Monday Morning, November 4, 2002

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-MoM

Nanotubes: Growth and Characterization
Moderator: S.B. Sinnott, University of Florida

8:20am **NT-MoM1 Synthesis and Applications of Vertically Aligned Carbon Nanofibers**, ***V.I. Merkulov***, *A.V. Melechko, M.A. Guillorn, D.K. Hensley, D.H. Lowndes, M.L. Simpson*, Oak Ridge National Laboratory **INVITED**

Vertically aligned carbon nanofibers (VACNFs) prepared by direct-current (dc) plasma enhanced chemical vapor deposition (PECVD) are important for various applications including electron field emitters, tips for scanning microscopy, and biological probes, among others. To date, the crucial advantage of using VACNFs is the ability to grow them deterministically, i.e. their location, height, tip and base diameters, and, to some extent, shape, orientation, and chemical composition can all be controlled, and mechanically and electrically reliable contact to the substrate can be established. We will discuss various aspects of the VACNF growth by dc PECVD including the effects of the growth parameters on the properties of resultant VACNFs, the VACNF alignment, etc. We will demonstrate significant progress toward the ability to deterministically synthesize VACNF-based carbon nanostructures in a large-scale synthesis process. In addition, phenomenological models that explain important aspects of VACNF growth will be presented. Finally, various potential applications of VACNFs will be discussed, and the possibility of large-scale fabrication of several types of devices based on individual VACNFs will be demonstrated.

9:00am **NT-MoM3 Facilitating Single-wall Nanotube Formation by Plasma Excitation**, *B. Simard*, ***C.T. Kingston***, *S. Denommee, D. Ruth*, National Research Council Canada

We have investigated the effects of laser excitation of the ablation plasma on single-wall nanotube (SWNT) formation using the laser-oven method. In the first study a high-power kilohertz YAG laser was used to thermally excite the target and ablation plasma. A sustainable production rate of 125 mg/hr of very pure SWNT material has been achieved. A second study involved the use of an argon-ion laser to electronically excite the C_2 molecule via the swan-band transition. The results with respect to nanotube yield, purity and characteristics for both studies will be presented.

9:20am **NT-MoM4 Directed Growth of Carbon Nanotubes on Anodized Aluminum Surfaces**, ***J.D. Whittaker***, *M. Housley, W. Wilson, R.C. Davis*, Brigham Young University

Aluminum oxide surfaces were prepared from 20 nm aluminum films by anodic oxidation. The anodization was performed in a solution of tartaric acid and propylene glycol yielding smooth alumina surfaces. Iron was then deposited by thermal evaporation, in varying thicknesses, to act as a catalyst. Carbon nanotubes were grown on the surface by chemical vapor deposition, and characterized using scanning electron microscopy and atomic force microscopy. We will also discuss NT growth from ordered porus alumina films. These growth methods are being developed to control the location and orientation of tubes grown on solid surfaces.

9:40am **NT-MoM5 A Novel CVD Method for Large-scale Synthesis of Carbon Nanotubes**, ***B. Simard***, *S. Denommee, Z. Yang, D. Ruth, C.T. Kingston*, National Research Council of Canada, *N. Braidy, G. Botton*, McMaster University, Canada

A novel CVD method for large scale synthesis of carbon nanotubes is demonstrated. It relies on the "in-situ" formation of metal nanoparticles into the feedstock solution, which is then vaporized from an aerosol nozzle into a furnace maintained between 800-1000 C. The nanoparticles are formed from laser vaporization of the bulk materials, either Ni/Co 50/50 or Co/Mo 50/50 directly in the feedstock. The nanoparticles are produced with a very narrow distribution of less than 1 nanometer with average size smaller than 3 nm. The technique is fully scalable. TEM of the synthesized nanotubes and the nanoparticles has been performed and the results will be shown at the meeting as well as more detailed description of the apparatus.

10:00am **NT-MoM6 Preparation, Chemical and Physical Properties of Large Area Free-Standing Carbon Nanofilms**, ***M.M. Kappes***, Universität Karlsruhe, Germany

Thin free standing films of single-walled carbon nanotubes (SWNT) were prepared by a novel ultrafiltration process. 1 cm x 1 cm films of less than 200 nm thickness can be routinely prepared for a variety of SWNT materials ranging from as-prepared to chemical derivatized (via amide coupling). Such films are particularly useful for transmission spectroscopic probes. We present results on gas-adsorption leading to changes in electronic structure. Furthermore we have investigated changes to optical properties associated with thermally induced deintercalation of SWNT bundles. Such processes may also be induced via visible laser irradiation thus allowing for spatial resolution.

10:20am **NT-MoM7 Growth of Aligned Arrays of Carbon Nanotubes from Patterned Catalyst Particles**, ***M.J. Bronikowski***, *D.S. Choi, M.E. Hoenk, R.S. Kowalczyk, F. Noca, M.E. Taylor, R.M. Williams, E.W. Wong, B.D. Hunt*, Jet Propulsion Laboratory

Carbon nanotubes (CNT) are expected to have a wide variety of uses due to their many exceptional properties. In particular, regular arrays of CNT are expected to have applications ranging from biomolecular filters to nano-scale electronics, oscillators, and signal processors. Of central importance in such applications is the ability to grow arrays of CNT with identical dimensions and tube-tube spacings. This talk will discuss our recent efforts in JPL's Microdevices Laboratory toward this goal. CNT are grown from gaseous carbon-containing precursors (hydrocarbons, CO) on substrate surfaces such as Si or SiO2 by chemical vapor deposition (CVD): CNT nucleate and grow from nanometer-size particles of catalytic metals (Fe, Ni, Mo) that have been pre-deposited on the substrate. CNT dimensions and arrangement are determined by the size and arrangement of the catalyst dots, and by the CVD growth parameters. Various methods for controllably placing catalyst particles on surfaces will be demonstrated and discussed. In particular, methods for patterning catalytic metals with nanometer precision using self-assembling thin films of block copolymers will be presented.

10:40am **NT-MoM8 Carbon Nanotube Growth for Nanomechanical Devices**, ***M.E. Hoenk***, *R.S. Kowalczyk, M.J. Bronikowski, E.W. Wong, D.S. Choi, F. Noca, R.M. Williams, M.E. Taylor, B.D. Hunt*, Jet Propulsion Laboratory, California Institute of Technology

Mechanical resonators with nanometer dimensions offer the capability for sensors and actuators to interact with materials at the molecular scale. We are developing device structures based on carbon nanotube mechanical resonators. While the unique mechanical and electronic properties of carbon nanotubes are promising for this application, the relationship between growth conditions and nanotube properties plays a major role in nanotube device development. In this paper, we will present our most recent results on the growth, processing, and characterization of carbon nanotube arrays. We have grown aligned carbon nanotube arrays over a wide range of pressures and temperatures using thermal and plasma-enhanced chemical vapor deposition. We have experimented with a variety of catalyst materials, growth conditions, and patterning techniques, and we have characterized the catalysts and nanotubes using scanning and transmission electron microscopy, Raman spectroscopy, and atomic force microscopy. We have demonstrated growth of aligned arrays of carbon nanotubes at temperatures as low as 411 C. The research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, and was jointly sponsored by the National Aeronautics and Space Administration, Office of Aerospace Technology, and the Defense Advanced Research Projects Agency, Microsystems Technology Office.

11:00am **NT-MoM9 High-resolution Transmission Electron Microscopy Study of Catalyst Metal Particle at the Tip of Carbon Nanotube**, ***T. Ikuno***, *S. Takahashi, K. Kamada, S. Ohkura, M. Katayama, T. Hirao, K. Oura*, Osaka University, Japan

Carbon nanotubes (CNTs) have been attracted much attention due to their fundamental research interest and potential applications. Control of alignement of CNT is essential for applications such as field emission display (FED), quantum wire, and field effect transistor. For FED application, to concentrate electric field at the CNT tip, vertically aligned CNT is desirable. On the other hand, lateral alignment is necessary for nanodevice application. In this study, we have performed high-resolution transmission electron microscopy (TEM) analysis focused on the metal particle at the tip of CNT to clarify correlation between growth mechanism of CNT and crystallography of metal catalyst. Specimens are randomly and vertically aligned CNTs which are synthesized on Ni (50 Å)/ Si (100) substrates by thermal chemical vapor deposition and RF-plasma CVD, respectively. From TEM observation of Ni particle at the tip, it was found that randomly CNT (bamboo-like CNT) has spherical Ni particle at the tip, and vertically CNT (multi-wall CNT) has a wedge shape with flat facets. Both particles were found to be monocrystalline. The crystalline orientations of the particles were also investigated. The axial directions of the vertically CNT are mainly parallel to the <111> and <311> direction of

Ni. From high-resolution TEM image of Ni / CNT interface, graphite layers were formed along the ridge line of Ni particle for randomly CNTs, whereas they were formed along specific planes parallel to the growth direction for vertically CNTs. On the basis of these results, we will discuss the mechanism of alignment process associated with growth front of graphite layers precipitated from the Ni particle. This work was performed with Japan Fine Ceramic Center under the Frontier Carbon Technology Project of the New Energy and Industrial Technology Development Organization.

11:20am **NT-MoM10 Nitrogenated Carbon Nanostructures Grown by Microwave Induced Hot-filament CVD Techniques**, ***D. Sarangi***, *A. Karimi*, FSB-IPMC, EPFL, Switzerland

Nitrogenated carbon nanotubes and nanostructures were grown by microwave induced hot-filament chemical vapor deposition (CVD) technique. The mixture of methane or acetylene gas with ammonia or nitrogen gas was used as feed gas. The nanostructures were gro wn on silicon substrates using iron (Fe) and nickel (Ni) as catalysts. The morphological properties of the nanotubes and nanostructures were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effect of microw a ve power and the influences of precursor gases on the structures of nanotubes were discussed. About 5 atomic percentage of nitrogen was observed as measured by electron energy loss spectroscopy (EELS). High-resolution TEM observation revealed that, wit h the increase of nitrogen concentration the outer graphane shell of the nanotube becomes more rough, retaining the crystallinity. In general, this paper will discuss the morphological properties of the carbon nanostructures with respect to the mechanical properties.

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-MoA

Nanotubes: Chemical Functionalization, Sensors
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

2:00pm **NT-MoA1 Photoenhanced Oxygen Adsorption in Carbon Nanotubes**, ***A.M. Rao***, Clemson Univeristy **INVITED**

Thermopower (TEP) measurements have been very effective for detecting trace amounts of absorbed gases in single walled carbon nanotube bundles (SWNTs). The dynamics of gas adsorption is extremely rapid with a short time constant (few seconds to hours) for achieving oxygen saturated TEP values of ~ +45 µV/K in SWNT bundles. Upon desorbing the oxygen from the sample, the TEP switches reversibly to ~ -45 µV/K. In this talk, we present TEP values in films of multiwalled carbon nanotubes (MWNTs) as a function of exposure to room air in the presence or absence of illumination from a UV lamp. The MWNT films were prepared on quartz substrates from a thermal decomposition of xylene-ferrocene mixtures at ~700 °C. In room air and room light, freshly prepared MWNT films exhibit a negative TEP value of ~ -12 µV/K that systematically changes to ~ +12 µV/K over a time period of ~ 4 months. Thus, MWNTs offer a unique opportunity to study photoinduced adsorption of gases in quasi one dimensional carbon system. Interestingly, upon UV illumination of the MWNT film in room air, the rate at which TEP sign reverses is drastically reduced to 7-10 days suggesting a photoenhanced oxidation phenomenon in carbon nanotubes. Based on our density functional calculations, we attribute this photoinduced phenomenon due to the lower energy barrier for adsorption of photogenerated singlet oxygen in the MWNT films. This work was done in collaboration with T. Savage, S. Bhattacharya, B. Sadanadan, J. Gaillard, T. M. Tritt, and Ya-Ping Sun (Clemson University), and S. Nayak (Rensselaer Polytechnic Institute). Research was supported by a grant from NASA Ames Research Center.

2:40pm **NT-MoA3 Strategies for Carbon Nanotube Functionalization**, ***S. Wong***, *S. Banerjee*, SUNY at Stony Brook

Understanding the chemistry of single-walled carbon nanotubes (SWNTs) is critical to rational manipulation of their properties. In one set of experiments, raw and oxidized SWNTs have been reacted with metal-containing molecular complexes. One of the molecular complexes studied was Vaska's compound. It has been found that Ir coordinates to these nanotubes by two distinctive pathways. With raw nanotubes, the metal attaches as if the tubes behaved as electron-deficient alkenes. With oxidized nanotubes, the reaction occurs by coordination through the increased number of oxygen atoms, forming a hexacoordinate structure around the Ir atom. Another compound analyzed was Wilkinson's complex. It has been found that the Rh metal similarly coordinates to these nanotubes through the increased number of oxygenated species. The functionalization reaction, in general, appears to significantly increase oxidized nanotube solubility in DMF (in the case of Vaska's) and in DMSO (with Wilkinson's). The derivatization process results in exfoliation of larger bundles of SWNTs and may select for the presence of distributions of smaller diameter tubes. An application has been made of this system as supports for homogeneous catalysis. In another set of experiments, oxidized SWNTs have been reacted with cadmium selenide nanocrystals (quantum dots) as well as with titanium dioxide nanocrystals to form nanoscale heterostructures, characterized by transmission electron microscopy and infrared spectroscopy. Based on the types of intermediary linking agents used, we have demonstrated a level of control over the spatial distribution of nanocrystals on these tubes. Optical data on the derivatized adducts suggest the possibility of interesting charge transfer behavior across the nanocrystal-nanotube interface.

3:00pm **NT-MoA4 The Fabrication and Characterization of Carbon Nanotube Nanoelectrode Array for Chemical/Biosensor Applications**, ***J. Li***, *R. Stevens*, NASA Ames Research Center / Eloret Corp., *H.T. Ng*, NASA Ames Research Center / SETI Institute, *L. Delzeit*, NASA Ames Research Center, *A. Cassell, C. Nguyen, B. Chen, J. Han*, NASA Ames Research Center / Eloret Corp., *M. Meyyappan*, NASA Ames Research Center

Nanoelectrode arrays are attractive electroanalytical tools with the potential to provide much higher sensitivity for chemical and biosensor applications. So far nanoelectrode arrays/ensembles were prepared by template synthesis using nanoporous membranes or nanoscale defects created in the self-assembled organic monolayers on an Au surface. We report here on a new approach to fabricate solid-state nanoelectrode array/ensemble by bottom-up scheme using well-aligned multi-walled carbon nanotube arrays on a conducting substrate. Carbon nanotubes were grown on a substrate prepatterned with metal catalysts. The density can be controlled precisely with e-beam lithography. The alignment, diameter, and length can be controlled by plasma CVD process. Dielectric material such as SiO2 was then filled into the gap between carbon nanotubes by TEOS CVD to insulate the sidewall of the carbon nanotubes as well as the conductive underlayers. This method also provides an added advantage by which the mechanical strength of the carbon nanotube array is dramatically improved. An aggressive mechanical polishing can thus be applied to planarize the surface, resulting in a flat surface with only the ends of carbon nanotubes exposed. SEM indicates that carbon nanotubes remain their integrity during these processes. AFM shows that carbon nanotubes extend out of the insulating matrix by a few nanometers due to the higher mechanical strength. The electrical properties of individual carbon nanotubes in the array are thoroughly characterized with current sensing AFM and I-V measurements. Both of metallic and semiconducting properties were observed, strongly depending on the growth conditions. Thus fabricated carbon nanotube array is essentially an ideal nanoelectrode array with graphite edge-plane like nanoelectrodes distributed in a controlled way. The electrochemical properties and the application of these nanoelectrode arrays as chemical and biosensors will be discussed.

3:20pm **NT-MoA5 Investigation on the NO2 Sensitivity Properties of Multi-Wall Carbon Nanotubes Prepared by Plasma Enhanced Chemical Vapor Deposition**, ***C. Cantalini***, University of L'Aquila, Italy, *L. Valentini, I. Armentano, J.M. Kenny*, University of Perugia, Italy, *L. Lozzi, S. Santucci*, University of L'Aquila, Italy

The special geometry and unique properties of carbon nanotubes offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and biosensors.[1-4] The effect of gas environment on the electronic properties of carbon nanotubes have recently attracted certain attentions.[5,6] In the present work multi-wall carbon nanotubes (MWNTs) deposited by plasma enhanced chemical vapor deposition have been investigated as resistive gas sensors towards NO2. The sensor design is a MWNT serpentine resistor, fabricated by photolithography defining a serpentine Si3N4 path upon silicon, and then growing MWNTs upon the Si3N4 structure. The electrical response has been measured exposing the films to NO2 (5 ppm) at different operating temperatures ranging between 50 and 250 Â°C. Upon exposure to NO2 the electrical resistance of MWNTs is found to decrease. The nanotube sensors exhibit a fast response and a substantially higher sensitivity than that of existing solid-state sensors at room temperature. Sensor reversibility is achieved by slow recovery under ambient conditions or by a higher recovery heating to 200 Â°C. Experimental findings revealed the chemisorption of oxidizer gas upon the surface of the NWNTs. Hence it appears that p-type semiconductor behavior is present in the MWNTs.

[1]Dresselhaus M S et al. 1996 Scienceof Fullenrenes and Carbon Nanotubes (New York:Academic)
[2]Ebbesen T (ed) 1997 Carbon Nanotube: Preparation andProperties (Boca Raton, FL: CRC Press)
[3]Saito R et al. 1998 PhysicsProperties of Carbon Nanotubes (New York: WorldScientific)
[4]Lu J P et al. 1998 Int. J. High Electron. Syst. 9 101
[5]Kong J et al. 2000 Science 287 622
[6]Collins P G et al. 2000 Science 287 1801 .

3:40pm **NT-MoA6 Invited Paper**, ***R. Baughman***, University of Texas at Dallas **INVITED**

4:20pm **NT-MoA8 Surface Modification of Aligned Carbon Nanotube Arrays**, ***L. Dai***, The University of Akron

The excellent optoelectronic, mechanical, and thermal properties of carbon nanotubes have made them very attractive for a wide range of potential applications. However, many applications require the growth of aligned/micropatterned carbon nanotubes, along with their surface modification. We have developed a simple pyrolytic method for large-scale production of aligned carbon nanotube arrays perpendicular to the substrate surface. We have also used photolithographic and soft-lithographic techniques for patterning the aligned carbon nanotubes with a sub-micrometer resolution. These aligned carbon nanotube arrays can be transferred onto various substrates of particular interest (e.g. polymer films for organic optoelectronic devices) in either a patterned or non-patterned fashion. The well-aligned structure further allows us not only to prepare novel aligned conducting polymer-carbon nanotube coaxial nanowires by electrochemically depositing a concentric layer of an appropriate conducting polymer onto the individual aligned carbon nanotubes, but also to develop a facile approach for modification of carbon nanotube surfaces via plasma activation followed by chemical reactions characteristic of the plasma-induced functionalities. These surface modification methods are

particularly attractive, which allow surface characteristics of the aligned carbon nanotubes to be tuned to meet specific requirements for particular applications while their alignment structure can be retained. In this talk, results from our recent work on microfabrication and chemical modification of aligned carbon nanotubes for certain device applications (e.g. biosensors) will be presented.

4:40pm **NT-MoA9 Comparing Light Gas Diffusion Rates in Carbon Nanotubes and Zeolites**, ***A.I. Skoulidas***, Carnegie Mellon University, *D. Ackerman*, *J.K. Johnson*, University of Pittsburgh, *D.S. Sholl*, Carnegie Mellon University

As in all microporous materials, the diffusion rates of molecules adsorbed in carbon nanotubes may have a large impact on the feasible applications of these materials. We have used atomistic simulations to compare the diffusion rates of H_2 and CH_4 in a range of defect-free single-walled carbon nanotubes with two silica zeolites with similar pore sizes, silicalite and ZSM-12. One advantage of comparing our results with these two zeolites is that we can validate the accuracy of our simulations against a large body of experimental data. We have used equlilibrium Molecular Dynamics and Monte Carlo methods to determine both the self diffusivity and the transport diffusivity of H2 and CH4 adsorbed as single components in carbon nanotubes. The transport diffusivity is the relevant quantity for describing macroscopic mass transfer in applications such as reversible adsorption cycles and membranes. We find that diffusion in carbon nanotubes is orders of magnitude faster than in the two zeolites over a broad range of pressure and temperature. These diffusivities are in fact among the fastest known for light gases in any environment, including bulk gas phases. This dramatic result can be understood in terms of the smoothness of the potential energy surface created by carbon nanotubes. We will discuss the implications of our results for using carbon nanotubes for highly permeable membranes.

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-TuM

Nanotubes: Electronics and Field Emission
Moderator: B. Simard, National Research Council of Canada

8:20am **NT-TuM1 Room Temperature Coulomb Diamond Characteristics in Single Electron Transistor with Position Controlled Grown Carbon Nanotube Channel**, ***K. Matsumoto***, National Institute of Advanced Industrial Science & Technology, Japan, *T. Kamimura*, Tsukuba University, Japan, *M. Maeda, K. Sakamoto, K. Kurachi*, Meiji University, Japan

Even at room temperature, the clear Coulomb diamond structures were obtained in the single electron transistor which used the position controlled grown carbon nanotube as a channel, and Coulomb energy of the device is as high as 400meV. The position contr ol of the carbon nanotube for the channel of the device was successfully achieved using the patterned chemical catalyst process without any difficulty, i.e., using the conventional photo-lithography process, 3 nm thick iron (Fe) catalyst was patterned fo r the source and drain structure on the SiO_2/Si substrate. Using the thermal CVD process, one carbon nanotube started to grow and bridged the gap between the source and drain patterned Fe catalysts. Ohmic metal was then deposited on to the source an d drain regions and on the backside of the Si substrate for the gate. The electrical properties of the device were all measured at room temperature. The device showed the large Coulomb gap of 800mV at around zero gate bias and the Coulomb energy of the de v ice is as high as 400meV that correspond to Coulomb temperature of 5000K. The Coulomb oscillation characteristics was also obtained and its modulation ratio is as high as 96~99% at the drain bias of around 20mV ~100mV even at room temperature. Five Coul omb diamond structures were obtained between the gate bias of @+ -@2V with the different structures sizes. This may come from the multi-islands formation by the residual chemical catalysts and/or the defects in the carbon nanotube. The corresponding island size is only 1nm diameter sphere. Using the position controlled grown carbon nanotube as a channel, ultra-high Coulomb energy of the single electron transistor is easily realized.

8:40am **NT-TuM2 Current Measurement with Tapping Mode AFM to Determine the Electrical Properties of Carbon Nanotubes**, ***M. Stadermann***, *J.J. Boland, M.R. Falvo, R. Superfine, S. Washburn*, University of North Carolina at Chapel Hill

Measurement of contact resistance and electronic transport properties of carbon nanotubes are typically performed with static contacts. Movable contacts provide many advantages over static contacts but difficulties arise from an inability to position the probe precisely on a nanotube, and to control the exact position of the electrical measurement due to thermal drift and piezoelectric hysteresis. The technique presented here allows characterization of the conductivity of different parts of a surface by applying a small voltage to a conductive AFM-tip and then scanning the surface in tapping mode. The resistance of the surface is determined from the current pulses flowing betwe en tip and sample whenever the tip intermittently makes contact with the surface. The advantage of this technique is that electrical and topographical data are taken simultaneously and are therefore in registry. A further advantage is the high number and density of data points taken at constant contact force during a single scan. This method is applied to map out the contact resistance of carbon nanotubes on graphite and examine the coupling between charge transfer modes along and across the tube. It is found that the contact resistance of the nanotube varies with the contact angle.

9:00am **NT-TuM3 Modeling of Gate Bias Modulation in Carbon Nanotube Field-Effect Transistors**, ***T. Yamada***, NASA Ames Research Center

The threshold voltages of a carbon nanotube (CNT) field-effect transistor (FET) are derived and compared with those of the metal-oxide-semiconductor (MOS) FETs. The CNT channel is so thin that there is no voltage drop in a CNT diameter direction perpendicular to the gate electrode plane, and this makes the CNTFET characteristics different from those in MOSFETs. The relation between the voltage and the electrochemical potentials, and the mass action law for electrons and holes are examined in the context of CNTs, and it is shown that the familiar relations are still valid because of the macroscopic number of states available in the CNTs. This situation is significantly different from that of quantum dots. Using these relations, we derive an inversion threshold voltage V_{Ti} and an accumulation threshold voltage V_{Ta} as a function of the Fermi level E_F in the CNT channel, where E_F is a measure of doping. V_{Ti} of the CNTFETs has a much stronger dependence on E_F than that of MOSFETs, while V_{Ta}s of both CNTFETs and MOSFETs depend quite weakly on E_F with the same functional form. This means that the transition from normally-off mode to normally-on mode is much sharper in CNTFETs as E_F is modulated through doping, and this property has to be taken into account in circuit design.

9:20am **NT-TuM4 Charge Imaging and Manipulation Using Carbon Nanotube Probes**, *S.-D. Tzeng, C.-L. Wu, Y.-C. You, T.T. Chen*, ***S. Gwo***, National Tsing-Hua University, Taiwan, ROC, *H. Tokumoto*, AIST, Japan

Direct imaging and manipulation of electric and magnetic domain structures (spontaneously or artificially formed) on the nanoscale has become increasingly important because of the recent developments in high-areal-density storage devices using charge-trapping, ferroelectric, or ferromagnetic materials. Electrostatic force microscopy (EFM) and magnetic force microscopy (MFM), variations of scanning force microscopy (SFM) which utilize nano-sized conducting or magnetic probes to sense the distributions of long-range forces, are two of the most widely used techniques for this purpose. To date, the major difficulty related to the long-range force imaging is to decouple the short-range interactions without degrading the lateral resolution. This problem is especially severe with the conventional micromachined EFM and MFM probes, typically consisted of a cantilever and a tip of conical or pyramidal shape. Carbon nanotubes (CNTs) are novel nanostructures which have a great potential to be used as the probing tips for the scanning probe techniques. It has been shown that CNTs are electrically conducting, mechanically robust with unprecedented elastic properties, chemically stable, and having a perfect cylindrical geometry with very large aspect ratio for imaging long-range forces. Recently, several groups have reported experimental approaches to attach a single CNT to a conventional SFM-tip. Among them, scanning electron microscope (SEM) based technique is the preferred method for preparing CNT tips with controllable tube diameters, lengths, and desired orientations. In this work, we show that CNT is an ideal tip material for "true" local probing of long-range electrostatic forces with a lateral resolution better than 5 nm. Moreover, we demonstrate that CNT tip can be used to manipulate charges on the charge-trapping media (such as Si_3N_4 thin films and Si_3N_4/SiO_2 dielectric multi-layers) with an areal density greater than 60 Gbit/in^2.

9:40am **NT-TuM5 Band Gap Engineering in Carbon Nanotubes**, ***J. Lee***, Seoul National University, *H. Kim, J. Ihm*, Seoul National University, Korea, *S.-J. Kahng*, Soongsil University, Korea, *H. Shinohara*, Nagoya University, Japan, *Y. Kuk*, Seoul National University, Korea

Carbon nanotubes have been successfully used for nanometer-sized devices such as diodes, transistors and random access memory cells. Despite these achievements, efforts to integrate these unit devices into functional systems have not yet succeeded. We report a method for constructing self-assembled, multiple quantum dots in a semiconducting carbon nanotube and demonstrate a spatial modulation of the band gap using a low-temperature scanning tunneling microscope.[1] When we imaged topographies of the semiconducting SWNTs at bias voltages of -0.8V to +1.0V, parts of the nanotubes appeared brighter than other areas, suggesting that the diameter may be greater there than at other areas or that the local electronic structure is modified by the inserted fullerene. In the dI/dV spectra, strong VHS peaks corresponding to conduction and valence band edges are clearly observed. The original band gap of about 0.5 eV is narrowed down to about 0.2 eV where the fullerene is expected to be located. There are two possible senarios to explain the observation: 1) Elastic strain can change the band gap significantly. For example, a strain of 4% in the tube axis direction can induce a gap reduction of 60% for the (15,1) tube. 2) Charge transfer from the nanotube to the metallofullerenes or the Au(111) substrate may also induce a change in the electronic structure. We have demonstrated that we can synthesize this band gap-engineered system by self-assembly instead of epitaxial growth.

[1]J. Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z.W. Wang, T. Okazaki, H. Shinohara, & Y. Kuk, Nature, 415, 1005 (2002).

10:00am **NT-TuM6 Modifying and Probing the Electrical Properties of Carbon Nanotube Devices using an Atomic Force Microscope**, ***J.-Y. Park***, *Y. Yaish, S. Rosenblatt, M. Brink, P.L. McEuen*, Cornell University

An atomic force microscope (AFM) is used to probe and modify electrical properties of nanotube devices. In one set of experiments, a metalized AFM tip in electrical contact with the nanotube is utilized as a local voltage

probe. These measurements reveal the voltage distribution along a nanotube as well as the contact resistance between the nanotube and the metal electrodes. For semiconducting nanotube field effect transistors, these measurements give important information about the bending of the semiconducting bands along the length of the tube. In other experiments, electrical pulses applied to the AFM tip are used to permanently modify the electrical properties of nanotube devices. By controlling the height and duration of the pulses, electrical breaks ("cuts") or tunneling barriers ("nicks") can be created at any point along the tube. The application of these modification techniques in combination with mechanical manipulation for the creation of more advanced device geometries will also be discussed.

10:20am **NT-TuM7 Electrostatically Focused Microfabricated Field Emission Electron Sources with Single Vertically Aligned Carbon Nanofiber Cathodes**, ***M.A. Guillorn***, Oak Ridge National Lab, *A.V. Melechko, M.D. Hale,* Univ. of Tennessee, Knoxville, *R.J. Kasica, V.I. Merkulov,* Oak Ridge National Lab, *E.D. Ellis,* Univ. of Tennessee, Knoxville, *D.K. Hensley, M.L. Simpson, L.R. Baylor, J.H. Whealton, D.H. Lowndes,* Oak Ridge National Lab

Electron beam lithography using a single beam cannot achieve acceptable throughput levels to become a viable manufacturing technology. The digital electrostatic e-beam array lithography (DEAL) concept under development at the Oak Ridge National Laboratory proposes circumventing this problem by writing simultaneously with millions of e-beams from a massively parallel and digitally programmable array of microfabricated electron sources. Such a system will require a robust field emission (FE) source of electrons capable of operation in moderate vacuum. In previous work we have shown that microfabricated FE sources using a single vertically aligned carbon nanofiber (VACNF) cathode are well suited for this application.[1] The ability to synthesize individual VACNF deterministically and incorporate them into conventional device fabrication processes distinguishes this material from other nanostructured graphitic carbon-based FE cathodes. By extending the fabrication process presented in our earlier work we have realized multi-electrode FE devices using this technology. Here we present the design, fabrication and characterization of prototype electrostatically focused FE electron sources intended for use in the DEAL system. The dc operating characteristics of these devices were investigated and fit well to the Fowler-Nordheim model of FE. The divergence of the emitted electron beam from unfocussed devices was evaluated using a microchannel plate system and found to be between 10 and 15 degrees. The effect of the focusing electrodes was analyzed using this system and shown to dramatically improve the focus of the beam. A discussion of these results along with modeling of the device behavior will be presented.

[1]M.A. Guillorn, A.V. Melechko, L.R. Baylor, E.D. Ellis, et al, Appl. Phys. Lett. 79, 3506 (2001).

10:40am **NT-TuM8 Fabrication and Electrical Characterization of Multiwalled Carbon Nanotube Field Emission Devices with Integrated Focusing Electrodes**, ***M.D. Hale***, University of Tennessee, *M.A. Guillorn, M.L. Simpson,* Oak Ridge National Laboratory and University of Tennessee, *C.L. Britton, G. Eres,* Oak Ridge National Laboratory

We report on the fabrication of field emission devices with integrated focusing electrodes that use dense films of multiwalled carbon nanotubes for the emitter material. The fabrication process used to realize these devices is completely compatible with large-scale integrated device production techniques. The current vs. voltage characteristics of these devices were examined and displayed a low turn-on voltage for initiation of electron emission. The effects of the focusing electrode on the field emission characteristics were explored along with the gain, frequency response, and output impedance of these devices. Details on the fabrication process and aspects of device performance will be discussed.

11:00am **NT-TuM9 Field Emission Properties of Nanostructures Based on Molybdenum Ternary Compounds**, ***V. Nemanic***, *M. Zumer, B. Zajec,* Institute of Surface Engineering and Optoelectronics, Slovenia, *M. Remskar, A. Mrzel, D. Mihailovic,* Jozef Stefan Institute, Slovenia

We have investigated the field emission (FE) properties of quasi one-dimensional molybdenum ternary compounds synthesized by a catalytic transport reaction. The self-assembly of tip-shaped nanofibres leads to the growth of a thin foil composed of mutually oriented bundles, below 500 nm in diameter and up to 20 micrometers in length. All FE measurements were performed in a dynamically pumped UHV system at 10^{-9} mbar base pressure. The samples were mounted on the top of metal pins positioned some mm from the aluminized luminescent screen biased as the anode. Current - voltage (I-V) measurements were performed under continuous bias conditions up to 4.5 kV where the resulting macroscopic field reached approx. 0.9 V μm^{-1}. The I-V behavior follows predominately the Fowler-Nordheim equation over the measured range. The emission current from a few sites reached a value of some ten micro amps and the emission spots of various shapes were observed. The current initially dropped, but became relatively stable even on the time scale of few hundred hours.

Tuesday Afternoon, November 5, 2002

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-TuA

Nanotubes: Mechanical Properties, NEMS
Moderator: L. Dai, College of Polymer Science and Polymer Engineering

2:00pm **NT-TuA1 Mechanics and Electrostatics of Nanotubes**, ***D.W. Brenner***, *D. Areshkin, J.D. Schall, O.A. Shenderova*, North Carolina State University **INVITED**

This talk will focus on modeling studies that have the aim of optimizing nanotube functionality in a number of applications, including nanocomposites and nanoelectromechanical (NEM) devices. The primary computational tools are a many-body bond-order potential energy function and a self-consistent hybrid density functional/tight binding scheme. The former is used for modeling structural and mechanical properties, including elastic properties of functionalized nanotubes. The latter method, which allows applied fields to be incorporated into a tight-binding Hamiltonian, is used to evaluate nanotube electrostatics and nonequilibrium electron transport. Topics to be discussed include the contribution of electrostatic interactions and nanotube polarizability to mechanical load transfer in nanotube-polymer composites, and alignment, kink formation and non-equilibrium transport in NEM devices.

[1] Funded by the Office of Naval Research and by NASA.

2:40pm **NT-TuA3 Carbon Nanotube/ Polymer Composite: Mechanical and Electrical Properties**, ***H.Z. Geng***, University of North Carolina at Chapel Hill, *B. Zheng*, Duke University, *H. Shimoda*, University of North Carolina at Chapel Hill, *J.L. Liu*, Duke University, *O. Zhou*, University of North Carolina at Chapel Hill

Carbon Nanotubes with elastic modulus ~1Tpa, and fracture strain ~5~10%, is interesting as filler for mechanical enhancement. Due to the poor dispersion and poor interfacial bonding between nanotube and polymer matrix, expected enhancement in mechanical properties by adding nanotube to polymer has by and large not been demonstrated. In this talk we present our results by using fluorinated nanotubes (F-SWNT). Differential scanning calorimetry (DSC) results show that our composite is macroscopically uniform. Tensile stress-strain curve and dynamic mechanical analysis (DMA) results show a significant enhancement of mechanical properties by adding only a few percentage of FSWNTs. Carbon black particle and carbon fiber filled polymer composites attract a lot of interest due to their Positive Temperature Coefficient (PTC) effect at percolation and therefore their potential application as temperature or current sensors. With large aspect ratio Carbon Nanotubes may offer some advantages over carbon black and carbon fiber, because percolation threshold is believed to be inverse of aspect ratio. In this talk we present our recent results on the dependence of percolation threshold on average length of nanotubes in CNT/polymer composites. Temperature effects on conductivities of composites at their percolations will also be presented.

3:00pm **NT-TuA4 Self-Aligned Mechanical Attachment of Carbon Nanotubes to Surfaces**, ***K. Bylund***, *J.D. Whittaker, D. Kitchen, M. Housley, R.C. Davis*, Brigham Young University

We have investigated self-aligned transition metal silicides and other thin film deposition based processes for the mechanical attachment of carbon nanotubes to silicon surfaces. These processes could aid in the mass production of carbon nanotube based AFM probes and NEMS devices. In each process, thin films are deposited and processed to secure nanotubes to silcon surfaces. An investigation of the efficacy of these processes has motivated fundamental research on the interaction of carbon nanotubes with transition metals and their silicides at varying temperatures. We will present the effects of the metal deposition, silicide formation, and wet chemical etching on the films and the nanotubes as observed by scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS).

3:20pm **NT-TuA5 Self-assembly of Carbon Nanotubes**, ***S.J. Oh***, *H. Shimoda, H.Z. Geng, R.J. Walker, L.E. McNeil, O. Zhou*, University of North Carolina, Chapel Hill

Self-assembly is an efficient process employed by nature to fabricate higher-level architectures of micro- and nano- objects with controlled functionality. Here we report that pre-formed individual CNTs can self assemble into macroscopically ordered films and membranes. Electron microscopy and polarized Raman spectroscopy measurements indicate orientational ordering of the CNTs in these self-assembled structures, which exhibit optical and electrical anisotropy. By controlling the functionality of the substrates, patterned CNT structures were obtained. Self-assembly of the CNTs is explained in terms of heterogeneous nucleation from a locally super-saturated suspension.

3:40pm **NT-TuA6 Fullerene Coalescence as a Junction Engineering for Nanoelectronics**, ***B.I. Yakobson***, Rice University

Relaxation and failure[1] of C or BN[2] nanotubes can be reversed in a well-defined sequence of atomic rearrangements. This process corresponds to cap-to-cap coalescence or welding of two nanotubes. Precise mechanism is revealed by topological analysis[3] and consists exclusively of number of Stone-Wales bond rotations, following the primary jump-to-contact polymerization with covalent bonding. This mechanism explains several "natural" phenomena like diameter doubling of nanotubes, coalescence of C_{60} in peapods, etc. It also generates a series of stable intermediate neck-shaped hetero-junctions with potentially useful electronic properties due to electrostatic dipoles,[4] density of states and conductance all varying along the series of emerging structures.

[1] B. I. Yakobson, Ph. Avouris, Topics Appl. Phys. 80, 287-329 (2001); Ge. G. Samsonidze, Gu. G. Samsonidze, B. I. Yakobson, Phys. Rev. Lett, 88, 065501 (2002).

[2] H. F. Bettinger, T. Dumitrica, G.E. Scuseria, B. I. Yakobson, Phys. Rev. B, 65, Rap. Comm,, 041406 (2002).

[3] Y. Zhao, B. I. Yakobson, R. E. Smalley, Phys. Rev. Lett., 88, 185501 (2002).

[4] T. Dumitrica, C. Landis, B. I. Yakobson, Chem. Phys. Lett. (submitted).

4:00pm **NT-TuA7 Synthesis and Properties of Plasma-polymerized Polypyrrole / Au Nanotube Composite Structures**, ***J. Zhou***, *E.R. Fisher*, Colorado State University

Composite nanostructures have a wide variety of potential applications in microelectronics, chemical sensors, and electrochemical energy production. Here, we report the synthesis of composite plasma-polymerized polypyrrole (PPPy)/Au nanotubes. The characteristics of both the PPPy films and the nanostructured composites have been investigated using FTIR, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and SEM. The gas phase species in the plasma have been investigated with mass spectrometry. The properties of PPPy films mostly depend on the applied plasma parameters, with both ring-opening reactions and the polymerization of pyrrole taking place simultaneously in the plasma. Decreasing the applied plasma power favors the retention of the rings of the pyrrole monomer. Mass spectra suggest that the plasma polymerization of pyrrole takes place on the substrate surface due to the diffusion of radicals produced in the plasma. In addition, thermal treatment after polymerization has been shown to enhance the conductivity of PPPy films. Thermally treated PPPy films can be partially oxidized or reduced electrochemically due to the exchange between cations and anions of PPPy films. From SEM analysis, it is apparent that reconstruction of PPPy films occurs after thermal treatment. However, non-thermally treated PPPy films coated on Au nanotubes demonstrate well-defined redox reversible peaks as results of the increasing of the interface areas between the surface of the PPPy films and electrolyte solution. The implications of these results for potential devices will also be presented.

Nanotubes: Science and Applications Topical Conference
Room: Exhibit Hall B2 - Session NT-TuP

Poster Session

NT-TuP1 Vertically Aligned Carbon Nanotubulated Fibers Grown by Microwave Plasma-Enhanced Chemical Vapor Deposition, *M. Hiramatsu, **K. Ito**, K. Kato,* Meijo University, Japan, *C.H. Lau, J.S. Foord*, University of Oxford, UK

Carbon nanotubes have attracted attention for several applications because of their unique properties such as high field electron emission capability and capacity for the storage of large amount of hydrogen. Carbon nanotubes with different structure and morphology can now be fabricated with several techniques. In the present work, carbon nanotubulated fibers were grown by microwave plasma-enhanced chemical vapor deposition (MWPCVD). These carbon nanotubulated fibers were in the form of the bundles of carbon nanotubes and were aligned perpendicular to the substrate. A mixture of methane and hydrogen was used as a carbon source gas. The applied microwave power and the pressure during the growth were 400-500 W and 25-30 Torr, respectively. The growth experiments were carried out for 5 - 15 min at a substrate temperature of 600 °C or less. The vertically aligned carbon nanotubulated fibers were grown selectively on a patterned Ni thin layer as a metal catalyst prepared on the silicon (100) substrate by electron beam evaporation. The diameters of the grown nanotubulated fibers were approximately 100 nm. Raman spectra for the carbon nanotubulated fibers fabricated were recorded, and the graphitised structure was clearly confirmed from the sharp G-line peak located at 1600 cm^{-1}. The field electron emission characteristics for the vertically aligned carbon nanotubulated fibers were investigated. The onset field of the field electron emission for the carbon nanotubulated fibers was 10 V/μm.

NT-TuP2 STM Investigation of Oxygen Adsorption on Carbon Nanotubes, ***S. Santucci**, L. Lozzi, M. Simeoni, M. Passacantando,* INFM and University of L'Aquila, Italy, *L. Valentini, I. Armentani, J.M. Kenny*, University of Perugia, Italy

Carbon nanotubes, thanks to their electronic and structural properties, are studied for many important applications. One recently interesting application is the gas sensing. In fact it has been shown that the electrical conductance of single-walled carbon nanotubes (SWNTs) can be drammaticaly changed upon exposure to gaseous molecules such as NO2, NH3[1]or O2.[2] These molecules can be adsorbed both at the nanotube surface or can be accepted inside the nanotube.[3] In this work we will present STM/STS data acquired onto multi-walled carbon nanotubes (MWNTs) during the exposure to O2 molecules. The MWNT films have been deposited by plasma enhanced chemical vapor deposition (PECVD) using Ni as catalyst particles on silicon. These samples have been exposed to O2, keeping the sample at different temperatures, in order to simulate the gas sensing processes (adsorption/desorption). The adsorption of O2 determines the variation of STS curves, showing the presence of new states, both filled and empty ones, which can be assigned to the interaction between molecules and MWNTs. These states also depend on the sample temperature, in particular the empty ones. The desorption process has been also followed, showing the missing of the oxygen-MWNT states when oxygen is removed from the STM chamber.

[1] J.Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Science 287 (2000) 622.
[2] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Science 287 (2000) 1801.
[3] A. Fujiwara, K. Ishii, H. suematsu, H. Kataura, Y. Maniwa, S. Sizuki, Y. Achiba, Chem. Phys. Lett. 336 (2001) 205. .

NT-TuP3 Synthesis of Single-walled Carbon Nanotubes on Thin Film Catalysts via Chemical Vapor Deposition, ***Y.J. Yoon**, J.C. Bae, H.K. Baik,* Yonsei University, Korea, *S.J. Lee,* Kyungsung University, Korea, *K.M. Song*, Konkuk University, Korea

Synthesis of single-walled carbon nanotubes (SWNTs) via chemical vapor deposition (CVD) has attracted notable attentions due to its low reaction temperature, compared to other processes. It enables SWNTs to be easily applied to electronic devices such as transistors, and chemical sensors. Recently, many researchers have been reported the synthesis of SWNTs on powder supports via CVD. However, synthetic method of SWNTs on flat Si substrates via CVD is not fully established due to the difficulty of catalyst control. The main issue of SWNT synthesis via CVD is the optimization of catalyst preparation. In this paper, to improve a yield and selectivity of SWNTs on patterned Si substrate, the optimization of catalyst was progressed by thermodynamic approaching. Catalysts were prepared by thin film deposition (Co, Ni, Fe, Mo and their alloys) on silicon substrate using D.C. magnetron sputtering system with an accurate thickness controller in angstrom scale. SWNTs were grown by catalytic decomposition of methane and hydrogen gas at the temperature range between 700°C and 1000°C. In order to investigate the formation mechanism of SWNTs, the characterization of nanoparticles and SWNTs by SEM, TEM, and Raman was performed. The nucleation and growth step for SWNTs on various catalysts will be presented by thermodynamic approaching.

NT-TuP4 Experimental and Theoretical Studies on the Gas Adsorption of Multi Walled Carbon Nanotubes Thin Films, ***S. Picozzi**, L. Lozzi, S. Santucci,* INFM, Univ. L'Aquila, Italy, *L. Valentini, I. Armentano, J.M. Kenny,* Univ. Perugia, Italy, *A. Pecchia, A. Di Carlo, P. Lugli*, Univ. Tor Vergata, Italy, *B. Delley*, Paul Scherrer Institut, Switzerland

The special geometry and unique properties of carbon nanotubes (CNT) offer relevant potential applications.[1] In particular, the effects of environment gases (such as O2, NO2, NH3) on the electronic and transport properties of carbon nanotubes have recently attracted great interests.[2,3] To date, the reported theoretical gas sensing studies have been based either on isolated single wall carbon nanotubes (SWNTs) or on SWNT mats. In the present work multi-wall carbon nanotubes (MWNTs) deposited by plasma enhanced chemical vapor deposition have been investigated as resistive gas sensors towards NO2. Experimental findings revealed the chemisorption of oxidizer gas upon the surface of the MWNTs, suggesting that p-type semiconductor behavior is present. The possibility of modulating the electronic properties of nanotubes using adsorption of gas molecules is investigated using first-principles density functional calculations. Transport characteristics are calculated using non-equilibrium Green's functions. The simulations account for the reaction dynamics between the CNT and the adsorbing gas,thus allowing the determination of the preferred adsorption site as well as the calculation of the current flowing along the nanotube as a function of time. The charge transport is dominated by the hopping mechanism across a bundle of several nanotubes. For this reason the influence that the adsorbed molecules have on the hopping rate between adjacent nanotubes has been also investigated. The results elucidate the mechanisms of adsorption and doping of CNTs and its influence on their conduction properties.

[1] M.S.Dresselhaus, G. Dresselhaus and P.C.Eklund, "Science of Fullerenes and Carbon Nanotubes" (Academic, New York, 1996).
[2] J. Kong, N.R. Franklin, C. Zhou, M.G.Chapline, S. Peng, K. Cho and H. Dai, Science 287, 622 (2000).
[3] P.G. Collins, K. Bradley, M. Ishigami and A. Zettl, Science 287, 1801 (2000).

NT-TuP5 Synthesis of Single-walled Carbon Nanotubes without Metal Catalysts by Arc Discharge, ***J.C. Bae**, Y.J. Yoon, H.K. Baik*, Yonsei University, Korea

Since single-walled carbon nanotubes (SWNTs) were discovered, great effort to control the nucleation and growth of SWNTs by selecting the metal catalysts, working pressure, ambient temperature, and feeding methods of carbons. Models proposed for nucleation and growth of SWNTs usually start from the carbon-metal gas phase or carbon-metal cluster. In other words, metal catalysts were believed to be necessary for the formation of SWNTs. In recent, new the technique for the formation SWNTs was reported. This technique did not require a metal catalyst and use as precursor amorphous carbon nano-sized particles generated by laser-induced chemical vapor deposition. In other words, the proper precursors are necessary for the formation of SWNTs, and metal catalysts are not. In arc discharge method, hemispherical fullerenes, which play a role in nucleation of carbon nanotubes, were easily formed in inert ambient. In addition, in case of CVD method flux control of carbon is key factor to determine which type of carbon nanotubes are formed. It indicates that SWNTs can be synthesized without metal catalysts by flux control of carbon in arc discharge. In this work, three types carbon anode were used to control the carbon flux. One was graphite rod (6mm diameter, 70 mm length), another was graphite rod (6mm diameter, 70 mm length) in which a hole (3 mm diameter, 50 mm deep) is drilled, and third was graphite rod (6mm diameter, 70 mm length) in which a hole (3 mm diameter, 50 mm deep) is drilled and filled with pure graphite powders. SWNTs were collected from round the cathode.

NT-TuP6 Field Emission Properties of Nanostructures Based on Molybdenum Ternary Compounds versus Carbon Single Wall Nanotubes, ***M. Zumer**, V. Nemanic, B. Zajec,* Institute of Surface Engineering and Optoelectronics (ITPO), Slovenia, *M. Remskar, A. Mrzel, D. Mihailovic*, Jozef Stefan Institute, Slovenia

As the single wall carbon nanotubes (SWCNT) were recognized as stable emitters for various electron devices, the performance of any new material

is well introduced when tested in comparison to them. From several reports on field emission (FE) measurements, it is difficult to eliminate all the experimental parameters that may influence the results. On a short term time scale, the characterization may be presented by the Fowler - Nordheim plot, while the long term behavior can only be presented by real measuring results. We have investigated the FE properties of quasi one-dimensional molybdenum ternary compounds. They were synthesized by a catalytic transport reaction and characterized by conventional microscopic methods. The results of FE measurements were compared to those obtained on commercially available purified SWCNT at identical experimental conditions. All FE measurements were performed in an UHV system at 10^{-9} mbar base pressure. The samples were mounted on the top of metal pins positioned some mm from the aluminized luminescent screen biased as the anode. Current - voltage (I-V) measurements were performed under continuous bias conditions up to 4.5 kV where the resulting macroscopic field reached approx. 0.9 V μm^{-1}. The emission current from a few sites reached a value of some ten micro amps in both cases. The current variation with time was related to onset and disappearance of emission spots of various shapes. The average current initially dropped, but became relatively stable even on the time scale of a few hundred hours for both FE materials studied.

Plasma Science
Room: C-103 - Session PS+NT-WeM

Plasma Science and Technology for Nanostructures
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

8:20am **PS+NT-WeM1 Plasma Enhanced Chemical Vapor Deposition of a Dense SiO_2 Cap Layer on Low-k Nanostructured Porous Silica**, ***Y.B. Jiang***, *N. Liu, C.J. Brinker, J.L. Cecchi*, University of New Mexico

Surfactant-templated self-assembled nanostructured porous silica is a promising material for low-k interlevel dielectrics (ILDs) in integrated circuits. With mono-dispersed pore sizes as small as 2 nm and an ordered pore structure, nanoporous silica has excellent mechanical and thermal properties, even at porosities high enough for k values of 2 and below. For ILD applications, the pores must be capped to prevent adsorption on pore surfaces during subsequent processing, such as the deposition of a copper diffusion barrier. In this work, we report on a process for capping nanoporous silica with a dense-but-thin SiO_2 layer that acts as a diffusion barrier without significantly increasing the overall dielectric constant of the ILD. Nanoporous silica was deposited on a silicon wafer by spin coating with a sol-gel solution. After spin coating, the films were solidified by heating. The pore surfaces were rendered hydrophobic by soaking the films in a 6% HMDS solution, which terminated the pore surfaces with methyl groups. An SiO_2 cap layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) in an inductively-coupled plasma reactor, using a SiH_4/O_2/Ar gas feed mixture. RF power, total pressure, gas composition, and flow rate were varied systematically to produce a high-density film with low surface roughness. The corresponding deposition rate resulted in 50 nm-thick films in approximately 15 minutes. N_2 absorption measurements performed with a surface acoustic wave (SAW) technique indicate a reduction of more 10 between the capped and the uncapped nanoporous film. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements both confirm that the pore structure in the nanoporous silica is unchanged by the capping process. Fourier transform infrared (FTIR) detection of methyl groups shows that the hydrophobicity of the nanoporous silica remains after the dense SiO_2 cap layer is deposited.

8:40am **PS+NT-WeM2 RIE processes of Formation of Nanometer-Scale Dot Arrays**, ***Y. Zhang***, *K.W. Guarini, E. Sikorski, C.T. Black, T.J. Dalton*, IBM T.J. Watson Research Center

Nanometer scale structures are increasingly merging into microelectronics and other applications. One of the challenges of fabricating nanometer scale structures is the simultaneous scaling of vertical and horizontal features. As the horizontal feature scale shrinks down to nanometer sizes, the vertical scale often shrinks at a faster rate. When using these materials for masking layers, this leads to new challenges in fabricating multi-layer nanometer scale structures for a variety of microelectronics applications. In this paper, we explore the challenges of plasma RIE processing to fabricate densely-spaced, uniformly-sized nanometer-scale dot arrays over large wafer areas based on self-organizing diblock copolymers. High selectivties among variety materials, precise CD control, real time process monitoring, and flexible and uniform plasma processing conditions are necessary for fabricating nano-scale structures with high aspect ratios (AR), e.g., ~ 20nm polysilicon hole or column arrays with AR > 15:1. The results show the versatility of RIE process techniques through examples of dot arrays formed of conducting, insulating, and polymeric materials. These fabrication processes vary in complexity, utility, and degree of optimization, and we discuss the relative merits of each. The ability to create uniform nanoscale features below lithographic resolution limits may enable key applications in fields such as magnetic recording and microelectronics.

9:00am **PS+NT-WeM3 Efficient Production of Single-Wall Carbon Nanotubes by Means of the Gravity-free Gas Arc Dischargee**, ***T. Mieno***, Shizuoka University, Japan, *M. Kanai*, University of London, UK, *H Shinohara*, Nagoya University, Japan **INVITED**

Single-wall carbon-nanotube (SWNT) are attracting much attention by their unique structures and properties, and applications of nanotubes are demonstrated as a cold electron emitter, strong wire, electronic devices and hydrogen absorber. The SWNT are produced by the gas-arc method as same as the fullerene production method. A carbon anode mixed with metal catalyst is arc sublimated in He gas (p> 40 kPa), and high density carbon particles deposit on metal particles in hot gas atmosphere making nano-pipe structures, diameter of which is about 1 nm. As these nanotubes, metal particles and another carbon clusters are flown up by the heat convection, the reaction time is limited by this heat convection. If the heat convection is suppressed by the gravity-free condition, diffusion speed of these particles is suppressed and longer reaction time can be expected.[1] In order to examine this gravity effect, the 12m-high vertical swing tower[1] is used and the carbon nanotubes are produced in the gravity-free condition.[2] Integrated gravity-free sublimation time is about 14 min. After the discharge, the carbon soot is collected and its weight is measured. As a result, production rate of the carbon soot including SWNT about 7 times increase in the gravity-free condition compared with that of the normal gravity condition. By the TEM (microscope method) their morphology is observed and more (about 2 times) dense bundle of SWNT is confirmed in the gravity-free condition. Thickness of the produced nanotube is measured by the Raman scattering method, and fatter nanotube (mainly d= 1.4 nm) is produced in the gravity-free condition compared with the normal-gravity case.

[1] T. Mieno, Jpn. J. Appl. Phys. 37 (1998) L761.
[2] M. Kanai, T. Mieno, H. Shinohara et al, Appl. Phys. Lett. 79 (2001) 2967.

9:40am **PS+NT-WeM5 Patterned Growth of Vertically Aligned Carbon Nanofibers using a High Density Plasma Enhanced Chemical Vapor Deposition Process**, ***J.B.O. Caughman***, *L.R. Baylor, M.A. Guillorn, V.I. Merkulov, D.H. Lowndes*, Oak Ridge National Laboratory

Patterned arrays of vertically aligned carbon nanofibers (VACNFs) have been grown using a high density plasma enhanced chemical vapor deposition process. The nanofibers are grown from a nickel catalyst that can be patterned to form arrays of individual isolated electron emitters. Forests of nanofibers, as well as single isolated nanofibers have been grown. An inductively coupled plasma source is used to grow the fibers. The plasma source operates at 13.56 MHz and couples power via a flat spiral coil. The plasma is composed of hydrogen and either acetylene or methane. The VACNFs are grown on a heated substrate located downstream from the ionization zone. Typical growth temperature is 700 degrees C. The energy of the ions impacting the growth surface is controlled by radio frequency bias, with typical self-bias voltages of between -50 and -300 volts. Plasma conditions are related to growth results by comparing optical emission from the plasma to the physical structure and electron emission from the nanofibers. For example, as the acetylene flow increases, the optical emission from the plasma indicates a decrease in atomic hydrogen production and an increase in molecular carbon production. The decrease in atomic hydrogen production results in a decrease in the chemical etching component during nanofiber growth. Plasmas that contain a high hydrogen to carbon ratio result in fairly narrow nanofibers, while plasmas with a high carbon to hydrogen ratio result in nanofibers with a broader base with more of a cone-like structure. The threshold electric field from isolated emitters has been measured and is typically 30-50 volts/micron and can vary with growth conditions. The relationship between plasma conditions and growth results/performance will be presented.[1]

[1]Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

10:00am **PS+NT-WeM6 Carbon Nanotubes by ICP-CVD: Growth, Characterization, Plasma Diagnostics, and Modeling**, ***D.B. Hash***, *L. Delzeit, K. Matthews*, NASA Ames Research Center, *B.A. Cruden*, Eloret Corporation, *M. Meyyappan*, NASA Ames Research Center

Applications in field emitter devices, electrode and sensor development require a very high degree of vertical orientation of carbon nanotubes (CNTs) on the substrate. This is not possible using thermal CVD. The inherent electric field in a direction normal to the substrate in a plasma process enables achievement of vertical orientation of the nanotubes. We have built an ICP reactor and grown multiwalled carbon nanotubes (MWNTs) from hydrocarbon feedstock (CH_4, C_2H_2, and C_2H_4) diluted with hydrogen. The MWNTs have been characterized using SEM, HRTEM, and Raman scattering. The MWNTs are highly aligned and suitable for the applications mentioned above. Results as a function of pressure, substrate power, and temperature will be discussed. To understand the effects of process parameters on growth as well as mechanisms - including identification of species responsible for nanotube growth, we have undertaken a 2-D plasma modeling of the process. Modeling results are compared with plasma diagnostics using optical emission spectroscopy, UV Absorption, and Residual Gas Analysis (RGA).

10:20am **PS+NT-WeM7 Zinc Oxide Nanowires Grown by Plasma Assisted Chemical Vapor Deposition**, ***J.B. Baxter***, *E.S. Aydil*, University of California, Santa Barbara

Zinc Oxide is a wide band gap semiconductor (Eg=3.37eV) that can exhibit visible and UV luminescence, piezoelectricity, and high conductivity. ZnO nanowires and hexagonal columns have been grown using plasma assisted chemical vapor deposition, using either metallic zinc or metalorganic

precursors. Nanowire growth is catalyzed by monodisperse gold nanoparticles (20 nm diameter) dispersed on a substrate from a colloidal solution. Transmission electron microscopy and electron diffraction show that single crystal ZnO nanowires grow from the gold particles in the <0001> direction. The nanowires have monodisperse diameters determined by the diameter of the gold particles (~ 20nm), and can grow to several microns in length. Energy dispersive x-ray spectroscopy confirms that the wires have a Zn:O ratio of 1:1. ZnO columns were formed by subliming metallic zinc in oxygen plasma, with the columns growing in the <0001> direction from the zinc surface. The columns are several 100 nm in diameter and are hexagonally faceted. Cathodoluminescence results show that both wires and columns emit photons upon excitation by electrons, with the columns emitting most light through the top face. This suggests that ZnO nanowires act as light pipes by internally reflecting the emitted light, making them good candidates for UV lasing. Because the gold particles from which the wires grow can be closely packed, the wires can be grown on a substrate in very dense, high surface area arrays. This property suggests that ZnO nanowires are also ideally suited toward application as the mesoporous semiconductor in dye sensitized (Gratzel) solar cells.

Authors Index

Bold page numbers indicate the presenter