanotubes produced using non-ferromagnetic Rh-Pt mixed catalysts by arc discharge method. Appropriate heat treatment was proved to be essential to open the tubule ends and cause Xenon gas adsorption inside the single wall carbon nanotubes. Detailed dynamics and thermodynamic properties of Xenon atoms obtained by adsorption isotherm and NMR measurements will be discussed.

**A14.41**  
**EFFECT OF ORGANIC POLYMER SOLUTION IN PURIFICATION AND CUTTING OF SINGLE-WALL CARBON NANOTUBES.** Masako Yudasaka, Minfang Zhang, Christoph Jabs, and Sumio Iijima, ICORP-JST, NEC, Tsukuba, JAPAN; Meijo Univ. Dept. of Physics, Nagoya, JAPAN.

Single-wall carbon nanotubes (SWNTs) formed by laser ablation and arc discharge contain various impurities which include amorphous carbon, metal catalysts, and graphite particles. It has been shown that oxidation using acids such as nitric acid helps to remove these impurities. Mizoguchi et al. has also suggested the use of ultra fine gold particles to catalyze the oxidation of amorphous carbon at lower temperatures[1]. Purification using strong acids has shown to generate shortened tubes, whose properties have been characterized by various analyses methods, such as scanning tunneling microscope. However, we think that purification using acids may cause safety and environmental problems if it were employed in large-scale production of SWNT in future. We have been searching for an alternative purification method that would not require the use of strong acids, and have found that a polymer solution is helpful to purify and shorten SWNTs. This method also facilitated the isolation of single SWNTs by allowing us to disperse the tubes on a substrate by spin coating. [1] E. Mizoguchi et al, *Chem. Phys. Lett.* 321(2000) 297.

**A14.42**  
**HYDROGEN STORAGE IN CARBON NANOTUBES.** Andrea Quintel, Youngmoon Choi, Ursula Dettlaff, Viera Skakalova and Siegmund Roth, Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, GERMANY; Marion Becher, Miro Haluska and Michael Hirscher, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY; Raimund Stroebel and Ludwig Joerissen, Zentrum fuer Solarenergie und Wasserstofforschung, Ulm, GERMANY.

Single walled carbon nanotubes (SWCNTs) seem to adsorb hydrogen at different temperature and pressure conditions[1-3]. Therefore SWCNTs could be ideal building blocks to construct safe, efficient and high energy density adsorbents for hydrogen storage applications like hydrogen tanks in fuel cell electric vehicles. The present contribution will first summarise the promising publications on hydrogen storage in carbon nanotubes. Then results on checking these published experiments will be shown. Systematic studies of hydrogen storage capacity as function of purification (chromatography, oxidation) and tube opening (sonication, ball milling) will be presented and discussed. References: 1. Dillon, A.C. et al. *Nature* 386, 377 (1997). 2. Ye, Y. et al. *Appl. Phys. Lett.* 74, 2307 (1999). 3. Liu, C. et al. *Science* 286, 1127 (1999).

SESSION A15: NANORODS/TUBES

Chair: Otto Zhou

Thursday Morning, November 30, 2000

Grand Ballroom (Sheraton)

**8:30 AM \*A15.1**  
**OXIDE-ASSISTED SYNTHESIS OF ONE-DIMENSIONAL SEMICONDUCTOR NANOMATERIALS.** S.T. Lee, Center of Super-Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, SAR, CHINA.

Our recent studies have shown that by using oxides as a starting material in a laser ablation, thermal evaporation or CVD process, it is possible to achieve bulk-quantity synthesis of high-purity (no metal contamination) one-dimensional nanoscale semiconductor materials.

In contrast to the classical VLS method based on metal particle catalysts, oxides have been discovered to play a critical role in promoting the formation and growth of one-dimensional semiconductor nanoscale structures. We thus propose a new mechanism, oxide-assisted one-dimensional growth. The essence of the new growth mechanism is in using oxides as a starting material, together with a proper activation method, e.g., laser ablation, CVD, or simple thermal evaporation. Using this new approach, we have synthesized various one-dimensional nanoscale semiconductor materials, including Si, Ge, C, SiC, Si<sub>3</sub>N<sub>4</sub>, GaN, GaAs, CdS. Our systematic study suggests that the new synthetic approach is generally applicable to a wide range of one-dimensional nanoscale materials, including semiconductors, metals and insulators. In particular, we find that by the proper choice of processing conditions, one-dimensional nanoscale materials of controlled dimension (diameter and length) and desired orientation or pattern can be achieved via this new method. It is further possible to fabricate nanoscale structures of desired morphologies, such as nanowires, nanochains, nanoribbons, nanoribbons. The morphology, microstructure, and optical and field-emission properties of some one-dimensional nanoscale materials have been systematically characterized. The capability of the present oxide-assisted method for synthesizing bulk-quantity one-dimensional nanoscale materials offers many exciting opportunities for fundamental research and applications in nano science and technology.

#### 9:00 AM **A15.2**

**SYNTHESIS AND CHARACTERIZATION OF SELENIUM NANOWIRES WITH UNIFORM, WELL-CONTROLLED LATERAL DIMENSIONS.** Byron Gates, Yadong Yin, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated an effective chemical approach to the large-scale synthesis of single crystalline selenium nanowires with uniform, well-controlled lateral dimensions in the range of 10-100 nm. In this talk, we will discuss the mechanism for the formation of these one-dimensional, anisotropic nanostructures versus zero-dimensional, isotropic colloidal particles. The unique optical and photoelectrical properties of these nanowires will also be presented.

#### 9:15 AM **A15.3**

**CATALYST-FREE SYNTHESIS OF SINGLE-WALL BORON NITRIDE NANOTUBES VIA LASER ABLATION.** Roland S. Lee, Julie Gavillet, Marc Lamy de la Chapelle, Annick Loiseau, LEM, CNRS-ONERA (UMR104), Chatillon Cedex, FRANCE; Jean-Lou Cochon, Daniel Pigache, ONERA, Palaiseau Cedex, FRANCE; Jany Thibault, SP2M: DRFMC, CENG, 85X, Grenoble Cedex, FRANCE; Francois Willaime, SRMP, CEA Saclay, Gif sur Yvette Cedex, FRANCE.

We present the results of catalyst-free synthesis of boron nitride nanotubes (BN-NTs) in "mass" quantities (~150 mg) using a continuous CO<sub>2</sub> laser ablation reactor described in the literature [1]. High-resolution transmission electron microscopy (HRTEM) analyses have shown the samples to be composed of single wall boron nitride nanotubes (BN-SWNTs) organized in long (~100 nm) perfectly crystallized "ropes" of ~5-10 nanotubes. The samples also contain a small percentage of BN-NTs composed of two layers and multi-wall boron nitride "cages". HRTEM images of BN-NTs were analyzed using Fast Fourier Transform to obtain their helicities; the majority of BN-SWNTs organized in "ropes" seems to have a zig-zag configuration. The BN-NTs also appear to grow from nanoparticles of pure boron whose composition was determined using electron energy loss spectroscopy (EELS). 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 was needed. Since bulk production of this material has now been realized, its characterization, using methods previously stymied by the paucity of available samples, is now possible. [1] J.L. Cochon et al., Electronic Properties of Novel Materials, American Institute of Physics 237 (1999).

#### 9:30 AM **A15.4**

**STRUCTURE AND MECHANICAL PROPERTIES OF SILICON CARBIDE-SILICA BIAXIAL NANOWIRES.** Z.R. Dai, Z.G. Bai, R.P. Gao, Z.L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA; J.L. Gole, J.D. Stout, School of Physics, Georgia Institute of Technology, Atlanta, GA.

One-dimensional quantum wires are of fundamental importance to the study of size-dependent chemical and physical phenomena. With a reduction in size, unique electrical, mechanical, chemical and optical properties are introduced, which are largely believed to be the result of surface and/or quantum confinement effects. Here we report a composite nanowire structure that may be potentially useful for nanodevice-nanointerconnect integration. The unique side-by-side biaxially structured silicon carbide-silica nanowires were produced using mixed SiO and carbon sources by means of high temperature

synthesis at 1500°C for 12 hours under a total pressure in the inner tube ranged from 200 to 300 Torr. The structure of these nanowires, their cross-sectional shape, and their structural transformation between a biaxial and coaxial configuration have been studied by transmission electron microscopy. The nanowires, which are typically 50-100 nanometer in width, can be as long as 100 micrometers. The axial growth direction approaches [311] for nanowires with a high density of microtwins and stacking faults, and is [211] for defect-free nanowires. The SiC nanowires have faceted shapes, as one type of the facets is {111}. Two biaxially structured nanowires can be linked by a coaxial nanowire, resulting in formation of an interface-junction between biaxial and coaxial nanowires in the same nanomaterial. The synthesized nanowires could be potentially useful for high-strength composites, in which the mechanical properties are critical. Using a novel in-situ TEM technique, the Young's modulus of the biaxially structured nanowires was measured to be 50-100 GPa depending on the size of the nanowire.

#### 9:45 AM **A15.5**

**A CATALYST-FREE APPROACH OF SYNTHESIZING NANORODS.** L.C. Chen, C.Y. Wen, F.G. Tarntair, National Taiwan University, Center for Condensed Matter Sciences, Taipei, TAIWAN; S.W. Chang, C.H. Chang, Y.F. Chen, National Taiwan University, Dept. of Physics, Taipei, TAIWAN; J.-J. Wu, K.H. Chen, Academia Sinica, Institute of Atomic and Molecular Sciences, Taipei, TAIWAN.

To explore and realize the exciting opportunities of the one-dimension nanostructures such as nanotubes, nanowires and nanorods requires producing these materials in a well-controlled manner. Most of the techniques that have been employed to synthesize these materials relate to the vapor-liquid-solid (VLS) process wherein a catalyst is involved. However, the catalyst usually remains in the materials and may affect their intrinsic properties. This work presents a non-VLS and catalyst-free approach of growing a variety of nanorods in a controllable manner directly on Si substrate. For instance, silicon carbon nitride (SiCN) nanorods with rod widths ranging from 10 to 60 nm and lengths of microns have been demonstrated with a two-stage approach that combines the use of electron cyclotron resonance (ECR) plasma enhanced chemical vapor deposition (PECVD) and microwave PECVD. The first stage involves formation of a buffer layer containing various densities of SiCN nanocrystals by ECR-PECVD; whereas the second stage involves high growth rate along a preferred orientation to produce nanorods by microwave PECVD. The number density and the diameter of the nanorods can be controlled by the corresponding values of the nanocrystals in the buffer layer. Production of quasi-aligned SiCN nanorods with a number density of the rods as high as 10<sup>10</sup> cm<sup>-2</sup> has been achieved. The high aspect ratios, sharp features and structural stability of the nanorods result in good field emission characteristics with a stable operation over a substantial period of time.

#### SESSION A16: TUBE FILLING

Chair: Patrick Bernier  
Thursday Morning, November 30, 2000  
Grand Ballroom (Sheraton)

#### 10:30 AM **\*A16.1**

**NANOSCALE HYBRID MATERIALS.** David E. Luzzi and Brian W. Smith, Univ. of Pennsylvania, Dept. of Materials Science, Philadelphia, PA.

A synthesis route for the efficient production of single-wall carbon nanotubes (SWNTs) filled with chains of C<sub>60</sub> molecules has been discovered and will be presented. The synthesis involves transport of C<sub>60</sub> molecules in the gas phase to partially-oxidized SWNTs where they enter through open ends and side-wall defects. The process is efficient and yields high concentrations of SWNTs filled over long lengths. The same process has now been used to fill SWNTs with the endohedral fullerene La<sub>2</sub>@C<sub>80</sub>. This molecule is interesting due to the large electron transfer that is predicted. These observations are the first direct experimental evidence that La<sub>2</sub>@C<sub>80</sub> is an endohedral molecule. Within the SWNT, the La-La atom separation is greater than 0.5 nm, significantly larger than the 0.36 nm predicted from ab-initio calculations of the isolated endohedral. Results on the filling of SWNTs with other molecules will be presented. Anneals of C<sub>60</sub>-filled SWNTs at high temperatures produces molecular coalescence of the C<sub>60</sub> chains into hemispherically-capped capsules and long tubes. Some of the produced structures are present in a metastable structural form. This work demonstrates that SWNTs can be used as nanoscopic reaction chambers for the production of new molecules. The SWNT plays a dual role of catalyzing the reaction by controlling the orientation and proximity of the reactants and as a steric template that limits the attainable conformations of the reaction product. The work will also show that SWNTs can be used

as effective 1-D substrates for high signal-noise studies of single molecules and atoms over a wide temperature range.

#### 11:00 AM **A16.2**

ONE-DIMENSIONAL CRYSTALS OF FULLERENE FORMED INSIDE SINGLE-WALL CARBON NANOTUBES. S. Iijima<sup>a,b,c</sup>, S.

Bandow<sup>c</sup>, K. Hirahara<sup>c</sup>, K. Suenaga<sup>a,c</sup>, T. Okazaki<sup>d</sup>, H. Kato<sup>d</sup>, H. Shinohara<sup>d</sup>, H. Kataura<sup>e</sup> and Y. Achiba; <sup>a</sup>Meijo Univ. and <sup>b</sup>NEC, <sup>c</sup>JST-ICORP, <sup>d</sup>Nagoya Univ., <sup>e</sup>Tokyo Metropolitan Univ.

In a rare occasion a SWNT could trap fullerenes in its central hollow during laser ablation of graphite(1), which is so called "peapod"(2). The observation motivated us to make SWNTs encapsulating fullerenes in a simple vapor phase reaction by doping with C<sub>60</sub> after an appropriate treatment of SWNTs (this symposium). The encapsulation of fullerenes succeeded equally with various higher fullerenes and metal-endhedral fullerenes (Metal@Cm)n@SWNT, where M is metal such as Gd, La, Sm, Sc. TEM and EELS revealed clearly individual metal atoms inside carbon cages (3). These fullerenes aligned so regularly inside the central hollows of SWNTs that they can be considered *one-dimensional fullerene crystal*. Such SWNTs will behave differently in their physical and chemical properties from conventional ones, providing a new series of hybrid structures of fullerene and nanotube. Some of their properties will be presented. Other aspects of SWNTs encapsulating fullerenes are concerning structural evolution of encapsulating fullerene molecules themselves within the central hollows of SWNTs. We observed that encapsulated fullerene molecules can be fused together at an elevated temperature to form a smaller diameter SWNT inside the host SWNTs, leading to double-walled carbon nanotubes(DWNTs) (4). In our ex situ heat treatment the DWNTs were formed in a large quantity so that their Raman signals showed clearly a characteristic co-relation among RBM peaks. The formation of DWNTs inside existing SWNTs does not involve any catalytic metal and thus their growth mechanisms is simpler, providing useful information for the growth of SWNTs.

1) Y. Zhang, S. Iijima, Z. Shi and Z. Gu, Phil. Mag. Lett. **79**, 473 (1999). 2) B.W. Smith, M. Monthieux and D.E. Luzzi, Nature **396**, 323 (1993). 3) K. Hirahara, et al. Physical Review Letters, accepted. 4) J. Sloan, et al. Chem. Phys. Lett., **316**, 191 (2000)

#### 11:15 AM **A16.3**

STATISTICAL MECHANICS OF NANOPEAPODS. Miroslav Hodak, Louis A. Girifalco, Dept of Material Science and Engineering, University of Pennsylvania, Philadelphia, PA.

A one dimensional lattice gas model is used to study nanopeapods. We study two different situations: Equilibrium of internal bucky balls with bucky balls outside in the gas phase and the equilibrium of balls in closed nanotube. By studying the open system we can determine conditions at which the nanotubes can be filled with bucky balls, whereas the closed system can give us information about clustering of internal balls. By mapping the lattice gas model onto the one-dimensional Ising model, the partition function for the open system can be solved exactly. However, using the same procedure, the closed system cannot be solved exactly, so we use the Monte Carlo method. Our results show that tubes can be filled very efficiently at room temperature provided we have enough external balls in the gas phase. For a closed system at room temperature we found a high degree of clustering which decreases with increasing temperature. At about 500K the system goes from a quasi-solid into a quasi-liquid state. Because of the strong interaction between bucky balls, the system is far from its random state even at 1000K - the highest temperature studied. These results are in the agreement with the experimental observations.

#### 11:30 AM **A16.4**

OPTICAL PROPERTIES OF ONE-DIMENSIONAL FULLERENE CHAINS ENCAPSULATED IN SINGLE-WALL CARBON NANOTUBES. H. Kataura, Y. Maniwa, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN; K. Hirahara, K. Suenaga, S. Iijima, Japan Science and Technology Corp, ICRP, Nagoya, JAPAN; T. Kodama, K. Kikuchi, S. Suzuki and Y. Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN.

Single-wall carbon nanotube encapsulating fullerenes (peapod) is an interesting material as a new solid phase of carbon constructing a hierarchical system from zero- to one-dimensional sp<sup>2</sup> network. [1-3] A theoretical calculation shows some flat electronic bands for (10,10) nanotube encapsulating C<sub>60</sub> chains. [4] However, no one succeeded to measure optical properties of peapods to date. We realized high-yield fullerene encapsulations in single-wall nanotubes using diameter-selected nanotubes and specified fullerenes. HRTEM and electron diffraction reveals very high-density packing of fullerenes inside single-wall nanotubes. At room temperature, time-resolved Raman spectra of C<sub>60</sub>-peas clearly indicate a photo-polymerization inside nanotubes by laser irradiation. Photo-polymerized C<sub>60</sub>-peas show a

similar Raman spectrum to that of the orthorhombic polymer phase. [5] At 4.2 K, however, no photo-polymerization reaction was observed. Since free rotations of C<sub>60</sub> molecules play an important role for the photo-polymerization, this result suggests that even in the one-dimensional space, C<sub>60</sub> molecules have a similar spinning nature to those in thin films. In the case of C<sub>70</sub>-peapod, no photo-polymerization was observed. Observed Raman intensity of the C<sub>70</sub>-peas is 1/10 of C<sub>70</sub> films.

**References:** [1] B.W. Smith *et al.*, Nature **396** (1998) 323, [2] B. Burtiaux *et al.*, Chem. Phys. Lett. **310** (1999) 21. [3] J. Sloan, *et al.*, Chem. Phys. Lett. **316** (2000) 191, [4] S. Saito and S. Okada, Proc. 3rd Symposium on Atomic-Scale Surface and Interface Dynamics (March 4-5, 1999, Fukuoka) p 307, [5] A.M. Rao *et al.*, Phys. Rev. B **55** (1997) 4766.

#### 11:45 AM **A16.5**

DOPING AND/OR FILLING CARBON NANOTUBES WITH NITROGEN: AN EELS INVESTIGATION. Susana Trasobares, Christian Colliex, Laboratoire de Physique de Solides, UMR 8502, Université Paris Sud, Orsay, FRANCE; Gilles Hug, LEM, ONERA-CNRS, UMR 104, Châtillon, FRANCE.

Synthesis of nanotubes containing nitrogen is attractive both for electronic and mechanical issues. The present study intends to investigate how far N atoms can be introduced into carbon based nanostructures, elaborated with different methods. Spatially and time-resolved EELS, respectively at the subnanometer and millisecond levels, is used as a local probe of the composition and of the electronic structure. Using a dedicated FEG-STEM instrument, the CN<sub>x</sub> nanotubes grown by catalytic pyrolysis of organic precursors have been characterised by Electron Energy Spectroscopy (EELS) and High Resolution Transmission Electron Microscopy (HRTEM). High-resolution EELS line-scans show a modulated composition across the tube section with an increase in carbon on the external surface of the nanotube. Considering the individual spectra in more detail, it is observed that the π\* peak of the C-K edge decreases with increasing concentration of nitrogen. The similar behaviour have previously been detected as well on CN<sub>x</sub> thin films grown by magnetron sputtering as by chemical vapour deposition. The σ\* band of the C K edge exhibits a similar shape to graphite close to the edge of the tube but becomes less structured when the nitrogen composition increases. It suggests that the structure consists of a graphitic stacking on the outside surface and an amorphous type CN<sub>x</sub> phase in the core. Furthermore, sequences of spectra recorded as a function of primary electron dose, rebuild that the insertion of the N atoms in the tube core may, in certain cases, be unstable, as demonstrated by the clear appearance of a N K line characteristic of N<sub>2</sub> molecules. We thank the collaboration of our colleagues at the University of Sussex, Brighton, UK and the supported of the TMR CT97-0103 network.

### SESSION A17: THERMAL AND TRIBOLOGICAL PROPERTIES

Chair: Rodney S. Ruoff  
Thursday Afternoon, November 30, 2000  
Grand Ballroom (Sheraton)

#### 1:30 PM **\*A17.1**

THERMAL PROPERTIES OF CARBON NANOTUBES. James Hone, California Institute of Technology, Dept of Physics, Pasadena, CA.

The thermal properties of carbon nanotubes reflect both their outstanding mechanical properties and their small size. The measured heat capacity of bulk samples of SWNTs is in excellent agreement with model calculations for individual nanotubes, and provides direct evidence of the quantization of the circumferential phonon wavevector. Detailed modelling provides a measurement of the energy spacing between 1-D phonon 'subbands', and shows that the mechanical coupling between nanotubes in a bundle is weaker than expected. The thermal conductivity of SWNTs is high, and in bulk samples of aligned SWNTs is within an order of magnitude of that of crystalline graphite.

#### 2:00 PM **A17.2**

MESOSCOPIC THERMAL TRANSPORT MEASUREMENT OF CARBON NANOTUBES. Philip Kim, Paul L. McEuen, Department of Physics, University of California, Berkeley, CA; Li Shi, Arunava Majumdar, Department of Mechanical Engineering, University of California, Berkeley, CA.

The thermal conductivity of nanotubes has been measured using a suspended mesoscopic device. The device was fabricated on silicon nitride membrane which is suspended above the substrate. It is connected to a thermal bath through a low thermal conductance path that isolates the heating and sensing elements. Carbon nanotubes

bridge two suspended structures to allow measurements of the thermal conductivity and thermopower of the tube. The observed thermal conductivity is an order of magnitude higher than the estimation obtained from previous experiments on macroscopic mat samples. The temperature dependence of the thermal conductivity and thermopower of these materials will be discussed.

#### 2:15 PM A17.3

MECHANICAL AND TRIBOLOGICAL PROPERTIES OF CARBON NANOTUBES INVESTIGATED WITH ATOMISTIC SIMULATIONS. Boris Ni, Susan B. Sinnott, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY.

Experimental studies and computational simulations have shown that carbon nanotubes have mechanical properties that are both unique and potentially important for their use in new composite materials that could find use in structural applications. Most of the studies to date have been on individual single-walled (SWNTs) or multi-walled (MWNTs) nanotubes. In this work we investigate the mechanical properties of SWNTs and MWNTs that have been filled with various gases, such as methane, xenon, and hydrogen, or clusters, such as buckyballs. The effect of the filling on the deformation of the nanotubes is examined with atomistic simulations using a many-body, reactive empirical bond-order potential that is coupled to long-range van der Waals potentials. The same method will be used to examine the tribological properties of SWNT bundles that are subjected to compressive and shear stresses between two sliding diamond surfaces. The simulations predict that the nanotubes are quite flexible and therefore can be subjected to high shear forces prior to wear. However, the exact nature of these responses is shown to depend on the orientation and attachment of the nanotube bundle with respect to the sliding surfaces.

#### 2:30 PM A17.4

APPLICATION OF CARBON NANOTUBES AND FULLERENES FOR THERMAL MANAGEMENT. Leonard Yowell, Enrique Barrera, Rice Univ, Dept of Mechanical Engineering and Materials Science, Houston, TX; Brian Mayeaux, NASA Johnson Space Center, Houston, TX.

New techniques for thermal management in ceramics at the nanoscale level are proposed using low percentages of fullerenes and carbon nanotubes to control the degree of isotropy in thermal conductivity. Samples of yttria-stabilized zirconia containing fullerenes and nanotubes are prepared by tape casting and are characterized using the laser flash method to map reductions and directional differences in thermal conductivity. Microstructural changes in zirconia due to the presence of fullerenes or nanotubes are related to differences in thermal conductivity and will be characterized using Raman, SEM, TEM, and XRD. Heat transport reductions normal to the sample surface will be analyzed and compared to previous research in thin ceramic-fullerene films to identify unique contributions to thermal management from the particle shape, size, and distribution. Support: Office of Naval Research, Contract #N00014-99-1-0246 and NASA Graduate Cooperative Education Program.

### SESSION A18: FIELD EMISSION PROPERTIES AND APPLICATIONS

Chair: Hiroshi Tokumoto  
Thursday Afternoon, November 30, 2000  
Grand Ballroom (Sheraton)

#### 3:15 PM \*A18.1

CARBON NANOTUBE ELECTRON SOURCES: EMISSION BEHAVIOR, ELECTRONIC STATES, AND CAP STRUCTURE. Kenneth A. Dean, Paul von Allmen, and Babu R. Chalamala, Motorola Inc., Tempe, AZ.

Developing functional electron devices based on carbon nanotubes requires a thorough understanding of fundamental electron emission phenomena in carbon nanotubes. To this end, we present recent results from field emission investigations of electron emission from individual single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Our experimental technique utilizes a field emission microscope to observe nanoscopic phenomena occurring on a nanotube cap during field emission. We find that surface electronic states due to adsorbates dominate the behavior of both SWNTs and MWNTs under typical conditions and lead to current instability and current saturation. However, the behavior of clean, adsorbate-free nanotube surfaces is quite different. The field emission current is extremely stable, and the spatially-resolved field emission microscope images are related to the electronic structure of the nanotube caps. The field emission images of clean SWNTs and MWNTs are found to differ significantly. Clean nanotube surfaces also possess surface states that affect the tunneling current, as indicated by current versus

temperature dependencies and electron energy distributions. We measure the maximum current per nanotube before field evaporation and show that through controlled field evaporation, the cap can be altered repeatedly to produce a set of different cap electronic structures. We will discuss the impact of these properties on the performance of nanotube-based field emission devices.

#### 3:45 PM \*A18.2

SYNTHESIS AND FIELD EMISSION PROPERTIES OF CARBON NANOTUBES. Chris Bower, Otto Zhou, Dept. of Physics and Astronomy, University of North Carolina, Chapel Hill, NC; Wei Zhu, G.P. Kochanski, Sungho Jin, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We will present our recent results on fabrication and characterization of cold cathodes based on carbon nanotube field emitters. The first portion of the talk will focus on the fabrication of carbon nanotube films, and the second half will be devoted to the field emission properties of these films. Specifically, we have successfully synthesized films consisting of well-aligned carbon nanotubes by microwave plasma-enhanced CVD. The nanotubes were found to nucleate and grow from catalytic cobalt islands on a standard silicon wafer, with their diameters and lengths dependent on the size of the cobalt islands. Electron microscopy revealed that the nanotubes grew via a base-growth mechanism, and studies of the growth kinetics revealed a very rapid initial growth that decreased sharply after the catalyst became fully encapsulated within the nanotube. A nucleation and growth model explaining our experimental observations will be proposed. Additionally, we will present data that suggests the nanotube alignment was induced by the plasma environment. We will show that nanotube films can be uniformly grown on contoured surfaces with the nanotube alignment always perpendicular to the local substrate surface. We will compare the field emission properties of various types of carbon nanotube films. These include randomly oriented SWNT and MWNT films, and aligned MWNT films. We will contrast the field emission properties of nanotubes with diamond and other types of cold cathodes, and consider the future of using nanotubes in vacuum microelectronic devices.

#### 4:15 PM \*A18.3

CARBON NANOTUBE AND ITS APPLICATION TO TRIODE-TYPE FIELD EMISSION DISPLAYS. W.B. Choi, M.J. Yun<sup>1</sup>, N.S. Park, C.G. Lee<sup>2</sup>, Y.W. Jin, H.Y. Kim<sup>1</sup>, S.J. Lee<sup>1</sup>, H.S. Han<sup>2</sup>, Y.W. Na<sup>2</sup>, B.G. Lee<sup>2</sup>, N.S. Lee, J.E. Jung<sup>1</sup>, J.H. You<sup>2</sup> and J.M. Kim<sup>1</sup>, Display Lab. <sup>1</sup>The National Creative Research Initiatives Center for Electron Emission Source. <sup>2</sup>CRD, Samsung SDI, Samsung Advanced Institute of Technology, Suwon, KOREA.

Carbon nanotube field emission displays (CNT-FEDs) have a strong potential to be applied to emissive devices including flat panel displays, cathode-ray tubes, back lights for liquid crystal displays, outdoor displays, and traffic signals. The CNT-FEDs have been demonstrated by our group based on the well-aligned nanotubes following paste squeeze and surface treatment [1]. The fabricated displays were fully scalable and showed a high brightness on the green phosphor. The current fluctuation was found to be about 7% over a 9-inch panel [2]. In order to generate high quality moving images with high gray scale, low power consumption, and high brightness, the triode-type geometry should be realized. Here we report fabrication processes and field emission characteristics of a triode-type CNT-FEDs. The CNT cathodes were prepared by the paste squeezing and electrophoresis technique. The gate electrode was inserted between the cathode and the anode plates. Uniform emission with high brightness was obtained. The electron emission was modulated at gate voltage of 100-300V. In this presentation, the effect of geometric factor upon the emission properties of the triode-type panel will be discussed together with the effects of fabrication process. [1] W.B. Choi, D. S. Chung, J.H. Kang, H.Y. Kim, Y.W. Jin, I.T. Han, Y.H. Lee, J.E. Jung, N.S. Lee, G. S. Park, and J.M. Kim, Appl. Phys. Lett. 75 3129 (1999). [2] W.B. Choi, N.S. Lee, W.K. Yi, Y.W. Jin, Y.S. Choi, I.T. Han, D.S. Chung, H.Y. Kim, J.H. Kang, Y.J. Lee, M.J. Yun, S.H. Park, S. Yu, J.E. Jang, J.H. You, J.M. Kim, "The first 9-inch carbon-nanotube based field-emission displays for large area and color applications", SID 2000 Digest, pp324-327

#### 4:45 PM A18.4

ELECTRON EMISSION FROM PENTAGONS ON A CARBON NANOTUBE TIP REVEALED BY FIELD EMISSION MICROSCOPY. Koichi Hata, Akihiro Takakura, Yahachi Saito, Mie Univ, Dept of Electronic Engineering, Tsu, JAPAN.

Field emission of electrons from multiwall carbon nanotubes (MWCNTs) has been investigated in ultra-high vacuum by field emission microscopy (FEM). MWCNTs whose tips are capped by curved graphite layers give FEM patterns consisting of 6 bright pentagons, each of which has a dark regions in its center. Interference fringes are also observed between adjacent pentagonal rings. The

present result shows a direct evidence of the presence of 6 pentagons on a tip of a closed carbon nanotube. In previous FEM experiments performed under a poor vacuum, bright solid spots that were randomly distributed or arranged with two- and four-fold symmetry were observed. These bright spots are revealed to be due to adsorbed molecules such as oxygen on nanotubes tips. Adsorption of molecules seems to raise the tunneling probability of electrons.