Tuesday Afternoon, October 16, 2007

Nanometer-scale Science and Technology

Room: 616 - Session NS+MS-TuA

Characterization of Nanostructures

Moderator: R.F. Klie, University of Illinois - Chicago

1:40pm **NS+MS-TuA1 Atomic-scale Deformation in N-doped Carbon Nanotubes**, ***C.-L. Sun***, Academia Sinica, Taiwan, *H.-W. Wang, M. Hayashi, L.-C. Chen,* National Taiwan University, *K.-H. Chen*, Academia Sinica, Taiwan

We present the N-doping induced atomic-scale structural deformation in N-doped carbon nanotubes (CNTs) by using energy-filtered transmission electron microscopy (EFTEM) and density functional theory calculations. EFTEM N mapping image shows that N is indeed incorporated in the bamboo-like CNTs with non-uniform distribution. The interlinked parts in CNTs are brighter than the sidewall, indicating that they contain higher N concentration. We then construct the finite cluster models for CNTs with pure and two doping types in order to study the detailed structural changes in atomic scale. For substitutional-N-doped nanotube clusters, the N dopant with an excess electron lone pair exhibits the high negative charge and the homogeneously-distributed dopants enlarge the tube diameter in both zigzag and armchair cases. On the other hand, in pyridine-like-N-doped ones, the concentrated N atoms result in positively curved graphene layer and thus can be responsible for tube wall roughness and the formation of interlinked structures. Several examples for its relevant applications in energy conversion and storage will be briefly introduced in the end.

2:00pm **NS+MS-TuA2 Four-Tip Scanning Tunneling Microscope for Measuring Transport in Nanostructures**, ***S. Hasegawa***, University of Tokyo, Japan **INVITED**

Since the establishment of techniques for surface conductivity measurement by microscopic four-point probes (M4PP).[1-5] with four-tip scanning tunneling microscope (4T-STM) and monolithic four-point probes, electronic transport through single-atomic layers on semiconductor crystals has attracted considerable interests. The electrical conduction through atomic chains and nanowires can also be measured by the methods. Interesting transport properties of such atomic-scale structures have been revealed; the instability and atomic-scale defects intrinsic to such nano-scale structures play decisive roles in transport. I will introduce and summarize the following several topics in the talk. Recent advancements with metal-coated carbon nanotube tips in 4T-STM are also introduced.[11]) (1) A metal-insulator transition and strong anisotropy in conductivity of Indium atomic wire arrays.[1,6] (2) Resistance caused by monatomic steps on surface .[12] (3) Non-metallic conduction of metallic Au wires and monolayers[7,10] (4) Conductance of individual silicide nano-wires and carbon nanotubes.[8,9,13]

[1]T. Kanagawa, et al., Phys. Rev. Lett. 91, 036805 (2003).
[2]T. Tanikawa, et al., e-J. Surf. Sci. Nanotech. 1, 50 (2003)[http://dx.doi.org/10.1380/ejssnt.2003.50]
[3]S. Hasegawa, et al., J. Phys.: Condens. Matter 14, 8379 (2002).
[4]S. Hasegawa, et al., Surf. Rev. Lett. 10, 963 (2002).
[5]R. Hobara, et al., Rev. Sci. Inst. 78, 053705 (2007).
[6]T. Tanikawa, et al., Phys. Rev. Lett. 93, 016801 (2004).
[7]H. Okino, et al., Phys. Rev. B 70, 113404 (2004).
[8]H. Okino, et al., Appl. Phys. Lett., submitted.
[9]R. Hobara, et al., Jpn. J. Appl. Phys. 43, L1081 (2004).
[10]S. Yamazaki, et al., submitted to Phys. Rev. Lett.
[11]Y. Murata, et al., Jpn. J. Appl. Phys. 44, 5336 (2005); S. Yosimodo, et al., ibid. 44, L1563 (2005).
[12]I. Matsuda, et al., Phys. Rev. Lett. 93, 236801 (2004).
[13]S. Yoshimoto, et al., Nano Letters 7, 956 (2007).

2:40pm **NS+MS-TuA4 A Novel Approach for Electronic Nanotechnology of Carbon Nanotubes**, ***K.E. Hurst***, National Institute of Standards and Technology, *R.K. Ahrenkiel,* National Renewable Energy Laboratory, *T. Campbell,* ADA Technologies, *J.H. Lehman*, National Institute of Standards and Technology

We present a new measurement technique for measuring the recombination lifetimes of carbon nanotubes called the resonant-coupled photoconductive decay (RCPCD) method.[1] The carrier recombination lifetime is a fundamental property of carbon nanotubes which is typically determined by contact-based techniques or spectroscopic methods which do not readily allow characterization of bulk material properties. The measurement is based on a pump-probe technique in which an optical pump and a low frequency microwave probe are employed. RCPCD offers the first rapid, non-contact technique for routine nanometrology of carbon nanotube electronic properties. We demonstrate measurements of carrier lifetimes for multi-walled carbon nanotube and single-walled carbon nanotube thin films, where the ~30 μm thick films are deposited on a glass slide by an air-brush technique. We also consider the influence of material purity on the measurement of lifetimes in these nano-scale systems. Raman spectroscopy and UV-VIS absorption measurements provide further identification and characterization of nanotube samples to enable correlation of nanotube properties with the efficiency of charge transport in these samples. RCPCD is shown to be a fast and effective method for measuring the lifetimes of bulk carbon nanotubes, thereby overcoming present issues of routine carbon nanotube electronic nanometrology.

[1]R.K. Ahrenkiel, S.W. Johnston Mater. Sci. Eng. B 102 (2003) 161

3:00pm **NS+MS-TuA5 Properties of the Surface and Core Region of Single CdS Nanowires**, ***S.F. Alvarado***, IBM Research, Zurich Research Laboratory, Switzerland, *O. Hayden*, Siemens AG, Germany

The properties of the surface and core region of single CdS nanowires are characterized by STM-based cathodoluminescence under ultrahigh-vacuum conditions at room temperature. The CdS nanowires were fabricated using pulsed laser deposition via metal-cluster-catalyzed growth. A diluted nanowire suspension was used to flow-align the nanowires on a p-type Si substrate using microfluidic channels. Cathodoluminescence is excited by using the tip of an STM as a source of low-energy electrons ($100 < E_{kin} < 1000$ eV) at currents in the pico- to microampere range. The penetration depth of the incident electrons is approx. 1 nm at 100 eV and increases with kinetic energy up to a few nanometers at 1 keV. Therefore this technique allows one to probe the surface region of single nanostructures. A typical spectrum collected on a single nanowire exhibits a relatively sharp emission line centered at approx. 510 nm, with a full width at half maximum of 20 nm, and a much broader band centered at 750 nm. The intensity ratio of the 510 nm to the 750 nm line increases with increasing electron energy, indicating that the 750-nm emission arises from the surface regions of the nanowires, whereas the 510 nm line originates mainly from their core regions. In addition, cathodoluminescence images of single CdS nanowires, collected at different wavelengths, exhibit regions of enhanced emission as well as local variations of the ratio of surface and core contributions. A comparison of cathodoluminescence spectra collected on nanowires, on a CdS nanosheet, and on other structures, suggests a relationship between the ratio of surface-to-core emission and the quality of the nanowires.

4:00pm **NS+MS-TuA8 Helium-ion Microscopy for Nanostructure Characterization**, ***N.P. Economou***, *B. Ward, J. Notte, R. Hill, L.A. Stern*, Carl Zeiss SMT **INVITED**

We have developed the first practical He ion microscope, based on a unique gas field ion source. The source has highly desirable performance characteristics for building scanning ion microscopes with sub-nanometer probe sizes. A unique construction allows the source to provide stable output over useful lifetimes of several hundred hours, thus enabling the development of practical systems for microscopy and nanostructure characterization. An important aspect of the He ion microscope is the interaction of He ions with the sample being observed. As compared with electrons interacting with the same sample, He ions penetrate less deeply, scatter less and produce higher yields of secondary electrons; back-scattered ions are also present. Images produced with a He ion beam exhibit greater material contrast, higher resolution due to reduced interaction volume, and better signal-to-noise ratio. These factors combine to produce He ion images that often contain more and better information than electron images. Because of these inherent advantages, we believe the He ion microscope will become an important tool for the study of nanostructures. We will discuss the unique characteristics of the source, and present images produced from the microscope that demonstrate its advantages over currently available instruments.

4:40pm **NS+MS-TuA10 Study of Characteristic Fragmentation of Nano Carbon by the Scanning Atom Probe**, ***O. Nishikawa***, *M. Taniguchi*, Kanazawa Institute of Technology, Japan, *Y. Saito,* Nagoya University, Japan, *M. Ushirozawa*, Japan Broadcasting Corporation

Since the characteristic fragmentation of a material is closely related with the binding state between the atoms forming the material, multiwall carbon nanotubes (MWCNT), graphite nanofibers (GNF) and ultrapure graphite are studied by field evaporating these specimens and by mass analyzing the fragmented cluster ions with the scanning atom probe. Two kinds of MWCNT were analyzed: commercially available and laboratory fabricated MWCNTs. GNF is grown on a 304 stainless steel tip by thermal CVD. Purity of the analyzed graphite is 99.9999%. The mass spectra of both MWCNTs are quite similar, particularly mass to charge ratio M/n from 0 to 100. However, the commercial MWCNT exhibits many unidentifiable small

mass peaks throughout the mass range up to a few thousands. The most significant feature is the large mass peak at M/n = 340 which could be $C_{28}H_4$. The proposed structure of this cluster is a squarely arranged 8 hexagonal rings. This structure is suitable to form a tube. The mass spectrum of GNF is quite different from that of MWCNT and shows the highest mass peak at M/n = 278, $C_{23}H_2$. The proposed structure of this cluster is the triangularly arranged six hexagonal cells. Two corner carbon atoms of the triangle are hydrogen-terminated and third corner carbon atom is bound with an extra carbon atom. Two dimensional extension of the fragments shows a hexagonal ring formed by 6 hydrogen atoms terminating the carbon bonds and 6 extra carbon atoms forming a hexagon. The hydrogen hexagonal ring is quite similar to that of a kekulene molecule. The graphite exhibits two completely different mass spectra. One is quite similar to that of MWCNT showing the characteristic large mass peaks. The other closely resembles those of silicon and diamond. The number of detected ions decreases with mass. Thus, the largest mass peak is C^{2+} and then C^+. The clusters formed by the odd number of carbon atoms are more abundant than those of even number. Most clusters are doubly charged. This implies that the binding between carbon atoms in this analyzed section is strong and uniform and that the graphite has two phases: diamond and graphite. Although only few H^+ ions are detected from MWCNTs and GNF, most fragments contain more than 1 hydrogen atom. On the other hand few ions detected from the diamond-like graphite are bound with hydrogen.

5:00pm **NS+MS-TuA11 Nano-scale Surface Effects of Field Electron Emission from Zirconium and Hafnium Carbide**, ***W.A. Mackie,*** *G.M. Magera, K.J. Kagarice*, Applied Physics Technologies

An electron source for a high resolution SEM/TEM application should produce a high brightness, have a minimal energy distribution, and should be highly stable. In an application in which the resolution is limited by chromatic aberrations, one can improve the performance over a commonly used thermal field emission source, such as a ZrOW Schottky emitter, by using a cold field emission source (CFE). In CFE, the emitting area of the usable beam is small and understanding surface chemistry and effects are crucial to controlling emission stability. Single crystalline transition metal carbides have electron emission properties making them attractive candidates for CFE applications. We are reporting on field emission from (310) oriented single crystal ZrC and HfC. ZrC(310) has a relatively low work function axial emitting surface (3.4 eV) that has a low evaporation rate, is resistant to ion bombardment and sputtering, has a high melting point (~3800 K), and a very low surface mobility. The robustness of this material allows for repeated cleaning via high temperature flashing without changing the geometry of the emitting end form. These crystals are electrochemically etched and mounted in a mini Vogel mount to enable flash cleaning. Experimental I(V) data were taken from which angular intensity and reduced brightness were calculated. Experimental I(t) data were then taken and analyzed for current stability in both long term drift and short term noise. Results are highlighted from a 160 nm ZrC (310) operating at 0.02 mA/sr. Noise spectra were analyzed by FFT and found to be consistent with step and spike like noise associated with foreign atom migration and ion bombardment. Emission from small areas comprising <100 atom sites are dominated by the mobility of foreign atoms from ion back streaming and surface diffusion both arising from the high electric field. Using an annular area surrounding the beam emission area as a current monitor we were able to control fluctuations in the beam. This control ability results from the overlapping currents from both areas. Data are presented which demonstrate improved stability over a variety of vacuum conditions.

Authors Index

Bold page numbers indicate the presenter