Nanometer-Scale Science and Technology
Room 210 - Session NS-FrM

Nanotube Processing and Properties

Moderator: N.A. Burnham, Worcester Polytechic Institute

8:20am **NS-FrM1 Precise Placement of a Multi-Wall Carbon Nanotube using Nano Manipulator in SEM**, ***H. Abe***, *M. Tanaka, M. Horikawa, Y. Naitoh, T. Shimizu,* AIST, Japan

There have been many studies for realizing electric devices using carbon nanotubes (CNTs). Particularly a variety of growth methods have been developed in order to control the diameter and the electric properties. In addition, we have thought that it is important to place precisely a CNT onto the designated position and make electrically and mechanically reliable contacts between CNT and electrodes for the realization electric circuit using CNT. From now, we have manipulated a multi-wall CNT (MWNT) and fabricated a MWNT tip for high-resolution SPM measurement using specially designed SEM manipulator. Then we developed several bonding methods by melting low melting point alloy and TiNi nano particles, whose bonding showed good conductivity of several 10k@ohm@ and mechanical strength of more than 2GPa. In addition to the techniques, we have tried to fabricate a bridge structure using a MWNT in the SEM manipulator. Then we succeeded in bridging a MWNT between electrodes whose distance is from 1µm to 4µm. This technique enables us to control the attaching position of less than 50nmx50nm and to float or touch MWNT from the substrate. We could really bridge a MWNT by floating between thermal heater of 300nm and thermal bath for precise thermal conductivity measurement of a single MWNT. We have thought that this technique could be applied to other nanotubesâ?T bridge structure fabrication and their physical property. The way of fabricating a MWNT bridge structure will be shown using video file in detail in our presentation.

8:40am **NS-FrM2 Hydrogenation of Single Wall Carbon Nanotubes**, ***A.S. Nikitin***, *H. Ogasawara,* Stanford Synchrotron Radiation Laboratory; *D. Mann, Z. Zhang, H. Dai, K.J. Cho,* Stanford University; *A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The hydrogenation of the single wall carbon nanotubes (SWCN) is considered as a mechanism of hydrogen storage in the nanotube materials. We present the hydrogenation of the single wall carbon nanotube films with an atomic hydrogen beam. Using X-ray absorption spectroscopy, we demonstrated that C-C bonds in the walls of SWCN decrease of sp@super 2@ character and increase of sp@super 3@ character simultaneously due to hydrogenation. On the basis of X-ray photoelectron spectroscopy results combined with theoretical calculations, we show 65+/-15% hydrogenation of carbon atoms in the SWCN films that corresponds to 5.1+/-1.2 wt % hydrogen weight capacity of the studied sample. The formed C-H bonds are stable at ambient temperature and can be broken in the temperature range from 300°C to 600°C. These results clearly demonstrate that a chemical interaction mechanism of hydrogen with SWCN is possible with a large hydrogen storage capacity.

9:00am **NS-FrM3 Well - Aligned Growth of Carbon Nanotubes/Fibers in Anodized Aluminum Oxide Pores by DC Plasma Enhanced Hot Filament Chemical Vapor Deposition**, ***H.W. Yap***, *B. Ramaker, A.V. Sumant, R.W. Carpick,* University of Wisconsin-Madison

In many carbon nanotube (CNT) or carbon nanofiber (CNF) applications - such as field emission flat panel displays, it is ideal to have an ordered and dense vertically aligned dense CNT/CNF array over a large area. The anodized aluminum oxide (AAO) template is favorable since it offers uniformly spaced pores for isolated and directional growth of these CNT/CNFs. Several research groups have already reported the use of the AAO template to grow CNT/CNFs via thermal chemical vapor deposition (CVD) but they were not successful in obtaining vertical and isolated growth once they emerged from the pores. Thus, etching of the AAO had to be subsequently performed. Microwave plasma enhanced MPECVD has been shown to give better alignment, however it is not cost effective in terms of power requirements and large area deposition. Here we report a cost effective, low power alternative approach: dc plasma enhanced hot filament CVD (dcPEHFCVD). To our knowledge, this is the first successful report to grow well aligned CNTs via AAO pores using dcPEHFCVD. Here, no anodization of the aluminum, pore widening of the AAO, post growth etching of the AAO or pretreatment of the catalyst are needed. Nickel nanowires electrodeposited in the pores act as catalysts. We find that tip growth mode is dominant here. The hot filament plays an important role in dissociating hydrocarbon species as well as heating the substrate to enhance the catalyst driven CNT/CNF growth. The plasma's electric field aligns the CNT/CNFs and is responsible for most of the growth chemistry. High resolution transmission electron microscopy reveals that both CNTs and CNFs are formed via the tip growth mode and have graphitic walls. The majority of CNTs have hollow interiors but some CNFs exhibit herringbone - like fringes in the interior. AFM images of the tubes are obtained and provide quantitative measurement of the length variations of the tubes.

9:20am **NS-FrM4 Carbon Nanosheets--A Sub-nanometer Two-dimensional Carbon Nanostructure**, ***M.Y. Zhu***, *J.J. Wang, X. Zhao, R.A. Outlaw, B. French, D.M. Manos, B.C. Holloway,* College of William and Mary

In this paper, we report a sub-nanometer scaled two-dimensional carbon nanostructure--Carbon nanosheets (CNS) by radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD). CNS were synthesized from mixed gases of methane (CH@sub 4@) and hydrogen (H@sub 2@) on various substrates, including Si, SiO@sub 2@, Al@sub 2@O@sub 3@, Mo, Zr, Ti, Hf, Nb, W, Ta, Cu and 304 stainless steel, without any catalyst or substrate pre-treatment. SEM, HRTEM, SAD, Raman spectroscopy, XRD, XPS and AES, were used to characterize the morphology and structure properties of the CNS. The results showed that CNS consist of graphene layers, oriented nearly vertically to the substrates. Typical CNS are hundreds of nanometers in width and height, but only few nanometers in thickness, sometimes as thin as a single-atomic-layer. Raman spectra of CNS featured D peaks and G peaks for sp@super 2@ bonded carbon, and low energy peaks, similar to RBM mode of single wall carbon nanotubes, were also observed. Analysis indicated that CNS is pure carbon without detectable contamination. BET measurement revealed a specific surface area of ~1300m@super 2@/g, which is the theoretical maximum value for a 2-layered graphene sheet. The high surface area makes CNS a potential candidate of catalyst support and hydrogen storage in fuel cell applications. Diode I-V curves, acquired to study the field emission property of nanosheets, showed a turn-on field as low as 1 V/µm and a current density of 2.2mA/mm@super 2@ over an area of 1mm@super 2@. This indicates that CNS is a good cathode material for cold field emission devices.

9:40am **NS-FrM5 Super Growth - Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes and its Applications**, ***K. Hata,*** AIST, Japan **INVITED**

We demonstrate an extremely efficient chemical vapour deposition synthesis of single-walled carbon nanotubes where the activity and lifetime of the catalysts are enhanced by an addition of water into the ambient of the CVD furnace, a growth mode we call "Super Growth".@footnote 1@ The enhanced catalytic activity of super growth results in massive growth of super-dense and vertically-aligned single-walled nanotubes forests with heights up to 2.5 millimeters. In addition, these SWNT forests were easily separated from the catalysts, producing the most pure SWNT material (over 99.98%) ever made, amazingly through an all-dry process without any purification. Moreover, patterned highly organized intrinsic single-walled nanotube structures were successfully fabricated. Super Growth simultaneously addresses many critical problems such as scalability, purity, and cost, and opens up innumerable opportunities ranging from fundamental research to real applications. @FootnoteText@ @footnote 1@K. Hata, et al.,Science 306. 1362 (2004)

10:20am **NS-FrM7 Microstructural Modifications of Multiwalled Carbon Nanotubes by keV Ar@super +@ Bombardment: a High Resolution TEM Study**, ***D.-Q. Yang***, *E. Sacher,* Ecole Polytechnique of Montreal, Canada

The surface functionalization and microstructural modification of carbon nanotubes (CNTs) have both attracted great interesting because of their potential applications to microelectronic devices and advanced functional CNT-based materials. One functionalization method is to break C-C bonds with keV Ar+ treatment, thus producing highly localized amorphous regions containing free radicals capable of further reaction. Such treatment of NTs has recently been found capable of changing the electronic properties and enhancing the field emission of multiwalled CNTs (MWCNTs). To better understand the interaction between the ion beam and CNTs, we have studied their microstructural evolution, under keV Ar+ beam irradiation, by high resolution TEM. We found that Ar+ treatment doses from 1013 to 1015 ions/cm2 produce free radical defects, an amorphous layer, as well as nanonodules that continue to grow and, on contacting another such growing nodule, crosslink the nanotubes. We discuss the formation mechanism of these microstructural modifications.

10:40am **NS-FrM8 Structural, Optical, and Electrical Properties of Functionalized SWNTs with DNA and Metal Nanoparticles**, ***G.-H. Jeong***, NTT Basic Research Laboratories, Japan; *A. Yamazaki,* Tokyo University of Science, Japan; *S. Suzuki, Y. Kobayashi, K. Furukawa, K. Torimitsu,* NTT Basic Research Laboratories, Japan; *Y. Homma,* Tokyo University of Science, Japan

Because of the outstanding physical, chemical and electrical properties of carbon nanotubes (CNT), a number of applications in various fields are expected. Especially, extensive CNT-functionalization researches have been performed to control electronic property because diameter- or chirality-controlled growth has not realized yet. Recently, we have performed the experimental approach to create CNT-based novel hybrid structures and demonstrate here the results. DNA and Au nanoparticles (NP) are selected to functionalize CNT due to their specific assembling property. By controlled chemical vapor deposition, single-walled carbon nanotubes (SWNTs) were successfully synthesized not only on flat substrate but also on Si-pillar substrate which allows suspending nanotubes. SWNTs-functionalization was performed by covalent coupling between carboxyl and amine groups. DNA/Au hybrids were made using thiolated-DNA and Au NP and confirmed by UV-visible absorption spectroscopy. Finally, SWNTs were modified with Au NP or DNA/Au hybrids. The density of Au NP attached along the suspended SWNTs was controlled by changing treatment time and concentration of the Au colloid. In Raman characterization, we observed new peaks at radial breathing band after Au NP attachment, which may be caused by surface-enhanced Raman scattering. Photoluminescence peaks were also detected from the SWNTs/Au hybrids and will be investigated the effect of Au functionalization. The intensity change of radial breathing band and defect band in Raman spectra was also observed from the SWNTs/DNA/Au hybrid, which implies the different electronic or optical properties are expected. These results show functionalized CNT can be further developed to electronic and optical applications. @FootnoteText@ @footnote 1@NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan @footnote 2@CREST, JST, c/o Dept. of Physics, Tokyo University of Science, Tokyo 162-8601, Japan

11:00am **NS-FrM9 Nanomechanical Resonance Studies of Carbon Nanotube Peapod Bundles**, *P. Jaroenapibal, C.Y. Nam, J.E. Fischer, D.E. Luzzi,* University of Pennsylvania; ***S. Evoy***, University of Alberta, Canada

The recent development of hybrid carbon nanotube materials, such as supramolecular self-assembled arrays of C60 molecules encapsulated within single-wall carbon nanotubes (C60@@SWNT), has opened new possibilities for the development of nanomechanical devices of tunable properties. We studied the mechanical properties of C60-filled SWNT bundles through analysis of their resonance in a transmission electron microscope (TEM). X-Ray diffraction was used to qualitatively study the filling of C60 in the bulk material. The intensity of the (1,0) bundle peak, located at Q = 0.45 A^-1, was reduced after filling of the tubes with C60. Electron diffraction analysis revealed a C60 spacing periodicity of 9.97 Ã. within the lumen of the SWNTs. Mechanical resonance measurements were conducted in a TEM by selecting bundles whose extremities were appropriately affixed. An average ratio of (E*/rho)^1/2 = 19002 Â± 2307 m/s was extracted from the resonance analysis of the C60-filled bundles, compared to a ratio of (E*/rho)^1/2 = 13230 Â± 3187 for the unfilled material. These values correspond to an effective average Young's modulus of E* = 240 Â± 105 GPa for empty bundles, and of up to E* = 650 Â± 156 GPa for the C60-filled materials. These moduli are significantly lower than the ~ 1 TPa usually reported for individual SWNTs due to the weak interaction and sliding effect that are known to exist between tube surfaces. However, the significant increase of stiffness upon filling is believed to be related to an increase of strain energy of the individual SWNTs within the bundle. A dependence of this modulus on bundle diameter was also observed. This dependence is explained by the increased importance of inter-tube slipping in bundles of larger diameter. We will also present recent results on the mechanical resonance properties of single-crystalline GaN nanowires. Preliminary resonant analysis of 30-160 nm wide wires suggest an average effective Young's modulus of E* = 120 Â± 20 GPa.

11:20am **NS-FrM10 Molecular Dynamics Simulation of Irradiation Effects on the Mechanical Failure of Multi-Walled Carbon Nanotubes**, ***S.K. Pregler***, *S.B. Sinnott,* University of Florida

Polyatomic ion-beam deposition on advanced materials, such as semiconductors, carbon nanotubes, polymers, and nanocomposites, to induce surface chemical modification is an important process used to achieve thin film growth, surface etching, and nano-texturing of the surface. Previous atomistic simulations have shown that particle beam deposition can induce crosslinking between the shells of unfunctionalized multiwalled carbon nanotubes. In this work, we investigate the effect of atomic, polyatomic, and electronic irradiation of chiral and armchair multiwalled carbon nanotubes. In particular, Ar and CF3+ ions are considered. The innermost shells of the irradiated nanotubes were then pulled at a constant rate of 40 m/s until axial load failure. The approach used is classical molecular dynamics simulations using reactive empirical bond-order potentials and the primary knock-on atom approach to model the effects of electron irradiation. The objectives of this study are to determine the degree to which multi-walled nanotube failure is mitigated by the irradiation-induced cross-links, and how irradiation affects the stability and structural integrity of the nanotubes. In addition, the influence of the irradiating species and nanotube chiral structure on the results is examined. Lastly, the predicted outcomes are compared to new and published experimental studies. This work is supported by the National Science Foundation (CHE-0200838).

11:40am **NS-FrM11 Direct Synthesis of Suspended Single-Walled Carbon Nanotubes Crossing Plasma Sharpened Carbon Nanofiber Tips**, *C.H. Weng,* ***K.C. Leou***, *W.Y. Lee, Z.Y. Juang, C.H. Tsai,* National Tsing Hua University, Taiwan

Single-walled carbon nanotubes are one of the most important quasi-one-dimensional nano-materials but their properties or associated device characteristics are very sensitive to the surroundings, e.g., surfactants or wrapping materials, and ambient gases, etc. It has been shown that such environmental perturbation effects could be minimized by suspending the SWNTs. Here we report a novel method for direct synthesis of suspended single-walled carbon nanotubes (su-SWNTs) using vertically-aligned carbon nanofibers (CNFs) as templates via a three-step fabrication process. Plasma enhanced chemical vapor deposition (PECVD) is first employed to grow vertically aligned CNFs on silicon substrates patterned with coated catalytic nickel film of 10 nm thickness. The CNFs are then post-treated by energetic argon plasma in the same reactor to yield structural transformation of CNFs with sharpening tips embedded with catalytic nanoparticles of a favorable size, presumably below 10 nm. A thermal CVD process then subsequently followed to directly synthesize SWNTs suspended across the tips or sidewalls of post-treated CNFs (PT-CNFs) with a span up to 10 µmm, as revealed by the analysis using scanning electron microscopy and resonance micro-Raman spectroscopy. We also demonstrated that one can maximize the yield of su-SWNTs on the tips of PT-CNFs by optimizing the post-treatment conditions to provide a protective coating to suppress the growth of SWNTs from sidewalls. The method of fabricating su-SWNTs described in this letter can be extended to position a single isolated SWNT for the purpose of either minimizing environmental perturbations during SWNT characterization or enhancing performance in nano-device applications.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the National Science Council of the Republic of China and the Center for Nano Science and Technology in the University System of Taiwan.

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