

Nanometer-scale Science and Technology

Room: 311 - Session NS+NC-FrM

Nanoscale Processes

Moderator: N.A. Burnham, Worcester Polytechnic Institute

8:20am **NS+NC-FrM1 Synthesis of Controlled (*n,m*) Identity Single-Walled Carbon Nanotubes**, *L. Pfefferle, C. Zoican*, Yale University
INVITED

Advanced electronic applications using single-walled carbon nanotubes (SWNT) require uniform property SWNT that are not degraded by compositional variation (*n,m* plurality) or side wall damage induced by cleaning or separation processes. The lack of uniform (*n,m*) identity SWNT with a low level of side-wall defects presents a major hurdle to device development. Thus, the ultimate goal of nanotube synthesis is to produce specific (*n,m*) nanotubes at high selectivity. In this talk we will discuss methods for controlling the diameter and *n,m* identity of a nanotubes produced in synthesis. Many investigators have shown that the use of a second metal or transition metal oxide in the catalyst can anchor small domains of the active phase or alter their morphology to narrow the distribution of nanotubes identities produced. In addition such methods can produce highly enriched semiconducting or metallic samples. In some of these catalyst systems using CO disproportionation as the growth reaction, changing reaction temperature can dramatically vary the diameter of the nanotubes produced. We will show our recent work and that of others using X-ray absorption spectroscopy to explore the interaction between the catalyst components and how the size of the active phase varies and is related to the nanotubes diameters observed. Longer term, in order to gain almost pure *n,m* identity nanotubes in an economically viable manner, regrowth of specific (*n,m*) nanotube would be the most effective technique. We have recently demonstrated regrowth of SWNT chopped into short "seeds", filled with iron or nickel functionalities and activated in a simple reaction step prior to the regrowth. Our exploratory results from the regrowth processes to be described in this talk resulted in a significant increase in SWNT weight, while at the same time showing a clear potential for retaining the (*n,m*)-distribution of the seed. This methodology offers advantages (e.g. scalability, fidelity, and does not require specialized seed cutting or functionalization) compared to other recent pioneering demonstration of SWNT regrowth by the Smalley research group.^{1,2}

¹ Smalley, R. E.; Li, Y.; Moore, V. C.; Price, B. K.; Colorado, R., Jr.; Schmidt, H. K.; Hauge, R. H.; Barron, A. R.; Tour, J. M., Single Wall Carbon Nanotube Amplification: En Route to a Type-Specific Growth Mechanism. *Journal of the American Chemical Society* **2006**, *128*, (49), 15824-15829.

² Wang, Y.; Kim, M. J.; Shan, H.; Kittrell, C.; Fan, H.; Ericson, L. M.; Hwang, W.-F.; Arepalli, S.; Hauge, R. H.; Smalley, R. E., Continued growth of single-walled carbon nanotubes. *Nano Letters* **2005**, *5*, (6), 997-1002.

9:00am **NS+NC-FrM3 Fullerene Growth on N-adsorbed Cu(001) Nanopatterned Surfaces**, *T. Iimori, B. Lu*, University of Tokyo, Japan, *K. Sakamoto*, Chiba University, Japan, *K. Nakatsuji*, University of Tokyo, Japan, *F. Rosei*, University of Quebec, Canada, *F. Komori*, University of Tokyo, Japan

Nitrogen (N)-adsorbed Cu(001)-c(2x2) nanopatterned surfaces are used as templates to guide the growth of low-dimensional C₆₀ molecular nanostructures. The detailed nucleation and growth behaviors are studied by in situ scanning tunneling microscopy (STM). At room temperature, on the 0.3 ML-N-covered surface, where 5x5 nm² patches of the c(2x2)-N surface are squarely arranged and bare Cu(001) surface. In other word, the bare Cu surface forms a nanogrid. Here ML is defined as the Cu atom density of the clean Cu(001) surface. During the initial stages of growth, C₆₀ molecules preferentially adsorb on the bare Cu regions on a partially N-covered grid surface. Subsequently a two-dimensional molecular nanomesh is formed after C₆₀ covers all the bare Cu regions. Further deposition leads to C₆₀ growth on the c(2x2)-N areas until the first molecular layer is completed. For N-saturated surface with trench structures, the <010> steps of these structures serve as initial anchoring sites for C₆₀ growth. From there, the growth proceeds two-dimensionally until a single C₆₀ layer is achieved due to island coalescence. In contrast, no nucleation site was observed when the <110> steps were predominant on the surface. At least up to 6 mono-molecule layer, the growth proceeds layer-by-layer i.e., the overlayer morphologies are directed by the underlying substrate pattern in both (partially and fully N-covered) surfaces. Four rotational domains are observed for the quasi-hexagonally close-packed C₆₀ overlayer with a nearest-neighbor C₆₀-C₆₀ distance of 1.02 nm. It is found that the interaction between C₆₀ and the c(2x2)-N surface is fairly weak, likely to be dominated by van der Waals forces, whereas the C₆₀-Cu interface is chemisorbed. Site-specific electronic effects between these two regions can be resolved by STM even for thick films.

9:20am **NS+NC-FrM4 Nanochemical Equilibrium Involving a Small Number of Molecules: a Prediction of a Distinct Confinement Effect**, *M. Polak, L. Rubinchik*, Ben-Gurion University, Israel

This study explores theoretically features unique to the chemical equilibrium in a nano-confined reaction mixture, which is closely related to newly developed routes for the synthesis of organic molecules and inorganic nanoclusters. Remarkable modifications in the equilibrium state of a closed small system compared to its (macroscopic) thermodynamic limit (TL) are predicted for several model reactions. Thus, canonical ensemble based statistical-mechanical formulation and computations show that a decrease in the overall number of molecules can lead to significant enhancement of the equilibrium extent of exothermic reactions. In particular, plots of lnK vs. 1/T exhibit below a certain temperature an increase in the slope, relative to the TL case, by a factor equal to the sum of the ingredient stoichiometric coefficients. In order to exemplify the smallness effect on K, the reaction 2AB(ad)=A₂(ad)+B₂(ad) on a surface is modeled for different overall number of molecules with emphasis on the roles of fluctuations and off-stoichiometric effects. The modeling is extended to the gaseous phase using the "harmonic oscillator-rigid rotor" approximation for the exothermic reaction 2NO(g)=N₂(g)+O₂(g), demonstrating the generality of the confinement-smallness effect. The enhancement is significant also in case of the addition reaction A+B=C, taking place in a closed tetrahedral "cage" as a model for a molecular capsule. The computations show that the temperature range of variations in the lnK vs. 1/T slope (from ΔH° to 2ΔH°) strongly depends on the reaction exothermicity. These phenomena are relevant to reactions taking place under certain conditions in a confined nano-space, such as catalytic nanoreactors ranging from molecular capsules and micelles¹ to zeolite cavities² and carbon nanotubes.³ While in catalysis the system is typically open, in nanoreactors there can be situations, such as the occurrence of rapid pre-equilibrium or "product inhibition", in which the reaction mixture is confined effectively. Then, conclusions of the closed system present modeling should be valid and taken into account as an appreciable contribution to the reaction equilibrium yield.

¹ T. S. Koblentz, J. Wassenaar, and J. N. H. Reek, *Chem. Soc. Rev.* **37**, 247 (2008).

² B. Smit, and T. L. M. Maesen, *Nature* **451**, 671 (2008).

³ D.A. Britz et al., *Chem. Commun.* **37** (2005).

9:40am **NS+NC-FrM5 Epitaxial Growth of InP Nanowires on Silicon**, *L. Gao, R.L. Woo, R.F. Hicks*, University of California, Los Angeles

Semiconductor nanowires have potential applications in new and high-performance one-dimensional devices. Epitaxial growth of high-quality semiconductor nanowires on Si surfaces is ideal for utilizing semiconductor nanowires within the frame of mainstream silicon technology. We have achieved epitaxial growth of InP nanowires on Si(111) and Si(100) surfaces by metalorganic vapor phase epitaxy (MOVPE). The silicon surfaces are wet cleaned before growth. Indium droplets are deposited onto the silicon surface as the seeds for InP nanowire growth. By finely controlling the experimental conditions, InP nanowires prefer to grow in the <111> directions of the silicon substrates, which makes it possible to grow vertical InP nanowires on Si(111) surface. By restraining the growth of non-vertical nanowires, the growth of all vertical nanowires can be achieved on Si(111) substrate. TEM and PL studies of as-grown InP nanowires will also be presented.

10:00am **NS+NC-FrM6 Structure and Electron Transport within Self-Assembled Monolayers (SAMs) of Discotic Molecules on Au-substrates**, *A. Bashir*, Ruhr Universität Bochum, Germany, *X. Dou*, Max Plank Institute of Polymer Research Mainz, Germany, *Z. Wang, D. Käfer, G. Witte*, Ruhr Universität Bochum, Germany, *K. Müllen*, Max Plank Institute of Polymer Research Mainz, Germany, *Ch. Wöll*, Ruhr Universität Bochum, Germany

Hexa-peri-hexabenzocoronene (HBC) and HBC-derivatives can self-assemble in form of columnar film structures, which have recently attracted a significant amount of attention with regard to one-dimensional charge transport. The HBC molecules are known to form the large ordered columnar rows studied by various methods. In previous work the preparation of vertically oriented columnar rows has been achieved by employing a zone casting technique.¹ Here, we demonstrate another approach to fabricate such columnar system by an immersion process, where one-dimensional columns are formed by the self organization of discotic HBC molecules modified by thiol (-SH) anchors adsorbed on Au(111) substrates. The molecular arrangements and charge transport of such columnar films is investigated by scanning tunneling microscopy (STM) and current imaging tunneling spectroscopy (CITS). The HBC self-assembled monolayer (SAMs) are found to consist of long range ordered

domains consisting of equidistant paired rows. Each row consists of a one-dimensional column of closely packed stacked HBC units. The periodicity between these rows amounts to be twice than the diameter of the HBC-molecules. From the STM data and the molecular orientation obtained from near-edge x-ray absorption spectroscopy (NEXAFS) a structural model is derived. The current-voltage (I-V) characteristics measured by locally positioned STM tip above the HBC-SAM at 298 K and at 80 K exhibit a pronounced temperature dependence, indicates the presence of an additional charge transport mechanism including a hopping between the adjacent HBC disks aside from direct tunneling

¹Simpson, C. D.; Wu, J.; Watson, M. D.; Müllen, K., From graphite molecules to columnar superstructures - an exercise in nanoscience. *Journal of Materials Chemistry* 2004, 14, (4), 494-504.

10:20am **NS+NC-FrM7 Nanoscale Ballistic Heat Conduction in Silicon**, *L.J. Klein*, IBM TJ Watson Research Center, *M. Ashegi*, Stanford University, *H.F. Hamann*, IBM TJ Watson Research Center

Today's electronic devices operations are affected by thermal issues determined by physical dimensions that are smaller or comparable to the mean free path of phonons in silicon. Controlling and understanding heat dissipation on nanometer scale can improve the thermal efficiency and power management of electronic circuits. Here we investigate heat conduction on nanometer scale employing metallic nanoheater with dimensions ranging from 100 nm up to 5 μ m. The nanoheaters are used both for heat generation and also for local temperature measurement. We investigate how the thermal resistance of individual nanoheaters and heat conduction across gaps ranging from 100 nm to 400 nm is changing as the sample temperature is varied from room temperature down to 30 K. As the temperature is lowered the phonon mean free path increases by more than 2 orders of magnitude compared with room temperature value and ballistic heat conduction (localized heating effects) start to play an important role. The thermal resistance of nanoheaters is a complex interplay between the thermal conductance of silicon substrate, localized heating effect and interface thermal resistance and their relative contribution changes as the phonon mean free path increases. A simple model considering the spreading thermal resistance, the interface thermal resistance, and the localized heating effect is proposed and used to model the experimental results. While for large heaters, the phonon mean free path is comparable to the size of the hot spots even at low temperature, for the small heaters, the mean free path is much larger than the heater size, and the localized heating effect plays a significant role in the total thermal resistance. The ballistic heat transport impact on nanoscale heat conduction has been evaluated in terms of heater size and phonon mean free path.

10:40am **NS+NC-FrM8 Understanding the Factors Driving Performance and Reproducibility for Spray-Coated Single Wall Carbon Nanotube Transparent Conductive Films**, *R.C. Tenent, J.L. Blackburn, T.M. Barnes, M.J. Heben*, National Renewable Energy Laboratory

Transparent and electrically conducting films of single wall carbon nanotubes (SWCNT) have been shown to be useful for integration into a variety of opto-electronic devices including solution-processed photovoltaics (PV). Several techniques have been introduced for the deposition of SWCNT networks including vacuum filtration, spin coating, ink jet printing and spray coating. We believe that spray coating represents the most cost effective technique for integrating transparent conductive SWCNT network films into large scale manufacturing. While a variety of groups have reported spray deposition techniques for SWCNT networks, there has been little detailed discussion of the issues relating to performance, reproducibility, and suitability for large scale manufacturing. A number of factors influence the electronic and optical properties of SWCNT networks. These factors include the tube source, purification protocol, ink formulation procedure (e.g. sonication power, duration, and choice of surfactant), the deposition method itself, and post-deposition processing. Our current work is focused on understanding the interplay of these factors in the spray coating process for SWCNT thin films. We pay special attention to optimizing film performance and reproducibility for photovoltaic applications. These studies have facilitated the reproducible fabrication of high performance organic photovoltaic devices on our SWCNT electrodes with efficiencies comparable to devices fabricated on traditional transparent conducting oxide films, such as indium tin oxide.

11:00am **NS+NC-FrM9 Electron Beam Irradiation Induced Mass Transport in Indium Filled Indium Oxide Tubular Nanoarrow Structures**, *M. Kumar, V. Singh, B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi

Indium filled indium oxide tubular nanoarrows have been synthesized on silicon substrates by using simple horizontal tube furnace kept at 960°C and atmospheric pressure. Indium oxide powder mixed with carbon (1:1) in the presence of reducing ambient has been used for the growth of indium oxide nanotubular structures. A constant flow of Ar gas at the rate of 200 ml/min.

was maintained during the growth. The transmission electron microscopy (TEM) studies show the presence of indium inside the indium oxide tubular base extended with octahedron tip. The octahedron tip is sharp and has the diameter as low as 10 nm. High resolution TEM studies reveal that the structures are crystalline in nature and growth direction to be $\langle 100 \rangle$. The bottom-vapor-solid growth mechanism has been used to explain the role of reducing ambient in self catalytic growth of indium filled indium oxide tubular nanoarrows. The electron-beam induced mass transport of indium filled in indium oxide nano structures has been studied using TEM with the background pressure of specimen chamber at 10^{-7} mbar and room temperature. The electron beam current has been varied from 0.8 μ A to 24.7 μ A to study the onset of phase transformation of indium from solid to liquid in different nanotube structures having diameter ranging from 30 nm to 150 nm. The electron-beam irradiation results in the melting and transport of indium inside the tubular structures. The real time imaging in TEM measurements have been used to study the mass transport properties. The synthesis of indium filled indium oxide tubular nanoarrows and the observed indium transport may have the potential nanotechnological applications.

11:20am **NS+NC-FrM10 Etch Stop Control and Low-Damage Atomic-Layer Etching of HfO₂ using BCl₃ and Ar Neutral Beam**, *J.B. Park, S.D. Park, W.S. Lim, G.Y. Yeom*, Sungkyunkwan University, Korea

The downscaling of metal-oxide-semiconductor field-effect transistors (MOSFETs) has created the need for high-dielectric-constant k materials to replace SiO₂ for reducing the gate-leakage current while maintaining the gate-dielectric capacitance. Therefore, there have been many studies on the dry etching of HfO₂ using halogen-based plasma etching for applications to MOSFET devices. A precise etch rate is required in the plasma etching for HfO₂ instead of a high etch rate due to the low thickness of the material. Moreover, an extremely high etch selectivity over the under layer material is required. In addition, the damage on the etched surface is intolerable. However, the conventional plasma-etching processes tend to physically damage the surface of the devices by creating surface defects, including structural disruption, an intermixing layer, or stoichiometry modification, and increasing surface roughness, due to use of energetic reactive ions to achieve vertical etch profiles. In addition, these halogen-based plasma etchings showed finite etch selectivity between HfO₂ and the under lying materials. These problems decrease the device performance. Atomic-layer etching (ALET) may be the most suitable method for etching HfO₂ in next-generation MOSFET devices because it may etch HfO₂ with no physical damage and with atomic-scale etch controllability. The etch characteristics of HfO₂ by ALET were investigated using a BCl₃/Ar neutral beam. The effect of ALET on surface modification and etch-depth control was also examined. Self-limited etching of HfO₂ could be obtained using BCl₃ ALET. This was attributed to the absorption of BCl₃ by the Langmuir isotherm during the absorption stage and the vaporization of hafnium-chlorides/boron oxychlorides formed on the surface during the desorption stage. In addition, the surface composition of HfO₂ was not altered by etching during ALET.

11:40am **NS+NC-FrM11 Assessment and Characterization of Exposures to Airborne Nanoparticles at Research Centers**, *S.J. Tsai, E. Ada*, University of Massachusetts Lowell, *J. Isaacs*, Northeastern University, *M. Ellenbecker*, University of Massachusetts Lowell

As part of ongoing efforts for the respiratory protection of researchers in the Center for High Rate Nanomanufacturing, nanoparticle exposure levels in various nanoparticle research laboratories were measured. The exposure assessments studied were associated with the use of nanoparticles during various machines processing and handling solid nanoparticles. Background particle number concentrations and particle size distributions varied significantly among the laboratories. Breathing zone particle number concentrations and particle size distributions were not significantly different from those of background when the process or handling was performed inside a laboratory fume hood or an effective local exhaust hood. However, high workers' breathing zone particle number concentrations were measured for a few operations that were performed without proper local exhaust ventilation. A TSI Fast Mobility Particle Sizer was used to measure airborne particle concentration from 5 nm to 560 nm in 32 size channels. Air samples were also collected on TEM grids placed on polycarbonate membrane filters and particles were characterized by transmission electron microscopy and scanning electron microscopy. Measurement locations were the room background, the researcher's breathing zone, and the source location. Airborne particle concentrations measured at breathing zone locations were analyzed to characterize exposure level. Elevated concentrations at the source location compared to the background concentration were found in most laboratories. Typically, nanoparticle agglomerates were formed at particle sizes ranging from nanometer to micrometer. Nanoalumina particles with individual particle size less than 100 nm formed airborne particle agglomerates as small as 200 nm and as

large as above a few micrometers. Exposure levels to airborne nanoparticles were affected by the properties of nanoparticles (size, shape, density), humidity and the airflow pattern of the environment. Our study is committed to ensuring that nanoparticle research is carried out in a healthful and environmentally beneficial manner. Complete results will be fully discussed in the presentation.

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