Electronic Materials and Processing
Room 309 - Session EM1-ThM

Molecular Electronics

Moderator: D.B. Janes, Purdue University

8:20am **EM1-ThM1 Molecular Conductance and Contact Resistance Measured in Nanoparticle-Bridged Nanogap Structures***, **C. Chu**, G.N. Parsons,* North Carolina State University

Understanding molecular conduction and contact resistance at organic-metal junctions is crucial for advanced organic electronic materials and devices. We have developed an angled metal evaporation technique to form planar metal (Au and Al) electrodes with separation distances of <50nm and electrode width of several microns, and used 80nm Au nanoparticles to form conductance pathways between the nanometer-spaced electrodes. Multiple nanoparticles can be measured in parallel, and the conductance increases with the number of nanoparticles in the gap. Before Au nanoparticle deposition, various molecular monolayers were adsorbed onto the Au electrodes, resulting in bridging structures that enable conductance of sets of molecules to be characterized. The conductance and contact resistances are evaluated from current-voltage characteristics and compared to results obtained by conductive probe AFM (CP-AFM) on the same monolayers. Molecules studied include various length alkanethiols and alkylamines, as well as conjugated molecules including xylyl thiol and phenylene derivatives. Current vs voltage is observed to follow the coherent tunneling model, and contact resistance (R@sub o@) was evaluated by measuring the effect of alkyl chain length for both thiol and amine head groups. Alkanethiols show R@sub o@ of ~18 k@OMEGA@, whereas amine head groups give R@sub o@ ~1k@OMEGA@. The number of molecules probed is not precisely known, but resistance for the nanoparticle bridge is larger than measured by CP-AFM, suggesting a smaller number of molecules are probed in the bridge structure. Furthermore conjugated molecules show conductivity that is ~400 times larger than for alkanedithiols. Results show that the bridged nano-gap structure can be used to evaluate conductance and resistance on the molecular scale, and it is capable of characterizing a variety of molecular and nanostructured elements.

8:40am **EM1-ThM2 The Effects of Molecular Environments on the Electrical Switching with Memory of Nitro Molecules***, **N. Gergel-Hackett**,* University of Virginia, US*; N. Majumdar, Z. Martin, G. Pattanaik,* University of Virginia*; Y. Yao, J.M. Tour,* Rice University*; G. Zangari, N. Swami, L.R. Harriott, J.C Bean,* University of Virginia

Since memory behavior was first reported for the "nitro" molecule (an OPE molecule with nitro side groups),@footnote 1@ other researchers have reported various combinations of electrical switching, memory, and/or negative differential resistance.@footnote 2,3,4@ These reports employed test structures that differed in the number of nitro molecules simultaneously contacted: some reports describe devices that contact thousands of molecules,@footnote1,3@ while others contact just a few.@footnote 2,4@ To address a possible correlation between contacting a large area of nitro molecules and observing memory behavior, we report on experiments that use a nanowell device where nitro molecules are seperated by insertion into a secondary matrix of alkanethiols. We observe memory behavior for "pure" nitro monolayers, but not for the monolayers of nitro molecules inserted into alkanethiols. Additionally, insertion into alkanethiol matrices adds the variable of order. STM images reveal that alkanethiol matrices are ordered, yet "pure" nitro monolayers are disordered. A recent report suggests a correlation between the rate of electrical switching and the ordering of a nitro molecule's environment.@footnote 4@ To test for a relationship between memory behavior and an ordered matrix environment, we have developed ways of forming disordered matrices. This is done by changing the exposure time of the substrate to the alkanethiol solution or by using COOH-terminated alkanethiols (16-mercapto hexadecanoic acid). We will report the electrical behavior of nitro molecules inserted into these disordered alkanethiol matrices and contrast the results with those obtained for nitro molecules inserted into ordered matrices, as well as those for "pure" nitro monolayers. @FootnoteText@ @footnote 1@M.A. Reed et al, Appl. Phys. Lett. 78, 3735 (2001)@footnote 2@I. Kratochvilova et al, J. Mater. Chem. 12, 2927 (2002)@footnote 3@F.Fan et al, J. Am. Chem. Soc.124, 5550 (2002)@footnote 4@Z.J. Donhauser et al, Science 292, 2303 (2001).

9:00am **EM1-ThM3 Electronic Structure and Charge Addition Effects in Phenylene Ethynylene Oligomers: a Comparison of Pristine versus -NO@sub2@ Substituted Molecules***, **S.W. Robey**, C.D. Zangmeister, R.D. van Zee,* NIST

Interest in aromatic systems based on phenylene ethynylene oligomers (OPE) has been spurred by reports of intriguing transport behavior in metal-molecule-metal junctions. There have been reports of the observation of negative differential resistance (NDR) characteristics by substitution of electron-withdrawing -NO@sub2@ groups on the central ring of a three-ring phenylene ethynylene oligomer, whereas this behavior is not observed for the "pristine", unsubstituted molecule. In this contribution, the relevant @pi@ electronic structure near the Fermi level, determined via photoelectron spectroscopy for self-assembled monolayers on gold, is compared and contrasted for three-ring phenylene ethynylene oligomers with and without substitution of -NO@sub2@ groups. Further comparison with -NH@sub2@ substituted oligomers and results of ab inito calculations will also be discussed. In addition, theoretical work has invoked redox-like or polaronic effects to provide an explanation for NDR behavior. We have performed measurements to shed light on this issue by comparison of the influence of additional charge in pristine versus nitro-substituted OPE, added by "doping" with K. For pristine OPE, sequential addition of K leads to a gradual shift of levels to higher binding energy reminiscent of "rigid band" behavior, although some distortion/conformation change is suggested by relative shifts of @pi@ levels. For large charge addition, two new states are observed in the original @pi@ to @pi@* gap. For the nitro-substituted oligomer, a similar spectrum is observed for large K addition, but the behavior as a function charge addition is quite different. After an initial shift by ~ 0.6 eV, the spectrum is nearly pinned for subsequent K addition before a final shift brings it to near coincidence with the pristine oligomer spectrum. These results will be discussed in the context of polaronic/bipolaronic effects and the influence of unoccupied levels related to the -NO@sub2@ substitution.

9:20am **EM1-ThM4 Probing Silicon Based Molecular Electronics with Ultra-High Vacuum Scanning Tunneling Microscopy***, **N.P. Guisinger**, N.L. Yoder, M.C. Hersam,* Northwestern University

A cryogenic variable temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM) is utilized for measuring the electrical properties of isolated cyclopentene molecules adsorbed to the degenerately p-type Si(100)-2x1 surface at a temperature of 80 K. Current-voltage curves taken under these conditions show negative differential resistance (NDR) at positive sample bias in agreement with previous observations at room temperature.@footnote 1-3@ The enhanced stability of the STM at cryogenic temperatures was utilized for repeated measurements taken over the same molecule. Current-voltage curves on isolated cyclopentene molecules are demonstrated to be repeatable and possess negligible hysteresis for a given tip-molecule distance. Subsequent measurements with variable tip position show that the NDR voltage increases with increasing tip-molecule distance. Using a one-dimensional capacitive equivalent circuit and a resonant tunneling model, this behavior can be quantitatively explained, thus providing insight into the electrostatic potential distribution across a semiconductor-molecule-vacuum-metal tunnel junction. This model also provides a quantitative estimate for the alignment of the highest occupied molecular orbital (HOMO) of cyclopentene with respect to the Fermi level of the silicon substrate, thus suggesting that this experimental approach can be used for performing chemical spectroscopy at the single molecule level on semiconductor surfaces. Overall, these results serve as the basis for a series of design rules that can be applied to silicon-based molecular electronic devices. @FootnoteText@ @footnote 1@ Guisinger, N. P., Basu, R., Baluch, A. S. & Hersam, M. C. (2003) Ann. N. Y. Acad. Sci. 1006, 227-234.@footnote 2@ Guisinger, N. P., Greene, M. E., Basu, R., Baluch, A. S. & Hersam, M. C. (2004) Nano Lett. 4, 55-59.@footnote 3@ Guisinger, N. P., Basu, R., Greene, M. E., Baluch, A. S. & Hersam, M. C. (2004) Nanotechnology 15, S452-S458.

9:40am **EM1-ThM5 Metal Molecule Silicon Devices***, **A. Scott**, D.B. Janes,* Purdue University

While the majority of molecular electronic devices have employed metal contacts, semiconductor contacts could allow more stable chemical bonds and enhanced electrical functionality. Integrating molecular devices on silicon is a promising approach to molecular electronics@footnote 1@ and would leverage capabilities of the microelectronics industry. In this study, metal-molecule-silicon devices have been fabricated and characterized. Molecules are grafted to 111 silicon surfaces by electrochemical reduction of diazonium salts,@footnote 2@ resulting in robust molecular layers that are covalently bound to the surface by C-Si bonds. Aromatic molecules with various headgroups have been grafted to Si and characterized using infrared spectroscopy and cyclic voltammetry. Metal top contacts are deposited using an indirect evaporation technique which minimizes metal penetration, as demonstrated previously on GaAs.@footnote 3@ Electrical testing of these devices indicates that transport can be modulated by both substrate doping and molecular chemistry. If a large metal-semiconductor barrier is present and the substrate is lightly doped, the current-voltage characteristics are only slightly modified by the addition of a molecular layer. N-type Si-Au Schottky diodes (N@sub D@=10@super 15@cm@super -3@) have current densities of 3 A/cm@super 2@ at 0.5 volt, and the addition of a molecular layer reduces the current density by less than an order of magnitude. In devices where the barrier height is small and the substrate heavily doped, transport is more dominated by molecular effects. P+ (N@sub A@=10@super 19@cm@super -3@) Si-Au Schottky diodes exhibit current densities of 10@super 6@ A/cm@super 2@, and the addition of a molecular layer decreases this by 1 to 4 orders of magnitude depending on the molecular species. @FootnoteText@ @footnote 1@Guisinger et al., Nano Let. 55-59, 2004@footnote 2@Allongue et al.,JEAC 161-174, 2003@footnote 3@Lodha and Janes, APL, 2809-2811, 2004.

10:00am **EM1-ThM6 Chemically Resolved Electrical Measurements within Monomolecular Layers***, **H. Cohen**, R. Yerushalmi, N. Granit, A. Shukla, M.E. van der Boom, A. Scherz,* Weizmann, Israel

Interesting electrical characteristics within monomolecular layers are revealed by chemically resolved electrical measurements (CREM).@footnote 1,2@ The method is based on slightly modified X-ray photoelectron spectroscopy (XPS), using energy-filtered electrons as fine and flexible electrodes. Our recent results manifest breakthrough capabilities for future molecular electronics applications. @FootnoteText@ @footnote 1@ H.Cohen, Applied Physics Letters 85, 1271 (2004).@footnote 2@ H. Cohen, C. Nogues, I. Zon and I. Lubomirsky, J. Appl. Phys., in press.

10:20am **EM1-ThM7 Conduction through Cytochrome c Molecules***, **T. Matsumoto**, M. Kataoka, T. Kawai,* Osaka University, Japan

Cytochrome c, which mediates electron transfer in biological system, is a candidate molecule with the suitable structure for electronic elements that comprise insulating and active parts. Since this redox center is isolated from the surroundings by the insulating part, the structure of cytochrome c can be regarded as a double tunneling junction for single electron tunneling. However, thin film of cytochrome c shows low conductivity, whereas, in vivo, single or several molecules derive electrons with high efficiency. For this reason, the measurement of the electrical conduction through single or several cyt.c molecules in solid state is a challenge to a critical stage towards the realization of bioelectronic devices using electron transfer proteins. Here, we demonstrate that cytochrome c molecules are electrically active on electrode surface modified with self-assembled monolayer. We also found that the strong influence of the variation of self-assembled monolayer on the conduction through cytochrome c. The gap-edge voltages observed are 0.5V for 2,2â?T-PySSPy and 1.3V for 4,4â?T-PySSPy. To confirm the participation of heme in the conduction through cytochrome c, the comparative experimenht for Zn cytochrome c, whose heme ion of Fe is replaced to Zn, was performed. In case of Zn cytochrome c, any detectable current has not been observed. This implies that the current goes through the ion in the reaction center of cytochrome c molecules suggesting that the conduction mechanism might be single electron tunneling. The SAM modification is also useful for nanogap electrode. The current through the molecule increases with increasing temperature suggesting the presence of thermal excitation.

10:40am **EM1-ThM8 Tunneling Transport through Benzoate on Cu(110)****, **D.B. Dougherty**, P. Maksymovych, J.T. Yates Jr.,* University of Pittsburgh

The possible use of single molecules as devices in electronic circuits requires a fundamental understanding of the influence of the details of the linkage and charge transport to a macroscopic contact. Molecular orientation, chemical bond strength and location, and energetic location of molecular orbitals may all play a role in determining the possible use of a given molecule/contact system. Thus, detailed experimental studies of simple molecules in well-defined and reproducible configurations are necessary to supplement and guide more technologically relevant work. Significant progress has been made in understanding the transport properties through long chain molecules linked to Au surfaces by a thiolate group.@footnote 1@ These linkages are not the only potentially interesting candidates for electronics. In fact, the enormous chemical variety available is one of the great advantages of using organic molecules in devices. We have studied the electronic transport properties of benzoate molecules on a clean Cu surface which are linked by a carboxylate group instead of a thiolate.@footnote 2@ Such a linkage can be strong and surface-site specific and may therefore result in useful and reproducible electrical contact. More importantly, it provides a tool for addressing fundamental issues in single molecule transport. Using scanning tunneling spectroscopy, we have measured the I/V and conductance characteristics of differently oriented benzoate molecules chemisorbed on a Cu(110) surface. Benzoate molecules adsorbed with their plane perpendicular to the surface have a diminished conductivity in the low bias regime when compared to molecules with their plane parallel to the surface. The conductivity is found to be independent of temperature. *Supported by the W.M. Keck Foundation and a Japanese NEDO grant. @FootnoteText@ @footnote 1@ W. Wang et al., Rep. Prog. Phys. 68 (2005) 523.@footnote 2@ B.G. Frederick et al., Surf. Rev. Lett. 3 (1996) 1523.

11:00am **EM1-ThM9 Hopping Transport through Self-Assembled Monolayer on a GaAs Surface***, **K. Lee**,* Purdue University

In organic solids, hopping transport is known to be a primary conduction mechanism. The prominent feature of hopping transport is its low mobility, which has been major limitation of utilizing organic solid as an active channel material. However, it has been known@footnote 1@ that, with efficient @pi@-@pi@ stacking of @pi@-conjugated molecules, the mobility of organic solids can be dramatically improved. To realize this idea, highly pure single crystals of organic molecules have been used to demonstrate much higher mobility,@footnote 2@ but it is questionable whether it would be feasible to fabricate a 3-terminal device with reasonable operating voltage. Another suggested solution is to use well-ordered self-assembled monolayer (SAM) of @pi@-conjugated molecules as an active channel component. In this study, a testbed for hopping transport through SAM has been fabricated using back-to-back schottky diode structure on semi-insulating GaAs. Before depositing molecules, pre-deposition current is less than 1nA. After forming SAM on GaAs surface, significant change in conductivity was observed in several molecules. For instance, thiophenol SAM increased conductivity by ~10 times, whereas ODT SAM suppressed bulk leakage current by one third. There are two possible conduction paths that can explain this conductivity increase: 1) hopping conduction through SAM 2) surface potential change due to the molecular dipole moments. However, it is not likely that the second possibility is a primary reason for enhanced conductivity because of the fact that ODT SAM, which has relatively strong molecular dipole moment but no @pi@-electrons, decreased conductivity. In addition, the dependence of mobility on temperature indicates that hopping transport is dominant. Finally, the application of the testbed to chemical sensors and organic transistors will be discussed. @FootnoteText@ @footnote 1@ J. L. Bredas, et al., PNAS, 99, 5084 (2002)@footnote 2@ Vikram C. Sundar, et al., Science, 303, 1644 (2004).

11:20am **EM1-ThM10 Charging and Discharging Nanoscale Domains in Thin Films of Arylamines Studied with Kelvin Probe Microscopy***, J. Sun, S.C. Blackstock, **G.J. Szulczewski**,* University of Alabama

The work reported here was motivated to assess the feasibility of a non-volatile molecular memory based on charge storage in amorphous thin films. Toward that end, thin films of a series of redox-gradient arylamines were vapor deposited on oxidized p-type Si(100) wafers and subsequently charged in tapping mode with a voltage applied to a metal-coated AFM tip. The redox-gradient is designed to facilitate one-way electron transfer from the periphery of the molecule to its core. The concept is realized by synthesizing molecules with an easy to oxidize (i.e. ionize) moiety at the interior of molecule and surrounding it with harder to oxidize redox moieties.@footnote1@ In effect the gradient acts as a charge funnel toward the interior of the molecule. The extent of charging was measured with Kelvin probe microscopy (KPM). The charged domains have an apparent diameter of about 200 nm in the KPM image, which is larger than the real area due to the long-range interaction of the charge and the tip/cantilever. The charge half-life was proportional to the magnitude of the redox-gradient. For example, amines without a redox gradient discharged within 1 hour. In contrast, amines with a redox-gradient of ~0.8 eV could retain 50% of their initial charge after 10 hours. The charging is reversible. By applying a negative bias on the KPM tip the charged region could be neutralized. Although the charge is stable for many hours and can be neutralized, there is diffusion of charge in the films due to Coulombic repulsion. @FootnoteText@ @footnote1@ T. D. Shelby and S. C. Blackstock, "Preparation of a Redox-gradient Dendrimer. Polyamines

Designed for One-Way Electron Transfer and Charge Capture" J. Am. Chem. Soc. 1998, 120, 12155.

11:40am **EM1-ThM11 Observation of trans-to-cis in Azobenzene by Spatially Resolved Scanning Tunneling Spectroscopy***, **B.-Y. Choi,*** Seoul National University, Korea*; S.-J. Kahng,* Korea University, Korea*; Y. Kuk,* Seoul National University, Korea

There have been serious efforts to apply various organic molecules to an organic based memory. These molecules change their configuration by a charge transfer between surrounding bonds or to reach an energy minimization state when a bias voltage is reached at a certain voltage. Similar but slightly different organic molecules, photo sensitive molecules, may be used for this application. Scanning tunneling microscopy/spectroscopy experiment was performed on azobenzene single molecule adsorbed on a Au(111) surface in UHV at 5K. Azobenzene has two stereoisomers; trans- and cis-azobenzene which can be transformed to each other by UV irradiation or thermal energy. We could induce the trans-to-cis transition of a single trans-azobenzene by injecting electric pulses by using STM tip and the electronic structure of them were observed in sub-atomic resolution. The tip bias for the trans-to-cis transition is ~1.5V and cis-azobenzene returned back under negative tip bias or in time at the adsorption site. The LUMO state of trans-azobenzene was confined mainly within the benzene segments which were lying parallel to gold substrate. The HOMO state was localized within the nitrogen. Cis-azobenzene shows several spectroscopy results depending on the molecule-surface configuration. We also observed an LDOS of azobenzene on NaCl layers deposited on Cu(111). Adsorbed on NaCl, the azobenzene shows an electronic states which are not coupled to that of the metal surface.

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