Friday Morning, November 17, 2006

Electronic Materials and Processing Room 2001 - Session EM-FrM

Molecular Electronics

Moderator: I.G. Hill, Dalhousie University, Canada

8:00am EM-FrM1 Scanning Tunneling Microscopy Study of Azobenzene and Azobenzene-Derivatives, Y.S. Cho, B.Y. Choi, H.J. Yang, Seoul National University, Korea; Y. Kuk, Seoul National University, Korea, South Korea Conjugated molecular chains exhibit good conductivity with @pi@ bonding for the carrier transport. If two disconnected parts of a conducting molecular chain are connected by a bond with two coupled potential energy surfaces with 2 degrees of freedom, the resulting chain will reveal non-linear characteristics. It has been shown experimentally in a scanning tunneling microscopy (STM) that these kinds of molecules switch between two potential energy minima and function as nano-molecular switches.@footnote 1@ Chemical isomers are the most appropriate target molecules, because they have the same molecular formula and connectivity but different geometric structures and conductivities. We studied geometric and electonic structures of isolated azobenzene and azobenzene derivative molecules adsorbed on Au (111) surface with scanning tunneling microscopy and spectroscopy(STM) at 5K. These molecules have two stereoisomers which can be transformed to each other by UV irradiation or thermal energy. We could induce this transformation by tunneling electrons using STM tip. In the case of azobenzne, the transto-cis transition is induced at ~-1.5V and the cis-azobenzene returned back ~+2.5 V. We studied three different kinds of azobenzene-derivatives; EtO-Az-C10, EtO-Az-C6, CF@sub 3@-Az-C10. Each derivative has a long alkylchain which enable us to control the length of switching molecules. We will show the coverage dependance of the HOMO-LUMO state and the conformational change by STM tip in azobenzene-derivatives. This results could be an possible implication to mechanism of organic-based conformational switch. @FootnoteText@ @footnote 1@ Byoung-Young Choi et al., PRL 96, 156106 (2006).

8:20am EM-FrM2 Structural Dependence of Charge Transport in Organic Molecular Films, Y. Qi, B.L.M. Hendriksen, D. Esteban, I. Ratera, M. Salmeron, J.Y. Park, F. Ogletree, UC Berkeley and Lawrence Berkeley National Laboratory

The charge transport properties and mechanical properties of alkanethiol and trans-stilbene based self-assembled molecules on Au(111) have been investigated by using a conducting probe atomic force microscope (CP-AFM) in ultrahigh vacuum. We found that there exists a clear correlation between them. The step-wise change previously found in alkanethiol molecular film thickness and friction upon pressing the molecules with atomic force microscope tip was observed in the tip-sample current. Increasing of tip-sample current is mainly due to tilt of molecules under the high pressure. We measured the decay constant β =0.58/Å for hexadecanethiol, significantly smaller than decay constant (~ 1/Å) that is caused by shortening the alkanethiol molecule length. Our calculation based on the two-pathway model is in good agreement with the current measurement upon molecular tilt. We will discuss the new scheme of Field Effect Transistor (FET) configuration that allows us to measure the electron transport parallel to the self-assembled monolayer.

8:40am EM-FrM3 Temperature Dependent Conduction and Charge Tunneling in Nanoparticle-Molecule-Nanoparticle Bridging Structures, J.-S. Na, J. Ayres, K. Chandra, C.B. Gorman, G.N. Parsons, North Carolina State University

Although electronic transport across organic molecules has been widely investigated, the conduction mechanisms across a single molecule is still not well defined because of instability of metal-molecule contacts, uncertainty of number of molecules in the junction, and unavailability of temperature variable current-voltage measurements. Here we report the dielectrophoretic trapping, contact stability, and conduction characteristics of a nanoparticle/molecule/nanoparticle bridge assembly, where two ~40nm nanoparticles are linked by a phenylacetylene oligomer. The molecule/nanoparticle structures are assembled across a nanoscale (~70nm) electrode gap fabricated by angled e-beam evaporation. The nanoparticle/molecule structures are trapped by applying а dielectrophoretic force across the nanoscale electrode gap. At the optimum trapping conditions (2VAC, 1MHz, and 60s), a success rate of ~78% achieved. Current versus voltage through is the nanoparticle/molecule structure is consistent with a single molecule

present between the nanoparticles, and IV results are obtained as a function of temperature (80K to 293K) and time in ambient. Analyses of ln(I/V@super 2@) versus 1/V indicates a transition from direct tunneling to Fowler-Nordheim tunneling, independent of temperature. A nonlinear fit of the IV data to the Simmons tunneling model results in barrier height of about 0.12eV, suggesting charge transport proceeds through hole tunneling. The stability of the nanoparticle electrode structure and molecular conduction over several weeks will also be presented and discussed.

9:00am EM-FrM4 Switching and Conductance Peaks in Metal-Molecule-Silicon Devices with Nitro-Containing Molecular Layers, A.D. Scott, D.B. Janes, Purdue University

Recently there has been a large amount of interest in developing molecular electronics for miniaturization and enhancing functionality of electronic devices. Interesting transport features have been observed in metalmolecule-metal devices containing nitro-substituted species.@footnote 1@ Silicon contacts to molecular devices offer advantages over metal contacts due to the covalent nature of the molecular attachment, the technological relevance of silicon, and the ability to tune the electrical properties of the contact through doping. In this study, we present interesting transport features observed in metal-molecule-silicon devices with nitro-containing molecular layers. These devices exhibit interesting transport behavior that varies with molecular species used and substrate doping. Devices with nitrobenzene layers on p+ Si substrates exhibit bistable switching in 63% of devices. This behavior has been characterized using current-voltage measurements and current vs. time measurements of switching transients. The voltage threshold at which switching takes place is 0.9±0.15 V and the ratio of on-current to off-current is approximately 10. Devices with 2-methyl 4-nitrobenzene layers on n Si exhibit non-ideal current-voltage behavior and show peaks in the conductance-voltage curves for all devices measured. The conductance peak occurs at 0.9V forward bias. It has been observed both by numerically differentiating DC current-voltage curves and by AC conductance measurements utilizing lock-in detection. Similar devices with molecular layers that do not contain nitro headgroups and those with different substrate dopings do not exhibit these features. @FootnoteText@ @footnote 1@ Chen J, Reed MA, Rawlett AM, Tour JM (1999) Large On-Off Ratios and Negative Differential Resistance in a Molecular Electronic Device. Science 286: 1550-1552.

9:20am EM-FrM5 Towards Molecular Electronics: Controlling and **Understanding Metallic Contact Formation on Patterned Self-Assembled** Monolavers, A.V. Walker, Washington University in St. Louis INVITED We have developed a robust method by which to construct complex twoand three- dimensional structures based on controlling interfacial chemistry. This work has important applications in molecular/organic electronics, sensing, and other technologies. Our method is extensible to many different materials, easily parallelized, affords precise nanoscale placement and is fully compatible with photolithography. Our work to date has provided a simple method for the construction of complex 2D molecular electronic circuitry using UV-photopatterning and the reaction of deposited metals with self-assembled monolayers (SAMs). To demonstrate the method we have selectively vapor-deposited Mg on a patterned -CH@sub 3@/-COOH terminated alkanethiolate surface. The deposited metal penetrates through the -CH@sub 3@ SAM to the Au/S interface while reacting with and accumulating on top of the -COOH SAM. Applying these ideas to the rational design of metal/organic structures requires a fundamental understanding of the underlying metal-molecule interactions; we therefore shall also discuss experiments that elucidate these.

10:00am EM-FrM7 Energy-Level Alignment at Thiol/Metal Interfaces: A Model "Molecular Wire" Chemisorbed on Ag, Cu, Au, and Pt., C.D. Zangmeister, R.D. van Zee, National Institute of Standards and Technology; C.A. Ventrice, University of New Orleans

Photoemission spectra have been used to determine the energy-level alignment for self-assembled monolayers of the "molecular wire" 4,4'-bis-(phenylethynyl)benzenethiol self-assembled on Ag, Cu, Au, and Pt. We measured a shift in the hole-transport barrier with metal work function due to changes in the interfacial electrostatics. The hole-transport barrier as a function of metal work function is near the common vacuum limit (S@subB@ = 0.8). The shift of the hole-transport barrier is analyzed as an interfacial dipole and decomposed with a three term model. The current through a model metal/molecule/metal junction is calculated using the measured values of the hole-transport barrier, and trends are found to be consistent with previously published results.

Friday Morning, November 17, 2006

10:20am EM-FrM8 Fabrication of Semiconductor-Molecule-Semiconductor (SMS) Devices, A. Mahapatro, M. Martinez, P. Carpenter, A.D. Scott, Purdue University; A. Yulius, Yale University; J. Woodall, D.B. Janes, Purdue University

Molecular electronic devices have typically been fabricated using metalmolecule-metal (MMM) configurations. Recently, several studies involving semiconductor-molecule-metal (SMM) junctions have been reported, motivated by the prospects of realizing covalent bonds to one contact and exploiting the semiconductor states in device properties. The MMM and SMM junctions are the commonly used device structures for studying the electrical behavior of single/few molecules. While the SMM structures address some of the problems with reliability of MMM structures, there is still the possibility of metal penetration through the molecular layer during deposition or device operation. This study illustrates a technique to fabricate large area molecular devices in a semiconductor-moleculesemiconductor (SMS) configuration by depositing a pre-formed semiconductor island (InAs) onto a molecular self-assembled monolayer (SAM) which has been formed on another semiconductor substrate (GaAs). Micron-scale InAs islands with Au top contact layers are formed on a sacrificial substrate and transferred onto the SAM-coated GaAs substrate. Identical topography of the grains on the surface of the settled islands and freshly prepared Au surfaces, confirm that the InAs side of the island is in contact with the SAM-coated GaAs surface. In order to verify that thiolbased bonds are possible on InAs (for the top contact), we have also developed SAMS of short thiol molecules on InAs surfaces. The resulting SAMs were characterized through X-ray photoemission spectroscopy. Electrical conduction has been measured for p@super +@GaAs/xylyldithiol/InAs structures of 100-400 µm@super 2@ contact areas. This study demonstrates that molecular devices can be realized using exclusively semiconductor contacts.

10:40am EM-FrM9 Molecular Tunnel Junctions Incorporating Nickel-Octanedithiol Multilayer Thin Film, L.H. Yu, J.G. Kushmerick, National Institute of Standards and Technology

We present measurement of tunneling junctions made using selfassembled nickel-octanedithiol multilayer thin film. Multilayer structures on evaporated gold and nickel surfaces were studied by ellipsometry, Fourier Transform Infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Superconducting quantum interference device (SQUID) measurements were performed on the nickel-dithiol multilayer thin films and bulk materials to characterize their magnetic properties. We will discuss the effect of applied magnetic field on the electronic transport of these ferromagnetic atoms containing tunneling junctions.

11:00am EM-FrM10 Electrical Transport Measurements on Conjugated Molecules using Nanogap Electrodes on Cleaved AlGaAs Planes, M. Tornow, S.M. Luber, S. Lingitz, A.G. Hansen, F. Zhang, Walter Schottky Institute, TU Munich, Germany; F. Scheliga, E. Thorn-Csányi, University of Hamburg, Germany; M. Bichler, Walter Schottky Institute, TU Munich, Germany

One of the major challenges in the realization of molecular electronic hybrid systems that comprise molecules as functional units is the reproducible fabrication of the inorganic contact electrodes. We have developed a novel technique to prepare such nanogap electrodes in a very precise manner, based on cleaved GaAs/AlGaAs semiconductor heterostructures grown by Molecular Beam Epitaxy (MBE).@footnote 1@ These electrodes of predetermined distance are macroscopically flat, coplanar and exceedingly clean. We report on electronic transport measurements on @pi@-conjugated, dithiolated Oligo-(phenylenvinylene) (OPV) derivatives of length 8.5 nm bridging a ~7 nm nanogap device. Starting from a high impedance behaviour before molecule deposition the OPV functionalized hybrid system develops a pronounced non-linear I-V characteristic measured at T=4.2 K. We compare our observations to model calculations on a simplified structure involving extended Hueckel theory and non-equilibrium Greens Function methods, and find qualitatively good agreement. @FootnoteText@ @footnote 1@ S.M. Luber et al., Nanotechnology 16, 1182 (2005).

11:20am EM-FrM11 Dynamics of Molecular Quantum-Dot Cellular Automata Devices and Circuits, Y. Lu, M. Liu, C. Lent, University of Notre Dame

Quantum-dot cellular automata (QCA) provides a non-transistor alternative for the design of molecular electronics. Binary information is encoded in the charge configuration of molecular cells. Information is transported from cell to cell through the Coulomb interaction. Clocked control of molecular QCA can be accomplished by employing an applied clocking field which varies regularly in both space and time. This enables binary information to be transported across molecular arrays without electrons moving between molecules. Power gain restores signal energy lost to unavoidable dissipative processes. Here we study dynamic properties of molecular QCA devices including energy dissipation, operating frequency, and defect tolerance. We use detailed quantum chemistry results for molecules to construct simpler effective Hamiltonians for each QCA molecular cell. We then solve the equation of motion of the whole molecular device using a coherence vector formalism which includes both quantum effects and dissipative coupling to the environment. This enables us to characterize non-equilibrium and finite-temperature effects on switching behavior. We explore the structure-function relation in molecular QCA at two levels: that of the individual molecules and that of the circuit layout. The specific character of the inter-dot intra-molecular linker plays a crucial role in the dynamics of molecular switching, particularly near the maximum possible switching speeds. At the level of the circuit as a whole, a key challenge for all molecular electronics is handling defects due to the fundamental thermodynamic inability to control exactly the position and orientation of each single-molecule device. The QCA approach has the advantage of being inherently robust against disorder and can be made even more so by simply using wider wires to build in redundancy.

Author Index

Bold page numbers indicate presenter - L -Lent, C.: EM-FrM11, 2 Ayres, J.: EM-FrM3, 1 Bichler, M.: EM-FrM10, 2

-A-

— B —

-C-

— E —

-G-

-H-

— J —

— К —

Carpenter, P.: EM-FrM8, 2

Chandra, K.: EM-FrM3, 1

Cho, Y.S.: EM-FrM1, 1

Choi, B.Y.: EM-FrM1, 1

Esteban, D.: EM-FrM2, 1

Gorman, C.B.: EM-FrM3, 1

Hansen, A.G.: EM-FrM10, 2

Kuk, Y.: EM-FrM1, 1

Hendriksen, B.L.M.: EM-FrM2, 1

Kushmerick, J.G.: EM-FrM9, 2

Janes, D.B.: EM-FrM4, 1; EM-FrM8, 2

Lingitz, S.: EM-FrM10, 2 Liu, M.: EM-FrM11, 2 Lu, Y.: EM-FrM11, 2 Luber, S.M.: EM-FrM10, 2 -M-Mahapatro, A.: EM-FrM8, 2 Martinez, M.: EM-FrM8, 2 -N-Na, J.-S.: EM-FrM3, 1 -0-Ogletree, F.: EM-FrM2, 1 — P — Park, J.Y.: EM-FrM2, 1 Parsons, G.N.: EM-FrM3, 1 - Q -Qi, Y.: EM-FrM2, 1 -R-Ratera, I.: EM-FrM2, 1

— S — Salmeron, M.: EM-FrM2, 1 Scheliga, F.: EM-FrM10, 2 Scott, A.D.: EM-FrM4, 1; EM-FrM8, 2 -T-Thorn-Csányi, E.: EM-FrM10, 2 Tornow, M.: EM-FrM10, 2 -vvan Zee, R.D.: EM-FrM7, 1 Ventrice, C.A.: EM-FrM7, 1 -w-Walker, A.V.: EM-FrM5, 1 Woodall, J.: EM-FrM8, 2 -Y-Yang, H.J.: EM-FrM1, 1 Yu, L.H.: EM-FrM9, 2 Yulius, A.: EM-FrM8, 2 — Z — Zangmeister, C.D.: EM-FrM7, 1 Zhang, F.: EM-FrM10, 2