Nanotubes
Room Hall A-C - Session NT-WeP
Poster Session

NT-WeP1 Reactor Design Considerations in the Hot Filament/DC Plasma Synthesis of Carbon Nanotubes/Nanofibers, ***B.A. Cruden**, A.M. Cassell, Q. Ye,* Eloret Corporation/NASA Ames Research Center*; M. Meyyappan,* NASA Ames Research Center

A combined hot filament/DC plasma approach to chemical vapor deposition (CVD) of carbon nanofibers (CNFs) has been explored. As a part of the study, the impact of filament usage and substrate holder design has been examined by SEM imaging of deposition products and monitoring of downstream products by residual gas analysis (RGA). It is demonstrated that the filament wire is important only in the pre-treatment of the substrate, where ammonia is dissociated and reacts with the substrate surface, improving CNF growth quality. However, the filament has no apparent impact when combined with the DC plasma, as demonstrated by RGA analysis of the plasma chemistry and the resultant films. The substrate holder is modified by introducing a graphite spacer into the electrode. By varying the size of the spacer, the effective surface.

NT-WeP2 Large-Area Growth of Aligned Carbon Nanotubes by Hot-Filament Assisted DC Plasma CVD, ***K. Ueda**, T. Negishi, Y. Hayashi, S. Nishino,* Kyoto Institute of Technology, Japan

Hot-filament assisted dc plasma chemical vapor deposition (HF/DC-PCVD),@footnote 1@ in which a plasma is generated between the anode of hot-filaments and the cathode of a substrate, was developed to grow carbon nanotubes in a large-scale. Carbon nanotubes are expected to be used for the field emitters of a field emission display (FED) because their high aspect ratio and small radius of curvature lead to large electric-field enhancement at their tips resulting in low operating voltage for electron emission. However the method of large area growth of vertically aligned carbon nanotubes should be developed to be applied to field emitters of FED. We have succeeded to grow well-aligned carbon nanotubes on an iron substrate of 5 X 5 cm@super 2@ in a CH@sub 4@/H@sub 2@ DC plasma at 2.7KPa (20Torr) by HF/DC-PCVD. In this process, the plasma sheath plays an important role for the growth of vertically aligned carbon nanotubes. The sheath was formed all over the substrate with uniform thickness, i.e., uniform electric field strength, when three hot-filaments spaced 5mm were stretched parallel to the substrate. In order to grow well-aligned carbon nanotubes on a larger substrate, we generated plasma above a substrate of 10 X 10 cm@super 2@ at 1.35KPa (10Torr) using three hot-filaments spaced 15mm. Therefore the large-area growth of well aligned carbon nanotubes on a 10 X 10 cm@super 2@ substrate is expected. @FootnoteText@ @footnote 1@Y.Hayashi, T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19(2001) 1796.

NT-WeP3 Carbon Nitride Nanostructures Prepared by Surface Treatments, ***J.H. Hong**, S.H. Kim, S. Lee, Y.B. Hahn,* Chonbuk National University, Korea

Nano-dots and nano-stripes of carbon nitride (CNX) were fabricated by surface treatment. Amorphous CNX thin films grown on Si (100) wafer by plasma enhanced chemical vapor deposition at room temperature were first treated by H2 plasma and then annealed at 200-300@degree@. The effects of surface treatments on chemical and structural properties of the films were investigated by Auger electron spectroscopy (AES), Fourier transform infrared sprectra(FT-IR). Well-defined nano-dots and nano-stripes were formed depending on temperature and treatment time. This was attributed to recombination of adatoms and rearrangement of film structure caused by surface energy change between the film and the substrate. The AES showed that the composition of the film is 90 at.% C and 9 at.% N. The FT-IR spectra showed the presence of C-N peak at 1260 cm-1 and C=N peak at 1640-1670 cm-1, respectively.

NT-WeP5 Preparation of Self-Assembled Carbon Nano-Ropes and Carbon Nanotubes Using Microwave Plasma-Enhanced Chemical Vapor Deposition@footnote 1@, ***M. Taniguchi**, M. Hiramatsu, Y. Ando,* Meijo University, Japan*; M. Hori,* Nagoya University, Japan

Carbon nano-structures such as carbon nanotubes, nanofibers and nanocrystalline diamond films are of tremendous interest from both a fundamental and an applied prospective. From the point of view of their wide applications, it is desirable to control properties such as the size, shape, and growth direction of surface structures during the growth. Carbon nano-structures with different structure and morphology can now be fabricated using several techniques. Among various techniques used for the growth of carbon nano-structures, plasma-enhanced chemical vapor deposition (PCVD) has gained considerable importance for the industrial application due to its feasibility and potentiality for large-area production with reasonable growth rates. In this work, aligned carbon nano-structures were grown using a conventional microwave plasma-enhanced chemical vapor deposition (MWPCVD) with a 1.5-kW microwave generator. A mixture of acetylene and hydrogen was used as a carbon source gas. The applied microwave power and the pressure during the growth were 400-1200 W and 25-80 Torr, respectively. The growth experiments were carried out for 1-15 min at substrate temperatures ranging from 500 to 800 °C. The morphologies of the grown carbon nano-structures depended strongly on the growth temperature. Vertically aligned, self-assembled, stranded carbon nano-fibers (carbon nano-ropes) were grown at relatively low temperature of about 500 °C. On the other hand, carbon nanotubes were grown on the catalyzed Si substrate at the temperature of about 800 °C. The field emission characteristics for the aligned carbon nano-structures were investigated. @FootnoteText@ @footnote 1@This work was supported by 21st century COE program, Nano Factory.

NT-WeP6 Synthesis of Multi-walled Carbon Nanotubes by CVD using Methane and Acetylene, ***S.A. Moshkalyov**,* UNICAMP, Brazil*; C. Reyes-Betanzo,* INAOE, Mexico*; A.C.S. Ramos, J.L. Gonçalves, J.W. Swart,* UNICAMP, Brazil

For the CNTs growth, a number of methods was developed, including different versions of chemical vapor deposition (CVD). CVD methods have certain advantages over other ones as they provide a way for controlled, directional growth of both single-walled and multi-walled CNTs. Here, results of CNTs synthesis using two different catalytic CVD techniques (plasma-enhanced low-pressure CVD and atmospheric-pressure thermal CVD) are presented. Thin Ni films (1-40 nm thick) were used as a catalyst material. For the film deposition, electron-beam thermal deposition was employed. Then, the films were thermally treated (~700 C) in a nitrogen atmosphere to provide formation of separate catalyst nanoparticles. As substrates, Si wafers were used previously covered by thin (50 nm) oxide films. CTNs synthesis was realized in two different reactors. The first one uses a low-pressure microwave plasma source, with low-pressure (~1Torr) nitrogen-acetylene gas mixtures. Samples are heated up to 700 C by a halogen lamp heater. In the second reactor, the flowing gas mixture and samples are heated in a resistive heating furnace to temperatures up to 900 C. Atmospheric pressure methane-hydrogen based mixtures were used in this case. After synthesis, the samples were examined using high-resolution scanning electron microscopes. The first results obtained here have shown fast CNT growth in both reactors. The process appears to depends critically on the catalyst thickness. For thin catalyst films, it was possible to grow long (randomly oriented), and small diameter (smaller than 10 nm) CNTs. In most cases, small catalyst particles were detected at the tip of the tubes. This suggests that the tip growth mechanism is responsible for the CNTs synthesis under the present conditions. The future work will focus on comparison of the two techniques and optimization of the processes, in particular, in order to achieve directional CNTs growth.

NT-WeP7 Growth of Cone-shaped Carbon Nanotubes by Arc Discharge in Anode, ***S.-C. Kung**,* Industrial Technology Research Institute,Taiwan*; C.-M. Hsu,* Industrial Technology Research Institute,Taiwan, Taiwan*; B.-J. Li, H.-J. Lai,* Industrial Technology Research Institute,Taiwan

Various synthetic methods are developed and the main method for the production of high quality CNTs (carbon nanotubes) is the DC (direct current) arc discharge between two graphite electrodes in a buffer atmosphere which is usually is helium, leading to the formation of nanotube-containing deposit on the end of the cathode. Many factors such as the velocity distribution of carbon ions, the density of carbon vapor, and the growth temperature have been suggested to affect the growth of CNTs. The pressure of carrier gas in the evaporation chamber is generally considered as the most important factor. Here, we report the production of CNTs without catalytic metals by DC arc discharge between two graphitic rods of the same diameter at the low pressure ambiance (ca. 10@super -2@ torr) and higher pressure helium atmosphere (ca. 900 torr). After the arcing was carried out, CNTs were discovered in the deposit on the anode instead of the cathode in low pressure working ambiance. The morphologies of CNTs on the anode deposit are specifically cone-shaped, 15 nm in diameter. The difference of nanometirc graphitic structures synthesized under the noble and higher vacuum atmosphere were discussed and characterized by FESEM, HRTEM, RAMAN spectrometer, TGA, and field emission properties measurement.

NT-WeP8 Growth of Carbon with Vertically Aligned Nano-scale Flake Structure by rf Sputtering, ***E. Kusano***, *H. Zhang,* Kanazawa Institute of Technology, Japan*; T. Kogure,* University of Tokyo, Japan*; I. Yoshimura, K. Yamamoto, A. Kinbara,* Kanazawa Institute of Technology, Japan

Carbon nanoflake has been deposited by rf sputtering using the mixture of Ar and CH@sub 4@ with a total pressure of 14.5Pa as a discharge gas and a graphite disk as a target. A Si (110) wafer was used as a substrate on which carbon nanoflakes was grown at 670°C. The rf (13.56MHz) discharge power was kept 100W for all deposition. Deposition time was changed from 15 min to 3 hours. Microstructure of deposited carbon was investigated by Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscope (HRTEM). Under the present conditions, high-density vertically aligned carbon nanoflakes with a thickness of about 30 nm were obtained. High intensity and symmetry of electron diffraction pattern indicated that carbon nanoflakes deposited by rf sputtering had the three dimensionally perfect crystallinity with an interlayer spacing of 335pm. In particular, there was no disorder in stacking of layer structure. It was further found that the thickness of the flakes was independent of deposition time while the length of the flakes increased to about 600-800 nm with increasing deposition time to 3 hours. Width of the carbon nanoflake was about 300 nm after 3-hour deposition. The results suggest that a critical thickness of carbon nanoflake exists, possibly depending on deposition conditions such as substrate temperature and discharge pressure. This critical thickness was almost equal to the layer number of about 90. Some potential applications of the carbon nanoflake film are being considered in vacuum electronic devices, chemical catalyst, frictional abrasion resistance, etc.

NT-WeP9 Synthesis of Aluminosilicate Nanotube "Imogolite" in the Presence of Polymer Solution, ***K. Yamamoto***, *H. Otsuka, S.-I. Wada, A. Takahara,* Kyushu University, Japan

Inorganic nanotube "Imogolite" is a hydrous aluminosilicate polymer with an external diameter of ca. 2.5 nm and lengths from several hundreds nanometer to a micrometer. The authors introduce a novel method for the preparation of polymer nanohybrid through in situ synthesis of imogolite in the aqueous solution of water-soluble polymer. A polymer nanohybrid prepared by this method can be expected to improve the dispersion of imogolite in the polymer matrix compared with that prepared by conventional blending.@footnote 1@ The aqueous dilute solution of aluminum chloride and tetraethoxysilane was stirred and refluxed at 369 K for several days and freeze-drying of the solution gave white powder of synthetic imogolite. The polymer nanohybrid was also prepared through in situ synthesis of imogolite in the presence of poly(vinylalcohol)(PVA) in solution and this reaction was carried out at various concentration of PVA. The formation of synthetic imogoltie was confirmed by IR, WAXD measurement, and AFM observation. The content of imogolite in the each polymer hybrid sample was evaluated by TGA measurement. WAXD profiles of PVA-imogolite nanohybrid showed the sharp diffraction peak of PVA and the diffractions corresponding to the parallel orientation of the bundle of imogolite nanotubes. It was confirmed that synthetic imogolite formed nanoscale fibrous network structure in PVA matrix by the above mentioned procedure. Furthermore, high transparency of synthetic imogolite/PVA hybrid film prepared by this method was attained because of the high dispersibility of synthetic imogolite in PVA solution. @FootnoteText@ @footnote 1@K. Yamamoto, H. Otsuka, S. -I. Wada, A. Takahara, J. Adhesion, 78, 591 (2002).

NT-WeP11 A Novel Field Emission Triode Configuration Based on a Cylinder/Plane Geometry and Carbon Nanotubes, ***V.P. Mammana***, *O. Shenderova, G.E. McGuire,* International Technology Center

Field emission devices are an excellent alternative for a myriad of applications requiring highly efficient and compact electron sources, such as flat panel displays, microwave tubes and plasma thrusters. Although field emission devices with several different triode configurations have been developed, there is still a need for devices with increased robustness, lower gate voltage and lower gate parasitic current that are easy to manufacture. In this work we propose a new configuration based on a cylinder/plane geometry, in which the cylinder plays the role of cathode and the plane performs as the gate. In the proposed configuration, an insulating dielectric is used between the cathode and the gate, in a way that the gate current is significantly reduced while the overall robustness is increased. Manufacturing this structure is straightforward, since it does not require patterning of the dielectric. The complexity is further reduced if no pixel addressing is needed (for non-display applications), since the dielectric may be blanket deposited or grown. We present electrostatic field calculations made in order to optimize the geometrical parameters of the device, and these calculations demonstrate that emission takes place at gate potentials of a few tens of volts, if carbon nanotubes are included into the structure in order to enhance the local electrostatic field. In this paper we address the dependence of the electrostatic field on the gate voltage, type of dielectric, cylinder/plane distance and cylinder cross-section. Some focusing issues are preliminarily addressed too. A process flow for the manufacture of the device is also proposed.

NT-WeP12 Field Emission Properties of Carbon Nanotubes Relative to Buffer Layer, ***C.-M. Hsu***, *S.-C. Kung, B.-J. Li, H.-J. Lai,* Industrial Technology Research Institute, Taiwan

Effect of field emission and growth of carbon nanotubes use various buffer layers Carbon nanotubes (CNTs) were synthesized with various buffer layers by electron cyclotron resonance chemical vapor deposition (ECR-CVD) and microwave plasma chemical vapor deposition (MPCVD) system. Growth was performed in a flowing mixture of H@sub2@, CH@sub4@ and N@sub2@ as precursors at temperature 600°C and -200 V substrate bias, sputter Co as catalysts material. The preliminary results indicate that well-aligned carbon nanotubes show significant emission current. Field emission property of carbon nanotubes and buffer layers relationship will be compared. Field emission scanning electron microscopy (FESEM) shows that the CNTs are well aligned with high aspect ratio and growth direction vertical to the substrate. The field emission properties of CNTs and buffer layers relationship will be characterized by I-V measurement, XRD, TEM, and RAMAN.

NT-WeP14 Modification of Contact Resistance by Nano-bonding and Thermal Treatment, *S. Lee, H.J. Chung,* CSNS and Seoul National University, Korea*; J.-Y. Park,* Cornell University*; Y.S. Cho,* ***Y.D. Park***, *J.H. Choi, Y. Kuk,* CSNS and Seoul National University, Korea

When we connect a nano-structure with conducting wires, we face difficulty fabricating them around ultra-fine and dense nanostructures. In order to use nanotubes or nanowires as interconnection materials, the contact resistance should be controllable because it may become main noise and dissipation sources with this low electrical current signal. In this study, the variation of the contact resistance in the carbon nanotubes (2-8 nm) on Au electrodes was investigated. The contact resistance between a nanotube and a electrode was changed the nanometer sized dots of Au and Ni formed by the field evaporation of the metals coated cantilever using atomic force microscopy (AFM) combined with a thermal treatment of 400-500 °C by a rapid thermal annealing (RTA). By using this method, the contact resistance of ~100 k@ohm@ is routinely produced despite of the geometry of nanotubes. This method can be used to other transport experiments to be required to modify the contact resistance.

NT-WeP15 Fabrication and Characterization of Active Nanoscale Electronic Devices Based on Vertically Aligned Carbon Nanofibers (VACNF), *M.L. Simpson,* Oak Ridge National Laboratory*;* ***X. Yang***, University of Tennessee*; M.A. Guillorn,* Oak Ridge National Laboratory*; D.W. Austin,* University of Tennessee*; V.I. Merkulov, A.V. Melechko, D.H. Lowndes,* Oak Ridge National Laboratory

Arrays of deterministically grown VACNFs were synthesized in a high-density Plasma-Enhanced Chemical Vapor Deposition (PECVD) process that provides a high degree of control of the growth conditions and, consequently, the resultant electronic properties. After inspection of fiber morphology and composition using scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis, a layer of SiO2 was deposited conformally onto the fibers by a silane-based RF PECVD process. Following planarization of the substrates by chemical mechanical polishing, the tips of the fibers were uncoverd by reactive ion etching of the SiO2 layer. Electrodes were patterned on the substrate surface to make contact to individual fiber tips within the array. Current versus voltage (I-V) curves indicate the presence of a metal-semiconductor (Schottky) junction and display a rectifying behavior. I-V measurements made with respect to temperature reveal an average barrier height of 300 mV. Additional experiments indicate that the junction occurs at the nanofiber/silicon interface. An empirical model of the material system will be presented along with an explanation of the experimentally observed charge transport behavior.

NT-WeP16 Fabrication of Top gated Single-Walled Carbon Nanotube Field Effect Transistor Utilizing Scanning Probe Lithography, ***S.H. Choi***, *J. Heo,* SungKyunKwan University, Korea*; W.B. Choi,* Samsung Advanced Institute of Technology, Korea*; I.S. Chung,* SungKyunKwan University, Korea

We attempted to fabricate top gated single wall carbon nanotube field effect transistor(SWNT FET) utilizing scanning probe lithography(SPL)

method. In SPL, electrons induce chemical reactions at the desired position during scanning. Thus, gate electrode as well as source/drain formation would be done using lift-off method without using e-beam lithography. N type or p type FET can be formed according whether the oxygen annealing process is given or not. Thus, we can easily form an inverter based on top gate structure. In this study, SWNTs were dispersed on pre-patterned substrate prior to deposit top gate oxide. Our device shows excellent electric characteristics by thinner gate oxide.

NT-WeP17 Large Paramagnetic Susceptibility and Field Induced Persistent Current for Carbon Nanotube Tori, ***R. Tamura,*** Shizuoka University, Japan*; M. Tsukada,* University of Tokyo, Japan

Magnetic susceptibilities have been calculated for a number of Carbon nanotube (CNT) tori with the tight binding model. We found large paramagnetic susceptibility which cannot be expected when the system size is larger than the order of the nanoscale. The CNT torus with six-fold rotational symmetry is composed of six unit cells. The unit cell is an armchair nanotube with two pentagonal defects and two heptagonal defects. Direction of the tube axis is changed by sixty degrees by the defects. When this unit cell is repeated periodically, on the other hand, the helical CNT is formed.@footnote 1@ The energy levels of the CNT torus can be obtained from the dispersion relation of the helical CNT, E(k), by choosing only the discrete wave number k=@pi@j/3 with an integer j. The magnetic field penetrating the torus surface change the dispersion relation E(k), while magnetic field through the hole shift the discrete wave number due to the AB effect. When the helical CNT is semi-metallic, it is possible that LUMO band bottom at k=0 is lower than the HOMO band over some k region.@footnote 2@ In that case, electron at the HOMO band makes a transition to the k=0 LUMO sate so that number of occupied levels with positive k is different from that with negative k. This causes the persistent current and large positive magnetic susceptibility, in spite of large negative magnetic susceptibility of graphite. @FootnoteText@@footnote 1@R. Tamura and M. Tsukada,Journal of Physical Society of Japan, Vol. 68, pp.910-922 (1999)@footnote 2@K. Akagi, R. Tamura, M. Tsukada, S. Itoh, and S. Ihara, Phys. Rev. B,Vol. 53, pp.2114-2120 (1996) .

NT-WeP19 Experimental and Theoretical Studies on the Ozone Reactivity with Carbon Nanotubes, *S. Picozzi, L. Lozzi, F. Di Gregorio, S. Santucci, C. Cantalini,* INFM and University of L'Aquila, Italy*; C. Baratto, G. Sberveglieri,* INFM and University of Brescia, Italy*; L. Valentini,* ***I. Armentano,*** University of Perugia, Italy*; B. Delley,* Paul Scherrer Institut, Switzerland

In a previous paper@footnote 1@ it has been reported how carbon nanotubes (CNTs) thin films deposited by plasma-enhanced chemical vapor deposition have a strong reactivity with NO2. In this work we investigate a CNT film as resistive gas sensors for O3. The sensor composed by the aligned CNT film with a thickness of 200 nm exhibits sensitivity to O3 gas at concentrations as low as 25 ppb, fast response time with a baseline drift that has been observed if the operating temperature of the sensor is increased over 70Â°C Upon the reaction with O3, the electrical resistance of the CNTs is found to decrease. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+O3 system within the density functional theory, using the all-electron Dmol3 (density functional theory for molecules and three-dimensional periodic solids) code.@footnote 2@ Our calculations show that the ozone molecule adsorbs on the tube with a binding energy of the order of 300 meV and gains about 0.1 electrons from the CNT. The calculated density of states shows that O3 adsorption gives rise to an acceptor peak at the Fermi level, which lies in correspondence to the tube valence band maximum, rendering the CNT+O3 system metallic. This is consistent with the experimentally observed increase in conductivity. The baseline shift of the sensor experimentally observed for the higher working temperatures may be ascribed to a consumption of the carbon nanotube under the ozone exposition at the defective sites.@footnote 3@ @FootnoteText@ @footnote 1@ L. Valentini, I. Armentano, J. M. Kenny, C. Cantalini, L. Lozzi, and S. Santucci, Applied Physics Letters Volume 82, Issue 6, pp. 961-963 (2003). @footnote 2@ B. Delley, J. Chem. Phys. 113, 7756 (2000); ibid. 92(1), 508 (1990) @footnote 3@ D.B. Mawhinney, V. Naumenko, A. Kuznetsova and J.T. Yates Jr., J. Am. Chem. Soc., 122, 2383 (2000).

NT-WeP20 Molecular Dynamics Study on the Non-equilibrium Flow of Small Molecules through Opened Carbon Nanotubes, ***K. Lee,*** *S.B. Sinnott,* University of Florida

Ultrafiltration membranes made of short, opened carbon nanotubes, which have relatively uniform nanometer-scale pore sizes and linear structures, may allow gases to selectively pass through the membrane. This potential selectivity can be predicted from atomistic simulations of the diffusion and adsorption of the gases into and within carbon nanotubes. The computational nanofluidics of hydrocarbons, oxygen, and carbon dioxide has been studied with molecular dynamics simulations in the work reported here. The microscopic behaviors of these gases can be simulated with multiple integrations of the interactions among the atoms in a system. The transport of gas molecules for long time periods is characterized by initial non-equilibrium states followed by equilibrium states. The non-equilibrium state is induced by the diffusive motion of the gas molecules from one end of the nanotubes into the vacuum or low-pressure region at the other end of the nanotubes, and lasts until the gases are evenly distributed in the nanotubes. During the non-equilibrium state, the gas molecules move back and forth through the nanotubes. It is found that this behavior, the time needed for the attainment of equilibrium, and the molecular motions at the openings of the nanotubes are affected by the density (or pressure) of gas molecules both inside and outside of the carbon nanotubes. When the gas molecules reach the end of the nanotubes, the attractive force between the tube end and the gas molecules prevent the molecules from leaving the nanotube. In order to leave the tube, the molecules must be acted on by a repulsive force, which is exerted by other gas molecules entering at the other end. The dynamics of these various nonequilibrium diffusion regions are characterized and will be discussed in detail. In addition, a discussion of how the results change with changes in nanotube chirality and diameter will be discussed. This work is supported by the NASA Ames Research Center.

Nanotubes
Room 317 - Session NT-WeA

Properties of Carbon Nanotubes
Moderator: J. Randall, Zyvex Corporation

2:00pm **NT-WeA1 Photoemission Spectromicroscopy and Spectroscopy of Carbon Nanotubes**, ***S. Suzuki***, *Y. Watanabe, T. Ogino, Y. Homma,* NTT Basic Research Laboratories, NTT Corporation, Japan*; S. Heun, L. Gregoratti, A. Barinov, B. Kaulich, M. Kiskinova,* Sincrotrone Trieste, Italy*; W. Zhu,* Bell Laboratories, Lucent Technologies*; C. Bower, O. Zhou,* University of North Carolina at Chapel Hill **INVITED**

Investigating the electronic structure of carbon nanotubes, especially their tips, is important for understanding the electron-field-emission properties of nanotubes. A specific electronic structure is expected at the hemispherical tips of nanotubes, where the graphene cylinders are believed to be closed by insertion of the five-member rings in the graphene network. The localized states in the vicinity of the Fermi level would largely contribute to the field emission properties for close-end nanotubes. For open-end nanotubes or nanotubes having imperfect structures, dangling bond states may significantly contribute to the field-emission properties. Moreover, the edge state, which is a characteristic electronic structure formed at a zigzag-type graphene edge, and has a large density of states at the Fermi level, may also play a key role. By means of scanning photoemission spectromicroscopy, we studied the local electronic structure at the tips of aligned multi-walled carbon nanotubes grown using microwave plasma-enhanced chemical vapor deposition. The valence band and the C 1s spectra, measured systematically from spatially selected regions along the tube axes, were the fingerprint for lateral variations in the electron density of states and in the band bending, respectively. The spatially selected photoemission spectra revealed that the tips have a larger density of states in a binding energy range of 0 to about 1 eV, whereas band bending, which would explain such a spectral difference, was not observed. It is suggested that the different density of states near the Fermi level is due to a larger dangling bond density at the tips. We also studied the electronic structure and work function of alkali-metal-doped carbon nanotubes. Drastic change in the electronic structure caused by the doping will also be presented.

2:40pm **NT-WeA3 Preparation and Field Emission Studies of Carbon Based Nanostructured Materials**, ***X. Xiao***, Argonne National Laboratory, U.S.*; O. Auciello, J.E. Gerbi, J. Wang, J. Birrell, J.A. Carlisle,* Argonne National Laboratory*; V.I. Merkulov, H. Cui, D.H. Lowndes,* Oak Ridge National Laboratory*; Y. Wang,* North Carolina State University

Four types of carbon based nanostructured materials were prepared, including nitrogen doped ultrananocrystalline diamond (UNCD) films, UNCD on vertically aligned carbon nanofibers (VACNFs), carbon nanotubes (CNTs), and nanocomposite of UNCD/CNTs. Different methods were employed to characterize the nanostructures, such as scanning electron microscopy, Raman spectroscopy, high-resolution transmission electron microscopy and quadrupole mass spectrometry. The field electron emission properties of these carbon nanostructured materials in different ambients (O@sub 2@, Ar, N@sub 2@) were extensively studied and compared with each other. The experimental results show that the UNCD/VACNFs composite is a good field emitter with low threshold value for electron emission, good stability and long lifetime. The excellent field emission property of the composite is believed to be due to the combined effect from the negative electron affinity of UNCD and high aspect ratio of carbon nanofibers. CNTs, especially vertically aligned CNTs, can not stand long-time ion bombardment from the residual gas in the field emission process, and distortion of CNTs has been observed subsequently to electron emission measurements. Possible damage mechanism is discussed. We acknowledge support from the US Department of Energy, Office of Science / Basic Energy Science-Materials Science, under Contract W-31-109-ENG-38.

3:00pm **NT-WeA4 Infrared Stimulated Emission and Optical Gain in Isolated Single-Walled Carbon Nanotubes**, ***M.S. Arnold***, *J.E. Sharping, S.I. Stupp, P. Kumar, M.C. Hersam,* Northwestern University

Bandgap fluorescence from single-walled carbon nanotubes (SWNTs) isolated in surfactant micelles has recently been reported.@footnote 1@ Since semiconducting SWNTs possess electronic bandgaps in the near infrared region of the optical spectrum, these nanomaterials have potential application in fiber optic communication and infrared medical imaging. In this talk, we will discuss experimental results characterizing stimulated emission of infrared radiation from SWNTs isolated in aqueous micellar suspensions. Solutions of nanotubes are optically pumped at the E@sub 22@ transition for a particular (n, m) chirality, and stimulated emission is probed at the corresponding E@sub 11@ transition. The stimulated emission in isolated SWNT solutions is observed to be more than 122 times larger than in a control sample of aggregated SWNTs. Pump and probe power, wavelength, and polarization; path length; and concentration dependencies have been characterized. For small probe intensities, the stimulated emission intensity increases linearly with probe intensity, while sub-linear behavior is observed for large probe intensities; and gain and stimulated emission are maximized for co-linear-polarization of pump and probe. Currently, measurements are underway to quantify the gain coefficient and carrier lifetimes using delayed pulsed pump-probe spectroscopy. These results suggest the conditions under which tunable infrared optical amplification devices may be realized with SWNTs. @FootnoteText@ @footnote 1@ M. J. O'Connell et al., Science, 291, 2002.

3:20pm **NT-WeA5 Defective Carbon Nanotube Channel Single Electron Transistor with Ultra-High Coulomb Energy of 5000K and its Applications**, ***K. Matsumoto***, Osaka University, Japan **INVITED**

Coulomb diamond characteristics with Signal/Noise ratio of 10000 and drain current level of ~10@mu@A was attained even at room temperature in the single electron transistor (SET) using the segmented carbon nanotube (CNT) of 1~2nm diameter as multi-isla nds for the SET. The position and direction of the carbon nanotube for the channel of the SET is controlled by the patterned chemical catalysts of 3nm thick iron (Fe) and applied field between them. Using methane gas in the CVD process, the single wall c a rbon nanotube was grown between two patterned catalysts on the Si0@sub2@/Si substrate. Most important technology is the introduction of defects into the carbon nanotube channel using the chemical process. The defects make the carbon nanotube to the segmen ted structure of 1~2nm diameter, which is used as multi-islands for the SET. The electrical property of the defective carbon nanotube channel single electron transistor was measured all at room temperature. The drain current shows the Coulomb gap of ~80 0mV, which corresponds to the Coulomb energy of 400meV and Coulomb temperature of 5000K. The drain current shows the Coulomb oscillation characteristics with the modulation ratio of as large as 96~99%. The effective island size is as small as ~1nm es tima ted from the electrical property. Coulomb diamond structures were observed even at room temperature. By improving the ohmic contact resistance, the drain current becomes of the order of ~10@mu@A and there is no noise observed in the Coulomb diamond characteristics. The signal/noise ratio becomes as high as 10000. This SET has a high sensitivity to the one electron because of the small gate capacitance of 1E-19~1E-20F, and is applicable to the single electron sensor at room temperature.

4:00pm **NT-WeA7 The Highly Robust Electrical Interconnects and Ultrasensitive Biosensors Based on Embedded Carbon Nanotube Arrays**, ***J. Li***, NASA Ames Res. Center*; A.M. Cassell,* NASA Ames Res. Center / Eloret Corp.*; J. Koehne,* NASA Ames Res. Center*; H. Chen, H.T. Ng, Q. Ye, R. Stevens, J. Han,* NASA Ames Res. Center / Eloret Corp.*; M. Meyyappan,* NASA Ames Res. Center **INVITED**

We report on our recent breakthroughs in two different applications using well-aligned carbon nanotube (CNT) arrays on Si chips, including (1) a novel processing solution for highly robust electrical interconnects in integrated circuit manufacturing,@footnote 1@ and (2) the development of ultrasensitive electrochemical DNA sensors.@footnote 2@ Both of them rely on the invention of a bottom-up fabrication scheme which includes six steps, including: (a) lithographic patterning, (b) depositing bottom conducting contacts, (c) depositing metal catalysts, (d) CNT growth by plasma enhanced chemical vapor deposition (PECVD), (e) dielectric gap-filling, and (f) chemical mechanical polishing (CMP). Such processes produce a stable planarized surface with only the open end of CNTs exposed, which can be further processed or modified for different applications. By depositing patterned top contacts, the CNT can serve as vertical interconnects between the two conducting layers. This method is fundamentally different from current damascene processes and avoids problems associated with etching and filling of high aspect ratio holes at nanoscales. In addition, multiwalled CNTs (MWCNTs) are highly robust and can carry a current density of 109 A/cm2 without degradation. It has great potential to help extending the current Si technology. The embedded MWCNT array without the top contact layer can be also used as a nanoelectrode array in electrochemical biosensors. The cell time-constant and sensitivity can be dramatically improved. By functionalizing the tube ends with specific oligonucleotide probes, specific DNA targets can be

detected with electrochemical methods down to subattomoles. @FootnoteText@@footnote 1@J. Li, Q. L. Ye Q, A. M. Cassell, H.T. Ng, R. Stevens, J. Han, M. Meyyappan, Appl. Phys. Lett., 82 (15), 2491 (2003). @footnote 2@J. Li, H. T. Ng, A. Cassell, W. Fan, H. Chen, Q. Ye, J. Koehne, J. Han, M. Meyyappan, Nanoletters, in press.

4:40pm **NT-WeA9 Photocurrents in Nanotube Junctions***, D.A. Stewart,* ***F. Léonard****,* Sandia National Laboratories

Carbon nanotubes have demonstrated great promise for future nano-electronic devices. However, their potential for opto-electronic applications has received much less attention, despite their seemingly ideal properties, such as a direct band-gap, quasi-one-dimensional density of states, low defect density and a high surface-to-volume ratio. In this talk, we present calculations of photocurrents in nanotube junctions using a non-equilibrium quantum transport theory. The dependence of the short-circuit photocurrent on incoming photon energy shows many fatures, due to band-to-band transitions and photon-assisted tunneling. The operation of such devices in the ballistic transport regime leads to unusual size effects.

5:00pm **NT-WeA10 Gas Adsorption on Multi-walled Carbon Nanotubes: An Experimental and Theoretical Study***, **S. Picozzi**, L. Lozzi, C. Cantalini,* University of L'Aquila, Italy*; L. Valentini, I. Armentano, J.M. Kenny,* Universita di Perugia, Italy*; S. Santucci,* University of L'Aquila, Italy

The effects of environment gases (such as O2, NO2, NH3) on the electronic and transport properties of carbon nanotubes have recently attracted great interests.@footnote 1@ In this work a combined experimental and theoretical study on CNT-based system for gas sensing applications is reported. Carbon nanotubes thin films have been deposited by plasma enhanced chemical vapor deposition on Si3N4/Si substrates provided with Pt electrodes. Microstructural features as determined by SEM, TEM and Raman spectroscopy highlight the growth of defective tubular carbon structures. CNTs show a p-type response with decreasing electrical resistance upon exposure to NO2 gas (100 ppb) and the highest sensitivity at 165° C working temperature. No response has been found by exposing the film to CO gas in the temperature range between 25 and 250° C. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+CO and CNT+NO2 systems.@footnote 2@ Our spin-unrestricted density functional calculations show that NO2 retains its spin-polarized state upon adsorption. Both CO and NO2 molecules adsorb weakly on the tube wall, with essentially no charge transfer between the tube and the molecules. The electronic properties of CNTs are sensitive to the adsorption of NO2, due to an acceptor-like peak close to the tube valence band maximum, while they are insensitive to the CO adsorption. According to the experimental findings, our theoretical results suggest that gas-induced modification of the density of states close to the Fermi level might significantly affect the transport properties of nanotubes. @FootnoteText@@footnote 1@ J. Kong, N.R. Franklin, C. Zhou, M.G.Chapline, S. Peng, K. Cho and H. Dai, Science 287, 622 (2000).@footnote 2@ B. Delley, J. Chem. Phys. 113, 7756 (2000).

Nanotubes
Room 317 - Session NT-ThM

Nanotube Growth and Processing
Moderator: K. Matsumoto, AIST, Japan

8:20am **NT-ThM1 Analyses of Early Stages of Vertically Aligned Carbon Nanotube Growth**, ***Y. Hayashi***, *K. Ueda, Y. Watanabe, S. Nishino,* Kyoto Institute of Technology, Japan

Vertically aligned carbon nanotubes are expected to be used for the electron emitters of a field emission display, which demands large-area and low-voltage operation. We have developed the method of large-area growth of well-aligned carbon nanotubes by hot-filament assisted dc plasma chemical vapor deposition (HF/DC-P CVD).@footnote 1,2@ In order to obtain high electron emission density at low voltage, the crystallinity and alignment of carbon nanotubes should be controlled. However the growing mechanisms of aligned carbon nanotubes, especially early stages, have not well been understood. Therefore we are analyzing substrate surface states in the early states of aligned carbon nanotube growth in HF/DC-P CVD by in-situ ellipsometry along with other ex-situ analytical methods. The ellipsometer is a rotating-analyzer type and the light source is a diode laser of the wavelength of 690 nm. Carbon nanotubes were grown on an iron film about 500 nm thick in the DC plasma of 20 % methane diluted in hydrogen after the pretreatment in a pure hydrogen plasma. The trajectory of ellipsometric parameters in the early stages was compared with that of simulation which was performed using the effective medium approximation for the calculation of the optical indexes of a film equivalent to aligned carbon nanotubes of a certain diameter and density. From the results of the ellipsometry and SEM observation, it was found that an incubation period of about 2 min exists before the growth of carbon nanotubes and the carbonization of iron fine particles, which were formed during the pretreatment process, was occurred in the incubation period. @FootnoteText@@footnote 1@Y.Hayashi , T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19 (2001) 1796. @footnote 2@K.Ueda, T.Negishi, Y.Hayashi and S.Nishino, in preparation for publication.

8:40am **NT-ThM2 Iron-carbide Cluster Thermal Dynamics for Catalysed Carbon Nanotube Growth**, *F. Ding, K. Bolton,* ***A. Rosen***, Goteborg/Chalmers University, Sweden

The mechanism of the growth of carbon nanotubes by chemical vapor deposition (CVD) method is still not well understood. It seems that the catalyst particles play a key role in controlling the size, defects, number of walls and chirality of the nanotubes. Knowledge about thermal properties of the catalyst particles in the temperature range (500-1200)@super o@C used in the CVD growth would be beneficial to the understanding of the growth mechanism. We have used molecular dynamics (MD) simulations for studies of the thermal behavior of C@sub m@Fe@sub N-m@ clusters with N up to 2400. Comparison of the computed results with experimental data shows that the simulations yield the correct trends for the liquid-solid region of the iron-carbide phase diagram as well as the correct dependence of cluster melting point as a function of cluster size. The calculations also show that the melting points of both pure Fe clusters (m=0) with diameter larger than 3 nm (about N>1000) and clusters composed of 10% C with diameter larger than 4 nm (about N>2400) are higher than 1000@super o@C. This indicates that, when nanotubes are grown on large catalyst particles at these lower temperatures, the catalyst particles are primarily in the solid - and not the liquid - state. The simulations indicate that nanotube growth may depend only on the surface melting of these clusters. This surface melting behavior and the coalescence of C@sub m@Fe@sub N-m@ clusters at temperatures lower than the melting point is also studied. At these low temperatures surface melting results in the coalescence of two clusters, where the final structure is similar to the minimum energy geometry.

9:00am **NT-ThM3 Growth & Control Mechanisms for Directed Assembly of Vertically Aligned Carbon Nanofibers: Fundamental Studies and Nanotech. Applications**, ***D.H. Lowndes***, *V.I. Merkulov,* ORNL*; A.V. Melechko,* ORNL, U. Tennessee*; M.A. Guillorn,* ORNL*; M.L. Simpson,* ORNL, U. Tennessee*; H. Cui,* ORNL*; J. Liu,* Duke U.*; J.B.O. Caughman, M.J. Doktycz, T.E. McKnight,* ORNL*; L. Zhang, X. Yang,* ORNL, U. Tennessee*; D.K. Hensley,* ORNL **INVITED**

Although vertically aligned carbon nanofibers (VACNFs) are structurally quite imperfect in comparison to single-wall carbon nanotubes (SWNTs), their synthesis and assembly is highly controllable using a DC plasma-enhanced method and--unlike SWNTs-- they can be precisely positioned in large arrays. VACNFs grow simultaneously by two mechanisms, catalytically controlled vertical growth and defect-mediated lateral growth, and the morphology of isolated VACNFs is readily controlled. Their growth rate can be increased by changing the feedstock transport from diffusive to forced flow, and their growth mode can be altered from 'base-type' to 'tip-type' without changing the type of substrate or catalyst. Their alignment angle relative to the substrate also can be controlled via the direction of local plasma electric-field lines, so that deliberately tilted or kinked CNFs can be grown. Recent extensions to grow VACNFs using radio frequency (RF) PECVD and from nanometer-scale metal catalyst particles also will be described. Phenomenological models that explain important aspects of VACNF growth will be presented and validated with experimental results. Potential nanotechnology applications of VACNFs will be demonstrated, including multi-electrode vacuum nanoelectronic devices using field emitting VACNF cathodes; tubular nanopipes that can be deterministically positioned using VACNFs as templates; the use of VACNFs as an intracellular interface for monitoring and controlled biochemical manipulation of phenomena within viable cells; and their use to form semi-permeable membranes that mimic some features of biological cells, in combination with microfluidic and electronic structures.

9:40am **NT-ThM5 Synthesis of Carbon Nanotube Array by Radio-frequency Plasma Enhanced Chemical Vapor Deposition for Field Emission Application**, ***J. Wang***, *M. Zhu, R.A. Outlaw, X. Zhao, N.D. Theodore, D. Manos, B.C. Holloway,* The College of William and Mary*; V.P. Mammana,* International Technology Center

In this presentation we report on the synthesis, characterization, and applications of large periodic carbon nanotube arrays. A polystyrene and silica nanosphere lithography technique was used to create nickel catalyst arrays on silicon substrates. Nanotubes, with a diameter of about 50 nm, were synthesized on the nanodot arrays by radio-frequency plasma enhanced chemical vapor deposition (CVD) using an acetylene and hydrogen mixture. Scanning electron microscopy has been used to determine the density, height, and interspacing of the carbon nanotubes as a function of array patterning and deposition conditions. The suitability of such arrays for use in field emission devices is discussed within the framework of field emission electron spectroscopy, Kelvin probe and diode measurements.

10:00am **NT-ThM6 Magnetic Entrapment of Carbon Nanotubes for the Fabrication of Electrically Conductive Bridging Structures**, ***D.P. Long***, *J.L. Lazorcik, R. Shashidhar,* Naval Research Laboratory

The unique electrical properties of carbon nanotubes have made them ideal candidates for their use in future molecular electronics. The successful application and mass production of CNT-based nanoelectronics will require methods for the efficient and reliable fabrication of large numbers of CNT devices simultaneously across a substrate. Here we present recent experiments on the generation of electrically conductive carbon nanotube bridged structures fabricated in parallel by magnetic entrapment. By utilizing devices composed of individually addressed nickel lines and containing gaps 1 micron wide, we have demonstrated that moderate external magnetic fields can induce domain alignment in the ferromagnetic material and generate locally intense fields within the feature junctions able to attract and bind carbon nanotubes. Magnetic field strength, nanotube solution concentration, and feature gap width and thickness are used to control the trapping process. Junctions ranging from 2-4 microns were selective for large tube bundles while devices containing gaps of 1 micron or less were more selective for individual CNTs or small ropes of tubes. By making use of electrically isolated devices on silicon containing a thermally grown oxide layer we have measured the basic electrical properties of the bridged structures.

10:20am **NT-ThM7 Novel Approaches to Developing Carbon Nanotube Based Polymer Composites**, *N. Raravikar, G. Viswanathan, N. Chakrapani, C.Y. Ryu,* ***P.M. Ajayan***, Rensselaer Polytechnic Institute **INVITED**

Polymer-carbon nanotube composites combine the unique properties of nanotubes with the ease of processability of polymers. Alignment of nanotubes, the nanotube-matrix interface and the dispersion of nanotubes are issues critical to successful applications. Infiltration of polymer into pre-aligned arrays of nanotubes provides simultaneous control over the degree of alignment as well as the dispersion of nanotubes. The infiltration is achieved by introduction of the monomer and subsequent polymerization into a pre-aligned array of multi-walled carbon nanotubes grown by chemical vapor deposition technique. The resultant composites show better hardness and thermal stability compared to the parent polymer, and

can have applications as thermo-mechanically strong, antistatic polymeric coatings. Especially for application as structural reinforcements, a good interface between the nanotubes and the host matrix should exist for efficient load-transfer. We have also developed a novel route for grafting polystyrene chains onto single-walled nanotubes to obtain homogeneous, well-dispersed composites, using an anionic polymerization scheme. The mechanism of functionalization and the enhancement of interfacial properties studied using thermal analysis and spectroscopic techniques will be discussed.

11:00am **NT-ThM9 Filling and Chemical Modification of Carbon Nanotubes**, ***N. Naguib***, *H. Ye, Y. Gogotsi,* Drexel University

The possibility of filling of carbon nanotubes at elevated temperatures and pressures has been demonstrated. Carbon nanotubes can be filled with different fluids such as water, ethylene glycol and isopropyl alcohol or different gases such as Argon and Nitrogen. Understanding the penetration of fluids in nanochannels is important for the efficient storage of gasses. The effect of changing variables (pressure and temperature) on the filling process has been demonstrated. Wall structure of the nanotubes after treatment has been investigated. Hydrothermal treatment makes nanotubes hydrophilic. During the hydrothermal treatment, nanotubes can be completely or partially filled with liquids. Lattice fringe imaging of the tube walls showed a very strong interaction between the tube walls and the liquid. If a liquid inclusion was present in the area where some graphite planes terminated within the tube (inner diameter change or bending of the tube), swelling of the tube walls was observed and the wetted graphite layers pointed away from the wall toward the tube axis. Polymerization of ethylene glycol and isopropyl alcohol occurred inside and outside of the nanotubes, producing nanotube-reinforced composites. The liquid could also penetrate between the carbon layers causing this behavior. The exact chemical composition of the fluid, as well as the presence of the gases inside the nanotubes after hydrothermal treatment, have been studied by using TEM, EELS, EDS, Raman and Infrared microspectroscopy techniques.

11:20am **NT-ThM10 Polyatomic-Ion Beam Induced Chemical Functionalization of Carbon Nanotube-Polystyrene Composites**, *Y. Hu,* ***S.B. Sinnott***, University of Florida

Classical molecular dynamics simulations with empirical potentials are used to study polyatomic-ion deposition on nanotube-polystyrene composites. The forces in the simulation are calculated with a many-body, reactive empirical bond-order potential for hydrocarbons and fluorocarbons. The ion beam consists of 50 C@sub 3@F@sub 5@@sup +@ ions and the composite consists of (10,10) single-walled carbon nanotubes embedded in crystalline polystyrene. The ions impact at random points on the composite slabs along the substrate normal. The composites differ in the embedding depth of the nanotube within the polystyrene matrix and the orientation of the nanotubes relative to the polystyrene chains. The simulations predict that chemical modification of the carbon nanotubes can be achieved through polyatomic-ion beam deposition. They also predict the dependence of such modifications on the incident energy of the ions and embedding depth of the carbon nanotubes. The findings could have important implications for the production of carbon nanotube-based nanocomposite materials with improved load-bearing capabilities. The work is supported by the National Science Foundation through grant CHE-0200838.

11:40am **NT-ThM11 AC Electrical Transport Behavior of Epoxy Matrix/Single-Walled Carbon Nanotube Composites**, ***L. Valentini***, *D. Puglia, I. Armentano, J.M. Kenny,* University of Perugia, Italy*; S. Santucci,* University of L'Aquila, Italy

A study of the ac electrical transport properties of a diglycidyl ether of bisphenol A-based epoxy resin (DGEBA) polymerized with a diethylene triamine (DETA) and reinforced with single wall carbon nanotubes (SWNTs) is presented. The main objective is the investigation of the particular electrical behavior of the conductive filler in the composite and the development of new nanocomposite materials based on epoxy resins with controlled structural and electrical properties. The structural and electrical characterization of the SWNTs-DGEBA/DETA hybrid system, performed by differential scanning calorimetry, Raman and ac impedance spectroscopy show interesting effects, including the particular interaction between the polymer and nanotubes, the tendency of the nanotube structure to increase the rate of reaction and substantial effects of the nanotubes bundle conformation, dependent on matrix intercalation, on the dielectric behavior of the composite.

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