

Nanotubes

Room 317 - Session NT-WeA

Properties of Carbon Nanotubes

Moderator: J. Randall, Zyvex Corporation

2:00pm **NT-WeA1 Photoemission Spectromicroscopy and Spectroscopy of Carbon Nanotubes**, *S. Suzuki, Y. Watanabe, T. Ogino, Y. Homma*, NTT Basic Research Laboratories, NTT Corporation, Japan; *S. Heun, L. Gregoratti, A. Barinov, B. Kaulich, M. Kiskinova*, Sincrotrone Trieste, Italy; *W. Zhu*, Bell Laboratories, Lucent Technologies; *C. Bower, O. Zhou*, University of North Carolina at Chapel Hill

INVITED

Investigating the electronic structure of carbon nanotubes, especially their tips, is important for understanding the electron-field-emission properties of nanotubes. A specific electronic structure is expected at the hemispherical tips of nanotubes, where the graphene cylinders are believed to be closed by insertion of the five-member rings in the graphene network. The localized states in the vicinity of the Fermi level would largely contribute to the field emission properties for close-end nanotubes. For open-end nanotubes or nanotubes having imperfect structures, dangling bond states may significantly contribute to the field-emission properties. Moreover, the edge state, which is a characteristic electronic structure formed at a zigzag-type graphene edge, and has a large density of states at the Fermi level, may also play a key role. By means of scanning photoemission spectromicroscopy, we studied the local electronic structure at the tips of aligned multi-walled carbon nanotubes grown using microwave plasma-enhanced chemical vapor deposition. The valence band and the C 1s spectra, measured systematically from spatially selected regions along the tube axes, were the fingerprint for lateral variations in the electron density of states and in the band bending, respectively. The spatially selected photoemission spectra revealed that the tips have a larger density of states in a binding energy range of 0 to about 1 eV, whereas band bending, which would explain such a spectral difference, was not observed. It is suggested that the different density of states near the Fermi level is due to a larger dangling bond density at the tips. We also studied the electronic structure and work function of alkali-metal-doped carbon nanotubes. Drastic change in the electronic structure caused by the doping will also be presented.

2:40pm **NT-WeA3 Preparation and Field Emission Studies of Carbon Based Nanostructured Materials**, *X. Xiao*, Argonne National Laboratory, U.S.; *O. Auciello, J.E. Gerbi, J. Wang, J. Birrell, J.A. Carlisle*, Argonne National Laboratory; *V.I. Merkulov, H. Cui, D.H. Lowndes*, Oak Ridge National Laboratory; *Y. Wang*, North Carolina State University

Four types of carbon based nanostructured materials were prepared, including nitrogen doped ultrananocrystalline diamond (UNCD) films, UNCD on vertically aligned carbon nanofibers (VACNFs), carbon nanotubes (CNTs), and nanocomposite of UNCD/CNTs. Different methods were employed to characterize the nanostructures, such as scanning electron microscopy, Raman spectroscopy, high-resolution transmission electron microscopy and quadrupole mass spectrometry. The field electron emission properties of these carbon nanostructured materials in different ambients (O₂, Ar, N₂) were extensively studied and compared with each other. The experimental results show that the UNCD/VACNFs composite is a good field emitter with low threshold value for electron emission, good stability and long lifetime. The excellent field emission property of the composite is believed to be due to the combined effect from the negative electron affinity of UNCD and high aspect ratio of carbon nanofibers. CNTs, especially vertically aligned CNTs, can not stand long-time ion bombardment from the residual gas in the field emission process, and distortion of CNTs has been observed subsequently to electron emission measurements. Possible damage mechanism is discussed. We acknowledge support from the US Department of Energy, Office of Science / Basic Energy Science-Materials Science, under Contract W-31-109-ENG-38.

3:00pm **NT-WeA4 Infrared Stimulated Emission and Optical Gain in Isolated Single-Walled Carbon Nanotubes**, *M.S. Arnold, J.E. Sharping, S.I. Stupp, P. Kumar, M.C. Hersam*, Northwestern University

Bandgap fluorescence from single-walled carbon nanotubes (SWNTs) isolated in surfactant micelles has recently been reported.¹ Since semiconducting SWNTs possess electronic bandgaps in the near infrared region of the optical spectrum, these nanomaterials have potential application in fiber optic communication and infrared medical imaging. In

this talk, we will discuss experimental results characterizing stimulated emission of infrared radiation from SWNTs isolated in aqueous micellar suspensions. Solutions of nanotubes are optically pumped at the E₂₂ transition for a particular (n, m) chirality, and stimulated emission is probed at the corresponding E₁₁ transition. The stimulated emission in isolated SWNT solutions is observed to be more than 122 times larger than in a control sample of aggregated SWNTs. Pump and probe power, wavelength, and polarization; path length; and concentration dependencies have been characterized. For small probe intensities, the stimulated emission intensity increases linearly with probe intensity, while sub-linear behavior is observed for large probe intensities; and gain and stimulated emission are maximized for co-linear-polarization of pump and probe. Currently, measurements are underway to quantify the gain coefficient and carrier lifetimes using delayed pulsed pump-probe spectroscopy. These results suggest the conditions under which tunable infrared optical amplification devices may be realized with SWNTs.¹

3:20pm **NT-WeA5 Defective Carbon Nanotube Channel Single Electron Transistor with Ultra-High Coulomb Energy of 5000K and its Applications**, *K. Matsumoto*, Osaka University, Japan

INVITED

Coulomb diamond characteristics with Signal/Noise ratio of 10000 and drain current level of $\sim 10^{-10}$ A was attained even at room temperature in the single electron transistor (SET) using the segmented carbon nanotube (CNT) of 1~2nm diameter as multi-islands for the SET. The position and direction of the carbon nanotube for the channel of the SET is controlled by the patterned chemical catalysts of 3nm thick iron (Fe) and applied field between them. Using methane gas in the CVD process, the single wall carbon nanotube was grown between two patterned catalysts on the SiO₂/Si substrate. Most important technology is the introduction of defects into the carbon nanotube channel using the chemical process. The defects make the carbon nanotube to the segmented structure of 1~2nm diameter, which is used as multi-islands for the SET. The electrical property of the defective carbon nanotube channel single electron transistor was measured all at room temperature. The drain current shows the Coulomb gap of ~ 80 mV, which corresponds to the Coulomb energy of 400meV and Coulomb temperature of 5000K. The drain current shows the Coulomb oscillation characteristics with the modulation ratio of as large as 96~99%. The effective island size is as small as ~ 1 nm estimated from the electrical property. Coulomb diamond structures were observed even at room temperature. By improving the ohmic contact resistance, the drain current becomes of the order of $\sim 10^{-10}$ A and there is no noise observed in the Coulomb diamond characteristics. The signal/noise ratio becomes as high as 10000. This SET has a high sensitivity to the one electron because of the small gate capacitance of $1E-19 \sim 1E-20$ F, and is applicable to the single electron sensor at room temperature.

4:00pm **NT-WeA7 The Highly Robust Electrical Interconnects and Ultrasensitive Biosensors Based on Embedded Carbon Nanotube Arrays**, *J. Li*, NASA Ames Res. Center; *A.M. Cassell*, NASA Ames Res. Center / Eloret Corp.; *J. Koehne*, NASA Ames Res. Center; *H. Chen, H.T. Ng, Q. Ye, R. Stevens, J. Han*, NASA Ames Res. Center / Eloret Corp.; *M. Meyyappan*, NASA Ames Res. Center

INVITED

We report on our recent breakthroughs in two different applications using well-aligned carbon nanotube (CNT) arrays on Si chips, including (1) a novel processing solution for highly robust electrical interconnects in integrated circuit manufacturing,¹ and (2) the development of ultrasensitive electrochemical DNA sensors.² Both of them rely on the invention of a bottom-up fabrication scheme which includes six steps, including: (a) lithographic patterning, (b) depositing bottom conducting contacts, (c) depositing metal catalysts, (d) CNT growth by plasma enhanced chemical vapor deposition (PECVD), (e) dielectric gap-filling, and (f) chemical mechanical polishing (CMP). Such processes produce a stable planarized surface with only the open end of CNTs exposed, which can be further processed or modified for different applications. By depositing patterned top contacts, the CNT can serve as vertical interconnects between the two conducting layers. This method is fundamentally different from current damascene processes and avoids problems associated with etching and filling of high aspect ratio holes at nanoscales. In addition, multiwalled CNTs (MWCNTs) are highly robust and can carry a current density of 109 A/cm² without degradation. It has great potential to help extending the current Si technology. The embedded MWCNT array without the top contact layer can be also used as a nanoelectrode array in electrochemical biosensors. The cell time-constant and sensitivity can be dramatically improved. By functionalizing the tube ends with specific oligonucleotide probes, specific DNA targets can be

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detected with electrochemical methods down to subattomoles.
@FootnoteText@@footnote 1@J. Li, Q. L. Ye Q, A. M. Cassell, H.T. Ng, R. Stevens, J. Han, M. Meyyappan, Appl. Phys. Lett., 82 (15), 2491 (2003).
@footnote 2@J. Li, H. T. Ng, A. Cassell, W. Fan, H. Chen, Q. Ye, J. Koehne, J. Han, M. Meyyappan, Nanoletters, in press.

4:40pm **NT-WeA9 Photocurrents in Nanotube Junctions**, *D.A. Stewart, F. Léonard*, Sandia National Laboratories

Carbon nanotubes have demonstrated great promise for future nano-electronic devices. However, their potential for opto-electronic applications has received much less attention, despite their seemingly ideal properties, such as a direct band-gap, quasi-one-dimensional density of states, low defect density and a high surface-to-volume ratio. In this talk, we present calculations of photocurrents in nanotube junctions using a non-equilibrium quantum transport theory. The dependence of the short-circuit photocurrent on incoming photon energy shows many features, due to band-to-band transitions and photon-assisted tunneling. The operation of such devices in the ballistic transport regime leads to unusual size effects.

5:00pm **NT-WeA10 Gas Adsorption on Multi-walled Carbon Nanotubes: An Experimental and Theoretical Study**, *S. Picozzi, L. Lozzi, C. Cantalini*, University of L'Aquila, Italy; *L. Valentini, I. Armentano, J.M. Kenny*, Università di Perugia, Italy; *S. Santucci*, University of L'Aquila, Italy

The effects of environment gases (such as O₂, NO₂, NH₃) on the electronic and transport properties of carbon nanotubes have recently attracted great interests.@footnote 1@ In this work a combined experimental and theoretical study on CNT-based system for gas sensing applications is reported. Carbon nanotubes thin films have been deposited by plasma enhanced chemical vapor deposition on Si₃N₄/Si substrates provided with Pt electrodes. Microstructural features as determined by SEM, TEM and Raman spectroscopy highlight the growth of defective tubular carbon structures. CNTs show a p-type response with decreasing electrical resistance upon exposure to NO₂ gas (100 ppb) and the highest sensitivity at 165° C working temperature. No response has been found by exposing the film to CO gas in the temperature range between 25 and 250° C. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+CO and CNT+NO₂ systems.@footnote 2@ Our spin-unrestricted density functional calculations show that NO₂ retains its spin-polarized state upon adsorption. Both CO and NO₂ molecules adsorb weakly on the tube wall, with essentially no charge transfer between the tube and the molecules. The electronic properties of CNTs are sensitive to the adsorption of NO₂, due to an acceptor-like peak close to the tube valence band maximum, while they are insensitive to the CO adsorption. According to the experimental findings, our theoretical results suggest that gas-induced modification of the density of states close to the Fermi level might significantly affect the transport properties of nanotubes.
@FootnoteText@@footnote 1@ J. Kong, N.R. Franklin, C. Zhou, M.G.Chapline, S. Peng, K. Cho and H. Dai, Science 287, 622 (2000).@footnote 2@ B. Delley, J. Chem. Phys. 113, 7756 (2000).

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