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.

Author Index

Bold page numbers indicate presenter