

Nanometer-scale Science and Technology Room 213D - Session NS-TuM

Nanotube Processing and Composite Materials

Moderator: S. Evoy, The University of Pennsylvania

8:20am **NS-TuM1 Controlled Fabrication and Modification of Organized Carbon Nanotube Architectures**, *Y.J. Jung*, Rensselaer Polytechnic Institute, U.S.A.; *R. Vajtai, N. Chakrapani, G. Meng, P.M. Ajayan*, Rensselaer Polytechnic Institute; *Y. Homma, Y. Kobayashi*, NTT Basic Research Laboratories; *T. Ogino*, Yokohama National University, Japan

An overview of our results on the controlled fabrication and modification of organized carbon nanotube architectures will be presented. The talk includes strategies for building suspended single-walled carbon nanotubes (SWNTs) forming self-directed networks on nano-scale patterned substrate using chemical vapor deposition (CVD). We elaborate the straightening process of nanotubes in the networks suspended on Si pillars by Ga ion irradiation in a Focused Ion Beam (FIB). Beyond the morphological changes of the nanotubes and nanotube bundles we will present our conclusions for carbon atom ejection and compare with previous electron beam and ion beam irradiation experiments. Although ion irradiation induces defective structures into the nanotube lattice, as micro-Raman mapping shows, the form and dimensions of the nanotubes remain close to that of the original grown morphology. To demonstrate another nanostructure modification we will discuss the formation of intriguing two-dimensional cellular foams from capillarity-induced perturbations during the drying of vertically aligned multi-walled carbon nanotubes (MWNT) architectures with the mechanisms giving rise to pattern formation and methods of controlling the structure and orientation. Similarly, we will briefly present our latest results for organized assembly of multiwalled nanotubes into various 2-D and 3-D structures on planar substrates as well as within anodic porous aluminum oxide templates.

8:40am **NS-TuM2 Growth of Arrays of mm Long, Straight Single-Walled Carbon Nanotubes**, *Z. Yu, S. Li, P. Burke*, UC Irvine

In this work, we demonstrate the growth of arrays of 1.5 mm long, straight single walled nanotubes fabricated using a single furnace with methane and H₂ as the feedstock. Recently Huang et al[1] have fabricated 3.7 mm long single walled carbon nanotubes using a two-furnace, dual temperature growth system with CO and H₂ as the feedstock. Our work shows arrays of long, straight nanotubes can be grown in a single furnace system. Using a home-built CVD system based on a 3 inch Lindberg furnace, we have synthesized long, straight nanotubes using CVD. The catalysts were prepared as follows: First, a lithographically patterned Ti(50 nm)/Au(200 nm) metallization layer is deposited and patterned using e-beam evaporation onto a Si wafer. Next, an aqueous solution containing nanoparticle catalyst is deposited and lifted off onto only the patterned Au. The growth procedure was as follows: First, the sample was heated to 900 C in Ar. Next, H₂ was flowed for 10 minutes. Next, methane/H₂ mixture was flowed for 15 minutes to activate the growth. Post-growth characterization was carried out with SEM. AFM growth from nanotubes grown under similar conditions in our lab yielded diameters of 1.5 nm. The growth results indicate an aligned array of nanotubes (6) with pitch of 50 microns and length of at least 200 microns. 3 of the 6 nanotubes were 1.5 mm in length. The growth of the longer nanotubes was terminated only by the presence of a neighboring catalyst site. With properly designed catalyst geometries with room to grow, cm long single walled nanotube growth should be possible. In the future it should be possible to grow 2d arrays by rotating the wafer and carrying out a second growth run. By engineering the nanotube pitch, ultra-dense electrical circuitry could be fabricated.

[1] S. Huang, B. Maynor, X. Cai, J. Liu, *Ultra-long Well-Aligned Single-Walled Carbon Nanotube Architectures on Surfaces*, *Advanced Materials*, vol. 15, pp. 1651-1655, 2003.

9:00am **NS-TuM3 Low-temperature Synthesis of Aligned Carbon Nanotubes by Hot-Filament Assisted DC Plasma CVD**, *Y. Watanabe, Y. Hayashi, S. Nishino*, Kyoto Institute of Technology, Japan

Carbon nanotubes (CNTs) are expected to be used for the field emitters of 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. The synthesis method of vertically aligned CNTs in low temperature below the softening point of a glass substrate should be developed to apply CNTs to field emitters of FED. Motivated by such a background, we carried out experiments of synthesis

of CNTs in low temperature by hot-filament assisted DC plasma chemical vapor deposition (HF/DC-PCVD)@super 1@. The growth method and conditions were as follow. First a Co foil substrate was heated by hot tungsten filaments in H@sub 2@ atmosphere. Then after 10 min pretreatment in a H@sub 2@ plasma, CH@sub 4@ gas was added for the growth of nanotubes. DC voltage of -450V was applied to the substrate with the hot-filaments grounded. During the growth, substrate temperature was controlled about 500°C, the gas pressure was 20Torr, and growth time was 10 min. Well-aligned CNTs about 60 nm in diameter were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the substrate. We have succeeded to synthesize well-aligned and high density carbon nanotubes on Co substrate at 500°C. @super 1@Y.Hayashi, T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19(2001) 1796.

9:20am **NS-TuM4 Theoretical Study of Catalytic Growth Single-Walled Carbon Nanotubes**, *F. Ding, K. Bolton, A. Rosen*, Goteborg University and Chalmers, Sweden

Molecular dynamics (MD) simulations based on an empirical potential energy surface (PES) were used to study iron catalyzed nucleation and growth of single-walled carbon nanotubes (SWNTs). The simulations show that SWNTs grow from the iron-carbide particle at temperatures between 800 and 1400 K, whereas graphene sheets encapsulate the particle at temperatures below 600 K and a three-dimensional (3D) soot-like structure is formed above 1600 K. The simulations also reveal other details of the growth mechanism. For example, it is seen that the growing SWNT maintains an open end on the FeC particle due to the strong bonding between the SWNT end atoms and the particle. The SWNT-particle enthalpy is minimized when the SWNT and FeC cluster have similar diameters. This leads to the growth of SWNTs that have similar diameters to the metal clusters, as has been seen experimentally.

9:40am **NS-TuM5 Controlling and Modeling the Interphase in Polymeric Nanocomposites**, *L.C. Brinson, H. Liu, T. Ramanathan*, Northwestern University

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Polymeric nanocomposites made by incorporating small amount of nanoscale inclusions into polymer matrices exhibit dramatic changes in thermomechanical properties over the pure polymers. Because the properties of the nanoscale fillers can be extraordinary, even small volume fractions can result in significant changes. Enhancing the effect is the extremely significant role that the interphase plays in these systems. Given the enormous surface to volume ratio for nanoparticles, the interphase volume fraction can dwarf that of the inclusions themselves. In this paper, experimental evidences of the existence of this interphase region are presented. We show that by properly-controlled functionalization of the nanoscale inclusions, we can impact the properties of the interphase region and consequently control the properties of the nanocomposites. In conjunction with the experimental results, the viscoelastic behavior of multi-phase polymeric nanocomposites is modeled using a novel hybrid numerical-analytical modeling method that can effectively take into account the existence of the interphase region. This hierarchical modeling approach couples the finite element technique and micromechanical approach and operates at low computational cost. Comparison between experimental and modeling results is reported.

10:20am **NS-TuM7 Wetting of Individual Carbon Nanotubes with Organic Liquids**, *A.H. Barber, S.R. Cohen, H.D. Wagner*, Weizmann Institute of Science, Israel

Carbon nanotubes show promise as reinforcements in polymer composites. For effective reinforcement, good adhesion between the nanotube and polymer is necessary. Adhesion at a polymer-nanotube interface involves many different types of bonding mechanisms, with wetting of fibers by the liquid polymer regarded as a necessary, but not a sufficient prerequisite for adhesion. Here we present a new experimental method to investigate the wetting behavior of single carbon nanotubes under ambient conditions. Carbon nanotubes, bound to probe tips in a scanning probe microscope are controllably dipped into various organic probe liquids. The changes in force due to the wetting of single carbon nanotubes thus can be accurately measured, giving insights on the interaction between liquid and nanotube. In particular, liquid-carbon nanotube contact angles are measured, which can be interpreted with respect to the nanotube surface characteristics. Using an Owens and Wendt analysis, the polar and dispersive components of the interaction can be separated. Our results show that the surface of the carbon nanotube displays hydrophilic behavior, in contrast to hydrophobic graphite surfaces. This project was supported by the (CNT) Thematic European network on 'Carbon Nanotubes for Future Industrial

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Composites' (EU), the Minerva Foundation, the G. M. J. Schmidt Minerva Centre of Supramolecular Architectures, and by the Israeli Academy of Science. H.D. Wagner is the recipient of the Livio Norzi Professorial Chair.

10:40am **NS-TuM8 Impregnation of Osmium Dioxide to MWCNTs and Improvement of the Electron Emission Characteristics**, *T. Noguchi, M. Shimamoto, M. Nishiwaki*, KEK, Japan; *K. Tatenuma*, KAKEN Inc., Japan; *S. Kato*, KEK, Japan

Osmium dioxide impregnation to MWCNTs was attempted in order to improve the electron emission characteristics. OsO₂ similar to RuO₂ has desirable properties including high conductivity (6x10⁴ Ω⁻¹cm at 300K), high catalytic performance, and good chemical and physical stabilities. In this study, OsO₂ impregnation to MWCNTs was conducted by utilizing osmium tetroxide in a solvent at ambient temperatures and pressures. When compared to MWNTs without impregnation treatment, those MWCNTs impregnated with OsO₂ have superior and more efficient electrical characteristics with stable emission at a lower electric field as observed for RuO₂ impregnated MWCNTs.

11:00am **NS-TuM9 Electron Emission Property from MWCNTs with Subnano Ruthenium Dioxide Clusters and with High Adhesivity on Substrate - High Current Endurance Test in UHV and Influence of H₂O or CO**, *M. Shimamoto, T. Noguchi, M. Nishiwaki*, KEK, Japan; *K. Tatenuma*, KAKEN Inc., Japan; *S. Kato*, KEK, Japan

Applications of MWCNTs to FEDs, electron sources of electron accelerators and surface analytical tools, and vacuum tubes for microwave amplifier, X-ray, light tube and so on require a high current density of its electron beams, a low threshold of electric field starting the field emission and a long life time with the emission. We reported the achievement of a remarkably high DC current density close to 300mA/cm² with a threshold electric field of 2V/μm using new technologies of subnano RuO₂ clusters on MWCNTs surface and of high CNT adhesivity on metallic substrate. An outstanding electron emission property achieved after those treatments would be explainable based on both further increase emission points due to the subnano clusters not only from MWCNT ends but also from strongly bent wall and better thermal conductivity resulted from the heat treatment. Reduction of work function of CNT owing impregnation of RuO₂ might contribute higher field emission current density as well. Base pressure of XHV should be also big help to make sure reasonable MWCNT life at very high emission current to drastically reduce physical and chemical ion sputtering. In this paper, endurance running tests of MWCNTs in UHV up to 700 hours with a relatively high DC current of 50 mA/cm² and degradation of the field emission characteristics due to residual gas such as H₂O or CO are focused.

11:20am **NS-TuM10 Synthesis of Y-Junction Singlewall Carbon Nanotubes**, *Y.C. Choi, W. Choi*, Florida International University

Y-junction singlewall carbon nanotubes were synthesized on thermally oxidized silicon substrates by chemical vapor deposition. Molybdenum, titanium, or zirconium-doped iron nanoparticles supported by aluminum oxide were used as catalysts for the synthesis. Most of singlewall carbon nanotubes have branches, forming Y-junctions. Transmission electron microscopy confirmed the formation of singlewalled structures of Y-junctions with diameters ranging from 2 nm to 4 nm. The density of Y-junctions could be controlled simply by variation of spinning rate when spin coating of catalyst solution was carried out. It was found from radial breathing mode peaks in Raman spectra that our sample has both metallic and semiconducting nanotubes, indicating the possible formation of Y-junctions with different electrical properties. The growth mechanism based on experimental results will be further proposed.

11:40am **NS-TuM11 Surface-Programmed Assembly Process of Large-Size Multi-Wall Carbon Nanotubes and Its Mechanism**, *J. Im, M. Lee, S. Hong*, Seoul National University, South Korea

Recently, the surface-programmed assembly (SPA) process that utilizes surface molecular patterns to guide the assembly of single wall carbon nanotubes (SWCNT) has been reported (Nature 425, 36 (2003)). Herein, we show that the SPA method can be utilized to assemble even large-size multi-walled carbon nanotube (MWNT) which is as large as 30nm in diameter. In addition, we studied the mechanism of the SPA process for both SWNTs and MWNTs by measuring 1) the adsorption probability distribution as a function of CNT size (diameter, length, etc.) and 2) interaction energy between molecular patterns and CNTs. This result implies that SPA method can be applied for electronic applications based on relatively large-size nanowires.

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