Wednesday Morning, November 11, 2009

Nanometer-scale Science and Technology
Room: L - Session NS-WeM

Nanoscale Devices and Sensors and Welch Award
Moderator: R.J. Colton, Naval Research Laboratory

8:00am **NS-WeM1 2009 Medard Welch Award Lecture - Molecular Interfaces to Nanoscale Materials: Making "Dumb" Materials "Smart"**, *R.J. Hamers**, University of Wisconsin-Madison **INVITED**
Recent years have seen dramatic increases in the ability to synthesize new bulk and nanostructured materials. For many applications, such as sensing and renewable energy, the need for high stability drives a motivation for working with two classes of 'ultra-stable' materials: (1) nanoscale carbon, and (2) nanocrystalline metal oxides. While these materials are highly stable they do not provide important properties such as chemical or biological selectivity. Molecular surface chemistry can be used to turn these into "smart" materials by linking molecules that will convey chemical or biological selectivity for sensing or desirable electron-transport properties for applications in renewable energy. We have found that photochemical grafting of alkenes provides a nearly universal method for producing molecular monolayers on a wide range of highly stable materials. Surprisingly, this method works on both wide-bandgap semiconductors such as diamond and TiO$_2$, as well as metallic materials such as carbon nanofibers. Through a series of studies we have identified the underlying mechanism as an internal photoemission process in which ultraviolet light ejects an electron from the material into an adjacent reactive liquid, leaving behind a reactive (and persistent) hole that serves as a reactive site for molecular grafting. With suitable chemistry, this approach can be used to fabricate (bio)molecular interfaces with a high degree of functionality that can be used (for example) to achieve direct biological-to-electronic signal conversion for sensing. Recent work also shows this to be an excellent approach for novel types of electrocatalytic interfaces of interest for applications in renewable energy. In this talk I will discuss some of our efforts in making and understanding "smart" molecular and biomolecular interfaces to nanocrystalline materials, and some of the resulting applications in sensing and in renewable energy.

8:40am **NS-WeM3 Plasmon Induced Molecular Conductivity in Devices**, *P. Banerjee*, University of Maryland, *D. Conklin, S.U. Nanayakkara*, University of Pennsylvania, *T.-H. Park*, University of Michigan, *M.J. Therien*, Duke University, **D.A. Bonnell**, University of Pennsylvania
Plasmonics and molecular electronics are two fields that explicitly exploit nanoscale physical phenomena. In the former, optical interactions with nanosized particles induce surface plasmons creating locally intense electric fields. In the latter, two decades of intense research has focused on electrical conduction in organic molecules to enable molecular electronics. The interaction of plasmons and electrical conduction has not been observed. Here we demonstrate the ability of a plasmon to alter the electrical properties of a molecular junction. Arrays of Au nanoparticles with different separations are assembled on an insulating substrate and functionalized with porphyrin compounds. These molecules posses unique optical properties and electron delocalization lengths on the order of 7-8nm. The wavelength and temperature dependence of transport in these hybrid devices reveal differences on photo conduction mechanism with wavelength. Three mechanisms are identified, one that operates in the dark current, one associated with electron-hole generation on absorption and one induced by surface plasmons. This ability of plasmons to directly influence electrical conductivity is a new mechanism of photoconduction that suggests a variety of optoelectronic applications.

9:00am **NS-WeM4 CMOS Compatible Silicon Nanowire Field Effect Transistor as Ultrasensitive Bio-sensor**, *S. Regonda, K. Trivedi, P. Fernandes, R. Tian, O. Seitz, J. Gao, E.M. Vogel, Y. Chabal, W. Hu*, University of Texas at Dallas
Among the emerging devices for the future technology in the nanoscale regime, silicon nanowire (SiNW) devices have received significant attention for applications in logic gates, interconnects, photo detectors and biological and chemical sensors. For biosensing, femtomolar (fM) level detection of protein in solution has been demonstrated using both chemically synthesized nanowires [1] and lithographically defined nanowire field effect transistors (FETs) [2]. This type of sensor offers ultrasensitivity, rapid

electronic readout, and does not require bulky sensing apparatus. It has a strong potential to be an ultra-portable and low cost biosensing platform that is badly needed for disease diagnostics and early detection.

In this work, we present our recent work on the similar nanowire FETs defined by e-beam lithography and standard Si processing technologies. This approach provides excellent manufacturability and feasibility of integrating circuitry with the sensor array on a single chip for ultimate system miniaturation and low manufacturing cost. In our process, SiNWs are defined by e-beam lithography in hydrogen silses quioxane resist, followed by a new two-step Si etch process, which is designed to improve the process reliability and controllability. SiNW FETs of 30-100 nm in widths, 10-30 nm in thickness, 5-80 µm in length have been successfully fabricated on Si on insulator (SOI) substrates. Uniform devices with sub threshold slope (SS) of 80 mV/dec and On/off ratio greater than 10^7 have been made reproducibly. We will present various device design and fabrication considerations for using nanoelectronic FETs as biosensors, e.g. source/drain doping effects, oxidation effects, plasma treatment effects, buffer solution effects and stability. These device issues are quite different from conventional use of nanowires in logic gates. We further integrate these SiNW FETs with SU8 microfluidic channels to detect proteins at low abundance in solution. Preliminary results have indicated a sensitivity or detection limit of 2fM. We expect to present controlled sensing results of protein biomarker under controlled flow conditions.

[1] Patolsky, F., Zheng, G and Lieber, C.M, *Nat.Protocols* 1, 1711-1724 (2006)

[2] Eric Stern, et al. *Nature* 445, 519-522 (2007)

9:20am **NS-WeM5 The Role of Surface Chemistry on the Properties of Nanoporous Gold**, *J. Biener, M.M. Biener, A.V. Hamza*, Lawrence Livermore National Laboratory, *A. Wittstock, M. Bäumer*, Universität Bremen, Germany, *D. Kramer, R.N. Viswanath, J. Weissmüller*, Forschungszentrum Karlsruhe, Germany
Although surfaces or, more precisely, surface atoms determine the way how materials interact with their environment, the influence of surface chemistry on the bulk of the material is generally considered to be small. However, in the case of high surface area materials such as nanoporous gold the influence of surface properties can no longer be neglected. Therefore, actively controlling surface properties such as diffusion barriers and surface stress by surface chemistry should provide an opportunity to manipulate and fine-tune material properties. Specifically, we will show that surface chemistry is an important factor in determining the stability of nanostructured gold surfaces, and that macroscopic strain can be generated by surface-chemistry induced changes of the surface stress. The latter effect can be used to directly convert chemical energy into a mechanical response without generating heat or electricity first and thus opens the door to surface-chemistry driven actuator and sensor technologies.

9:40am **NS-WeM6 Surface Plasmon Induced Enhancement of Hot Electron Flow Generated by Photons Probed with Metal-Semiconductor Nanodiodes**, *J.Y. Park, H.S. Lee, J.R. Renzas, R. Baker, G.A. Somorjai*, University of California, Berkeley and Lawrence Berkeley National Laboratory
We present hot electron generation from photon absorption on metal-semiconductor Schottky diodes and its amplification by localized surface plasmon resonance. Hot electron flow was generated on a gold thin film (< 10 nm) by photon absorption and directly measured as a form of photocurrent on chemically modified gold thin film metal-semiconductor (TiO$_2$) Schottky diodes. The short-circuit photocurrent obtained with low energy photons (lower than the 3.1 eV bandgap of TiO$_2$) is consistent with Fowler's law, which confirms the presence of hot electron flow. The morphology of the metal thin film was modified to a connected gold island structure with a lateral length scale of 50- 100 nm after heating in oxygen. The nanometer scale domains in the gold island structures were electrically connected to the Ohmic pad, ensuring the measurement of the flow of hot electrons. These connected island structures exhibit a localized surface plasmon with peak energy at 550- 570 nm, which was separately characterized with UV-Vis. Hot electron flow (after normalizing photon absorption) was enhanced by a factor of three on the connected gold island structure. This result indicates correlation between the hot electron flow and localized surface plasmon resonance. Possible mechanisms for surface plasmon induced enhancement of hot electron generation are also discussed.

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* Medard W. Welch Award Winner

10:40am NS-WeM9 Gallium Nanoparticles: An Alternative Metal for Surface-Enhanced Raman Scattering, *P.C. Wu, C.G. Khoury, T.H. Kim, Y. Yang,* Duke University, *M. Losurdo, G. Bruno,* IMIP-CNR, Italy, *T. Vo-Dinh,* Duke University, *H.O. Everitt,* Army AMRDEC, *A.S. Brown,* Duke University

The recent increased use of surface-enhanced Raman spectroscopy (SERS) for chemical and biological sensing is intimately tied to the surging interest in developing plasmonic metallic nanostructures. Typically silver or gold, SERS substrates exploit the plasmon resonance and the associated localized surface fields to enhance Raman scattering from the molecule of interest. We will present an alternative plasmonic metal, gallium, for use as SERS substrates. Gallium's prevalence in optoelectronic device growth also suggests their potential for integrated SERS structures. Our previous work has demonstrated interesting properties of gallium that make it an attractive metal for SERS sensing schemes compared to Ag or Au; these include its thermal and oxidative stability. Also in contrast to the properties of Ag and Au, Ga plasmonic nanoparticles can be tuned for size resulting in a plasmon resonance that varies from the near IR through the visible and into the deep UV.

Gallium nanoparticles (NPs) deposited onto dielectric substrates (glass and sapphire) were grown by molecular beam epitaxy. Nanoparticles were tuned to different plasmon resonances (i.e. mean size) to discern the effect NP geometry (size, distribution, and interparticle spacing) has on the strength of the Raman enhancement. In this work, solutions of the standard Raman dye Cresyl Fast Violet were dropcast onto the NP substrate at varying concentrations to evaluate the linear correlation between SERS intensity and molecular concentration. Direct comparison between bare (unmetallized) surfaces and metallized surfaces were made to quantify the Raman enhancement resulting specifically from the presence of Ga NPs. The enhanced Raman signal in the presence of Ga NPs suggest that Ga NP are effective alternatives to Ag and Au for SERS applications.

11:00am NS-WeM10 Effect of Functional Substrates on Optoelectronic Properties of Hybrid Nanostructures, *D. Conklin,* University of Pennsylvania, *P. Banerjee,* University of Maryland, *S.U. Nanayakkara,* University of Pennsylvania, *T.-H. Park,* University of Michigan, *M.J. Therien,* Duke University, *D.A. Bonnell,* University of Pennsylvania

Functionalized gold nanoparticles are assembled on ferroelectric and non ferroelectric substrates. The assemblies are designed to exhibit photoconductivity by controlling particle size, distribution, density, and by linking with optically active porphyrin complexes. The wavelength and temperature dependence of transport is used to determine the effect of the substrate on the optoelectronic properties. Specifically, the effect of substrate local field due to the domain polarization is determined by comparing the response of similar nanostructures on non ferroelectric (SiOx) substrates. Activation energies of high temperature transport mechanisms and tunneling parameters of low temperature transport mechanisms are compared. The combination of optoelectronic molecular nanostructures and a functional substrate suggests new device strategies.

11:20am NS-WeM11 Control of Coupled Silicon Atomic Quantum Dots for Nano-Electronic Computing Architectures, *J. Pitters,* National Institute for Nanotechnology, Canada, *B. Haider,* University of Alberta, Canada, *G. Dilabio,* National Institute for Nanotechnology, Canada, *L. Livadaru, J. Mutus, R. Wolkow,* University of Alberta, Canada

Coupled quantum dots form an attractive basis both for fundamental studies of single electron control and as potential building blocks for future nano-electronic devices. One computing scheme, Quantum-dot Cellular Automata (QCA), is based upon "cells" of tunnel coupled quantum dots and electrostatic interactions between adjacent cells to transmit binary information and perform calculations with minuscule power consumption. Efforts to fabricate electrostatic QCA devices have been limited by the need for extreme cryogenic conditions. We have demonstrated a new approach using the scanning tunneling microscope (STM) at room temperature. We show that the silicon atom dangling bond (DB) state, on an otherwise hydrogen terminated surface, serves as a quantum dot. These atomic quantum dots can be assembled into multi-DB ensembles through precise hydrogen atom removal using the STM tip. Assembly at critical distances leads to electron tunnel coupling between DBs and control over the net electron occupation of assembled quantum dot DBs is also demonstrated. Additionally, it is shown that a pair of tunnel-coupled DBs can be switched, using electrostatic control, from a symmetric bi-stable state to one exhibiting an asymmetric electron occupation. Similarly, the setting of an antipodal state in a square assembly of four DBs is achieved, demonstrating at room temperature the essential building block of a quantum cellular automata device.

11:40am NS-WeM12 Towards Wafer-Scale Fabrication of Room-Temperature Single-Electron Transistors, *P. Bhadrachalam, V. Ray, R. Subramanian, S.J. Koh,* University of Texas at Arlington

We recently demonstrated CMOS-compatible fabrication of single-electron transistors (SETs) that operate at room temperature (Nature Nanotech. V.3, p.603, 2008). This was realized using a new device architecture in which source and drain electrodes are vertically separated with a Coulomb island placed between the electrodes. Here, we present two important advancements toward wafer-scale fabrication of room-temperature SETs for practical applications. Firstly, we present a technique for placing Coulomb islands between the source and the drain electrodes with nanoscale precision, which significantly improves the yield of device fabrication. This accurate placement was made possible by electrostatically guiding Coulomb islands onto the center of the electrode gap. The electrostatic guiding structures were made on a large scale using self-assembled monolayers (SAMs) of positively- and negatively- charged molecules. Secondly, we present a very small fluctuation of the background charges for our fabricated SETs. The uncontrolled fluctuation of background charges has been one of the major obstacles to the practical implementation of SET devices. The shift of background charges was directly measured from the phase shift of Coulomb oscillations at room temperature and it was found that the charge shift was only ~0.01e (e: electron charge) over a time span of more than a week. These two advancements show a great promise for realization of integrated systems of room-temperature SETs for practical use. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), THECB (003656-0014-2006))

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