Wednesday Afternoon, October 27, 1999

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-WeA

Nanotubes: Growth, Characterization and Properties I
Moderator: S.B. Sinnott, University of Kentucky

2:00pm **NT+NS+EM+MS-WeA1 Making and Modifying Carbon Nanotubes***,* ***R.E. Smalley****,* Rice University **INVITED**

The last year has produced exciting developments in our ability to produce and modify single wall carbon nanotubes (SWNT). New experiments have shown the feasibility of producing nanotubes in an efficient gas-phase process, sometimes having diameters down to approximately 0.6 nm. These methods involve chemical vapor deposition in high-pressure carbon monoxide. We are now pursuing this growth technique as a potentially viable means for cost-effective production of large amounts of SWNT. Development of new methods for purification and characterization of nanotubes has given new insight into their growth mechanisms. I will present new data on the morphology and length distributions of SWNT grown by traditional laser-oven methods, and outline new results on the behavior and characteristics of tube samples. Perhaps the most remarkable developments have been in the chemistry of SWNT as a new molecular species. Several groups have discovered means of covalent attachment of other chemical species to the tube ends and sidewalls. This derivatization significantly modifies the properties of SWNTs, permits the first true solutions of tube segments, and opens the door to a remarkable new realm of chemistry, materials science, and electronics.

2:40pm **NT+NS+EM+MS-WeA3 Roles of Fe, Co, and Ni in the Formation of Single-Walled Carbon Nanotubes and Encapsulated Nanoparticles***,* ***J. Jiao****,* Portland State University

The preparation and structural properties of carbon nanoclusters synthesized by having the transition metals Fe, Co, and Ni react with carbon in three different methods were investigated comparatively with the focus on single-walled nanotubes and encapsulated nanoparticles. The carbon nanoclusters were synthesized first by the high temperature (~3000°C) and high carbon-content process of the conventional arc discharge, secondly by the high temperature but low carbon-content process of the modified arc-discharge, and finally by the relatively low temperature (~500°C) process of catalytic decomposition of carbon monoxide (CO). The samples were characterized with respect to morphology, internal structure, and related properties. The carbon nanoclusters prepared by three different methods appear quite different on the surface, but have features in common that this report emphasizes. The same element can apparently serve different functions, serving as catalyst under one set of condition, and being encapsulated into the growing cages in a different environment. The elements of the iron group (Fe, Co, and Ni) were known as catalysts for growing the single-walled nanotubes and strings of spherical particles in conventional arc discharge, but could be encapsulated into the graphitic particles in the modified arc discharge and the CO disproportion that this study demonstrates. It was found that variation of the metal-to-carbon ratio is required to make these elements assume the double roles of either catalyst or encapsulant. In this report, an assembly of growth phenomena of carbon nanoclusters indicating the roles of the Fe, Co, and Ni will be presented. The growth mechanisms of these structural phenomena in relation to the preparation conditions in particular to the ratio of carbon content in the reaction chamber during the preparation are discussed.

3:00pm **NT+NS+EM+MS-WeA4 Plume Diagnostics During Carbon Nanotube Production by Laser Ablation***,* ***S. Arepalli****,* G. B. Tech./Lockheed Martin*; C.D. Scott,* NASA/Johnson Space Center

We report recent results of our plume diagnostics during carbon nanotube production by double pulse laser oven method. The evolution characteristics of different species in the plume from different regions of the laser ablated plume will be presented. Transient emission data is compared with plume images to formulate dynamics of plume expansion. Vibrational and rotational temperatures of C@sub 2@ and C@sub 3@ are estimated by comparison with computations. Excitation spectra of LIF are used to deduce ground state temperatures and populations.

3:20pm **NT+NS+EM+MS-WeA5 Synthesis and Integration of Carbon Nanotubes***,* ***H. Dai****,* Stanford University **INVITED**

This talk focuses on controlled growth and properties of multi-walled and single-walled carbon nanotubes on catalytically patterned substrates. It will be shown that new possibilities are opened up in nanotube science and applications by synthesizing nanotubes at desired locations and orientations in ordered fashions. A recently developed chemical vapor deposition method for high quality single-walled nanotubes is combined with microfabrication methods to reliably integrate single-walled nanotubes into various electrical architectures. The transport properties of individual single-walled nanotubes will be presented. Functional nanotube electrical devices with advanced performances will be shown. Issues in further control of nanotube growth will be addressed.

4:00pm **NT+NS+EM+MS-WeA7 Growth of Vertically Aligned Carbon Nanotubes on Transition-metal Catalyzed Plain Silicon Substrates using Thermal Chemical Vapor Deposition***,* ***Y.H. Lee****, Y.C. Choi,* Jeonbuk National University, Korea*; C.J. Lee,* Kunsan National University, Korea*; Y.B. Han,* Jeonbuk National University, Korea

Vertically aligned carbon nanotubes have been grown on a large area of transition-metal coated plain silicon substrates by thermal chemical vapor deposition method. We find that vertically aligned growth is critically dependent on the domain density in the transition metal cluster. Steric hindrance between nanotubes at an initial stage of the growth forces nanotubes to align vertically. Nanotubes are then further grown by the catalyst-cap growth mechanism. We also show emission patterns from aligned nanotubes. Our current approach of simple integration of stable field-emission displays on a large area puts a step forward to future display applications.

4:20pm **NT+NS+EM+MS-WeA8 Carbon Nanotube Tips: Structures and Properties***,* ***J. Han****, L. Yang, R.L. Jaffe,* NASA

A variety of structures and properties of carbon nanotube tips present challenges in understanding of electron tunneling and field emission of carbon nanotube materials. Topologically, a nanotube tip can be formed by joining a tube bulk and a cone or a half the fullerene. Different configurations can be resulted from arrangement of topological defects. Energetically favorable configurations are identified and classified using functional theory and molecular mechanics calculations. They are further used for electronic structure calculations based on tight-binding approaches. The location and intensity of localizes states at tips are studied as functions of the size and configurations of tips. The differences in localized stated between one and four-orbital calculations are also compared. Experimental results of carbon nanotube field emission properties are related to the calculations of the localized stated of nanotube tips.

4:40pm **NT+NS+EM+MS-WeA9 Electrochemical Deposition of Carbon Nanofilaments***, E. Anoshkina,* **D. Zhou***, L. Chow, V. Desai,* University of Central Florida

Carbon nanofilaments are conventionally made from thermal catalytic chemical vapor deposition with carbonaceous gases as growth precursors. Based on their unique mechanical, thermal, and electrical properties, many applications of carbon nanofilaments have been realized in advanced technologies. We report here on a new method to prepare carbon nanofilaments, in which the nanofilaments have been made from organic solvents such as methanol through an electrochemical deposition process. Silicon wafers coated with Fe or Ni nanoparticles were employed as the electrodes, and the depositions were carried out at room temperature. It has been found that electrical field between the electrodes, conductivity of the solvent, and size of the catalysts play important roles in control of morphologies of the carbonaceous deposits. Furthermore, based on characterization of the nanofilaments using scanning electron microscopy, transmission electron microscopy, and energy dispersive x-ray spectroscopy, the formation and growth mechanism of carbon nanofilaments from the electrochemical deposition has been discussed.

5:00pm **NT+NS+EM+MS-WeA10 A Study on the Growth of Carbon Nanotubes with Respect to Process Conditions***, J.N. Srivastava, K.K. Awasthi,* **C.D. Dwivedi***, G.N. Mathur,* Defence Materials & Stores Research & Development Establishment, India

Carbon nanotubes have been produced by graphite evaporation method in macroscopic quantities with reproducible results at different conditions. A study on the growth of CNT against the variation in Helium / Argon / Nitrogen pressure has been done and some interesting results are found with respect to geometry, density and alignment of the tubes. Total yield of the material is also found to be having correlation with the pressure and current. Material produced in different conditions has been characterized by XRD, SEM, TEM, TGA and FTIR techniques.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 4C - Session NT+NS+EM+MS-WeP
Poster Session

NT+NS+EM+MS-WeP1 Growth of Carbon Nanotubes at Low Temperature by Microwave Plasma-enhanced Chemical Vapor Deposition*, **Y.C. Choi**, D.J. Bae, Y.H. Lee, B.S. Lee,* Jeonbuk National University, Korea

We have grown carbon nanotubes at temperatures below 520 C by microwave plasma-enhanced chemical vapor deposition using methane and hydrogen gases. Carbon nanotubes were uniformly grown in large area of transition metal-coated Si substrates with high density. Each nanotube is terminated by transition metal cap, suggesting that the transition metals play an important role in the nanotube growth. Carbon nanotubes are curly in all cases, indicating the nanotubes to be defective due to very low growth temperature. Diameters and lengths of the nanotubes could be controlled by changing the ratio of methane to hydrogen and growth time. Raman spectum clearly shows the peak at 1592 cm-1 (G-band), indicating the formation of well graphitized carbon nanotubes.

NT+NS+EM+MS-WeP2 Nanoscale-controlled Handling of Carbon Nanotubes*, **O. Jaschinski**, P. Bernier, L. Vaccarini, C. Goze,* Universite Montpellier II, France*; G. Duesberg,* Trinity College Dublin, Ireland*; C. Journet, S. Roth,* Max-Planck-Institut fuer Festkoerperforschung Stuttgart, Germany

Carbon nanotubes are the most promising materials for applications in nanoelectronics and nanomechanics. For the determination of the electrical and mechanical properties of nanotubes and for the production of nanotube devices one needs the ability to handle nanoscale materials in a controlled way . We demonstrate how atomic force microscopy (AFM) can be used as a tool for manipulating and investigating carbon nanotubes. For an optimal use of AFM it is necessary to control the substrate-nanotube interaction. We present results of measurements of the mechanical properties of nanotubes obtained with various kinds of substrates. We show how the combination of lithography, manipulation by AFM and control of the adsorption process of nanotubes allow to prepare well defined sample configurations for very sophisticated measurements of the electrical and mechanical properties of carbon nanotubes. Based on these methods, techniques for the production of nanotube devices can be developed. This work was supported by European TMR contract NAMITECH ERBFMRX-CT96-0067 (DG12-MIHT)

NT+NS+EM+MS-WeP3 Aligned Carbon Nanotubes with Controlled Diameters Using Anodic Alumina Template*, **S.-H. Tsai**, H.C. Shih,* National Tsing Hua University, R.O.C.

The microwave plasma enhanced chemical vapor deposition (MPECVD) system had been successfully fabricated the well-controlled diameters of aligned carbon nanotubes on the anodic alumina template with a mixture of methane and hydrogen. Prier to test, the anodic alumina with pore arrays in various diameters were prepared by anodizing aluminum using oxalic, sulfuric, and phosphoric acid solutions. By adjusting the pore size of the anodic alumina, various carbon nanotube diameters can be obtained in a range of 30 to 100 nm and were examined by scanning electron microscopy and transmission electron microscopy.

NT+NS+EM+MS-WeP4 The Selective Growth of Aligned Carbon Nanotubes by PECVD Using Nickel Catalyst*, **H. Jeon**, K. Ryu, M. Kang,* Hanyang University, Korea

Carbon nanotubes have been studied extensively because of their own unique physical properties and also of their application potential for field emitters. One of the interesting applications is reported for display application, but neither industrial fabrication technology nor performance has been reported for practical display application. Here we tried to grow aligned carbon nanotubes selectively by plasma enhanced chemical vapor deposition (PECVD) method using nickel catalyst@footnote 1@ at temperatures below 600°C. These conditions for low temperature growths are suitable for field emission display which requires carbon nanotube emitters grown perpendicular to the Si substrate. In our experiment, a thin film of nickel(10-100nm) was deposited through a pattern mask on a Si substrate in UHV e-beam evaporator and was agglomerated by in-situ annealing for thirty minutes at 700°C. The use of a patterned catalyst enhanced the formation of selectively aligned nanotubes at low temperatures. After this process, Ni particles deposited on Si substrate were examined by AFM and SEM. Carbon nanotubes were selectively grown on Ni particle by PECVD with using the mixture of CH@sub 4@ and NH@sub 3@ at 600°C. In this process, CH@sub 4@ was used as the carbon source and NH@sub 3@ was used as a catalyst and dilution gas. During the process, many carboneous impurities can be produced and tried to eliminated by introducing H@sub 2@ plasmas. We examined the physical properties of carbon nanotubes by SEM, XRD and Raman spectroscopy. And we investigated the formation temperature of carbon nanotubes on silicon substrate and controlled the selective growth of aligned nanotubes. @FootnoteText@ @footnote 1@ Masako Yudasaka, et al.,Appl. Phys. Lett. 70(14), 7 April 1997.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThM

Nanotubes: Nanoelectronics and Field Emission
Moderator: N.J. Halas, Rice University

8:20am **NT+NS+EM+MS-ThM1 Carbon Nanotube Molecular Electronics*, C. Dekker,*** Delft University of Technology, The Netherlands **INVITED**

I will present various recent results from electron transport measurements and scanning-probe microscopy on individual single-wall carbon nanotubes. Our early electrical transport work showed mesoscopic signatures at cryogenic temperatures. Additionally, a room-temperature transistor based on an individual semiconducting nanotube was established. Recent results in transport studies include first measurements on samples with low-ohmic contacts. The nanotubes are found to sustain very high current densities (~10^9 A/cm^2). I will show first measurements on kinked nanotubes, which act as an ontube intramolecular junctions. If time allows I may also present our results on AFM manipulation of nanotubes, and electrical measurements on manipulated nanotubes.

9:00am **NT+NS+EM+MS-ThM3 Electrical Transport in Single-Wall Nanotube Rings: Coherence and Localization***, H.R. Shea, R. Martel,* ***Ph. Avouris,*** IBM T.J. Watson Research Center

Understanding electrical transport in carbon nanotubes is essential for their possible use in nanoelectronics. Furthermore single-walled carbon nanotubes (SWNTs) provide ideal model systems on which to test theories of transport phenomena in 1D-systems. Linear SWNTs, however, do not have self-folding electron trajectories which can enclose magnetic flux. Thus, the technique of magneto-resistance (MR) cannot be applied directly to obtain information on the mechanism of electrical transport. Recently, we have developed a procedure by which linear SWNTs can be induced to form ring structures. Despite the high flexural rigidity of these materials, coils stabilized only by van der Waals forces can be produced in yields of ~50 %. These rings provide an ideal geometry for MR measurements. The MR is negative over the range of 0-5 T and from it we are able to determine the coherence length of the electrons in the rings. We found that over the entire range of 3 K - 60 K the SWNT-rings are in a state of weak localization induced by the constructive interference of electron waves propagating in opposite directions around the ring. Electric transport is not ballistic, and the coherence length reaches 520 nm at 3 K. From the temperature dependence of the coherence length we determine that the dominant dephasing mechanism at low T involves electron-electron interactions (Nyquist mechanism). Below ~1 K we observe an electronic phase transition to a strongly localized state. This transition is accompanied by the opening of a small energy gap and very strong MR and universal conductance fluctuations. An interesting zero bias anomaly (ZBA) is also observed below ~0.7 K. This ZBA is sensitive to magnetic fields and is ascribed to Kondo-type scattering from localized magnetic moments.

9:20am **NT+NS+EM+MS-ThM4 Analysis of Carbon Nanotube Field-Effect-Transistors (FETs)*, T. Yamada,*** NASA Ames Research Center

Recent experiments on carbon nanotube FETs@footnote 1@ are analyzed theoretically. Comparing to the familiar Metal-oxide-semiconductor (MOS) FET characteristics, two qualitatively different behaviors can be pointed out:@footnote 1@ (1) the channel conductance g@sub d@ as a function of gate voltage V@sub g@ is not linear but somehow saturates, and (2) the drain current I@sub d@ does not saturate with the drain voltage V@sub d@ but rather monotonically increases. As for g@sub d@(V@sub g@), a staircase-like curve is expected with possible rounding. Each time the Fermi energy crosses a degenerate new subband, the nanotube conductance increases by double the quantum conductance, and thus g@sub d@ forms steps. When moving up to a next step, one new additional degenerate subband needs to be filled in the inversion layer, where larger V@sub g@ has to be applied. This will be a mechanism for the g@sub d@ saturation. The absence of I@sub d@(V@sub d@) saturation is due to the infrequent inelastic scattering by phonons or other carriers in the channel, regardless of the frequent elastic scattering by defects or impurities determining the small g@sub d@ (1/g@sub d@ ~ 2.9 M@ohm@).@footnote 1@ Carriers are not thermalized in the channel without efficient inelastic scattering, resulting in no channel pinch-off formation and no I@sub d@ saturation. These reflect the nanotube electronic properties. We need to take them into account in the future device/circuit design, and develop a scheme best suitable for nanotube FETs. @FootnoteText@ @footnote 1@S.J. Tans, R.M. Verschueren & C. Dekker, Nature, 393, 49 (1998); R. Martel, T. Schmidt, H.R. Shea, T. Hertel, Ph. Avouris, Appl. Phys. Lett. 73, 2447 (1998).

9:40am **NT+NS+EM+MS-ThM5 Novel Length Scales in Nanotube Devices*, F. Léonard,*** *J. Tersoff,* IBM T.J. Watson Research Center

We calculate the properties of p-n junctions, n-i junctions, and Schottky barriers made on a single-wall carbon nanotube. In contrast to planar bulk junctions, the depletion width for nanotubes varies exponentially with inverse doping. In addition, there is a very long-range (logarithmic) tail in the charge distribution, extending over the entire tube. These effects can render traditional devices unworkable, while opening new possibilities for device design. Our general conclusions should apply to a broad class of nanotube heterojunctions, and to other quasi-one-dimensional ``molecular wire" devices.

10:00am **NT+NS+EM+MS-ThM6 Field Emission from Carbon Nanotubes and Its Application to Electron Sources in Display Elements*, Y. Saito,*** Mie University, Japan*; S. Uemura,* Ise Electronics Corp., Japan **INVITED**

Carbon nanotubes posses the following properties favorable for field emitters: (1) high aspect ratio, (2) small radius of curvature at their tips , (3) high chemical stability and (4) high mechanical strength. Field emission microscopy was carried out for both multiwall nanotubes (MWNTs) and single-wall nanotubes (SWNTs) produced by arc discharge between carbon. Four kinds of nanotubes were investigated; viz., (1) as-grown MWNTs prepared in the helium arc (called "pristine MWNTs"), (2) as-grown MWNTs in hydrogen ("nanog rafibers"), (3) purified MWNTs with open ends ("purified MWNTs" or "open MWN Ts"), and (4) purified SWNTs. Field emission patterns as well as current versus voltage characteristics and Fowler-Nordheim plots for respective nanotubes will be discussed. As an application of nanotube field emitters, we manufactured cathode-ray tube (CRT) type lighting-elements and vacuum-fluorescence display (VFD) panels. In both display elements, conventional thermionic cathodes were replaced with MWNT field emitters which were fixed onto a stainless steel cathode by using conductive paste. In CRT-type lighting elements, the nanotube cold cathode was covered with a grid electrode, the gap between the cathode and the grid being in a range from 0.2 to 0.7 mm. Current density on the cathode surface was on the order of 10 - 100 mA/cm@super 2@ at an average field strength of 1.5 V/ µm. Luminance of the phosphor was intense enough for practical use; e.g., 6.3x10@super 4@ cd/m@super 2@ for green light at an anode current of 0.2 mA and an anode voltage of 10 kV. A direct-current driving test revealed a lifetime over 10,000 hours.

10:40am **NT+NS+EM+MS-ThM8 Emission Properties of Large-area, Fully-sealed Carbon Nanotube Field Emission Display*, W.B. Choi,*** *H.Y. Kim, D.S. Chung, J.H. Kang, I.T. Han, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Fully sealed field emission display (FED) in size of 4.5 inch has been fabricated by using carbon nanotubes. Carbon nanotubes were fabricated by arc discharge technique. Carbon nanotube aligning techniques with the aid of slurry squeezing and electrophoresis were used for making large-area cathode. The Y@sub 2@O@sub 2@S:Eu, ZnS:Cu,Al, and ZnS:Ag,Cl, phosphors are deposited on the anode glass for red, green, and blue colors, respectively. The assembled structure was sealed in an atmosphere of highly purified Ar gas by means of a glass frit. The display plate was evacuated down to the pressure level of 1x10@super -7@ Torr. Three non-evaporable getters of Ti-Zr-V-Fe were activated during the final heat-exhausting procedure. Finally, the active area of 4.5-inch panel with fully sealed carbon nanotubes was produced. The turn-on field for lighting phosphor was 1.5 V/µm. Brightness of over 1000 cd/m@super 2@ at 4V/µm was achieved on the entire area of 4.5-inch panel from the green phosphor-ITO glass. The fluctuation of the current was satisfied for the field emission display. These reliable results enable us to produce carbon nanotube-based large area full-color FEDs in the near future. In this presentation, fabrication techniques and emission properties of large area carbon nanotube FED will be demonstrated.

11:00am **NT+NS+EM+MS-ThM9 The Structure of Nanotubes Observed with Thermal Field Emission*, K.A. Dean,*** *B.R. Chalamala,* Motorola Flat Panel Display Division*; O. Groening, O.M. Kuettel,* University of Fribourg, Switzerland

We studied the structure of single-walled nanotubes (SWNTs) using field emission microscopy. The field emission images obtained after thermal cleaning depict the spatially-resolved electronic structure of the individual SWNT caps. Using high temperature field emission, we demonstrate how to distinguish between the patterns of individual SWNTs and those of clusters, how to alter the structure of the nanotube cap, and how to extract information about the SWNT structure and chirality from the field emission image. In addition, we demonstrate a technique for measuring the SWNT local density of states through thermal field emission energy distribution measurements. With this technique, we observe that nanotubes have discrete electronic states several eV above the Fermi level, and we suggest that these states are responsible for the large variation in emission current vs. temperature behavior observed among nanotubes.

11:20am **NT+NS+EM+MS-ThM10 Fabrication and Field Emission Properties of Adherent Carbon Nanotube Films***, **C. Bower,*** University of North Carolina at Chapel Hill*; W. Zhu, G. Kochanski, S. Jin,* Bell Laboratories, Lucent Technologies*; O. Zhou,* University of North Carolina at Chapel Hill

We report on the fabrication and field emission properties of carbon nanotube films. Films of randomly oriented carbon nanotubes were deposited onto substrates using a variety of techniques. The nanotube films exhibited stable field emission current at low turn-on fields (electric field needed to generate 1 nA of current) and threshold fields (electric field needed to generate 10 mA/cm@super 2@). A single-walled carbon nanotube film with approximately 20% surface coverage showed a turn-on field of 1-1.2 V/µm and a threshold field of 1.3-1.7 V/µm. The emission characteristics deviated from typical Fowler-Nordheim behavior at high current densities. The nanotube films were capable of generating large current densities (> 4 A/cm@super 2@). The emission properties were found to be stable over several days of emitting at 10 mA/cm@super 2@. The emission site density of the films was measured to be 10@super 4@-10@super 5@ sites/cm@super 2@ and the emission patterns were studied.

11:40am **NT+NS+EM+MS-ThM11 Characterization of Oriented Carbon Nanotube Cathodes for Field Emission Flat Panel Display and Light Source Applications***, **N.N. Chubun,*** SRPC Istok, Friazino, Russia*; A.G. Chakhovskoi, C.E. Hunt,* University of California, Davis*; A.N. Obraztsov,* Moscow State University, Russia

Oriented carbon nanotubes were recently reported as a viable material for fabrication of field emission cathodes applicable to flat panel displays and vacuum light sources.@footnote 1@ Field emission properties of diode and triode structures with oriented nanotube cathodes were studied in DC-mode in ultra-high vacuum chamber and in sealed glass prototype devices. Cathodes of 9x9mm grown using glow-activated direct current discharge CVD method on molybdenum and single crystal silicon substrates were studied at currents up to 2 milliamps using metal or phosphor coated anodes. The nanotubes exhibited various degrees of initial surface orientation depending on parameters of the deposition process. An additional orientation of the nanotubes in electric filed during first activation of the cathodes was observed. Monochrome low-voltage FPD phosphors were used for cathodoluminescent brightness/light efficiency characterization and for monitoring of distribution of the filed emission sites. Turn-on voltages varied from 1 to 5 V per micron depending on the extraction electrode configuration. Influence of vacuum conditions and initial training on stability and lifetime of the cathodes was studied. I/V characteristics of the nanotube cathodes were directly compared to those of carbon fiber and carbon foam emitters and to diamond-coated field emission arrays showing potentially greater reproducibility and uniformity of filed emission of the oriented nanotube cathodes. @FootnoteText@ @footnote 1@ A.N.Obraztsov, I.Yu.Pavlovsky, A.P.Volkov, V.L.Kuztetsov, A.L.Chuvilin. MRS 1999 Spring Meeting, San Francisco, CA, April 1999, p.B.4.9/C.2.9.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThA

Nanotubes: Functionalization and Metrology

Moderator: D. Herr, Semiconductor Research Corporation

2:00pm **NT+NS+EM+MS-ThA1 Opportunities and Challenges for Nanotubes in Future Integrated Circuits**, ***R.R. Doering,*** Texas Instruments **INVITED**

We speculate about a few potential research opportunities that may be of mutual interest to both the microelectronics and nanotube communities. Perhaps the most evolutionary use of nanotubes in integrated circuits would be in the form of "thin films." Such use would capitalize on "bulk" material properties. For example, a layer of nanotubes (with "best metallic" conductivity) might serve as an interconnect film. Alternatively, an insulating nanotube layer (e.g, "modified" CNTs or other tube chemistries) might be used as a low-K dielectric. Even lower K might be achieved by using high-conductivity CNTs as "self-supporting wires," taking advantage of their inherent mechanical strength to eliminate the need for solid insulating layers. Another type of evolutionary use might involve nanotube structures for passive IC components. For example, the huge volume density of surface area looks appealing for DRAM capacitors. A significant amount of current nanotube research is aimed at active devices, which might ultimately replace today's silicon semiconductor switches. One of the most exciting prospects is the potential for more extensive and effective use of the "third-dimension" in integrated circuits. However, as with today's "planar" IC technology, the benefit/cost of "going 3D" will depend on details of the practical fabrication techniques. For nanotubes, this brings up "formation/place/route" issues. Nanotubes may also play a role in future "atomically perfect manufacturing," which may be needed to scale much below about 50-nm features regardless of the type of device technology employed.

3:00pm **NT+NS+EM+MS-ThA4 Simulations of Plasticity and Kink Catalyzed Functionalization of C and BN Nanotubes**, ***D. Srivastava,*** NASA Ames Research Center*; M. Menon,* University of Kentucky

Routes to plasticity and kink catalyzed chemistry for functinlaization of C and BN nanotubes are investigated via classical molecular dynamics (MD) and generalized tight-bonding quantum molecular dynamics (QMD) methods. The critical strain for plasticity of BN nanotube is found to be more than that for the similar C nanotube. The structural collapse of nanotubes under compression is explored in which we find that the accumulated strain drives the tube in a plastic deformation in which four-fold coordinated tetrahedral bonds form at the location of the collapse. This lowers the elastic limit of compressed nanotubes to much less than what was predicted earlier with classical MD potential methods alone.@footnote 1@ The critical stress needed for this transition, as computed with QMD method, is in good agreement with experimental values observed for compressed nanotubes in polymer composites and graphite to diamond like transition in a bucky-onion pressure cell. Mechanical kink driven side-wall functionalization of C and BN nanotubes is also explored. We find that mechanical twisting and bending of the tube enhances the binding energy (and lowers the cohesive energy) at kink or edge sites by 1-2 eV as compared to the reactivity of undeformed tubes. Highly localized selective functionalization and etching of sidewalls could thus be possible through kink catalyzed chemical reactivity of nanotubes. A preliminary example of the experimental evidence will be shown.@footnote 2@ @FootnoteText@ @footnote 1@D. Srivastava, M. Menon, and K. Cho, submitted (1999). @footnote 2@D. Srivastava, D. W. Brenner, J. D. Schall, K. D. Ausman, M. F. Yu and R. S. Ruoff, to appear J. Phys. Chem. (1999).

3:20pm **NT+NS+EM+MS-ThA5 Nanoindentation and Nanotribology with Carbon Nanotubes**, *B. Ni, A. Garg,* ***S.B. Sinnott,*** University of Kentucky

The mechanisms by which carbon nanotubule (CNT) proximal probe tips deform during the nanometer-scale indentation and scratching of surfaces are explored using classical molecular dynamics simulations. The forces acting on the atoms in the simulations are calculated using a many-body, reactive bond-order potential for hydrocarbons. The results show that single-walled and multiwalled CNT tips indented against hydrogen-terminated diamond and graphene surfaces buckle and slip to relieve the applied stress. However, in the case of reactive surfaces, tip-surface adhesion occurs on contact that ultimately destroys the tubule. Furthermore, while shell-shell interactions have little effect on the deformation mechanisms, the multiwalled tubule is stiffer than comparably sized single-walled tubules. Finally, the way in which the deformation of these tubules changes during scratching of diamond and graphene surfaces will be discussed and the results compared to available experimental data. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

3:40pm **NT+NS+EM+MS-ThA6 Quantum Chemistry Study of Carbon Nanotube Fluorination**, ***R.L. Jaffe,*** NASA Ames Research Center

Quantum chemistry calculations are carried out to characterize the products of fluorination reactions of C@sub 60@, C@sub 70@ and carbon nanotubes. The calculations utilize density functional theory with a widely used hybrid nonlocal functional (B3LYP-DFT). C@sub 60@ is known to readily undergo reaction with molecular fluorine to form C@sub 60@F@sub n@ with n<44. C@sub 60@F@sub 18@ and C@sub 60@F@sub 36@ are the predominate products. C@sub 70@ also is known to undergo similar reaction, but the products have not been completely characterized. Less is known about the possibility of fluorinating nanotubes. However, it has been conjectured that highly fluorinated nanotubes may have attractive chemical and dielectric properties. Fluorination of C@sub 60@ and C@sub 70@ is used to benchmark the calculations for nanotubes. Previous studies have demonstrated that polycyclic aromatic hydrocarbons with an externally constrained curvature are good model molecules for studying the functionalization reactions of single-walled carbon nanotubes. Reaction is likely if the products are energetically stable and any activation energy barriers are small. Initial studies for C@sub 60@ and (10,10) nanotubes have shown that the difluoronated products are quite stable and the fluorination reaction is highly exothermic.

4:00pm **NT+NS+EM+MS-ThA7 Gear-like Rolling Motion of Carbon Nanotubes on HOPG**, ***M.R. Falvo,*** *J. Steele, A. Buldum,* University of North Carolina, Chapel Hill*; D. Schall,* North Carolina State University*; R.M. Taylor II,* University of North Carolina, Chapel Hill*; D.W. Brenner,* North Carolina State University*; J. Lu, R. Superfine,* University of North Carolina, Chapel Hill

Though much work has been done in recent years in exploring nanometer and atomic scale sliding friction, little experimental or theoretical work has been done on rolling and its relation to sliding at this scale. We will present lateral force microscope investigations of frictional phenomena of multiwall carbon nanotubes (MWCNTs) on highly oriented pyrolytic graphite (HOPG), that include all the rigid body motions: sliding, rotating in-plane, and rolling. Using an advanced manipulation interface for AFMs, the nanoManipulator, we study these friction phenomena through sophisticated manipulation experiments where lateral forces are monitored during manipulations. We have manipulated MWCNTs into a state of atomic registry between the lattice of the tube and underlying substrate. Out of atomic registry the friction is smooth and uniform. As the CNT is rotated in the plane of the substrate, three discrete atomically registered orientations are observed marked by a 3-10 fold increase in the lateral force required to remove them from these orientations. Results of molecular statics calculations for this system show that the potential energy as a function of in-plane rotation angle has three deep minima spaced sixty degrees apart corresponding to atomic lattice registry. When the CNT locks into atomic registry, there is a transition from an in-plane rotational motion to a stick-slip rolling motion. Rather than being perfectly cylindrical, our lateral force data during rolling indicate that the CNT may be faceted (polygonal cross section). MS calculations indicate that faceting is to be expected for MWCNT depending on diameter and wall thickness. The calculated friction expected for rolling a faceted MWCNT agrees well with experimental lateral force data. Molecular dynamics calculations will be shown that lend insight into the energy loss mechanisms for both the sliding and rolling case. This work is supported by the NIH (NCRR), NSF, ONR (MURI), and ARO (DURIP).

4:20pm **NT+NS+EM+MS-ThA8 Selectivity and Diffusion of Binary Fluids in Carbon Nanotubes**, ***Z. Mao,*** *S.B. Sinnott,* University of Kentucky

Carbon nanotube bundles have been proposed as good materials for the manufacture of tailored ultrafiltration membranes due to their uniform, porous structure. In contrast to conventional membranes produced by only partially sintering a ceramic or stretching a polymer, a nanotube membrane would offer the advantages of fewer blocked pores and a narrower distribution of pore sizes. To investigate the properties of a nanotube membrane, the adsorption of simple binary fluids within single tubules and tubule bundles are modeled using atomistic simulations. Specifically, classical molecular dynamics simulations are performed using a combined many-body, reactive bond-order and Lennard-Jones potential. The results show how the diffusion of these molecules proceeds at differing rates within the nanotubes as a function of the diameter and helical structure of the tubules, the density of the fluid, the size difference between the molecules, and temperature. An example of a binary fluid that has been studied is a mixture of CH_4 and C_4H_{10} at room temperature. The simulations predict high selectivity in the diffusion of these molecules through the nanotubes. They also allow for the determination of the type of diffusion followed by each type of fluid molecule. Comparisons will be made between these simulation results and the results of similar studies in the literature of diffusion in zeolites and other molecular sieves. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

4:40pm **NT+NS+EM+MS-ThA9 Improved Tungsten Disulfide Nanotubes as Tips for Scanning Probe Microscopy***, **A. Rothschild**, G. Frey, M. Homyonfer, M. Rappaport, S.R. Cohen, R. Tenne,* Weizmann Institute of Science, Israel

Synthesis and applications of long and hollow WS_2 nanotubes are described. Although synthesis of nanotubes from various inorganic compounds have been reported, the high yields of uncontaminated nanotubes reported here represents a significant improvement over past efforts by ourselves and others.[1],[2] The nanotubes are synthesized in a two-step process the first being the creation of WO_3 nanoparticles by heating a tungsten filament in the controlled presence of water. The second step, sulfidization, resulted in a 30 times increase in the length of these particles without change in width so that nanotubes up to 10 microns in length and 20-40 nm width were formed. These tubes were attached to scanning force microscope (SFM) tips and used to image deep and sharp features inaccessible by sharp silicon tips. Due to their sandwich S-W-S structure, these nanotubes are probably stiffer than the carbon analogs and hence less prone to instabilities under such rigorous scanning conditions. We propose application of these probes for nanophotolithography, aided by the facile excitation of these compounds by visible and infra-red light. Support by the Israel Ministry of Science, Israel Science Foundation, and Applied Materials-Weizmann Foundation are gratefully acknowledged. A.R. is a recipient of the Lavoisier fellowship (France). @FootnoteText@ [1] Y. Feldman, E. Wasserman, D.J. Srolovitz, R. Tenne, Science 267, 222 (1995). [2] N.G. Chopra, et al, Science 269, 966 (1995).

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-FrM

Nanotubes: Growth, Characterization and Properties II
Moderator: R.L. Jaffe, NASA Ames Research Center

8:20am **NT+NS+EM+MS-FrM1 Gas-phase Nanotube Production at High Pressure By Disproportionation of Carbon Monoxide***, **P. Nikolaev**,* G. B. Tech Inc. / NASA - JSC*; M. Bronikowski, K. Bradley, D. Colbert, K. Smith, R.E. Smalley,* Rice University

Single-wall carbon nanotubes (SWNTs) were produced in gas phase, in a flow tube reactor in 3 - 15 atm. of CO at 850@super o@ - 1200@super o@C. Nanotube growth was catalyzed by unsupported iron particles created in-situ by decomposition of iron pentacarbonyl vapor which was added to the CO feedstock at a few ppm level. We find that low Fe(CO)@sub 5@ concentration combined with fast heating rate of feedstock gas allows us to produce very small iron particles, while high pressure increases the rate of CO disproportionation, leading to effective nucleation and growth of SWNTs. Unlike pyrolysis of hydrocarbons, CO disproportionation is a "clean" process which proceeds only on the catalyst surface, resulting in essentially no amorphous carbon overcoating. Diameter distribution of the SWNTs is rather narrow and depends on CO pressure. Higher CO pressures (10 atm.) yield smaller nanotubes, with distribution centered at 0.7 nm (which is roughly the size of C@sub 60@ molecule). Nanotube yield relative to the amount of iron catalyst increases as the heating rate and mixing of Fe(CO)@sub 5@ are enhanced, indicating better catalyst utilization. In order to further increase nanotube yield, we have designed a "shower head" injector, in which cold CO/Fe(CO)@sub 5@ feedstock enters furnace through water-cooled injector, surrounded by "shower head" carrying CO pre-heated to 1200@super o@. Nanotube yield is also increased by addition of small amount of methane, while more CH@sub 4@ results in amorphous overcoating on the nanotube surface. In contrast to previously reported SWNT production methods, this scheme constitutes a continuous flow gas phase SWNT production process. It should therefore be readily amenable to scale up for bulk SWNT production.

8:40am **NT+NS+EM+MS-FrM2 The Optical Properties of Carbon Nanotubes and Their Use in the Characterisation of Bulk SWNT Material***, **M.S. Golden**, T. Pichler, R. Friedlein, M. Knupfer, J. Fink,* IFW Dresden, Germany*; O. Jost, A.A. Gorbunov, W. Pompe,* TU Dresden, Germany

The investigation of the optical properties of carbon nanotubes,@footnote 1,2@ either using UV-Vis or electron energy loss spectroscopies, offers insight into carbon nanotubes on two levels. Firstly, analysis of the energy positions of the characteristic electronic transitions between the singularities in the density of states enables a quick and easy determination of the overall NT yield, the diameter distribution and the ratio of semiconducting-to-metallic SWNTs in bulk samples. This represents an ideal express characterisation method to accompany tuning of the nanotube preparation process parameters. Secondly, the momentum dependence of the collective excitations of the @pi@-electron system in nanotubes measured using high resolution electron energy loss spectroscopy in transmission proves to be a sensitive probe of the effective dimensionality of the electron system and inter-tube interaction, both in bulk samples of SWNT and MWNT. @FootnoteText@ @footnote 1@ T. Pichler, M. Knupfer, M. S. Golden, J. Fink, A. Rinzler, R. E. Smalley, PRL 80 4729 (1998) @footnote 2@ T. Pichler, M. Sing, M. Knupfer, M. S. Golden, J. Fink, Solid State Commun., 109, 721 (1999).

9:00am **NT+NS+EM+MS-FrM3 Li Intercalated Carbon Nanotubes Ropes***, J. Lu, J. Zhao, **A. Buldum**, B. Gao, O. Zhou,* University of North Carolina, Chapel Hill **INVITED**

The electronic and electrochemical properties of Li intercalated single-wall nanotube ropes are studied theoretically using ab initio method@footnote 1@ and experimentally in an electrochemical cell.@footnote 2@ Complete charge transfer is found between Li atoms and nanotubes. The energetic and electrochemical potential of intercalated Li atoms on both the inside and the outside of tubes are investigated. The intercalated ropes are metallic with conduction band resides on C atoms. Both theoretical and experimental studies suggest that it is possible to achieve a Li intercalation density significant larger than that in the graphite, making the Li intercalated nanoropes a promising material for battery applications. @FootnoteText@ @footnote 1@ J. Zhao, A. Buldum, J. P. Lu, to be published. @footnote 2@ B. Gao and O. Zhou, to be published.

9:40am **NT+NS+EM+MS-FrM5 Mechanical and Electronic Properties of Carbon Nanotubes Under Bending***, **L. Yang**, M.P. Anantram, J. Han, R.L. Jaffe,* NASA

Bending, buckling and even collapsing of carbon nanotubes have been more frequently observed experimentally. They could be elastic or plastic deformations, and responsible for a variety of mechanical and electronic measurements. We systematically investigate mechanical and elecronical properties of carbon nanotubes under these deformations. They are correlated with tube configuration and stress - strain relations. Some interesting observations are made. For example, electron transport can be enhanced or suppressed, depending on the configuration and deformation of a tube. We also apply the simulation results in understanding some related experimental observations.

10:00am **NT+NS+EM+MS-FrM6 Effect of Strain on Electrical Properties of Carbon Nanotubes***, **S. Paulson**, N. Snider, M.R. Falvo, A. Seeger, A. Helser, R.M. Taylor III, R. Superfine, S. Washburn,* University of North Carolina, Chapel Hill

We have used an advanced interface to an Atomic Force Microscope to apply strain to carbon nanotubes. Simultaneously, we measure the current voltage characteristics, and see how they change as a function of strain in the tube. We have applied enough strain to fracture nanotubes, causing the resistance to become infinitely large, and then reassembled the ends to form junctions. The characteristics of these junctions will be discussed, as well as other strain dependant effects.

10:20am **NT+NS+EM+MS-FrM7 Molecular Dynamics Simulation of the Thermal Conductivity of Carbon Nanotubes***, **M.A. Osman**,* NASA Ames Research Center, US*; D. Srivastava,* NASA Ames Research Center

Carbon nanotubes (CNT) have very attractive electronic, mechanical, and thermal properties. Recently, measurements of thermal conductivity in single wall CNTs showed thermal conductivity magnitudes ranging from 17.5 to 58 W/cm-K at room temperature, which are better than bulk graphite.@footnote 1@ The cylinderical symmetry of CNT leads to large thermal conductivity along the tube axis which is an improvement over the strongly anisotropic nature of thermal conductivity of graphite. Additionally, unlike graphite, CNTs can be made into ropes that can be used as heat pipes. We have investigated the thermal concutivity of single wall CNTs Using non-equilibrium molecular dynamics (MD) with Brennar potential. The results of the simulation are in good agreement with the experimental results. We will discuss the results of our simluation and report on the effects of tube diameter and chirality on the thermal conductivity. @FootnoteText@ @footnote 1@ J. Hone, M. Whitney, C. Piskoti, and A. Zettl, Phys. Rev. B59, R2514 (1999).

10:40am **NT+NS+EM+MS-FrM8 Materials Applications of Carbon Nanotubes: Hydrogen Storage and Polymer Composites***, **S.J.V. Frankland**, D.W. Brenner,* North Carolina State University

Simulations addressing two applications of carbon nanotubes will be presented. Nanotubes have been proposed as storage media for hydrogen in fuel cells. Experiments have shown that the nanotube samples contain more hydrogen than will fit densely packed into the tubules themselves. Therefore, the location of the hydrogen is in question. The Raman shift of the hydrogen may provide a useful indicator of its placement. So far, two qualitative trends have been identified with molecular dynamics simulation which should enable the distinction of internal versus intercalated hydrogen. For internal hydrogen a decreasing Raman shift is observed with increasing nanotube radius. For intercalated hydrogen, the simulations predict a broadened Raman band with relatively little dependence on nanotube radius. The second application being considered is the usage of nanotubes to strengthen polymer composites. Molecular dynamics simulations are in progress to understand the load transfer mechanism between the polymer and the nanotube.

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