Tuesday Morning, October 3, 2000

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

Carbon Nanotubes: Synthesis

Moderator: D. Herr, Semiconductor Research Corporation

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

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

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

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

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

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

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

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

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

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

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

Carbon nanotubes are expected for the electron emitters of a field emitter display (FED). In order to realize the FED, a growth method of carbon nanotubes perpendicularly well-aligned on a large-area substrate has to be developed. Recently it was reported that such aligned carbon nanotubes were grown on nickel by plasma-enhanced hot filament chemical vapor deposition (CVD) and microwave plasma CVD. We have succeeded to grow well-aligned carbon nanotubes in the area of 4 cm in diameter by hot-filament-assisted DC plasma (HF-DCP) CVD in the gas of CH@sub 4@/H@sub 2@. The growth method and conditions were as follows. DC voltage of -250V was applied to substrates relative to hot filaments. A luminous region was observed just above the substrates. By the optical emission spectroscopy, it was confirmed that the luminescence was derived from excited hydrogen and hydrocarbon radicals. Therefore the process is called HF-DCP CVD. Nickel substrates were heated by the

filaments around 600 °C. The substrates were pretreated in pure hydrogen plasma for 15 min before the growth of carbon nanotubes in 20% CH@sub 4@/H@sub 2@ for 15 min. Well-aligned carbon nanotubes about 100 nm in diameter and about 5 microns in length were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the treated specimens. Positive ions of hydrogen, carbon and hydrocarbon are accelerated in the plasma sheath toward substrates. The sheath region of DC plasma plays important roles in the growth, while hot filaments assist the maintenance of DC plasma under such low voltage. By this method, the large-area growth of well-aligned carbon nanotubes is expected.

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

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

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

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

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

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

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

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

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