Nanotubes - Science and Applications
Room 309 - Session NM+NS-MoM

Carbon Nanotubes: Functionalization and Applications

Moderator: P.M. Ajayan, Rensselaer Polytechnic Institute

8:20am **NM+NS-MoM1 Surface Interactions Used to Probe Metallic Carbon Nanotubes*, M. Dresselhaus,*** MIT **INVITED**

A brief overview will be given of the remarkable structure and properties of carbon nanotubes and how surface interactions are used for some of these studies. Carbon nanotubes are tiny structures of molecular dimensions in the form of hollow cylinders with about 20 carbon atoms around the circumference of the cylinders and microns in length. The unique electronic properties of carbon nanotubes are that they can be either semiconducting or metallic depending only on their geometry. From this, stem other remarkable and unique properties of their vibrational spectra, allowing us a means to distinguish metallic from semiconducting nanotubes in samples containing both. Interactions of the nanotubes with nanostructured metallic substrates have provided a powerful tool to gain a fundamental understanding about why the Raman spectra of metallic nanotubes are different from those for semiconducting nanotubes. Though less than a decade since their discovery, carbon nanotubes are already finding practical applications based on their unique properties.

9:00am **NM+NS-MoM3 Purification and Functionalization of Single-wall Carbon Nanotubes*, I. Chiang***, *R. Saini, J. Margrave, R. Hauge, R.E. Smalley, R. Billups,* Rice University

A purification method has been developed which leads to 99.9% pure single wall nanotubes. It combines the well-known nitric acid treatment with water reflux and a two-stage gas-phase oxidation. Air oxidation of SWNTs is correlated to the amount of metals in the samples. For sidewall fluorinated SWNTs, two distinct types of C-F bonds have been observed, ionic and covalent bonds. These 'fluorotubes' have served as precursors for further substitution on the nanotubes, such as sidewall alkylation etc. The degree of substitution is found to correlate with the extent of covalent sidewall C-F bonding.

9:20am **NM+NS-MoM4 Chemical Functionalization of Single-Walled and Multi-Walled Carbon Nanotubes through Ion Bombardment: Predictions from Molecular Dynamics Simulations Nanotubes***, B. Ni,* ***S.B. Sinott,*** The University of Kentucky

Molecular dynamics simulations have been performed to study the bombardment of single-walled and multi-walled (double and triple) nanotube bundles by CH@sub 3@@sup +@ ions at impacting energies 10, 45, and 80 eV. The reactive empirical bond order potential for hydrocarbons was used in the classical simulations.@footnote 1@ The simulations predict that there is a high probability of radical or fragment adsorption to the nanotube walls which could serve as precursors to the chemical functionalization of the nanotube walls.@footnote 2@ In addition, the simulations show that ion bombardment at 80 eV can lead to cross-linking among the single-walled nanotubes that could stabilize the bundle relative to shear. The multi-walled nanotubes are predicted to be stiffer to scattering than the single-walled nanotubes, leading to increased fragmentation of the incident ions at lower energies. The results are compared to preliminary experimental results for the ion bombardment of muli-walled nanotubes and found to be in good agreement. This work was supported by the NSF (CHE-9708049 and the NSF MRSEC at the University of Kentucky, DMR-9809686) and by the NASA Ames Research Center (NAG 2-1121). @FootnoteText@ @footnote 1@S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Brenner, in Chapter 1 of Volume IV of ADVANCES IN CLASSICAL TRAJECTORY METHODS, Molecular Dynamics of Clusters, Surfaces,Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999), pp. 1-26. @footnote 2@B. Ni and S.B. Sinnott, Physical Review B 61, 2000 (in press).

9:40am **NM+NS-MoM5 A Novel Mechanism of Hydrogen Storage in Carbon Nanotubes*, Y.H. Lee***, *S.M. Lee,* Jeonbuk National University, Korea

We have carried out systematic calculations for hydrogen adsorption and storage mechanism in the nanotubes. Hydrogen atoms first adsorb on the tube wall in an arch type and zigzag type up to a coverage of @theta@=1.0, and are stored in the capillary as a form of H@sub 2@ molecule at higher coverages. Hydrogen atoms can be stored dominantly through the tube wall by breaking the C-C midbond, %with relatively low activation barrier of 1.51 eV, while preserving the wall stability of a nanotube after complete hydrogen insertion, rather than by the capillarity effect through the ends of nanotubes. In the hydrogen extraction processes, H@sub 2@ molecule in the capillary of nanotubes first dissociates and adsorbs onto the inner wall, and is further extracted to the outer wall by the flip-out mechanism. Our calculations describe suitably an electrochemical storage process of hydrogen, which is applicable for the secondary hydrogen-battery.

10:00am **NM+NS-MoM6 Local Solvation Shell Measurement in Water using a Carbon Nanotube Probe***, S.P. Jarvis,* JRCAT-NAIR, Japan*; T. Uchihashi,* JRCAT-ATP, Japan*;* ***H. Tokumoto,*** JRCAT-NAIR, Japan

Oscillatory forces between two approaching surfaces in solvent have long been the subject of study due to their possible influence on any surface-surface interactions mediated through a liquid or in the presence of a fluid film. Of particular interest is water, due to its omnipresence in all but the most stringently controlled environments and its role as the primary medium for biological interactions. Combining a carbon nanotube probe with an AFM has enabled us to measure oscillatory forces in water on approaching a surface that has been laterally characterized on a nanometer scale. One important aspect of the utilization of carbon nanotubes as the AFM probe is to remove the unwanted hydrodynamic damping effect caused by the bulk of the tip. We used a multi-walled carbon nanotube attached to a PtIr coated silicon lever in a specially designed FE-SEM. Another aspect is the usage of a magnetically activated AFM, which has been possible to resolve molecular layers of large molecules. With this method, magnetic material is deposited directly behind an AFM tip on the back-side of the cantilever so that the tip position can be controlled by the addition of a magnetic field. The lever can be vibrated in an oscillating magnetic field in order to make dynamic measurements. This success opens up the possibility of investigating water layers under a variety of experimental conditions and as a function of precise lateral position on any surface including biological membranes and macromolecules. Among the many and varied roles of water layers are effects on biomolecular adhesion, colloid dispersion and tribology, which can now be investigated with nanometer lateral resolution.

10:20am **NM+NS-MoM7 Single Wall Nanotube Probes for Structural and Functional Imaging in Fluid*, L. Chen***, *J. Hafner, C. Cheung, C.M. Lieber,* Harvard University

Scanning force microscopy is a powerful tool for probing nanometer scale objects in fluid, ambient and vacuum environments. The contrast of SFM is based on the interaction between surface and probe which is additive over a wide spectrum of forces including Van der Waals, electrostatic and magnetic forces. Therefore, the resolution of SFM imaging greatly depends on the geometrical and mechanical properties of the probes. Carbon nanotubes make potentially ideal tips for SFM. First, carbon nanotubes can give unprecedented high resolution in structural imaging because of the intrinsic small diameters, high aspect ratio and reversible buckling. Second, carbon nanotubes can be functionalized to give chemically well-defined SFM probes, which enables functional or chemically sensitive imaging. Here we report recent progress in addressing critical issues associated with nanotube probes including the preparation of nanotube tips, structural imaging in fluid, and the functionalization of nanotube ends. Nanotube probes have been prepared by chemical vapor deposition (CVD) on commercial cantilever-probe surfaces. CVD nanotube probes have been used to image individual molecules of supercoiled DNA plasmid pBR322 on mica-fluid interface with high resolution. The relaxation of the supercoiled molecules was observed in real time in aqueous buffer solution. The chemical functionality of the nanotube end group was identified as carboxylic groups, by carrying out force titration experiments. Nanotube probes have been functionalized with synthetic oligonucleotides, and the resulting probes were capable of recognizing complementary oligonucleotide strands on surfaces. The force needed to unbind the 14 base pair duplexes was shown to be 450pN, which is in agreement with previous chemical force microscopy measurements.

10:40am **NM+NS-MoM8 Nonlinear Optical Properties of Some Polymer/Multi-walled Carbon Nanotube Composites***,* ***Z.X. Jin,*** National University of Singapore, Singapore*; X. Sun, G.Q. Xu, S.H. Goh, W. Ji,* National University of Singapore

Several polymer-coated and polymer-grafted multi-walled carbon nanotubes(MWNTs) were synthesized and characterized using TEM and HRTEM. The polymer-coated or polymer-grafted MWNTs formed stable solutions in DMF. Their nonlinear optical properties were investigated using 532 nm nanosecond laser pulses. These polymer-MWNT composites still possess strong nonlinear optical properties.

Nanotubes - Science and Applications
Room 309 - Session NM+NS-MoA

Carbon Nanotubes: Nanoelectronics and Field Emission

Moderator: S. Sinnott, University of Kentucky

2:20pm **NM+NS-MoA2 Analysis of Long-Channel Nanotube Field-Effect-Transistors (NT FETs)*, T. Yamada,*** NASA Ames Research Center

Recent experiment on carbon NT p-channel FETs with a long channel (3 µm)@footnote 1@ is analyzed theoretically. They observed saturation of drain current (I@sub d@) as a function of drain voltage (V@sub d@), which plays a crucial role in digital applications. Two possible mechanisms can make the carrier acceleration by V@sub d@ ineffective and bring about the I@sub d@ saturation: (1) Coulomb repulsion from other carriers forming a self-consistent spatial distribution, leading to channel pinch-off; (2) phonon scattering due to a large field created by V@sub d@, leading to carrier velocity saturation. Since the former causes the saturated current I@sub dsat@ to depend quadratically on gate voltage (V@sub g@) and the latter linearly, two mechanisms are distinguishable. Noticing the quadratic dependence in their measurement, we argue that the Coulomb-induced pinch-off formation was the mechanism in these long-channel NT FETs. The maximum field was about 10 kV/cm and the velocity saturation for holes still did not occur. This field is comparable to that of electrons in silicon. |I@sub d@|-V@sub g@ characteristics did not show a sharp rise at the onset of strong inversion, during the transition from accumulation to inversion, as V@sub g@ was increased. This is significantly different from the familiar behavior of metal-oxide-semiconductor FETs. In NT FETs, I@sub d@ was practically zero for a wide range V@sub g@ = 3 to 40 V beyond accumulation. We argue that a high Schottky barrier for electrons existed at the source/drain metal-semiconductor contact and the electron flow was blocked in the inverted case although the hole flow was not in the accumulated case. Making Ohmic contact to both p- and n-NTs is mandatory for complementary circuitry, and will have to be explored for future electronics. @FootnoteText@ @footnote 1@C. Zhou, J. Kong, and H. Dai, Appl. Phys. Lett. 76, 1597 (2000).

2:40pm **NM+NS-MoA3 Electrical Transport in Carbon Nanotubes*, Ph. Avouris,*** *P.G. Collins, R. Martel, H.R. Shea,* IBM T.J. Watson Research Center*; H. Stahl, J. Appenzeller,* Physikalisches Institut, Germany **INVITED**

We will discuss studies of the electronic structure and electrical transport properties of individual and ropes of single-wall (SW) and multi-wall (MW) carbon nanotubes (CNTs). Both metallic and semiconducting NTs have been investigated. In the case of metallic NTs we will present results on the observation and interpretation of negative magneto-resistance, weak localization, strong localization, anti-localization, and Coulomb blockade phenomena. In the case of semiconducting NTs, we have observed band-bending, field switching, carrier depletion and inversion phenomena. Some evidence for non-local transport at elevated temperatures in MWNTs will be discussed. In the case of SWNTs ropes we have been able to obtain results on the efficiency of inter-tube electrical transport. Finally, the operation and characteristics of model NT-based devices such as field-effect transistors, single-electron transistors and low-pass filters will be discussed.

3:20pm **NM+NS-MoA5 First Principles Study of Electronic Properties of Molecule Functionalized Carbon Nanotube*, J. Zhao*,** *A. Buldum, J.P. Lu,* University of North Carolina at Chapel Hill*; J. Han,* NASA Ames Research Center

We studied the functionalized carbon nanotubes by using first principles methods based on density functional theory (DFT). The adsorption energy and structures are studied for various molecules including: O@sub 2@, N@sub 2@, H@sub 2@O, NO@sub 2@, CO@sub 2@, NH@sub 3@, He. The electronic structures calculations show 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.

3:40pm **NM+NS-MoA6 Effect of Commensurate Contact on the Resistance Across the CNT/HOPG Interface*, S. Paulson*,** *M.R. Falvo, A. Seeger, R.M. Taylor II, S. Washburn, R. Superfine,* The University of North Carolina

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, therefor 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 (NCRR).

4:00pm **NM+NS-MoA7 Ultra-Low Bias Operation of Field Emitter using Single Wall Carbon Nanotube Directly Grown onto Silicon Tip by Thermal CVD*, K. Matsumoto,*** Electrotechnical Laboratory, Japan*; S. Kinoshita,* Meiji University, Japan*; Y. Gotoh,* Tsukuba University, Japan*; T. Uchiyama,* Advanced Technology Institute, Japan*; S. Manalis,* Massachusetts Institute of Technology*; C. Quate,* Stanford University

The new carbon nanotube field emitter with single wall carbon nanotubes of a diameter of 1~2nm which were grown directly by thermal CVD onto the Si tips and protruded from them@footnote 1@ was developed. Owing to the 10 to 20 times smaller diameter of nanotube than the conventional Si tip, the new carbon nanotube field emitter showed the ultra-low threshold bias of 10V for the field emission of electron which is more than 10~50 times smaller value than the conventional Si emitter. The n-type silicon was etched by SF@sub 6@gas to form the 10900 silicon tips . After the chemical catalyst was spin coated, the sample was set in the furnace with hydro-carbonate gas flow at high temperature. The single wall carbon nanotube then started to grow and followed up the wall of the silicon tip to the top and protruded from the silicon tip. Three kinds of spacers of 6µm, 10µm, 21µm were prepared to change the distance between the anode and the carbon nanotube emitter. When the spacer is 21µm, the electrons began to emit at the applied bias of ~25V. The narrower the spacer, the threshold bias becomes smaller. When the spacer is 6µm, the electron starts to emit at the applied bias of as small as 10V. In the Fowler-Nordheim plot, the current follows the linear lines in 4~5 orders of magnitudes even at the different spacer thickness, which means the electrons are really field emitted from the carbon nanotube through the Fowler-Nordheim tunneling. This single wall carbon nanotube field emitter could be applicable to any kind of low power consumption flat panel displays in future. @FootnoteText@ @footnote 1@ J. Kong, C. Zhou, A. Morpurgo, H. T. Soh, C. F. Quate, C. Marcus, H. Dai, Applied Physics A69, p. 305, (1999).

4:20pm **NM+NS-MoA8 Field Emission Properties of Vertically Aligned Carbon Nanotubes Dependent Upon Gas Exposures and Growth Conditions*, S.C Lim*,** *D.J. Bae, K.H. An, Y.C. Choi, H.J. Jeong, Y.H. Lee,* Jeonbuk National University, Korea

Vertically aligned carbon nanotubes have been grown with different growth conditions by microwave plasma chemical vapor deposition and thermal chemical vapor deposition. The field emission properties of such grown carbon nanotubes are studied. Carbon nanotubes under high bias voltage are exposed to hydrogen, nitrogen, and oxygen. After each exposure, changes on turn-on volatage and slpoe of Fowler-Nordheim plots are observed. The saturation region of emission current at high bias voltage has been shifted. Degradation of field emission current from hydrogen and oxygen exposures has been observed. The ratio of change of emission current shows that oxygen exposure degrades the emission current more severely.

4:40pm **NM+NS-MoA9 Study on Field Emission Mechanism of Carbon Nanotube using High-resolution Electron Microscopy*, T. Kuzumaki*,** *H. Ichinose, Y. Horiike,* The University of Tokyo, Japan

In investigation of the relation between the tip structures and the field electron emission characteristics of the nanotube, we have found that the nanotube tip is plastically deformed during cold emission. Our studies with a high-resolution transmission electron microscope reveal that the deformation occurred at the local domain containing an isolated pentagonal carbon ring in the polyhedral cap and a convexity is formed along the electric field direction. Semi-empirical molecular orbital calculations show that the pentagon and heptagon pair is introduced into the hexagonal network with a pentagonal carbon ring by heterogeneous nucleation mechanism, and the resulting convexity structure is formed at the tip. The electron emission characteristics of the closed nanotube show that the threshold voltage was high for the first run and the current increased quickly. After the second run the emission started at rather lower voltage and increased gradually. Fowler - Nordheim (F-N) plots show that the first run does not show a straight line. There is no marked change to gradient the second run. The decreasing of the threshold voltage after the second run is possibly due to the structural change of the nanotube tip. The opened nanotubes also show the notable structural change at the tip. The deformed structure can be explained by introducing sp@super 3@ - like line defects in the hexagonal carbon network. In the opened nanotube, the gradient of the F-N plots is decreasing corresponding to change of structure. The formation of the emission site contributes greatly to the stable and highly efficient electron emission from the nanotubes.

5:00pm **NM+NS-MoA10 A Carbon Nano-Tube Based Electron Gun for Electron Microscopy***, O. Zik,* El-Mul Technologies Ltd., Israel*; **J.G. Leopold,*** Dept. of Appl Phys., Rafael Labs, Israel*; D. Rosenblatt,* Rosenblatt Associates

A novel electron gun geometry is proposed with a carbon nano-tube (CNT) grown in a conducting microfabricated crater separated from a gate by an insulating layer. Electron microscopy preferably utilizes point sources. Field enhancement is responsible for the increased emitted current. The field decreases after a very short range to the free space field of the device and the beam diverges. Because the point source and the electron optics are in practice far from ideal, large angular emission density is required with apertures cropping the diverging beam. Thus, a very small portion of the emitted current is useful. Best performance for point sources is gained when the emitter is a rounded, long and very sharp whisker - a 'point on plane' geometry. Such geometry can be realized with CNT's which have exceptional electron emission properties with very low energy spread. However, due to beam divergence, bare CNT's 'on a plane' are inadequate for Scanning Electron Microscopy (SEM) and to miniature SEM's, termed 'microcolumns', in particular. The crater geometry decreases field enhancement on the tip by an order of magnitude so that increased voltage is needed. Due to the excellent field emission of CNT's this voltage is acceptably low so as to obtain about 500nA while not exceeding the breakdown limit of the insulating layer. Our computer simulations support these results. For such geometry the CNT is immersed in a gun which in itself comprises a lens aligning the beam. Almost all the emitted current can be used in a micro-column. In addition to the low energy spread inherent to CNT's, this electron gun has very high brightness which is an advantage for SEM and lithography applications.

Nanotubes - Science and Applications
Room 309 - Session NM+NS-TuM

Carbon Nanotubes: Synthesis

Moderator: D. Herr, Semiconductor Research Corporation

8:20am **NM+NS-TuM1 Orientated Nanotube Growth with Cobalt Catalyst***, **S. Shah**,* University of Illinois at Urbana-Champaign*; L. Rotkina, H. Choi,* Beckman Institute for Advanced Science and Technology*; J.W. Lyding,* University of Illinois at Urbana-Champaign

Growth of carbon nanotubes (CNTs) is an important area of research in the area of molecular nanotechnology. The full potential of these devices as a building block for nanometer scale structures has not been fully realized and therefore new processing techniques and observations could have impact on the field. This paper will focus on the main aspects of our cobalt catalyst based growth process as well as our observations of the resulting carbon nanotubes. We will then suggest some applications of this technique for the development in the area of nanometer scale research. With the purpose of observing the growth behavior on a Si(100) surface, we have grown carbon nanotubes by means of chemical vapor deposition (CVD). Two distinct types of growth orientations were observed on the surface using a cobalt based catalyst and methane gas as a source of carbon. The first is a series of catalyst islands that have nanotubes growing randomly from them. The patterning of these tubes seems to "bridge" islands of catalyst together. The second growth mechanism is cobalt silicide based, where orientation of both the silicide and carbon nanotubes, appears highly oriented. Growth of oriented CNTs on silicon is particularly important to integrate CNTs with silicon devices. From the observations stated above, we hope to demonstrate a processing technique in which we can grow and characterize nanotubes grown in a highly oriented manner. Finally, our main objective will be to integrate our fabrication techniques to form the basis for the growth of nanotubes of nanometer scale devices.

8:40am **NM+NS-TuM2 Carbon Nanotube Growth on Nanoparticle Catalyst Patterns by Chemical Vapor Deposition***, **J.W. Ward**, P.M. Ajayan, G. Ramanath,* Rensselaer Polytechnic Institute*; L. Kish, R. Vajtar,* Uppsala University, Sweden

Growing nanotubes on catalyst template patterns on flat substrates by chemical vapor deposition (CVD) is a promising approach for creating nano- and meso-scale architectures for a variety of applications such as micro- and bio- electronics devices, and skeletal reinforcements for layered composites. Here, we report the unique morphology and junction-formation potential of CVD-grown carbon nanotubes on catalyst patterns fabricated by a nanoparticle writer. Patterns of Ni, Co, and Ni-Co alloys with different average particle sizes and spatial distributions were prepared on Si substrates and exposed to methane at 1000 °C. Our results show that multiwalled carbon nanotubes grow on nanoparticles. There is a close correlation between the nanotube diameter and the catalyst particle size. The nanotubes exhibit a large number of bends and turns. In several cases, the nanotubes grow from one particle and terminate at another, thereby connecting two nanoparticles lying on the substrate. Based upon our results, we propose a phenomenological explanation for nanotube-bridging. Controlling the formation of such nanobridges could provide a basis for simultaneous selection of both nucleation and termination sites, which is an important requirement for realizing nanotube-based network architectures.

9:00am **NM+NS-TuM3 Carbon Nanotube Catalyst Optimization Using Combinatorial Methods***, **A.M. Cassell**, M. Meyyappan, S. Verma, J. Han,* NASA Ames Research Center

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) of ethylene. The catalyst precursors were composed of inorganic salt solutions of Al, Si, Fe, Co, Ni, and a removable tri-block copolymer structure-directing agent. Scanning electron microscopy (SEM) was used to rapidly screen the catalyst libraries for activity. The optimized catalysts were then employed in the growth of aligned multi-walled carbon nanotube arrays. Successful implementation of combinatorial optimization methods in the development of high yielding carbon nanotube catalysts is demonstrated, as well as useful techniques for obtaining nanotube films of various configurations.

9:20am **NM+NS-TuM4 Effects Gas Adsorption and Collisions on the Physical Properties of Single-Walled Carbon Nanotubes@footnote 1@***, **P. Eklund**,* Pennsylvania State University **INVITED**

A single-walled carbon nanotube (SWNT) can be thought of as a graphene sheet rolled into a seamless cylinder. They are usually found in bundles containing several hundred tubes, and these bundles present an ideal microporous medium accessible to small gas molecules and ions. For this reason SWNTs are expected to be a sensitive chemical sensor, as has been reported recently. Bundles of SWNTs undergo charge transfer reactions similar to graphite, and this charge transfer when large enough can be monitored by Raman scattering. Even when very weak charge transfer, or just gas collisions with tube walls occurs, electrical transport (resistivity and thermopower) is found to be a very sensitive probe of the perturbation on the nanotube. We first review the effects on the physical properties with reagents that produce large amounts of charge transfer (e.g., alkali metals and iodine), then move to results on gases suspected of weak charge transfer reactions with SWNT (i.e., NH3) and then finally to weaker perturbations caused by physisorbed gases, such as CO. Finally, the surprizingly strong effects on the resistivity and thermoelectric power from collisions of inert gas molecules (e.g., He) with the SWNT walls will be presented. @FootnoteText@@footnote 1@Work supported by the ONR and NSF.

10:00am **NM+NS-TuM6 Time-Resolved Diagnostic Investigations of Carbon Nanotube Synthesis***, **D.B. Geohegan**, A.A. Puretzky, X. Fan, M.A. Guillorn, D.C. Joy, M.L. Simpson, V.I. Merkulov, S.J. Pennycook,* Oak Ridge National Laboratory

Time-resolved imaging and spectroscopy measurements are applied in conjunction with ex situ TEM and FESEM investigations to understand the growth rate and mechanisms of carbon nanotube growth during laser vaporization synthesis inside a hot oven. Condensation times of atomic and molecular species in the plume are estimated using population densities of ground state species as measured by laser-induced fluorescence. Rayleigh scattering, induced blackbody emission, and real-time video techniques are used to measure the dynamics and annealing time of these condensed aggregates of clusters, nanoparticles, and nanotubes as they propagate inside the oven. By varying the growth time with these diagnostics, we have explored the rate and mechanism of single-wall carbon nanotube growth by laser vaporization through the use of high-resolution transmission electron microscopy and field emission scanning electron microscopy of deposits collected for various growth times. Z-contrast STEM combined with EELS is used to investigate the effects of size and composition of metal catalyst nanoparticles through the ability to compositionally profile individual catalyst nanoparticles. FESEM imaging in bright and backscatter modes is also used to provide a three-dimensional perspective of nanotube growth. We conclude that nanotube growth during the laser vaporization process occurs over seconds of time by the condensed phase conversion of nanoparticle feedstock by the metal catalyst nanoparticles. Ex situ annealing experiments of incompletely-converted, short nanotube 'seeds' are described which show that nanotube growth can occur outside the hot oven, supporting the condensed phase conversion growth mechanism. The possibility of varying the growth conditions to enable economically viable scale-up of nanotubes by this technique will be discussed. Research sponsored by the Laboratory Directed Research and Development program at Oak Ridge National Laboratory.

10:20am **NM+NS-TuM7 Growth of Well-Aligned Carbon Nanotubes on Nickel by Hot-Filament-Assisted DC Plasma Chemical Vapor Deposition in a CH@sub 4@/H@sub 2@ Plasma***, **Y. Hayashi**, T. Negishi, S. Nishino,* Kyoto Institute of Technology, Japan

Carbon nanotubes are expected for the electron emitters of a field emitter display (FED). In order to realize the FED, a growth method of carbon nanotubes perpendicularly well-aligned on a large-area substrate has to be developed. Recently it was reported that such aligned carbon nanotubes were grown on nickel by plasma-enhanced hot filament chemical vapor deposition (CVD) and microwave plasma CVD. We have succeeded to grow well-aligned carbon nanotubes in the area of 4 cm in diameter by hot-filament-assisted DC plasma (HF-DCP) CVD in the gas of CH@sub 4@/H@sub 2@. The growth method and conditions were as follows. DC voltage of -250V was applied to substrates relative to hot filaments. A luminous region was observed just above the substrates. By the optical emission spectroscopy, it was confirmed that the luminescence was derived from excited hydrogen and hydrocarbon radicals. Therefore the process is called HF-DCP CVD. Nickel substrates were heated by the filaments around 600 °C. The substrates were pretreated in pure hydrogen plasma for 15 min before the growth of carbon nanotubes in 20% CH@sub 4@/H@sub 2@ for 15 min. Well-aligned carbon nanotubes about 100 nm in diameter and about 5 microns in length were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the treated specimens. Positive ions of hydrogen, carbon and hydrocarbon are accelerated in the plasma sheath toward substrates. The sheath region of DC plasma plays important roles in the growth, while hot filaments assist the maintenance of DC plasma under such low voltage. By this method, the large-area growth of well-aligned carbon nanotubes is expected.

10:40am **NM+NS-TuM8 Modeling of HiPco Process for Carbon Nanotube Production***, **T. Gokcen**, C.E. Dateo,* Eloret Corporation, NASA Ames Research Center*; M. Meyyappan,* NASA Ames Research Center*; D.T. Colbert, K.A. Smith, R.E. Smalley,* CNST, Rice University

High-pressure carbon monoxide (HiPco) reactor, developed at Rice University, is used to produce single-walled carbon nanotubes (SWNT) from gas-phase reactions of iron carbonyl and nickel carbonyl in carbon monoxide at high pressures (10 - 100 atm). Comput ational modeling is used to better understand the HiPco process. In the present model, decomposition of the precursor, metal cluster formation and growth, and carbon nanotube growth are addressed. Decomposition of precursor molecules is necessary to init i ate metal cluster formation. The metal clusters serve as catalysts for carbon nanotube growth. Diameter of metal clusters and number of atoms in these clusters are some of the essential information for predicting carbon nanotube formation and growth, which is then modeled by Boudouard reaction (2CO ---> C(s) + CO2) with metal catalysts. The growth kinetic model is integrated with a two-dimensional axisymmetric reactor flow model to predict reactor performance.

11:00am **NM+NS-TuM9 A Gas-Phase Method for Large-scale Production of Carbon Single-walled Nanotubes***, **M.J. Bronikowski**, R.K. Bradley, P.A. Willis, D.T. Colbert, K.A. Smith, R.E. Smalley,* Rice University

We have demonstrated large-scale production of high-purity carbon single-walled nanotubes (SWNT) using a gas-phase CVD process we call the HiPCO process. SWNT grow in high-pressure (10 - 100 atm), high-temperature (700 - 1200 °C) flowing CO, on clusters of catalytic metals such as iron and nickel. The metal clusters are formed in situ: metal is added to the gas flow in the form of organometallic compounds such as Fe(CO)@sub 5@ and Ni(CO)@sub 4@. Upon heating, the organometallics decompose and the metal atoms condense into clusters of 10 - 100 atoms. These clusters serve as catalytic particles upon which SWNT nucleate and grow (in gas phase) via CO disproportionation: CO + CO -> CO@sub 2@ + C(SWNT). SWNT material of up to 99 mole-% purity has been produced at rates of up to 350 mg/hr. The dependence of the quantity and quality of SWNT material produced on parameters such as temperature, pressure, catalyst concentration, catalyst composition and the presence of various catalyst enhancers (e.g., hydrogen and sulfur) will be discussed. The HiPCO process is currently being optimized and scaled for bulk production of 10 - 100 grams/day of high-purity SWNT material.

11:20am **NM+NS-TuM10 Diameter Selective Laser Ablation Synthesis of SWNTs: from 0.8 to 1.8 nm***, **M. Kappes**,* Universitaet Karlsruhe and Forschungszentrum Karlsruhe, Germany*; S. Lebedkin,* Forschungszentrum Karlsruhe, Germany

Two-pulse Laser ablation of carbon/catalyst composite rods comprising a variety of different metal combinations has been used to generate single-walled carbon nanotubes of widely varied diameter distribution. Resulting SWNTs have been characterized by (n)IR absorption and Raman spectroscopy as well as by dynamic light scattering, SEM and NMR.

11:40am **NM+NS-TuM11 Initial Growth Study of Well-aligned Carbon Nanotubes on Fe-coated Silicon Substrate by MWCVD Process***, **C.-Y. Wen**,* National Taiwan University*; L.C. Chen,* National Taiwan University, Taiwan*; C.S. Shen, Y.F. Chen,* National Taiwan University*; K.H. Chen,* Institute of Atomic and Molecular Sciences, Taiwan

Synthesis of well-aligned carbon nanotubes (CNTs) on a large area unveils the possibility to explore their properties and applications. Many synthesis methods have been reported for the growth of CNTs. Generally, it is relatively easy to generate aligned CNTs by the CVD processes. In our study, well-aligned multi-walled CNTs have been synthesized on 70 Å iron-coated silicon substrate by microwave plasma enhanced chemical vapor deposition process, wherein methane was used as carbon source. To further investigate the growth mechanism, we adopted ex-situ microscopic observation of the CNTs grown in very short growth time of several seconds. The high-resolution SEM image shows that clusters formed at the very initial stage. As the growth time extended to 40 seconds, the back-scattering image shows that metal particles were present at the tips of CNTs while metal cones appeared in the root of CNTs. After careful Ar ion beam thinning, CNTs specimens without contamination were analyzed by high-resolution TEM. The HRTEM image indicates that the clusters were precipitated iron particles of about 10 nm in diameter and graphene layers surrounded each of them. The iron precipitation continued to form cones and part of the iron was separated and encapsulated at the tip of CNTs. The growth mechanism of CNTs could be proposed from these microscopic observations. We attempt to postulate the growth kinetics of CNTs and diffusion paths of carbon species and the catalyst iron.

Nanotubes - Science and Applications
Room Exhibit Hall C & D - Session NM-TuP
Poster Session

NM-TuP1 Growth and Purification Characteristics of Isolated and Aligned Carbon Nanotubes*, **M. Kang**, K. Ryu, Y.C. Kim,* Hanyang University, Korea*; H. Jeon,* Hanyang University, Korea, South Korea

Carbon nanotubes of the interesting applications is reported for display application, but neither industrial fabrication technology nor performance has been reported for practical display application. Therefore, we studied that carbon nanotubes (CNTs) were grown on nickel deposited glass substrates at low temperature (about 650°C) by plasma enhanced chemical vapor deposition (PECVD) method using a mixture of CH@sub 4@, NH@sub 3@, and H@sub 2@ gaseous sources. CH@sub 4@and H@sub 2@ were used as main reactant gases, and NH@sub 3@ was used as both dilution and nickel layer pretreatment source. Nickel layer with a thickness of several hundreds nm was deposited using ultra high vacuum (UHV) e-beam evaporator and pretreated with NH@sub 3@ plasma to form isolated nano size nickel island before CNTs deposition. Nickel catalyst thickness and NH@sub 3@ plasma treatment significantly affected CNTs microstructure and alignment. CNTs size was generally increased with increasing nickel thickness. Aligned@footnote 1,2@ and isolated CNTs with a typical dimension of a few hundreds nm in diameter and several @micro@m in length were observed. Post hydrogen and oxygen plasma treatments successfully eliminated carboneous impurities and nickel caps on CNTs. In this presentation, a comprehensive understanding of the effect of NH@sub 3@ plasma treatment on nickel catalyst layer and plasma purification processing will be described. We examined the properties of carbon nanotubes by SEM, XRD, Raman spectroscopy and TEM. @FootnoteText@ @footnote 1@ Synthetic Metals 108(2000) 159-163 @footnote 2@ Appl.Phys.Lett., Vol.75, No.8, 23 .

NM-TuP2 Selective Area Growth of Carbon Nanotubes on Glass Substrate*, **J.B. Yoo**, J.H. Han, H.J. Kim, W.S. Yang, J.H. Yang, C.Y. Park,* Sungkyunkwan University, Korea

Carbon nanotubes have received considerable attention because of their own unique physical properties and many of potential applications. Selective area growth of carbon nanotubes is very important for the electronic device applications such as FED, TubeFET, SET, interconnects, sensor etc. In this study, selective area growth of vertically aligned carbon nanotubes was performed on nickel-coated glass and silicon (100) with and without buffer layer at temperatures below 600°C by hot filament plasma enhanced chemical vapor deposition (HFPECVD). The effects of growth parameters on the growth and emission characteristics of carbon nanotubes were investigated and compared to planar growth. Growth mechanism of selective area growth was proposed. The morphology of nanotubes was examined by field emission scanning electron microscopy (FESEM), and the microstructure of selective area growth of carbon nanotubes was investigated by high resolution transmission electron microscopy (HRTEM).

NM-TuP3 Effects of Metal-Catalyst and Buffer Layer on Growth and Emission Properties of Carbon Nanotubes*, **J.H. Han**, H.J. Kim, W.S. Yang, J.B. Yoo, J.H. Yang, C.Y. Park,* Sungkyunkwan University, Korea*; Y.H. Song, K.S. Nam,* ETRI, Korea

Carbon nanotubes have been extensively studied because of their own unique physical properties and their potential applications such as flat panel displays and vacuum microelectronics. In practical applications, roles of metal-catalyst and buffer layer, particularly, are very important to growth and adhesion of carbon nanotubes respectively. Therefore, a systematic study for metal-catalyst and buffer layer has been so indispensable. In our experiments, we have used buffer layer such as chrome or molybdenum or titanium to improve the adhesion between metal-catalyst layer (such as nickel, cobalt, and nickel-cobalt composite) and glass substrate. We have grown the vertically aligned carbon nanotube arrays on nickel-coated glass and silicon (100) with adhesive buffer layer at temperatures below 600°C by plasma enhanced chemical vapor deposition (PECVD). In this work, a dc plasma was employed, and acetylene gas was used as a carbon source and ammonia gas was used as a catalyst and dilution gas. We examined the effect of thickness of metal-catalyst and buffer layer on the growth and emission properties of carbon nanotubes. The emission characteristics of nanotubes were evaluated in vacuum chamber using phosphor-coated anode. The morphology of nanotubes was examined by field emission scanning electron microscopy (FESEM), and the microstructures of interface between metal-catalyst and buffer layer or buffer layer and glass (or silicon) were investigated by high resolution transmission electron microscopy (HRTEM).

NM-TuP4 Emission Properties of Field Emission Triode using Carbon Nanotubes Grown on Glass Substrate*, **H.J. Kim**, J.H. Han, W.S. Yang, J.B. Yoo, Y.W. Jin, J.E. Jung, J.H. Yang, C.Y. Park,* Sungkyunkwan University, Korea*; N.S. Lee, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Carbon nanotubes are potential candidates for cold cathode field emitter because of high aspect ratio and small radii of curvature at their tips with high chemical stability, thermal conductivity, and mechanical strength. The vertical alignment of carbon nanotubes in large area is important to FED application. We have fabricated the triode for field emission display using carbon nanotube as an emission tip. First, 1.2 @micro@m thick SiN@sub x@ as an insulator was deposited on the Ni coated glass substrate with Cr buffer layer by PECVD, and 100nm thick Mo as a gate electrode was deposited by DC sputter. Carbon nanotubes were directly grown on substrate using selective area growth technique after gate opening and insulator etching using conventional lithography process. Vertically well-aligned multiwall carbon nanotubes weres grown by PEHFCVD(Plasma Enhanced Hot Filament Chemical Vapor Deposition). The carbon nanotubes were about 40nm in diameter. The emission characteristics of the fabricated carbon nanotube triode shows very low operating voltage compared to that of conventional Spindt-type FEDs. The uniformity of emission characteristics of nanotubes were evaluated in vacuum chamber using phosphor-coated anode. The morphology of nanotubes was examined by field emission scanning electron microscopy (FESEM).

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