

Wednesday Afternoon, October 22, 2008

Electronic Materials and Processing

Room: 210 - Session EM+NC-WeA

Molecular and Organic Electronics

Moderator: L.M. Porter, Carnegie Mellon University

1:40pm EM+NC-WeA1 Metal-Molecule-Semiconductor Devices: Accurate Extraction of Device Parameters from Transport Measurements, A. Scott, D. Janes, Purdue University

In recent years there has been considerable interest in integrating molecular components into solid-state electronic devices for high-density memory, nanoelectronic, and sensing applications. Molecular devices directly grafted to semiconductors are of particular interest due to the electrically tunable nature and technological relevance of the substrates. Considerable experimental efforts have been invested in the fabrication and electrical characterization of metal-molecule-semiconductor (MMS) devices. When moderately-doped semiconductors are used in MMS structures, the devices exhibit Schottky diode-like behavior. Typically, current-voltage or capacitance-voltage characteristics of the devices are measured at room temperature and the results are analyzed by using well-known ideal Schottky diode relationships.¹ The Schottky barrier height, Φ_B , is experimentally determined assuming that the electronic and structural properties of the interfaced are not significantly modified by the presence of the molecular layer. Although this approach has been used to offer valuable qualitative insights about effects such as the influence molecular dipole on Φ_B ,² it does not consider the detailed structural and electronic properties of the interface. Additional experimental and theoretical tools are needed to capture the interfacial physics introduced by the molecular electronic structure as well as non-idealities which are present at such hybrid interfaces. We present a MMS device model which considers the molecular electronic structure, semiconductor interface states, junction non-uniformity, and other important physical phenomena which are not present in the ideal Schottky diode model. The influence of various effects on current-voltage and capacitance-voltage characteristics are illustrated. Theoretical and experimental evidence is presented to show that temperature dependent transport allows for more accurate extraction of device parameters with fewer assumptions. The improved description MMS devices will shed additional light on the transport mechanisms that dominate these structures as the substrate and molecular properties are varied, leading to improved device design and characterization.

¹ Sze, S. M., Physics of Semiconductor Devices, 2nd ed. Wiley-Interscience, New York, 1981.

² Haick, H.; Ambrico, M.; Ligonzo, T.; Tung, R. T.; Cahen, D., J. Am. Chem. Soc. 128 (2006) 6854-6869.

2:00pm EM+NC-WeA2 Silicon-on-Insulator based sub 10 nm Spaced Metal Electrodes for Hybrid Molecular Electronics, S. Strobel, Technische Universität München, Germany, R. Sondergaard, Technical University of Denmark, R. Murcia Hernandez, Technische Universität München, Germany, A. Hansen, F. Krebs, Technical University of Denmark, P. Lugli, Technische Universität München, Germany, M. Tornow, Technische Universität Braunschweig, Germany

In future microelectronic circuits a partial replacement of certain electronic functions by organic molecule junctions may become feasible. For such "hybrid" integration the fabrication of nanoscale contacts on the same semiconductor wafer using existing microelectronic process technology, only, will be advantageous. We investigated the fabrication of nanogap electrode devices based on silicon-on-insulator, by using optical lithography, a combination of dry and wet etching techniques and thin-film metal deposition. The prepared, smooth metallic contact pairs are separated by predetermined distances down to below 10 nm, and feature a well tailored material layer structure, as characterized by cross-sectional scanning TEM analysis. We studied the electronic transport properties of molecular wires based on conjugated organic molecules and molecule-nanoparticle hybrid systems. In the case of approx. 12 nm long dithiolated, oligo-phenylene-vinylene derivatives we observed a pronounced non-linear current-voltage characteristic at 4.2 K. The electronic states of the molecule have been studied by Density Functional Theory (DFT) in order to show the effect of the ligands and of the gold contacts. By using the results of the DFT calculations in a Non Equilibrium Green Function model, the current-voltage characteristics of OPVs have been analyzed, showing a good agreement with the experimental data. Low temperature transport through 30 nm gold nanoparticles positioned onto electrodes coated by a self-assembled monolayer of mercaptohexanol features a distinct Coulomb staircase behavior. These measurements are in excellent agreement with classical Coulomb blockade theory for an asymmetric double barrier tunneling system.

2:20pm EM+NC-WeA3 Single Molecule Electronics and Sensors, N.J. Tao, Arizona State University

INVITED

The ability to measure and control current through a single molecule is a basic requirement towards the ultimate goal of building an electronic device using single molecules. It also allows one to read the chemical and biological information of the molecule electronically, which opens the door to chemical and biological sensor applications based on electrical measurement of individually wired molecules. To reliably measure the current, one must: 1) provide a reproducible contact between the molecule and two probing electrodes; 2) find a signature to identify that the measured conductance is due to not only the sample molecules but also a single sample molecule; 3) provide a third gate electrode to control the current; and 4) carry out the measurement in aqueous solutions for biologically relevant molecules in order to preserve their native conformations. We will describe methods to attach a single molecule to two electrodes via covalent bonds and control the current through the molecule with an electrochemical gate, and report on sensor applications of the molecular junctions. We will also discuss unresolved issues in the attempt to measure and control electron transport in single molecules.

3:00pm EM+NC-WeA5 Spectroscopic Observation of Conductance Switching with Inelastic Electron Tunneling Spectroscopy, B.G. Willis, University of Delaware

Molecular electronics is a promising area of research for creating electronic devices that can be integrated with semiconductor based nanoelectronics for novel capabilities such as molecular sensors. Recent literature data has shown that the electrical transport properties of molecules can be tuned through chemistry, and the long term expectation is that useful devices can be engineered through a combination of chemistry and electrical transport properties. It is also known that the electrical contact between a molecule and an electrode has a significant influence on electrical transport measurements, and these contact effects complicate the interpretation and design of molecular electronics devices. The contact effects become increasingly important as the number of molecules in the molecular transport junction is reduced toward the limit of a single molecule, and there is an urgent need to investigate contact effects in transport measurements. This is difficult due to the inherent nanoscopic nature of the experiments and the general lack of appropriate experimental tools. In this paper, we present an approach using inelastic electron tunneling spectroscopy (IETS) to investigate the chemistry and chemical bonding in electrode-molecule-electrode tunnel junctions. We present IETS spectroscopic observation of conductance switching for carbon monoxide bonded to a Cu/Pd bimetallic surface in a nanoelectrode junction. It is shown that the conductance switching is caused by the formation of an adatom on the surface that leads to an abrupt increase in the current of almost an order of magnitude. The new bonding arrangement leads to intense IETS features including the metal-CO bond stretch that has not previously been observed in related scanning tunneling microscopy IETS experiments. This work demonstrates that conductance changes in molecular electronics junctions can be studied and understood using IETS as a spectroscopic probe of the chemistry and bonding in the junction. Furthermore, it is shown that small molecules such as CO may be useful for characterizing electrode structure in molecular electronics measurements.

4:00pm EM+NC-WeA8 Nanocontacts Inducing Surface Initiated Polymerization of Nanowires on Molybdenum Carbide, I. Temprano, Université Laval, Canada

The ability to develop new methods to enhance electrical contact between organic molecules and electrodes is fundamental to the design of devices that require electron flow between an organic and a metallic component. Metal-organic contacts using double and triple bonds is a promising approach in that it combines three advantages. First it offers a transmission coefficient not yet seen way ahead of any other molecular linkages yet known,^{1,2} second they have enhanced thermal stability^{3,9-10} over 900 K, and they show activity for olefin-metathesis add-on chemistry.¹ The dissociative adsorption of carbonyl compounds leads to the formation of C=Mo double bonds on the surface of molybdenum carbide.³⁻⁶ These metal alkylidenes are mimics of well defined homogeneous metathesis catalysts, and present similar activity face to transalkylidenation and ring-opening polymerization (ROMP)⁸ reaction. The data presented will show this breakthrough catalytic system and its performance, paying especial attention to the formation and characterization of surface initiated metathesis polymerization of polyacetylene,⁹ the simplest of the conjugated polymers, and an ideal candidate to study the special properties this system can develop. This study opens a whole new era in which a very controllable reaction as olefin-metathesis may be used to grow

technologically very interesting conjugated polymers, directly from a metallic surface, and hence, to interconnect electrodes, as nanowires, in nanodevices with great control and precision. Self-assembly of conjugated polymers may allow their targeted insertion into electronic and electrooptical devices.

¹ Tulevski, G.S., Myers, M.B., Hybertsen, M.S., Steigerwald, M.L., Nuckolls C., *Science*, 309 (2005) 591.

² J. Ning, Z. Qian, R. Li, S. Hou, A. R. Rocha, S. Sanvito. *J. Chem. Phys.*, 126 (2007), 174706

³ Zahidi, E-M., Oudghiri-Hassani, H., McBreen, P.H., *Nature*, 409 (2001), 1023

⁴ Sijaj, M., Reed, C., Oyama, T., Scott, S.L., McBreen, P.H., *J. Am. Chem. Soc.*, 126 (2004) 9514

⁵ Sijaj, M., Oudghiri-Hassani, H., Zahidi, E-M., McBreen, P.H., *Surf. Sci.*, 579 (2005) 1

⁶ Oudghiri-Hassani, H., Zahidi, E-M., Sijaj, M., McBreen, P.H., *App. Surf. Sci.*, 212-213 (2003) 4

⁷ Sijaj, M., McBreen, P.H., *Science*, 309 (2005) 588.

4:20pm **EM+NC-WeA9 Spatially Resolved Conductance Measurements of Novel Porphyrin-Chromophore Molecular Assemblies**, *S.U. Nanayakkara, L. Kraya*, University of Pennsylvania, *T.-H. Park, J.T. Stecher, M.J. Therien*, Duke University, *D.A. Bonnell*, University of Pennsylvania

We have measured charge transport in individual porphyrin-chromophore molecules using an ultra-high vacuum scanning tunneling microscope. This class of fully conjugated molecules can include a mono- or multi-chromophoric center and a linker-group that terminates with a thiol or dithioate functionality. These functionalities facilitate attachment to a gold substrate. Therefore, in order to isolate individual and small groups of molecules we have utilized self- and directed-assembly using alkanethiolate self-assembled monolayers (SAMs) on Au(111). The alkanethiolate SAMs provide a support matrix confining the porphyrin-chromophore molecules into precise assemblies for charge transport measurements. We have further coupled a laser to the tunneling junction in order to record photo-induced single molecule charge transport measurements. We aim to understand the conductance pathways of these molecules with and without illumination, and as a function of its chemical structure and the molecule-substrate interface.

4:40pm **EM+NC-WeA10 Phase Selection in TiOPc/Ag (111) Molecular Films: Combined STM:STS Investigations***, *Y.Y Wei*, University of Maryland, College Park, *S.W. Robey*, National Institute of Standards and Technology, *J.E. Reutt-Robey*, University of Maryland, College Park

Titanyl phthalocyanine (TiOPc) has emerged as an important molecular component in building organic electronic devices. Its broad optical absorption spans the near infrared - visible region and high photoconductivity are most promising features, yet a tendency for polymorphism may limit TiOPc applications. Understanding how to control the molecular architecture in thin TiOPc films, and relate structure to electronic properties, is thus an important scientific goal. We present STM/STS studies of growth and two-dimensional crystallization of TiOPc films prepared by vapor deposition on Ag (111). We show how three distinctive TiOPc monolayer phases can be fabricated via flux control. At lowest TiOPc fluxes, a honeycomb phase forms, in which molecules organize into interlocked pairs. This phase optimizes quadrupole attraction and minimizes lateral dipole repulsion between TiOPc neighbors. At medium fluxes, a higher-energy hexagonal phase, stabilized by partly overlapped Pc rings between neighboring molecules emerges. At yet higher fluxes, a triangular network of misfit dislocations, with a characteristic domain size of ca. 14 nm is produced. We present molecular models of these three distinctive phases and describe how the film architecture is controlled primarily by electrostatic TiOPc-TiOPc interactions. Comparative STS Studies of the honeycomb and hexagonal monolayers reveal a metallic-like conductivity for both films. Finally, we show how these different TiOPc phases, employed as substrates for sequential C₆₀ deposition, yield distinctive donor-acceptor heterostructures with unique electronic characteristics.

*This work has been supported by the Department of Commerce through the Nanomanufacturing Center of NIST, the Nanotechnology Fund of NASA, and the National Science Foundation under Surface Analytical Chemistry grant CHE0750203.

5:00pm **EM+NC-WeA11 Spin Polarized Electron Tunneling Through Conjugated Molecules**, *P. LeClair, W. Xu, G. Szulczewski, A. Gupta*, University of Alabama

Electron tunneling across organic/inorganic interfaces is important to the performance of organic based electronic devices, such as organic light emitting diodes and organic field effect transistors. However, spin dependent electron tunneling across organic/inorganic interfaces is not well understood.¹ In this presentation we will demonstrate the injection, transport, and detection of a spin-polarized current through pi-conjugated molecules. Specifically we highlight the results for tetraphenyl porphyrin (TPP), but the results are similar for other conjugated organic semiconductors.² Tunnel junctions were made by depositing TPP between La_{0.7}Sr_{0.3}MnO₃ (LSMO) and Co electrodes. At cryogenic temperatures the devices show a negative magnetoresistance of 15-25%. A tunneling model

that explains the temperature, bias voltage and sign of the magnetoresistance will be presented. In addition, we have directly measured the spin polarization (~37%) for electrons tunneling from Co through TPP monolayers using superconductor Al films as the spin detector. Collectively these results clearly demonstrate that spin polarized electrons tunnel through conjugated organic semiconductors with negligible spin-flipping and suggest that such molecules may find use in spintronic applications. For comparison, we will also present recent results utilizing halogen-substituted benzoic acid self-assembled monolayers as a "model" system. In this case, the presence or absence of spin-flip scattering during tunneling is highly dependent on the choice of the halogen substituent.

¹T. S. Santos, J. S. Lee, P. Migdal, I. C. Lekshmi, B. Satpati, and J. S. Moodera, *Physical Review Letters* 98, 016601 (2007).

²W. Xu, G. J. Szulczewski, P. LeClair, I. Navarrete, R. Schad, G. Miao, H. Guo, and A. Gupta, *Applied Physics Letters* 90,072506 (2007).

5:20pm **EM+NC-WeA12 Influence of Structural Ordering on Conductivity of Pentathiophene Based Langmuir-Blodgett Monolayers**, *Y. Qi*, University of California, Berkeley and Lawrence Berkeley National Laboratory, *B.L.M. Hendriksen, F. Martin, D.F. Ogletree*, Lawrence Berkeley National Laboratory, *C. Mauldin, J.M.J. Frechet*, University of California, Berkeley, *M. Salmeron*, Lawrence Berkeley National Laboratory

Good understanding of the mechanisms responsible for electrical conduction in organic molecules is essential for the development of organic and molecular electronics. In this study we correlate structural and electrical conduction properties of decyl-pentathiophenyl butyric acid monolayers using a conductance atomic force microscope (C-AFM). We used the Langmuir-Blodgett technique to prepare monolayers on heavily doped p-type Si, mica and flat Au substrates. For all substrates we find that two types of structures coexist in the monolayers: one consisting of compact and crystalline islands; the other phase is poorly packed and contains many holes. The magnitude of the friction on crystalline islands is significantly lower than on the poorly packed structure, while the current is at least an order of magnitude higher on the crystalline islands. Scanning on the well-order phase at high loads destroys the lateral order and reduces the conductivity. Our data show that there is a lateral, structural component to the conduction perpendicularly through the monolayer.

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