Tuesday Afternoon, October 19, 2010

Nanometer-scale Science and Technology
Room: La Cienega - Session NS-TuA

Carbon-Based Nanomaterials

Moderator: N.A. Burnham, Worcester Polytechnic Institute

2:00pm **NS-TuA1 Covalent Synthesis and Optical Characterization of Double-Walled Carbon Nanotube - Nanocrystal Heterostructures**, ***X. Peng***, State University of New York at Stony Brook, *M.Y. Sfeir, J.A. Misewich,* Brookhaven National Laboratory, *S.S. Wong*, State University of New York at Stony Brook

Double-walled carbon nanotubes (DWNTs) have been a key focus material of research in recent years owing to their unique electronic structure and properties. However, the incorporation of DWNTs with quantum dots (QDs) into nanocomposites via a covalent chemical approach as well as the optical properties of the composites have rarely been explored. In particular, the investigation based on CNT-QD systems, one of well-studied nanomaterial heterostructures, provides insights into a fundamental understanding of efficient charge separation within heterostructures via charge transfer relative to other relaxation pathways such as exciton recombination. In this specific work, DWNT-CdSe heterostructures were obtained by covalently conjugating 2-aminoethanethiol (AET)-modified CdSe QDs with terminal amino groups onto the surfaces of oxidized DWNTs via the formation of amide bonds. For AET-CdSe, a characteristic emission in NIR was observed due to the trap states induced by the presence of AET capping ligands. Besides, the magnitude of the trap emission was found to be associated with the concentration of AET added into systems. Interestingly, the observed trap emission is effectively quenched upon conjugation with the DWNT as a result of the charge transfer from trap states of CdSe to DWNTs. More strikingly, the time-resolved photoluminescence studies showed the exciton decay of DWNT-CdSe composites was recovered from multi-exponential to nearly mono-exponential behavior, thereby suggesting that a unique exciton dynamic occurred in the DWNT-CdSe heterostructure. More careful kinetic studies are in progress.

2:20pm **NS-TuA2 Carbon Nanotube Nonvolatile Memory**, ***K. Matsumoto***, Osaka University, Japan

Since single-walled carbon nanotubes (SWNTs) have small diameter of ~1 nm, high-electric field concentration is easily generated around SWNTs. Therefore, the carbon nanotube field-effect transistors (CNTFETs) using SWNTs as a channel are expected for low power consumption nonvolatile memory. The conventional CNTFETs, however, whose channels are exposed to the atmosphere, exhibit large hysteresis due to charge trapping by impurities, such as water molecules, around SWNT channels. In the present paper, we have fabricated nonvolatile memory based on top-gated CNTFETs with double gate insulator layers after removal of the impurities around SWNT channels.

A double layer thin SiNX /SiO2 films were deposited on SWNT channels using catalytic chemical vapor deposition. After the double layers deposition, a top gate electrode was fabricated. The interface between SiNX and SiO2 films in the device is expected as a charge storage node of nonvolatile memory. The transfer characteristics of the CNTFET as a function of back- and top-gated voltages at 300 K in vacuum were measured. The negligible hysteresis is observed for sweeping the back-gated voltage, indicating that impurities around the SWNT channel are completely removed. In contrast, hysteresis increases with increasing sweep range for top-gated voltage. The counterclockwise hysteresis loops are due to the charging and discharging processes of holes in the top-gated CNTFETs. These results mean that the charge was trapped at the interface of SiNX /SiO2 films by the applied top gate bias. Due to the small diameter of the CNT, the electric field concentration occurs, and only 2V application of the top gate bias produces the hysteresis. This gate bias is 10 times smaller value than that of the conventional planer type memory. The single-charge effects are observed using the CNT-based memory devices. When top-gated voltage was swept forth and backward for the ranging of ± 0.7 V, the abrupt peaks on the currents are observed for both directions. The abrupt drop or increase in drain currents corresponds to single-hole charging and discharging phenomena in CNT-based memory devices, respectively. The same measurements were carried out twenty times, and four discrete Id-Vg curves are clearly observed, which are attributed from the effect of single-holes traps.

We have fabricated the CNTFETs nonvolatile memory, which operate 10 times smaller bias owing to the electric field concentration effects. Single charge detection was also demonstrated in the CNT memory device.

2:40pm **NS-TuA3 Single Walled Nanotube (SWNT) Fiber Field Emission Cathodes**, ***S.B. Fairchild***, *B. Maruyama, J.J. Boeckl, D.A. Shiffler, N.P. Lockwood,* Air Force Research Laboratory, *M. Pasquali*, Rice University

High power THz sources and amplifiers hold the potential to revolutionize the remote sensing and communication industries. Traveling wave tubes (TWT) are the most promising technology for compact high power amplifiers at THz frequencies. High frequency applications necessitate the need for small diameter beam tunnels and thus small diameter high current electron beams. Small diameter beams are typically achieved by emitting electrons from a thermionic cathode surface much larger than the THz TWT beam tunnel and focusing the beam using either electrostatic or magnetic field electron beam optics. To avoid using focusing optics, a micron sized high aspect ratio field emission (FE) cathode can be immersed in the confining magnetic field and used to generate an electron beam with a smaller diameter than the THz TWT beam tunnel. The key technical challenge with using a micron sized FE cathode is achieving the high current densities, long life time, and uniform current densities within the electron beam. The Air Force Research Laboratory (AFRL) began research on small diameter (<100 micron) single fiber DC cathodes for this application. Two types of fibers were tested, 1) those made from carbon with graphitized outer shells, and 2) fibers made solely from single walled carbon nanotubes (SWNT) that are densely packed and highly aligned along the axial direction of the fiber. Carbon fiber cathodes suffered serious degradation due to joule heating after only 25 hours of operation while only producing up to 200 microamps of current. A single SWNT fiber cathode has emitted approximately 3 milliamps of current for hundreds of hours while suffering minimal damage, as well as an 8x reduction in turn-on voltage over carbon fiber cathodes. Efforts are currently underway to optimize these SWNT fiber FE cathodes by tip shaping and applying low work function coatings.

3:00pm **NS-TuA4 Spectroscopic Identification of Bond Strain and P Interactions in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane**, ***T.M. Willey***, *J.R.I. Lee,* Lawrence Livermore National Lab, *D. Brehmer,* SLAC National Accelerator Lab, *L. Landt,* Lawrence Livermore National Lab, *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina,* Justus-Liebig Univ. Giessen, Germany, *T. van Buuren*, Lawrence Livermore National Lab

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes or graphene, or defects within or at the surfaces of nanodiamond crystallites) can modify the electronic states of the nanocarbon material. Understanding the effects of bond strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how bond strain affects electronic structure in a benchmark series of novel saturated carbon cage compounds. Adamantane, $C_{10}H_{16}$, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of the series. Twistane has the same stoichiometry ($C_{10}H_{16}$), but introduces some strain into the cage. Octahedrane ($C_{12}H_{12}$) and cubane (C_8H_8) contain increasing amounts of bond strain, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge x-ray absorption fine structure spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C-C σ* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as octadedrane, even though these two molecules have similar stoichiometries (C_xH_x). We attribute the additional intensity to π* states, indicating a high degree of π interaction between parallel C-C bonds in the cubane.

4:00pm **NS-TuA7 Self-Assembly of Photo-reduced Graphene-Titania Films**, ***C.A. Chavez***, *T.N. Lambert, C.M. Washburn, N.S. Bell, B.B. Mckenzie, M.T. Brumbach, D.R. Wheeler*, Sandia National Laboratories

In an aim to develop photo-responsive composites, the UV photo-reduction of aqueous titanium oxide nanoparticle-graphene oxide (TiO_2-GO) dispersions (Lambert et al. J Phys. Chem. 2010 113 (46), 19812-19823) was undertaken. Photo-reduction led to the formation of a black precipitate as well as a soluble portion, comprised of titanium oxide nanoparticle-reduced graphene oxide (TiO_2-RGO). When allowed to slowly evaporate, self assembled titanium oxide nanoparticle-graphene oxide (SA-TiO_2-RGO)

films formed at the air-liquid interface of the solution. The thickness of SA-RGO-TiO_2 films range from ~30-100 nm when deposited on substrates, and appear to be comprised of a mosaic assembly of graphene nanosheets and TiO_2, as observed by scanning electron microscopy. Raman spectroscopy and X-ray photoelectron spectroscopy indicate that the graphene oxide is only partially reduced in the SA-TiO_2-RGO material. These films were also deposited onto inter-digitated electrodes and their photo-responsive behavior was examined. UV-exposure lead to a ~ 200 kOhm decrease in resistance across the device, resulting in a cathodically biased film. The cathodic bias of the films was utilized for the subsequent reduction of $Ag(NO_3)$ into silver (Ag) nanoparticles, forming a ternary Ag-(SA-RGO-TiO_2) composite. Various aspects of the self assembled films, their photoconductive properties as well as potential applications will be presented.

This work supported by the Department of Energy, Office of Basic Energy Sciences and the United States Department of Energy under contract number DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

4:20pm **NS-TuA8 Temperature Dependence of Carbon Nanofiber Resistance**, ***S. Maeda***, *T. Yamada, H. Yabutani, T. Saito, C. Yang*, Santa Clara University

Carbon nanostructures such as nanotube (CNT) and nanofiber (CNF) are the most promising materials for applications in next-generation silicon integrated circuits. Knowledge of the temperature dependence of these materials is critically important as it relates directly to circuit performance. However, in practice, it is extremely difficult to measure and control the temperature of each test device and maintain thermal equilibrium because of its small thermal capacity. Therefore, one must determine the temperature of test devices by other means. Here we report results of such a study on vertical via and horizontal CNF test devices. CNF can potentially be a replacement for copper in on-chip via interconnects [1], as well as in through-silicon-vias (TSVs) in three-dimensional chips [2,3]. The horizontal CNF test device can be used as a prototype of interconnect lines between adjacent transistors in the same silicon layer. In the horizontal structure, the temperature of the CNF is extracted from current stress measurements using our heat transport model [4] . For the via test device, the CNF temperature is estimated from that of the temperature-controlled measurement system [1]. In both cases, the conductivity of CNF is determined from the measured current-voltage characteristics. We find that in either case, the conductivity increases with increasing temperature as expected. However, the measured resistance of the test device in each case contains a very different contact resistance component, due to the much higher contact resistance in the horizontal structure [5]. From the conductivity versus temperature behavior, we extract the activation energy, which turns out to be about 30 meV in each case. This finding suggests that the change in conductivity in CNF, regardless of device configuration, is due to electron trapping and detrapping at defect sites within the carbon nanostructure.

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4:40pm **NS-TuA9 New Concepts in Molecular and Energy Transport Within Carbon Nanotubes: Thermopower Waves and Stochastically Resonant Ion Channels**, ***M. Strano***, Massachusetts Institute of Technology

INVITED

Our laboratory has been interested in how carbon nanotubes can be utilized to illustrate new concepts in molecular and energy transfer. In the first example, we predict and demonstrate the concept of thermopower waves for energy generation. Coupling an exothermic chemical reaction with a thermally conductive CNT creates a self-propagating reactive wave driven along its length. We realize such waves in MWNT and show that they produce concomitant electrical pulses of high specific power >7 kW/kg. Such waves of high power density may find uses as unique energy sources. In the second system, we fabricate and study SWNT ion channels for the first time and show that the longest, highest aspect ratio, and smallest diameter synthetic nanopore examined to date, a 500 μm SWNT, demonstrates oscillations in electro-osmotic current at specific ranges of electric field, that are the signatures of coherence resonance, yielding self-generated rhythmic and frequency locked transport. The observed oscillations in the current occur due to a coupling between stochastic pore blocking and a diffusion limitation that develops at the pore mouth during proton transport.

5:20pm **NS-TuA11 All-Diamond Particles Prepared by Layer-by-Layer Deposition for High Performance Liquid Chromatography**, ***M.R. Linford***, *L.A. Wiest, D.S. Jensen*, Brigham Young University, *A. Dadson, M.A. Vail*, U.S. Synthetic

All-diamond, core-shell particles for HPLC have been prepared by layer-by-layer deposition. The process begins with the amine functionalization of ca. 2 micron diamond particles by their immersion in an aqueous solution of a primary amine-containing polymer, polyallylamine (PAAm). The amine-functionalized microdiamond is then immersed in an aqueous suspension of nanodiamond, which leads to adsorption of the nanodiamond. Alternating immersions in the solutions of PAAm and the nanodiamond suspension are continued until the desired number of nanodiamond layers is formed around the core particle. Finally, the core-shell particles are functionalied with 1,2-epoxyoctadecane to create a C18 phase. Other surface modifications, including cross linking of the PAAm polymer have been demonstrated. Scanning electron microscopy and Brunauer Emmett Teller (BET) surface area and pore size measurements show formation of the expected particles. To date, we have made core-shell particles that can be used for an HPLC separation of a four-component mixture with more than 40,000 plates/m.

5:40pm **NS-TuA12 Fabrication of High-Performance Carbon Nanotube Field-Effect Transistors with Dense and Aligned Nanotubes**, ***Z. Xiao***, Alabama A&M University

Multilayered dense single-walled carbon nanotubes (SWCNTs) were deposited and aligned for fabrication of carbon nanotube field-effect transistors (CNTFETs) using the alternating electric field-directed dielectrophoresis (DEP) method. Ultrapurified high-pressure carbon monoxide (HiPCO)-grown SWCNTs were ultrasonically dispersed in n-methyl pyrrolidone (NMP) for deposition and alignment. High-performance CNTFETs with high on/off drain-source current ratios and good saturation of drain-source current were fabricated using semiconductors as the source/drain contact materials. The current-voltage (IV) electrical property of the fabricated CNTFETs was measured. The processes for alignment of multilayered dense SWCNTs and fabrication of CNTFETs and the electrical property of the fabricated CNTFETs will be reported in the conference.

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