

Tuesday Morning, October 16, 2007

Electronic Materials and Processing

Room: 612 - Session EM-TuM

Molecular Electronics

Moderator: I. Hill, Dalhousie University

8:00am **EM-TuM1 Dynamics of Molecular Switch Molecules Imaged by Alternating Current Scanning Tunneling Microscopy**, *A.M. Moore, P.S. Weiss*, The Pennsylvania State University

We have studied oligo(phenylene-ethylene) (OPE) molecules as candidates for molecular electronic switches. We previously determined the switching mechanism to rely on hybridization changes between the substrate and molecule. Here, we have determined which molecules will be more or less active in our samples using a custom-built alternating current scanning tunneling microscope (ACSTM). The polarizabilities of the OPE molecules are observed using the ACSTM magnitude signal. The stability of the ACSTM magnitude correlates to the stability of the switches in our samples. From this, we can determine which molecules are more likely to exhibit motion and/or switching events and which molecules will remain stable in our images.

8:20am **EM-TuM2 Probing the Polarization and Dielectric Function of Molecules with Higher-Harmonic Demodulation in s-NSOM**, *M.P. Nikiforov*, University of Pennsylvania, *S. Schneider*, Dresden University of Technology, Germany, *T.-H. Park*, University of Pennsylvania, *U. Zerwek, C. Loppacher, L. Eng*, Dresden University of Technology, Germany, *M.J. Therien, D.A. Bonnell*, University of Pennsylvania

In recent years a family of scanning probe microscopy (SPM) techniques has been evolved basing on applying multiple modulations to samples and tips and accessing optical higher-order harmonics. Scanning surface potential microscopy (SSPM or KPFM) based on noncontact atomic force microscopy (nc-AFM) is the first and most basic of the implementations exploiting multiple modulations. SSPM allows the analysis of local work functions on metallic samples and of surface charge distributions on insulators. In addition to the electric modulation, nc-AFM can be extended to optical investigations with the potential to access dielectric functions at surfaces. Of these scanning optical microscopes, so-called scattering near field optical microscopy (S-NSOM) offers the best opportunity for high spatial resolution. In s-NSOM a sharp probe tip is positioned near a surface and illuminated with optical radiation. The electric field is highly enhanced underneath the tip which acts as an optical antenna. Is a sample placed close to the tip, the local dielectric constant of the sample is probed by the tip and may be detected in the far-field scattered light. The strongly nonlinear distance dependence of the near-field may be used to separate its contribution from background signals by so-called higher-harmonic demodulation. In the present study the properties of porphyrin monolayers deposited on highly oriented pyrolytic graphite (HOPG) by evaporation in vacuum are probed. The molecular structure of the monolayer is known from nc-AFM. The polarization dependence of light scattering on the optically active molecules (porphyrin) was measured at four harmonics of the tip oscillation frequency. The contrast differences in the higher harmonics related to the dielectric properties of the molecules is compared with an analytical description of the signal transfer function. The limits in quantifying dielectric function and spatial resolution will be discussed as will the potential to probe dielectric function at the molecular level in the future.

8:40am **EM-TuM3 Electronic and Vibronic Spectroscopy of Molecular Junctions**, *J.G. Kushmerick*, NIST **INVITED**

Transition voltage spectroscopy and inelastic electron tunneling spectroscopy are used to explore charge transport in molecular junctions. Our recent work has shown that a mechanistic transition occurs from direct tunneling to field emission in molecular junctions. The magnitude of the voltage required to enact this transition is molecule-specific, and thus constitutes a form of spectroscopy. We demonstrate that the transition voltage of a conjugated molecule depends directly on the manner in which the conjugation path is extended. Furthermore using inelastic electron tunneling spectroscopy to measure the vibronic structure of non-equilibrium molecular transport, aided by a quantitative interpretation scheme based on non-equilibrium Greens function/density functional theory methods, we are able to characterize the actual pathways that the electrons traverse when moving through a molecule in a molecular transport junction.

9:20am **EM-TuM5 Real-time Conductivity Analysis through Single-Molecule Electrical Junctions**, *J.-S. Na, J. Ayres, K.L. Chandra, C.B. Gorman, G.N. Parsons*, North Carolina State University

We have recently developed a molecular electronic characterization test-bed that utilizes a symmetric pair of gold nanoparticles, 40 nm in diameter, joined together by a single or small group of conjugated oligomeric phenylene ethynylene (OPE) molecules. These nanoparticle/molecule/nanoparticle structures are subsequently assembled between nanoscale test electrodes to enable current through the molecule to be characterized. At low voltage ($< \pm 1.5$ V) the observed current is consistent with common non-resonant tunneling (i.e., I vs V is independent of temperature between 80 and 300 K). This molecular analysis approach is unique because it enables the stability of the molecular conductance to be observed and characterized over extended periods (several weeks so far) after fabrication. Conductance through single molecule junctions was monitored in real-time during several process sequences, including dielectrophoretic directed self assembly and post-assembly modification. Assembly faults are directly detected in real-time when non-ideal assembly conditions result in molecular junction failure and nanoparticle fusion in the junction. Real-time conductivity measured through the junction was sensitive to ambient conditions, and changes persisted over several days of exposure. Atomic layer deposition of Al_2O_3 was used to encapsulate and isolate the molecular junctions, and the effect of the deposition process sequence on current through the junction was evaluated in real-time. Results indicate that the current measured during atomic layer deposition is sensitive to the chemical oxidation and reduction reactions proceeding in the 1-2 nanometer confined region between assembled nanoparticles.

9:40am **EM-TuM6 Electronic Transport through Redox-Active Organic Molecules in Nanogap Molecular Junctions**, *A.K. Mahapatro, J. Ying, B. Muralidharan, S. Datta, T. Ren, D.B. Janes*, Purdue University

Electronic properties of various organic molecules have been studied for potential nanoelectronics and sensor applications. Studies of redox active molecules can allow investigation of the energy-band alignments of the molecular levels with respect to the contact Fermi levels and studies of molecules in specific charge states. A recently developed technique to efficiently fabricate stable nanogap molecular junctions (NMJs)¹ are used in this study for room-temperature electrical measurements through single/few molecule systems. Electronic properties of redox active molecules Oligo(phenylene ethylene), OPE and trans- $Ru_2(ap)_4(C=CC_6H_4S)_2$, where $(ap)_4$ is 2-anilinoipyridinate, are studied by localizing the molecules in the NMJs. The current-voltage characteristics of the OPE devices exhibit switching behavior at a threshold voltage between 1.6 V and 3.0 V. The di-ruthenium devices exhibit a negative differential resistance region, corresponding to an irreversible current peak at a bias voltage of ~ 0.3 - 0.4 V, followed by a conductance peak at higher bias. A theoretical model using sequential tunneling Coulomb blockade model² explains the current peak in terms of a blocking transport level that cannot be emptied easily, causing the conducting level to float out of the bias window as a result of Coulomb repulsion. Assuming equal capacitive coupling at both the metal-molecule contacts,³ the observed conductance peak positions at $\pm 0.25 \pm 0.05$ V and $\pm 1.05 \pm 0.15$ V correspond to molecular level energies of $E_{HOMO} = 5.23$ eV and $E_{LUMO} = 4.6$ eV for the di-ruthenium molecule. These values are in close agreement with the molecular level energies estimated from the measured oxidation and reduction peaks in cyclic voltammetry.⁴ The current study demonstrates that devices employing redox active molecules, in which the molecular levels are close to the metal Fermi level, allow resonant tunneling and could provide suitable structures for memory or chemical sensing applications.

¹ A. K. Mahapatro, S. Ghosh, and D. B. Janes, IEEE Trans. Nanotech., 5, 232 (2006).

² B. Muralidharan and S. Datta, Preprint, arXiv:cond-mat/0702161 (2007).

³ S. Datta, W. Tian, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Phys. Rev. Lett. 79, 2530 (1997).

⁴ T. Ren et. al., J. Organ. Chem., 690, 4734 (2005).

10:40am **EM-TuM9 Electron Transport through Silicon-Based Molecular Electronic Devices: Effects of Molecular Chainlength and Molecular Dipole**, *N. Gergel-Hackett, L.J. Richter, C.D. Zangmeister, C.A. Hacker, C.A. Richter*, National Institute of Standards and Technology

It is important for the advancement of the field of molecular electronics to develop an improved understanding the electron transport through molecular junctions, specifically silicon-based junctions that may enable the integration of molecular devices with traditional semiconducting technologies. In this work we examine the effects of molecular length and dipole on the electrical behavior of a metal-molecule-silicon, planar, enclosed devices. Devices with alkanethiol molecules of different lengths, with semi-fluorinated and non-fluorinated molecules, and with differently

doped silicon were characterized to systematically understand the energetics of the metal-molecule-silicon junction and how the electron transport through the device is affected. We characterized devices with monolayers of various chainlengths of alkanethiols and observed the device current to decrease with increased molecular length. This inverse dependence on chainlength has been widely observed from metal-molecule-metal devices, but is an important characterization metric for silicon-based devices. However, we observed a different dependence of the current density on the chainlength than has been observed for metal-molecule-metal junctions. We attribute this difference in dependence to the Schottky barrier between top metal and bottom silicon contact in the metal-molecule-silicon devices that is not present in metal-molecule-metal devices. This will be explained in greater detail. We also compare the electrical characteristics of alkanethiol molecules with those of semi-fluorinated alkanethiols. The molecular dipole is dramatically different for semi-fluorinated alkanethiols than for non-fluorinated alkanethiols, and we observed current-voltage characteristics that depend on the fluorination. In order to confirm that the differences in current observed were due to the molecular dipoles shifting the Schottky contact barrier, we characterized devices with differently doped substrates. The relative effects of the molecular dipoles on the different starting Schottky contact barriers are used to develop an energetic model of the junction and the effects of surface dipoles. The observed changes in electrical behaviors as a result of changes in the chainlength and dipole of the molecular monolayer help us to understand the electrical transport through these devices and to verify that the energetic behavior of the devices has a molecular dependence.

11:00am **EM-TuM10 Characterization of Aryl Monolayers on Silicon for Molecular Electronics Applications**, *A. Scott, D.B. Janes*, Purdue University

Recently there has been a significant amount of interest in developing molecular electronics to miniaturize and enhance functionality of integrated circuits. Molecular electronic devices with silicon contacts are of particular interest due to the relevance of silicon as an electronic material and the ability to engineer the substrate properties through doping. Molecular layers have been grafted to <111> silicon by electrochemical reduction of para-substituted aryl-diazonium salts for use in silicon-based molecular electronics. These molecular layers were characterized using atomic force microscopy, ellipsometry, x-ray photoemission spectroscopy, infrared spectroscopy, and contact angle measurements. It was found that the surface characteristics were dependent both on monolayer headgroup chemistry and substrate doping. Consequences for the application of these molecular layers to electronic devices on silicon were examined. Hydrogen-terminated silicon samples were prepared by etching cleaned silicon in deoxygenated ammonium fluoride. Various doping densities of silicon were used and it was determined that oxide-free surfaces could be realized on all of them using this method, however the doping affected the surface topology. Lightly doped samples exhibited atomically flat surfaces with well-defined step edges corresponding to individual planes of silicon atoms, whereas heavily doped samples maintained a low surface roughness, but had no defined structure. Molecular layers were prepared on hydrogen-terminated silicon by electrochemical reduction of various commercially available para-substituted aryl-diazonium salts in acidic aqueous solution.¹ Chemical characterization of the surfaces indicates that the substituent plays an important role in monolayer quality. Nitro-substituted species exhibited chemical instability and significant oxidation of the silicon substrate. Other molecular layers showed more ideal monolayer characteristics. These findings can be correlated with observations about electronic transport in gold-molecule-silicon devices.²

¹ P. Allongue, C. H. de Villeneuve, J. Pinson, F. Ozanam, J. N. Chazalviel, and X. Wallart, *Electrochim. Acta* 43, 2791 (1998).

² A. Scott, C. Risko, M. A. Ratner, D. B. Janes, *Appl. Phys. Lett.*, to be published.

11:20am **EM-TuM11 Nanoscale Electrical and Structural Characterization of Gold/Monolayer/Silicon Junctions**, *W. Li, M.A. Kuikka, H.Z. Yu, K.L. Kavanagh*, Simon Fraser University, Canada

The effect of molecular modification of metal-Si diode junctions has been investigated by electrical and structural measurements at both the macroscale and the nanoscale. Molecular junctions prepared with carbon-silicon bonded, n-alkyl monolayers and thermally evaporated gold contacts yield identical barrier heights and ideality factors irrespective of the alkyl chain length and end-group of the molecular layer. Nanoscale electrical and structural measurements, using ballistic emission electron microscopy (BEEM), and transmission electron microscopy (TEM), indicate laterally uniform penetration of deposited gold atoms into the junctions except for thiol-terminated monolayers where BEEM transmission is laterally non-uniform and TEM shows a continuous interfacial layer. In all cases, average BEEM transmission is reduced by the presence of a molecular layer with the largest effects also observed for the thiol terminated system.

11:40am **EM-TuM12 New Methods for Metal Deposition on Self-Assembled Monolayers: Towards Molecular Electronic Circuitry**, *P. Lu, A.V. Walker*, Washington University in St. Louis

We have investigated the deposition of metals on alkanethiolate self-assembled monolayers (SAMs) adsorbed on Au using chemical vapor deposition (CVD) and electroless deposition. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Chemical vapor deposition (CVD) is a widely employed technique for the deposition of metals on semiconductor substrates. CVD has not been widely employed to deposit films on organic materials because high temperatures ($T_{\text{substrate}} > 200\text{ }^{\circ}\text{C}$) are often required that are not compatible with most organic thin films. However, by exploiting the chemical reactivity of functional groups at the SAM surface it is possible to deposit thin metallic films at room temperature. We demonstrate this method using trimethyl aluminum (TMA). TMA reacts at room temperature with a -COOH terminated SAM to form an Al overlayer, whereas TMA does not react with a -CH₃ terminated SAM. We have also investigated the mechanism of electroless deposition of copper on functionalized SAMs using a copper sulphate/formaldehyde reaction. Copper is deposited on -CH₃ and -COOH terminated SAMs but not on -OH terminated SAMs. For -CH₃ and -COOH SAMs, the deposited Cu is weakly stabilized at the SAM/vacuum interface and so slowly penetrates through the SAMs to the Au/S interface. Further, Cu does not deposit on -OH terminated SAMs because the formaldehyde reacts with the -OH terminal groups rather than reducing the copper.

12:00pm **EM-TuM13 Contact Properties in Molecular Electronics: The Effect of Molecular Orientation on Potential at Organic- Metal Interfaces**, *M.P. Nikiforov*, University of Pennsylvania, *U. Zerwek, C. Loppacher*, Dresden University of Technology, Germany, *T.-H. Park, M.J. Therman*, University of Pennsylvania, *L. Eng*, Dresden University of Technology, Germany, *D.A. Bonnell*, University of Pennsylvania

Developments in molecular electronics over the last 5 years emphasize that the contact between molecules and electric contacts often define the behavior of the device. Controlling the structure and consequent properties of these junctions is of paramount importance. To date, it has not been possible to probe the relation between molecular structure and properties at the nm scale. The combination of molecular structure and local property measurement is demonstrated here. Vapor deposition of TET - H₂ - TET porphyrin on HOPG results in islands that self assemble into 2 structures; one with the molecules oriented perpendicular to the film, one with a parallel orientation. The molecular structures are determined by nc-AFM. Variations in surface potential determined by Kelvin Force Microscopy (Scanning Surface Potential Microscopy) are correlated with the orientation of the porphyrin monolayers. The difference between the potential of the two structures is about 50mV. The difference in work function with orientation reflects a difference in the coupling between the molecule and the substrate. Perpendicular porphyrin does not alter the work function implying the absence of reaction and self assembly is dominated by van der Waals interactions. The decrease in work function with parallel orientation is indicative of a substrate-molecule interaction. The mechanism of this interaction will be discussed in terms of atomic orbitals. This is a direct measure of the effect of molecular orientation on the electronic properties of the junction.

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