

# Thursday Afternoon, October 18, 2007

## Nanometer-scale Science and Technology

Room: 616 - Session NS-ThA

### Nanoscale Sensors

**Moderator:** N.A. Burnham, Worcester Polytechnic Institute, V. Vogel, ETH Zürich, Switzerland

2:00pm **NS-ThA1 Nanomechanics in Life Science, M. Hegner**, CRANN, University of Dublin, Ireland **INVITED**

Future diagnostics will depend on fast, specific assays to allow personalized medical diagnostics. Increasing efforts in our group have therefore been put into the development of instrumental measurement- and functionalization schemes for cantilever-based sensors for the label-free detection of physical- and chemical phenomena of biological interactions. Cantilevers arrays offer an elegant approach where physiological ligand-receptor binding interactions occurring on the sensor generate nanomechanical signals like bending or a change in mass that is optically detected in-situ. This allows a comprehensive characterization of biological interactions: The measured mass gives information about the binding event whereas the measured surface stress (structural changes) gives insights in the effects of the ligand on the biological systems. We report on new styles of combined measurements in the field of proteomics, genomics and present fast dynamic assessments of micro-organism growth on cantilever arrays.

2:40pm **NS-ThA3 Nanomechanical Resonance of Clamped Silicon Nanowires Measured by Optical Interferometry, M. Belov**, University of Alberta, Canada, *N.J. Quidoriano, S. Sharma, T.I. Kamins*, Hewlett-Packard Laboratories, *S. Evoy*, University of Alberta, Canada

Highly-sensitive transducers for the detection and assaying of molecular systems based on nanomechanical beams have been proposed. Mechanical objects with lateral dimensions reaching the sub-100 nm range, with high resonant frequencies and quality factors, are now routinely fabricated using surface micromachining. The surface machining procedures employed in NEMS fabrication are inherently slow, offer limited yield and usually employ plasma-assisted etching techniques that may introduce surface damage and significantly change the mechanical properties of the resonating element. The direct growth of cantilevered nanowires by chemical vapor deposition methods (CVD) offers, alternatively, a potent way for the efficient production of high-quality NEMS resonators, with sub-50nm diameters, circular profiles and small clamping losses. We report the synthesis and characterization of vibrating silicon nanowires grown by CVD. These highly-oriented and clamped silicon structures were laterally grown from the sides of etched silicon posts using a metal-catalyzed chemical vapor deposition process. The diameters and lengths of the structures ranged from 40 to 400 nanometers and from 2 to 20 micrometers, respectively. The substrates were mounted onto a piezoceramic disc, installed in a vacuum chamber and actuated at varying frequencies. The laser beam focused onto the vibrating structure was reflected back and the detected signal, proportional to the deflection of the beam relatively to the substrate, was processed by a spectrum analyzer. The data were acquired at temperatures ranging from 77°K up to 293°K, and at pressures ranging from atmospheric down to the low 10<sup>-6</sup> Torr. Typical resonant frequencies ranged from 1 to 20 MHz, in agreement with the Euler-Bernoulli analysis of vibrating structures. The resonant frequency of the nanowires typically showed a 0.25% increase as the nanowires were cooled from T = 293°K to T = 77°K as a result of changing Young's modulus. We also measured qualities of the resonators over the same temperature range. We discuss the energy dissipation processes that dominate the performance of these devices at various temperatures and pressures. This work was partially supported by Alberta Innovation and Science and by Hewlett-Packard Laboratories.

3:00pm **NS-ThA4 Electronic and Structural Properties of Ti and Pd Decorated Carbon Nanotubes, A. Felten, J. Ghijsen**, Namur University, Belgium, *W. Drube*, HASYLAB, Germany, *R.L. Johnson*, University of Hamburg, Germany, *D. Liand, G. Van Tendeloo*, University of Antwerp, Belgium, *M. Hecq*, Mons University, Belgium, *C. Bittencourt*, Materianova, Belgium, *J.J. Pireaux*, Namur University, Belgium

The study of the electronic interaction between metal atoms and carbon nanotubes is essential in order to improve performances of devices such as nano-transistors or gas sensors, for example to achieve low-resistance electrical contacts. Palladium and titanium decorated multiwall carbon nanotubes appear to be good candidates for such applications. In this work, both high resolution transmission electron microscopy (HRTEM) and

photoemission spectroscopy have been used. Different amounts of Ti and Pd were evaporated onto both pristine and oxygen plasma functionalized carbon nanotubes. HRTEM images show the evolution of the morphology of the metal overlayer onto the nanotube surface. Evaporation of Ti on pristine nanotubes leads to a continuous coverage even for a very low amount of evaporated metal. In contrast, Pd deposition is characterized by the formation of small clusters. Oxygen plasma treatment is seen to improve the Pd cluster dispersion and size distribution. Analysis of the core and valence bands in photoemission spectroscopy reveals also strong differences between the two metals. The appearance of a new peak at lower binding energy on the C 1s level for Ti decorated nanotube is associated to the formation of Ti-C bonds (high coverage), with evidence of a charge transfer from titanium atoms to the carbon nanotube at low coverage. For Pd on the contrary, the absence of new features in both Pd 3d and C 1s spectra are suggesting the absence of a mixed Pd-C phase.

This work is financially supported by the Nano2Hybrids (EC-STREP-033311) and PAI 6/1 projects, and by DESY and the EC under contract RII3-CT 2004-506008 (IASFS).

3:40pm **NS-ThA6 Albert Nerken Award Lecture - On Surface Analysis and Nanotechnology: A Personal Odyssey, R.J. Colton\***, Naval Research Laboratory **INVITED**

This Albert Nerken Award address recounts some science and technology highlights of my career in areas of surface analysis and nanoscience—a personal odyssey on SIMS, SERS, STM, AFM, nanomechanics, molecular dynamics, and single molecule biosensing. This presentation will recount the early observation of cationized molecular ions, magic numbers in large inorganic ion clusters, and UHV-SERS (of pyridine on silver of course). Early STM and AFM work addressed the then mysterious graphite imaging mechanism and the usefulness (once realized) of tip-surface force interactions. Examples of just how useful these force measurements can be led to new technology for surface and molecular mechanics with the help of molecular dynamics simulation. But can you really make a single molecule biosensor? We'll see. My presentation will close with a brief overview of NRL nanoscience programs on nanomaterials, nanoelectronics and nanosensors/devices.

4:20pm **NS-ThA8 Combined Scanning Tunnelling Microscopy & Stress Measurements to Elucidate the Origins of Surface Forces, D.E. Meehan, N.T. Kinahan**, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland, *T. Narushima*, National Institutes of Natural Sciences, Japan, *J.J. Boland*, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland

The concept of surface stress has been discussed extensively in terms of its role in controlling single crystal reconstruction and the growth morphology of thin films. In contrast, much less is known about the role of surface stress in surface chemical reactions, where differences in atomic size, electronegativity, and the incorporation of surface vacancies are likely to be of great importance, particularly in the case of nanoscale systems where surface effects are expected to dominate. In order to address the role of stress in surface chemical reactivity, we have developed a novel measurement system capable of investigating the underlying origins of surface stress in the context of atomic surface structure.<sup>1</sup> This system combines for the first time two distinct measurement capabilities: (i) measurement of surface stress based on the displacement of a large (50x10x0.28mm) silicon cantilever sample; and (ii) atomic resolution observation of the surface structure of the same cantilever sample. The former measurement incorporates a capacitive detection method capable of detecting energy changes with meV/atom resolution, while the latter measurement incorporates a scanning tunnelling microscope (STM) capable of observing structural changes occurring on the surface of the cantilever sample. Although non-trivial, the development of this combined measurement system was accomplished through careful electrical and mechanical design, accompanied by the incorporation of a novel sample heating method permitting localized heating of the cantilever sample. The system is also equipped with a device capable of applying external mechanical stress to the cantilever sample, thus enabling investigation of the effects of artificially induced stress on surface-based chemical reactions. The combined application of these two measurement capabilities yields detailed information regarding the atomic-scale structure, dynamics and interactions of the surface under investigation, which will ultimately be used to elucidate the origins of surface forces, and contribute to a deeper understanding of atomic-scale phenomena. Here, we present an introduction to the measurement system, a discussion on the challenges encountered

\* Albert Nerken Award Winner

during the development process, followed by a demonstration of the capabilities of the system itself.

<sup>1</sup> T. Narushima, N. T. Kinahan, J. J. Boland, *Rev. Sci. Instrum.* 78, 053903 (2007).

**4:40pm NS-ThA9 A Hydrogen-Sensitive Polymer Nanostructure with Reversible Conductance**, *A.R. Laracuente, M. Yang, W.K. Lee, L. Senapati, P.E. Sheehan, S.C. Erwin, L.J. Whitman*, Naval Research Laboratory

There is considerable interest in the use of polymer nanostructures for flexible electronics and sensors. We have previously written poly(3-dodecylthiophene-2,5-diyl) (PDDT) nanostructures between gold electrodes using thermal Dip-Pen Nanolithography (tDPN). tDPN uses a heatable atomic force microscopy cantilever to directly deposit "inks" that are solid at room temperature. When a PDDT-coated tip is heated close to or above the PDDT glass transition temperature, PDDT flows from the tip to the substrate surface with molecular-scale order.<sup>1</sup> We have discovered a novel property of such PDDT nanostructures: their conductivity can be increased by more than five orders of magnitude (from  $<10^{-4}$  S  $\text{cm}^{-1}$  to 10 S  $\text{cm}^{-1}$ ) by exposure to energetic electrons (5 keV). In contrast, spin-coated polymer thin films deposited on similar gold electrodes do not show any electron-induced conductivity. Interestingly, the electron-induced conductivity of the PDDT device reverts to a semi-insulating state by exposure to  $\text{H}_2$ , with a measurable change in conductance occurring following exposures as low as  $6 \times 10^{-4}$  Torr-s. Repeated shifting between the high and low conductivity states is possible. Significantly, exposure to oxygen, argon, or ambient air does not affect the conductance, suggesting that PDDT nanostructure devices deposited by tDPN have potential as  $\text{H}_2$  sensors. We propose a mechanism for the conductance modulation based on H desorption and re-sorption from the side-chains of the polymer. This mechanism is supported by a two terminal response theory based on Green's-function-based Landauer-Büttiker multichannel formalism.

<sup>1</sup> Yang et al., *J. Amer. Chem. Soc.* 128, 6774 (2006).

**5:00pm NS-ThA10  $\text{CO}_2$  Sensing and CO and  $\text{H}_2\text{O}$  Interactions on Mats of Gold Nanoparticle Decorated GaN Nanowires**, *C. Berven, S. Chava, A. Heieren, R. Abdelrahman, D. McIlroy*, University of Idaho, *M.G. Norton*, Washington State University

We report on the use of macroscopic mats of gold-nanoparticle-decorated GaN nanowires for the detection of  $\text{CO}_2$  and the possible generation of  $\text{CO}_2$  along with  $\text{H}_2$  by interactions of CO and  $\text{H}_2\text{O}$  on the surfaces of the gold nanoparticles. The sensor consisted of a mat of GaN nanowires grown on a sapphire substrate ( $d \sim 1$  cm) using a vapor-liquid-solid growth technique.<sup>1</sup> The mat was  $\sim 20$   $\mu\text{m}$  thick and the nanowire diameters and lengths were  $\sim 200$  nm and  $\sim 5$   $\mu\text{m}$ , respectively. The nanowires were decorated with gold nanoparticles using a chemical vapor deposition process resulting in a continuous layer.<sup>2</sup> The gold was reduced by selective wet etching to create a sparse coverage of nanoparticles. Current-voltage (I-V) measurements were performed when exposed to vacuum, CO,  $\text{CO}_2$  and water vapor. All measurements were performed at 300 K and in the dark at pressures of 50 Torr to 1 atm with a maximum vacuum of 5 mTorr. When exposed to just water vapor or CO the currents were only attenuated slightly from the vacuum state. When exposed to  $\text{CO}_2$ , the current was attenuated to a much larger degree. We have previously published data and a model to explain the sensitivity of similar device to methane<sup>3</sup> which was due to the nanowires acting like Chem-FETs and where the selectivity was attributed to the morphology of the nanoparticles. When the device was exposed to CO followed by  $\text{H}_2\text{O}$ , we saw significant reduction in the current, similar to that of just  $\text{CO}_2$  implying that what is being sensed is  $\text{CO}_2$  that was the by-product of the reaction of  $\text{CO} + \text{H}_2\text{O}$  occurring on the gold nanoparticles. This is not unreasonable since nanoparticle gold is known to be quite reactive.<sup>4</sup> As a consequence of  $\text{CO}_2$  being detected after the mixing of CO and  $\text{H}_2\text{O}$  on the nanoparticles, we speculate that  $\text{H}_2$  is also being generated giving a possible new mechanism for  $\text{H}_2$  generation for fuel cells.

<sup>1</sup>V. Dobrokhotov, C. Berven et al., *J. Appl. Phys.* 99, 104302 (2006)

<sup>2</sup>A. D. LaLonde, et al., *J. Mater. Res.* 20, 549 (2005)

<sup>3</sup> V. V. Dobrokhotov, C. Berven et al., *Nanotechnology* 17, 4135-4142 (2006)

<sup>4</sup> M. Haruta, *Applied Catalysis A: General* 222, 427 (2001).

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