

# Thursday Morning, October 18, 2007

## Nanometer-scale Science and Technology

Room: 616 - Session NS-ThM

## Nanotube Devices and Processes

**Moderator:** S.V. Kalinin, Oak Ridge National Laboratory, S. Evoy, University of Alberta, Canada

### 8:00am NS-ThM1 Single Charge Sensing by Carbon Nanotube Single-Hole Transistor, *K. Matsumoto*, Osaka University, Japan

We have succeeded in detecting the single charge transition near the channel of single walled carbon nanotube (SWNT) single-hole transistor (SHT). Abrupt discrete switching of the source-drain current is observed in the electrical measurements of SWNT SHT. These random telegraph signals (RTS) are attributed to charge fluctuating near the SWNT SHT conduction channels. The sample has a back gate FET structure with the source-drain spacing of 73 nm. The channel is formed by thermal CVD grown single walled carbon nanotube on the SiO<sub>2</sub> substrate. The silicon dioxide layer was deposited on the SWNT SHT to prevent the adsorption & desorption of the molecules to the carbon nanotube channel. In the drain current-voltage characteristics of SWNT SHT under the drain voltage of 11 mV at 7.3 K, drain current showed periodic peaks and valleys structure, with two. The large period of 3 V was attributed to Coulomb oscillation characteristic, the small period of 0.5 V to the quantum interference property of hole. The drain current was observed only in negative gate voltage region, which indicates that the measured SWNT SHT has the p type semiconductor property. The SWNT SHT shows random telegraph signals (RTS), which were attributed to fluctuating charge traps near the SWNT SHT conduction channels. The RTS appeared two levels, upper level and lower level in drain current, the occupation probabilities of which was depended on the applied gate voltage. Using the simple model we assumed, we could estimate the distance between the trap and the channel of SWNT SHT to be  $L=1.03$  nm. The potential energy barrier between the trap state and the Fermi level of carbon nanotube channel was also founded to be 3.2 meV. Thus, using the carbon nanotube single hole transistor, we have succeeded in detecting and analyzing the single charge transition.

### 8:20am NS-ThM2 Single Molecule Sensing with Carbon Nanotubes, *B.G. Goldsmith, J.G. Coroneus, V.R. Khalap, A.A. Kane, G.A. Weiss, P.G. Collins*, University of California at Irvine

Due to their extremely small size, single walled carbon nanotubes (SWCNTs) provide a promising framework for building single molecule electronic devices. We have developed a procedure to controllably form single carboxyl groups on a CNT's sidewall. By limiting the chemically sensitive region of a nanostructure to a single binding site, single molecule bonding dynamics become visible. Discrete changes in the circuit conductance reveal chemical processes happening in real-time and allow SWNT sidewalls to be deterministically broken, reformed, and conjugated to target species, creating new possibilities for chemical sensing and molecular electronics.

### 8:40am NS-ThM3 STM and STS Studies of SWCNT on NaCl/Ag(100), *H.-J. Shin, S. Clair, Y. Kim*, Riken, Japan, *M. Kawai*, Riken and University of Tokyo, Japan

Single-walled carbon nanotubes (SWCNTs) have been considered as one of the most promising candidates for future electronic devices due to their unique electrical properties. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) have provided a lot of information about the structure and electronic properties of SWCNTs.<sup>1,2</sup> In most STM studies of SWCNT, it was carried out on metals or semiconductors so far. In these cases, the electronic structure of SWCNT can be perturbed by the presence of the electrons of the surface. For example, the charge transfer between metal substrate and SWCNT results in the shift of Fermi-level of SWCNT on Au(111) to the valence band.<sup>2</sup> In this study, we studied electronic structure of SWCNT on NaCl thin film by STM and STS. We introduced insulating layer to reduce the influence of metal surface. We deposited SWCNT on the NaCl(100) film, grown on Ag(100) single crystal by dry contact transfer technique in UHV.<sup>3</sup> Interestingly, the Fermi-level of SWCNT shifted to the conduction band on Ag(100), while it shifted to the valence band on NaCl film. The charge transfer due to work function difference between Ag(100) (4.3eV) and SWCNT (4.8 ~ 5.0eV) was the main reason for the Fermi-level shift of SWCNT on Ag surface. On NaCl film, it is thought that the dipole moment at the interface between NaCl and

Ag brought about Fermi-level shift to the conduction band, though the work function of NaCl on Ag(100) is 3.6 ~ 4.0eV, much lower than that of Ag(100). The influence of dipole moment on the electronic structure of SWCNT will be discussed in details.

<sup>1</sup> J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, and C. Dekker, *Nature* 391, 59 (1998).

<sup>2</sup> M. Ouyang, J.-L. Huang, and C.M. Lieber, *Annu. Rev. Phys. Chem.* 53, 201 (2002).

<sup>3</sup> P.M. Albrecht and J.W. Lyding, *Appl. Phys. Lett.* 83, 5029 (2003).

### 9:00am NS-ThM4 Evaluation of High k Dielectric Films for Carbon Nanotube FETs, *W. Miller, S.V. Krishnaswamy, J.M. Murduck, H. Zhang, J. Baumgardner, A.A. Pesetski, J.X. Przybysz, J.D. Adam*, Northrop Grumman Electronic Systems

Carbon nanotube FETs are promising candidates for future RF applications because they simultaneously offer high speed, high linearity, low power and low noise. Carbon nanotube FETs are projected to have a cut-off frequency of over 1 THz due to their small size and high carrier mobility, 1000x lower dissipated power than current GaAs devices without sacrificing linearity. Successful development of CNT electronics will enable the fielding of RF systems that are not currently possible because of prime power requirements. CNT FETs will have a large impact in RF electronics applications where linearity is critical. Based on our simulations, CNT FETs can be designed to be intrinsically linear provided one uses a gate dielectric material with dielectric constant >15. In our work we have evaluated several candidate materials such as HfO<sub>2</sub>, ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> etc. Thin films of these gate dielectric materials have been grown at various laboratories using different techniques. While sputtering is a standard technique used in the semiconductor industry, sputtering of these materials on to CNT significantly deteriorated the performance of the devices. Dielectric for gate oxide in our CNT IC process must have high dielectric constant, be compatible with CNT, have good dielectric integrity and have reasonable breakdown voltages. We will report our results on atomically smooth TiO<sub>2</sub> films using rf magnetron sputtering with auxiliary magnet under the substrate. In addition we will report on ALD HfO<sub>2</sub> and evaporated Ta<sub>2</sub>O<sub>5</sub> films along with our results obtained from CNT FETs using these different gate dielectrics.

### 9:20am NS-ThM5 Erbium and/or Ytterbium Doped Yttrium Oxide Nanotubes for Optical Amplifier Application, *Y. Mao, J.P. Chang*, University of California at Los Angeles

Yttria is one promising hosting material for rare-earth-ion-activated phosphors with applications including amplifiers, lasers, waveguides, X-ray imaging, bioimaging, and displays due to their luminescent characteristics and stability in high vacuum. In fact, in our most recent study, we have deposited Er-doped Y<sub>2</sub>O<sub>3</sub> thin films by radical-enhanced atomic layer deposition (ALD)<sup>1</sup> and demonstrated that the Er incorporated in Y<sub>2</sub>O<sub>3</sub> can reach a concentration as high as 10<sup>21</sup> cm<sup>-3</sup> with outstanding room temperature photoluminescence (PL) at 1.54 μm in thin Er-doped (6-14 at. %) Y<sub>2</sub>O<sub>3</sub> films deposited at 350°C.<sup>2</sup> Meanwhile, nanomaterials exhibit physical properties, in particular, increased luminescence efficiency, which are not observed with their bulk counterparts. Hence, in this talk, we present our recent work on the synthesis of nanotubes of rare-earth (RE, Er and Yb) doped Y<sub>2</sub>O<sub>3</sub>, by a solution synthetic method. The processing temperature, pH, time, addition rate of NaOH, the concentration of precursors, and the annealing temperature dictated the nucleation/growth of RE doped Y(OH)<sub>3</sub> nanotubes. These tubes were converted to RE doped yttria by high temperature annealing and the resulting nanotubes had varying RE dopant concentrations (0-100%) with sizes ranging from 40-500 nm in diameter and 2-10 μm in length. X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and extended x-ray absorption fine structure (EXAFS) were combined to delineate the structure and composition of these nanotubes. The erbium coordination number and local bonding environment are assessed by synchrotron based EXAFS analysis, and are shown to dictate the measured photoluminescence intensity.<sup>3</sup> Their room luminescent properties (PL and cathodoluminescence, CL) are outstanding and even superior than the thin films synthesized by ALD. Finally, we will discuss their electronic properties and the application of these doped yttria nanostructures as small and compact planar optical amplifier.

<sup>1</sup> T.T. Van and J.P. Chang, *Appl Phys Lett*, 87, 011907 (2005).

<sup>2</sup> T.T. Van, J. Hoang, R. Ostroumov, K. L. Wang, J. R. Bargar, J. Lu, H.-O. Blom, and J.P. Chang, *J Appl Phys*, 100, 073512 (2006).

<sup>3</sup> T.T. Van, J. R. Bargar, and J.P. Chang, *J Appl Phys*, 100, 023115 (2006).

9:40am **NS-ThM6 Ultrahigh-Vacuum Scanning Tunneling Microscopy Study Into the Adsorption of N-methyl-pyrrolidone Molecules on Carbon Nanotubes**, *Z.T. Wang, P.M. Ryan, N.P.P. Niraj, J.J. Boland*, Trinity College Dublin, Ireland

The most common processing technique for carbon nanotubes involves dispersing them in a liquid media. However, due to their high molecular weight, nanotubes suspend and are not soluble in all known solvents. Usually, surfactants are used to overcome this obstacle.<sup>1</sup> Recently people found that pristine single wall carbon nanotubes can be spontaneously dispersed and even exfoliated in an N-methyl-pyrrolidone (NMP) solvent, forming a carbon nanotube solution.<sup>2</sup> The negative free energy of mixing NMP with nanotubes leads to the strongly adsorption of a huge number of NMP molecules on the nanotubes in NMP solution and even dried-powder. In our experiments, carbon nanotubes processed by the NMP solvent are deposited on clean Si(001) substrates using a dry deposition method<sup>3</sup> and investigated using an ultrahigh-vacuum (UHV) scanning tunneling microscope (STM). We find that NMP molecules diffuse from the nanotubes and become irreversibly chemically adsorbed on Si(001) surfaces due to the strong interaction of nitrogen with Si dangling bonds, indicating NMP molecules remain bound to nanotubes even under UHV conditions. However a few remaining molecules reversibly bound to the nanotubes are observed using STM and are seen to emerge from tube bundles. The molecules can migrate on the bundles during imaging and finally become bound to the Si(001) substrate. After all NMP molecules are removed, there is no defect left on the nanotubes.

<sup>1</sup> G. S. Duesberg et al, Chemical Communications, 435 (Feb, 1998)

<sup>2</sup> S. D. Bergin et al, unpublished.

<sup>3</sup> P.M. Albrecht and J. W. Lyding, App. Phys. Lett. 83, 5029 (2003).

10:00am **NS-ThM7 Growth Promotion and Etching of Carbon Nanotubes by CO<sub>2</sub> in Chemical Vapor Deposition using CH<sub>4</sub> Gas**, *Y. Suda, T. Saito, A. Okita, J. Takayama*, Hokkaido University, Japan, *J. Nakamura*, Tsukuba University, Japan, *Y. Sakai, H. Sugawara*, Hokkaido University, Japan

Oxidant has been used for growth promotion of carbon nanotubes (CNTs) in CVD since the work by Hata, et al.<sup>1</sup> We report the effect of CO<sub>2</sub> addition to CH<sub>4</sub> gas on CNT growth. The CVD chamber is evacuated down to 10<sup>-6</sup> Torr by a turbo-molecular pump followed by a rotary pump. We used Mo<sub>(0.025)/Fe<sub>(0.05)/MgO<sub>(0.925)</sub></sub> or Mo<sub>(0.025)/Ni<sub>(0.05)/MgO<sub>(0.925)</sub></sub> as a catalyst, H<sub>2</sub> gas as a reductant and CH<sub>4</sub> gas as a feedstock.<sup>2</sup> CO<sub>2</sub> gas was introduced during the CNT growth at a temperature of 800°C and its concentration in CH<sub>4</sub> was varied from 0.0037% (37 ppm) to 50%. The other experimental parameters are as follows: H<sub>2</sub> gas pressure = 100 Torr and flow rate = 100 sccm for reduction; CO<sub>2</sub>/CH<sub>4</sub> gas pressure = 100 Torr and flow rate = 76 sccm for growth. The CNT yield and the G/D ratio in the Raman spectra of CNTs grown in 10%-CO<sub>2</sub>/CH<sub>4</sub> were slightly higher (~86%) than that grown in CH<sub>4</sub> only (~71%). However, CNTs were hardly grown when the CO<sub>2</sub> concentration was more than 20%. Decreasing the CO<sub>2</sub> concentration down to 37 ppm, it was found that single-walled CNTs (SWCNTs) with a yield of ~10% were grown and that the yield for 60 min was 1.5 times higher than that for 10 min. This suggests that the SWCNT growth in a CO<sub>2</sub>/CH<sub>4</sub> gas mixture continued for 60 min. The G/D ratio obtained from 37 ppm-CO<sub>2</sub>/CH<sub>4</sub> was almost the same as that grown from CH<sub>4</sub> only. The radial breathing mode (RBM) obtained by a 632.8 nm excitation shows that the SWCNT diameter ranges from 0.9 to 1.3 nm and that a few metallic SWCNTs were eliminated but most of semiconducting SWCNTs remained.</sub></sub>

<sup>1</sup>K. Hata, et al, Science, 306 (2004) 1362-1364

<sup>2</sup>L.-P. Zhou, et al, J. Phys. Chem. B, 109 (2005) 4439-4447.

10:40am **NS-ThM9 Effect of Nitrogen Dopant on the Structure and Electrocatalytic Activity of Arrayed Multi-Walled Carbon Nanotubes**, *Y.-G. Lin*, National Chiao Tung University, Taiwan, *Y.-K. Hsu*, Academia Sinica, Taiwan, *J.-L. Yang, S.-Y. Chen*, National Chiao Tung University, Taiwan, *K.-H. Chen*, Academia Sinica, Taiwan, *L.-C. Chen*, National Taiwan University

With the recent advancements in nanoscience and nanotechnology, carbon nanotubes (CNTs) have drawn a great deal of attention as novel catalyst supports due to their unique structure, high surface area, stability, and excellent mechanical and electrical properties, all of which could offer improvements for fuel cell applications. We have developed a method to synthesize well-aligned nitrogen-containing carbon nanotube (CNx NT) by microwave-enhanced chemical vapour deposition with a source gas of CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub>. Here we report our recent results on employing different flow rate of nitrogen to control the structure and electrochemical activity of CNx NTs. The effect of nitrogen on the structure and electrochemistry has been examined by Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV) using the redox probe of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup>. From the structural investigation, as the flow rate of N<sub>2</sub> gas is higher than 120 sccm, the average diameter of the nanotubes goes beyond 100 nm. The intensity ratio

of the D band to G band of Raman spectrum increased with increasing N<sub>2</sub> flow rate from 0 to 40 sccm, and then rapidly decreased with further increase in the flow rate of N<sub>2</sub>. Similarly, XPS results showed the highest nitrogen concentration occurred at 40 sccm and the intensity of pyridine-type N bonding which causes the interlinked node morphology inside the CNx NTs increased with increasing N<sub>2</sub> gas flow rate. Hence, the nitrogen-incorporation promotes the disorder in graphitic structure in the initial stage; however, further increase in the N<sub>2</sub> flow rate won't enrich the nitrogen concentration in CNx NTs, but raise the growth temperature leading to enhanced graphitization. In addition, CNx NT electrode with N<sub>2</sub> flow rate of 40 sccm was found to significantly improve the electron transfer kinetics of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> redox couple, approaching almost reversible electron transfer kinetics. The reason could be ascribed that the nitrogen treatment at 40 sccm creates disordered and chemically active sites which play a key role to facilitate electron transfer.

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