SYMPOSIUM K
Molecular-Scale Electronics and Optoelectronics
April 22 – 24, 2003

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*Invited paper
SESSION K1: MOLECULAR DEVICES
Chair: Paul S. Weiss
Tuesday Morning, April 22, 2008
Nob Hill C/D (Merriott)

8:30 AM *K1.1 TOWARD MONOMOLECULAR DIODES, TRANSISTORS, AND CIRCUITS. J.C. Ellenbogen, Nanosystems Group, The MITRE Corporation, McLean, VA

Despite the recent remarkable progress toward fabricating and operating electronic nanocomputers [1,2, there remains an important scaling and density threshold yet to be reached. Thus, the development of multi-device nanocircuits within single molecules. The speaker will discuss a comprehensive design strategy for achieving this goal [3].


9:00 AM *K1.2 MOLECULAR SCALE ELECTRONIC TRANSPORT. Mark Reed, Yale University, New Haven, CT

Electronic transport in SAMs will be reviewed.

9:30 AM *K1.3 TRANSPORT AND SCANNED PROBE INVESTIGATION OF CHEMICAL NANOARRAYS. Hongwan Park, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA

In this presentation, I will discuss (1) the fabrication and characterization of nanoscale electroactive transistors that incorporate individual chemical nanostructures, including molecules, single-walled carbon nanotubes, and organic nanostructures and (2) the synthesis and characterization of transition-metal-oxide nanowires.

10:30 AM *K1.4 A NOVEL FABRICATION APPROACH FOR MOLECULAR MEMORY ARRAYS. Chao Li, Da-Hui Zhang, Xue-Qi Liu, Chongwu Zhou, Univ. of Southern California, Dept. of E.E. -Electrophysics, Los Angeles, CA, and Jes USEP, BNIB, Hoe and Nasya\nMeyyappan, NASA Ames Research Center, Moffett Field, CA; A.M. Rawlett, D.W. Price, and J.M. Tour, Rice Univ, Dept of Chemistry and Center for Nanoscale Science and Technology, Houston, TX.

Molecular electronics has been considered to be one of the best solutions to the scaling limit problem the semiconductor industry may have to face in the next decade. Past decade has witnessed the tremendous potential through demonstrations of molecular rectifiers, devices exhibiting negative differential resistance, electrically configurable switches and logic gates, but it has also seen great challenges in the device fabrication and integration. Here, we present an approach to tackle long-standing problems in contacts, thermal damage, pinhole induced short circuits and interconnects in molecular electronic device fabrication and integration. Our approach uses metallic nanostructures as top electrodes to connect and interconnect molecular wires assembled on electrode arrays in crossbar architectures. Using this simple and reliable approach, we have revealed intriguing memory effects with several kinds of novel molecular wires containing redox centers such as pyridine and NO2 groups. Our results are typical time constants above 30s, and can be repeatedly written and read without significant degradation. Our approach has great potential to be used for fast scanning of molecular wire candidates and construction of integrated molecular systems.


During the last five years, Molecular Electronics has seen very significant advances and raised prospects of mid-term applications. Self-assembly is generally considered as the way to be used for the fabrication of future molecular electronics circuits. Self-assembling molecules into devices has been central to our activity during the last few years with the aim to engineer i) metal-molecule interfaces to improve their transport properties and ii) molecules-surface interactions to localize the assembly of the molecules-including carbon nanotubes. In this lecture, I will focus on recent results developed in our group along these two axes. I will first discuss the relationship between the molecular structure of the organic monolayer and the transport properties and show that the metal - molecule coupling plays a key role. I will illustrate this based i) on combined Photoelectron Spectroscopy-STM experiments where similar conjugated molecules with different alkyl chains have been systematically compared and ii) on experiments in nanoparticle assemblies with various bifunctional bridging molecules. In a second part, it will be shown how carbon nanotubes (NTs) can be self-assembled at predefined location of a substrate using for example a localized functionalization of the substrate by a self-assembling monolayer. The FET devices prepared in that way are functional with state-of-the-art performances. I will discuss the role played by the environment (including that of the self-assembled monolayer) directing the deposition of the NTs and that of molecules adsorbed on the NTs on the device characteristics. Finally, I will discuss improvements of the self-assembly technique using the recognition properties of biomolecules.

SESSION K2/L2: JOINT SESSION
MOLECULAR ELECTRONICS
Chair: Massimiliano Di Ventra and Junji Kido
Tuesday Afternoon, April 22, 2008
Salon 1-3 (Merriott)

1:30 PM K2.1/L2.1 ORGANIC MOLECULES ON METAL SURFACES BY HIGH RESOLUTION STM. Frederic Ressier*, Y. Naitoh, M. Schanze, E. Levendorf, J. Bengtsson, Physics Department and L-Nano, University of Aarhus, DENMARK; P. Jiang, A. Grudin, and C. Joachim, CESBES CNRS, Toulouse, FRANCE.
*Present address: INRS-EMT, Université de Quebec, Varennes (QC), CANADA.

The adsorption of large organic molecules on surfaces plays a vital role in the emerging field of nanotechnology. Here we show how the understanding the resolved structure of Scanning Tunneling Microscopy (STM) gives new information on molecular diffusion and assembly. First, we address the issue of surface diffusion. Adsorbate movement across surfaces can be followed by time-resolved "STM movie". In the simplest picture of surface diffusion, the adsorbate jumps to the nearest neighbor sites. Recent results suggest this is not necessarily true for complex molecules. By studying the diffusion of two related aromatic molecules, DC (C$_{10}$H$_8$) and HBD (C$_{11}$H$_{10}$), on Cu[110], we find that their diffusion is dominated by long jumps, spanning multiple lattice spacings [1]. The HBD molecule has a core identical to DC, and the six additional spacer legs, which increase its diffusion coefficient by four orders of magnitude with respect to DC. This ultimately...
demonstrates how molecules can be predefined to engineer their diffusion properties. Second, we describe the adsorption of the Lander molecule [2] (C9H18O) on Cu(110) by STM and show that the absence of a Goldstone mode introduces an onset for local heating and the latter increases substantially with increasing bias. Work supported in part by NSF, Carillion Biomedical Institute and ACS-Petroleum Research Fund.

3:30 PM *K3.3
ELECTRON TRANSPORT IN MOLECULAR NANOSTRUCTURES: RECTIFICATION, SWITCHING, AND HYSTERESIS
A.M. Bruckovsky, Hewlett-Packard Laboratories, Palo Alto, CA.

Transport in conjugated organic molecular films, produced by either self-assembly [SAM] or Langmuir-Blodgett method, are of most interest for applications as possible microelectronics components. In short molecules the transport is mainly due to resonant tunneling through extended molecular states. It is shown that the current through molecular films strongly depends on the orientation of the molecules in the film with respect to electrodes [1,2]. This is a consequence of a strong directional character of orbitals that determine the conductance through the conjugated molecules. Gating of the molecule is studied for various attachments to the electrodes. The results may be relevant to recent experiments on conformational dependence of current through certain SAMs (switching) and field effect on some molecules exhibiting Coulomb blockade. In short molecules, where the molecular quantum dot (conjugated) is insuited from the electrodes by asymmetric saturated groups (e.g. aliphatic chains) the current rectification can be in excess of 100 [3]. Switching of the current can be achieved in conformationally bistable molecular components with a field-switchable dipole group [4]. Switching without retardation and current hysteresis can also be obtained in tunneling through molecular quantum dot with attractive electron-electron correlations [5]. The results will be discussed with current experimental situation.

In collaboration with A.S. Alexandrov, P.E. Kornilovich, and R.S. Williams.

K4.4 PURIFICATION OF SINGLE-WALL CARBON NANOTUBES (SWNTs) AND THE PREPARATION OF HIGH QUALITY SWNT/SILICON SURFACES. Robert M. Farrel, Jr., Peter Albuquerque, Joseph Liding, University of Illinois at Urbana-Champaign, Dept of Electrical and Computer Engineering, Beckman Institute for Advanced Science and Technology, Champaign, IL; We Ye, University of Illinois at Urbana-Champaign, Dept of Material Science and Engineering, Beckman Institute for Advanced Science and Technology, Urbana, IL.

We have developed a purification process for as-produced HPCO SWNTs that combines vacuum annealing at temperatures ranging from 1400 – 1600°C with either a subsequent gas-phase atmospheric oxidation or liquid-phase acid oxidation process. The purified SWNTs are then sonicated in several different organic solvents and deposited on a hydrogen-passivated 2x1 silicon surface for examination via UHV STM. For unpurified SWNTs, the STM images are dominated by SWNT ropes with attached catalyst particles. However, the purified samples show that removal of the catalyst facilitates the extraction of the ropes into individual SWNTs. After annealing (in a graphite crucible) we typically observe a factor of two mass reduction, which agrees well with the known HPCO SWNT catalyst content. We will show the results of various intermediate stages of the purification process and the effects of using a wide range of solvents for depositing SWNTs on H-passivated Si(100) surfaces. The conditions for preparing atomically clean SWNT/Si surfaces will be shown. Atomic resolution UHV STM and spectroscopy are also being used to determine the optimal processing conditions that minimize defect creation in SWNTs. TEM and SEM analysis results will be presented as well.


The utilization of individual molecules for digital device structures, so-called molechips, holds the promise of orders of magnitude increase in the level of device functionality and performance compared to today’s integrated circuits [ICs]. Similar advances in the area of on-chip interconnects may also benefit from a molecular approach wherein individual molecular structures can serve as signal conductors and switches. This work describes results to date on the development of self-assembling, genetically-derived molecular arrays, essentially one-dimensional molecular crystals, to serve as “building blocks” for nanoscale interconnects. These crystals have been demonstrated to be amenable to the attachment of functional groups to enable charge transport functionality. Scanning probe microscopy investigations of the assembly of genetically engineered polypeptide beta sheets are presented. Genetic sequencing of the synthesized materials confirmed the expected peptide structure. Scanning force microscopy (SFM) studies investigated the self-assembling behavior of the polypeptide materials as a function of deposition parameters on mica substrates. Spontaneous polypeptide aggregation has been observed in addition to aggregation induced by the scanning probe tip. Aggregate size ranges from tens of nanometers (< 10 beta sheets) to hundreds of nanometers (< 50 beta sheets). Similar size trends were observed for both mica and gold substrates. The self-assembled features were able to be transferred to a Au(111) substrate for topographical and current-voltage (L-V) characterization. The L-V results showed the self-assembled interconnects were functional on the Au(111) substrate.

K4.6 STM/STS ON OLIGO(PHENYLENEETHYNYLENE) MOLECULAR WIRES. Gheorghe Dohaliciu, Wendy Fan, Jessica Kochen, Jie Han, and M. Meyyappan, NASA Ames Research Institute, Moffett Field, CA.

Conjugated phenylene(ethynylene) molecules are of interest as potential candidates for molecular electronic devices. We study the topography and current-voltage (L-V) characteristics of self-assembled monolayers of two types of molecular wires. Both the wires have a three ring conjugated structure, connected by triple bonds. One of the wires differs from the other by the substitution of an electron-attracting substituent in the central phenyl ring. The scanning tunneling studies on the monolayers of these wires self assembled on Au(111) substrate show that the topography and L-Vs, for small scan voltages, of the two wires are quite similar and that the electronic and structural changes introduced by the substitution of an electron-attracting group in the central phenyl ring of these wires does not significantly alter the self assembly or the transport properties.

K4.7 RESISTANCE MEASUREMENTS OF CONAU MONOLAYERS FORMED ON NOBLE METAL FILMS. Ryos Notsui and Iku Kamo, Department of Nuclear Engineering, Kyoto University, Kyoto, JAPAN.

The superconductivity in alkali fullerenes is caused by the low work function of alkali metals and the high electron count of C60 molecules which favor charge transfer across C60 metal interfaces. This charge transfer effect is not particular to alkali or alkali-earth metal alks. Electrons can be transferred from noble metals to C60 molecules, although the work function of noble metals is higher than those of alkali metals. In alkali fullerenes, alkali metals occupy the interstitial sites of the C60 lattice, for the cohesive energy of alkali metals is sufficiently low. Noble metals, however, have higher cohesive energy, and cannot intercalate into the C60 lattice to form a three-dimensional solid solution. For the case of depositing C60 on noble metal films, therefore, the bilayer structure is formed. Electrons transfer to the adjacent monolayer of C60 from metal atoms and make a conducting C60 monolayer through it. In this report, we present the resistance measurements, which enabled us to see the charge transfer by the change in sheet resistance while depositing C60 on thin noble metal films or vice versa, for the C60/Cu bilayer structure and reported that the resistance of the C60 monolayer on a Cu underlayer was approximately 8 Ω. In this presentation, we report on the influence of the work functions of underlayer metals on the resistances of conducting C60 monolayers formed on noble metal (Au, Cu, Ag) underlays by i.e., their resistance measurements. [1] A.F. Hebard, R.R. Ruel, and C.B. Eom, Phys. Rev. B 54, 14052 (1996).

We have investigated methyl and carboxyl terminated alkylthiols (hexadecanethiol and mercaptohexadecanoic acid), and other more complex self-assembled monolayers (SAMs) on Au(111). We characterize these SAMs using x-ray absorption at the Carbon and Oxygen K-edges. Near-edge x-ray Absorption polarization effects in these spectra probe the orientation of chemical bonds. Simple, carboxyl terminated alkylthiols do not form well ordered films. We currently investigate attachment, uniformity, and order of these films as a function of solvent, chemical state of the carboxyl group, and by intermixing with well-ordered methylterminated alkylthiols. More complex thiocarboxylic acids are being investigated and order of more complex, thioic acid derivatives. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LNL, U.S. Atomic Energy Research Center, Mumbai, INDIA.

Recently, the molecular electronics has attracted strong attention as a "post-silicon technology" to realize a future nanoscale electronics device. A quarter century ago Aviram and Ratner [1] have first demonstrated how an organic molecule could function as a molecular rectifying diode. Further this has been supported by many experimental reports and theoretical calculations on organic molecules having conjugated systems through which electrons can flow easily. By substituting different functional groups on an aromatic system it is possible to increase or decrease the electronic density and thereby creating an acceptor (p-type) and donor (n-type) subunit. Therefore, a rectifier may be built by combining these two molecular subunits between two electrodes in which electrons can flow from cathode to the acceptor or from donor to the anode [23]. Porphyrin possesses good electron-donating properties due to its large easily ionized meso-electron system, and a long molecular wire of fully conjugated porphyrin polymer was reported by Tsuura et al. [4]. In this study, we propose rectifier diode can be created by combining two metal porphyrin molecules with different metal atoms. To realize the electron transport through this molecule, we have analyzed the spatial extent of the frontier orbitals (HOMO and LUMO), providing a strategy by which the rectifying properties of the porphyrin polymer can be understood. This study was performed through Special Coordination Funds for Promoting Science and Technology of the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government. [1] A. Aviram and M.A. Ratner, Chem. Phys. Lett. Vol. 29 (1974) 277. [2] C. Majumder, H. Mizusaki, and Y. Kawazoe, J. Phys. Chem. A, Vol. 105 (2001) 9454. [3] H. Mizusaki, K. Nishura, C. Majumder, and Y. Kawawoe, Comput. Mater. Sci., in press. [4] A. Tsuura and A. Osaka, Science Vol. 293 (2001) 79.

K4.10 NANOSCALE BLOCKS AND NGOASSEMBLY OF STRUCTURES
Srikanth Ramakrishna, Mah Raza Khan, University of California Riverside, Department of Chemistry, Engineering, Riverside, CA; Brooke Colburn, Cengiz Ozkan, University of California Riverside, Dept of Mechanical Engineering, Riverside, CA.

Electromechanics and photonics industries are highly interested in developing new methods for nanofabrication in order to be able to continue their long-term trend of building ever smaller, faster and less expensive devices. Conventional patterning strategies must be augmented by new techniques in order to truly take advantage of the quantum nature of novel nanoscale devices. In our research, we are developing a bottom-up approach to fabricate building blocks, which can be used to make a new generation of nanomachines. To do this, we start from the electronic transport properties of the molecules and nanostructures made of them. We have focused our research on the quantization of electronic transport in two-dimensional quantum dots and discrete nanostructures. This allows us to create quantum dot arrays and one-dimensional quantum wires. We are investigating the electronic transport properties of the molecules and how they can be used to build devices with new functionalities. These include electronic devices, nanoelectromechanical systems, and nanomotors.

K4.11 SYNTHESIS AND ELECTRON TRANSPORT PROPERTY OF DITHIOL-TERMINATED 2,2'-BIPYRIDINE TRANSITION METAL COMPLEXES
Sylvia Ann, Wendy Fan, Geetha Dhidhikie, Jie Han, ELORET Corp., Mountain View, CA; Jessica Kuehne, M. Meyyappan, ELORET Corp., Mountain View, CA; NASA Ames Res. Ctr., Mountain View, CA; Chonggu Zhou, Dept of Physics and Engineering, University of Southern California, Los Angeles, CA.

One of the goals in molecular nanoelectronics is to understand the influence of structural characteristics of a molecule on its electron transport properties. Studies by Reed and coworkers have shown that oligo[phenylenevinylene] containing nitro groups exhibit NDR (negative differential resistance) effect and thus have potential applications as an electronic switching and memory device. However, the origin of this observation is not well understood. Both the redox properties and the conformational changes of the molecule under an external electric field could be important factors. Despite the rigorous investigation, it is difficult to isolate the two factors in practical study. It appeared to us that molecules that are free of conformational change may shed light on this problem. Within this context, we designed and synthesized 4,4-dithio-2,2'-bipyridine and its Ru (II) and Co (II) coordination complexes. We chose the 2,2'-bipyridine unit since it possesses rigid rod-like structure, low band gap and the ability to coordinate transition metal ions to yield integrated molecular-metal platforms that could allow electron transport to be studied through well-defined charge states. The facile redox chemistries of Ru (II) and Co (II) provide another parameter for study. Here we report a novel method for a one-pot synthesis of these molecules as well as their electron transport properties obtained from both scanning tunneling microscopy study and break junction technique.

K4.12 SYNTHESIS AND ELECTRON TRANSPORT PROPERTY STUDIES OF Oligo[PHENYLENEVINYLENENE]ELECTRICAL ENGINEERING
Jessica Kuehne, NASA Ames Research Center, Moffett Field, CA; Wendy Fan, ELORET Corporation, Moffett Field, CA; Chao Li, University of Southern California, Los Angeles, CA; Chonggu Zhou, University of Southern California, Los Angeles, CA; Jie Han, ELORET Corporation, Moffett Field, CA; M. Meyyappan, NASA Ames Research Center, Moffett Field, CA.

Currently an important goal in molecular-scale electronics is to understand the influence of structural characteristics of a molecule on its electron transport properties. Studies by Reed and coworkers have shown that oligo[phenylenevinylene] containing nitro groups exhibit NDR (negative differential resistance) effect and thus have potential applications as electronic switching and memory devices. The physical mechanism of the spontaneous switching effect is not well understood. It was hypothesized that either the redox properties or the conformational changes of the molecule under external electric field could be responsible. Within this context, we prepared a series of oligo[phenylenevinylene] molecules bearing nitro group in various coupling reactions. Differing in the nature of the substituents, these molecules have different charge density on their conducting backbones. The rigid rod-like structures and terminal thiol groups allow the molecules to form self-assembled monolayers (SAM) on metal surfaces. The electron transport property was studied through a small-scale memory array that uses the SAM as the active component and nanowires as interconnects. Reproducible memory effects have been observed from molecules containing electron deficient backbones. Furthermore, molecules containing the resonance stabilizing nitro group gave more stable and reproducible LC curves, as well as longer retention times. The results strongly indicate that the redox properties of the molecule at least partially responsible for the electron transport behavior.

K4.13 NEW METHODS TOWARDS PREPARATION OF CONJUGATED OLIGOMERS CONTAINING AXYL THIOLS
Sylvia Ann, Wendy Fan, Sylvia Ann, Jie Han, ELORET Corp., Moffett Field, CA; Jessica Kuehne, M. Meyyappan, NASA Ames Research Center, Moffett Field, CA.

Formation of self-assembled monolayer (SAM) containing highly conjugated organic molecules not only facilitates the investigation of interfacial electron transfer but also is indispensable towards practical molecular device development. Within this context, systems with axyl terminal are particularly useful because they readily self-assemble onto gold surface and allow maximum electronic coupling. To date, the most successful route for preparation of such molecules involves incorporation of gold into the organic systems through metal-mediated coupling reactions. Due to the high
reactivity of the aryl thionocarbamate, the coupling chemistry that can be employed in very limited, consequently limiting the structures of the molecules that can be synthesized. Here we report two new methods that readily transform an aryl halide or a primary arylamine into thio or thiolate in high yields. We further demonstrate the usefulness of these methods by efficient synthesis of two classes of conjugated oligomers, which were previously difficult to prepare. These syntheses use a new approach in which the entire molecules were constructed with thiol/thioether groups masked in the form of halide or amine, bypassing the dilemma where the thionocarbamate is incompatible with the thiol or amine conditions required for preparation of the molecule. The transformation and the synthetic approach described here offer easy access towards a wide variety of conjugated molecules with terminal aryl thioles.

**SESSION K5.**

Chair: Jean-Philippe Bourgoin
Wednesday, May 25, 2003
Nab Hill C/D (M descr.)

8:30 AM *K5.1*

**THE NEAR FIELD OF AN OPTICAL TIP: PROBING IT WITH MOLECULAR OBJECTS AND USING IT FOR SINGLE OBJECT ADDRESSING**

A. Devez, M. Brunn, M. Nosse, N. Chevalier, J.C. Wehrl, S. Hunot, Laboratoire de Spectrométrie Physique, Grenoble University and CNRS, FRANCE.

Scanning-Probe Microscopy allows to explore various physical phenomena of molecules and nanostructures and to manipulate them on a single object basis. Here we describe two recent studies that sustain a scenario for the case of near-field scanning optical microscopy (NSOM). First, we show experimentally that fluorescent nanospheres act as volume detectors of the electric field intensity emanating from the NSOM tip. This allows us to build a realistic model of the optical near-field of such a tip. We have found that the Bethe-Bouwkamp model [1], widely used in NSOM for example for analyzing fluorescence images of single molecules [2], is at fault in predicting this intensity and, consequently, in interpreting the orientation of molecular transition moments from the experimental images. Implications on optical studies of single-molecule based devices will be discussed. Secondly, we describe a way of optically addressing single quantum dots. The method is inspired from Ref. 3 which demonstrated the addressing of single nanoholes in a metal film by exciting surface plasmons by the NSOM tip. We have extended this procedure to optically active semiconductor structures, namely self-assembled CdTe quantum dots, on which a thin aluminum film with well-defined nanoholes has been deposited. We show that launching of surface plasmons into these holes allows to excite the luminescence of underlying dots. Furthermore, monitoring the light polarization allows to control the propagation of 2D plasmons towards a selected nanohole, thereby permitting a well-controlled addressing of single dots located under different nano-holes. Possible implications of this control of optical processes over a single dot scale will be discussed. [1] C.J. Bouwkamp, Philips Res. Rep., 5, 166 (1960). [2] F. Bethe, Ann. der Physik, 322, 1422 (1993). [3] C. Soenensche et al., APL 76, 140 (2000)

9:00 AM *K5.2*

**CONTACT EFFECTS IN MOLECULAR JUNCTIONS**

C. Daniel Finshie, Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, MN.

The importance of metal-molecule interfaces in determining the current-voltage (LV) characteristics of molecular junctions has been made clear in theoretical work over the past 5 years. Yet systematic experimental investigations, in which the contact effects are mapped out as a function of the metal work function and the type of surface linker used to bind the molecules to the electrodes, have not been carried out. This talk describes a conducting probe atomic force microscopy (CP-AFM) approach to the experimental examination of contact effects in molecular junctions. Junctions are fabricated by contacting self-assembled monolayers (SAMs) on metal substrates with metal-coated AFM tips; it is possible to contact SAMs with any metal that can be coated onto an AFM tip. Contact resistances are examined by measuring total junction resistance (at different bias voltages) as a function of the length of the molecule between the tip and substrate contacts, and then extrapolating resistance versus length to zero length. We find that contact resistances in molecular junctions, irrespective of the metal work function, the type of surface linker (e.g., SiH vs. NCO), and the bonding in the molecular backbone (i.e., conjugated or saturated). Importantly, the work function dependence allows qualitative estimation of where the Fermi level of the junction lies with respect to the HOMO and LUMO of the molecules. We will summarize our findings to date on contact effects in junctions composed of molecules with alkane or oligophenylene backbones.

9:30 AM *K5.3*

**INVESTIGATING SINGLE MOLECULE SWITCHES USING SCANNING TUNNELING MICROSCOPY**

Zachary Donhouser, Amanda Moore, Thomas Pill, Brent Martz, Claudia N. Nangyal, Paul Weiss, Penn State University, Dept of Chemistry, University Park, PA.

We use intermolecular interactions to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to form structures for comprehension of single or bundles of molecules. We use and develop scanning probe microscopy to determine both local structures and electronic properties. We have applied these to isolate molecules with electronic functions to determine the mechanism of function, and the relationships between molecular structure, environment, connection, coupling, and function. We have been able to demonstrate that single molecules can function as multistate switches, and have determined important aspects of the mechanical function, and the mechanism of switching. We will discuss our molecular-scale measurements of these systems as well as our approaches to pattern design and creation using these methods.

10:30 AM *K5.4*

**NEW ROUTES TO DITHIOPHOSPHINES FOR FETS**

Joseph Frey, Steffen Proemmel, Kai Segenbacher, Andrew B. Holmes, University of Cambridge, Mobile Laboratory, Cambridge, UNITED KINGDOM.

Dithiophosphines has recently emerged as a promising building block for high mobility materials forming the active layer in field effect transistors. However, its synthesis has been problematic owing to side reactions in the ring closure step. In this paper we demonstrate a simple synthesis procedure based on conjugate addition of thiophenec esters to 2,4,5-dithiophenec-3,4,5-dithiophosphine. The procedure can be adapted to the corresponding 2,5-dicyanothiophenes and readily delivers full differentiation of the substituents. Using novel directed metallization procedures we have been able to prepare a range of suitably substituted dithiophosphine derivatives for Sisfe and Suzuki cross coupling polycondensations. The synthesis and device properties of the new materials will be reported.

10:45 AM *K5.5*

**STRUCTURE AND ELECTRICAL CHARACTERIZATION OF ORGANIC MONOLAYERS ON Au**

Weirong Jiang, Alexei Ermakov, Yves Chabal, and Eric Garfunkel, Rutgers - The State University, Department of Chemistry, Piscataway, NJ. Bert de Boer, David Abadts Magier, Shu Yang, Nikolai Zhitelev, and Zhennao Xoo, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Basic studies of molecules and monolayer films are a necessary focus of research if nanometer-scale molecular electronic devices are to be designed from first principles. Stimulating work involving imaging and electrical measurements has been reported over the past decade, with only a few being based on Au[111]. Here we report, for the first time, scanning tunneling microscopy (STM), conductive-tip atomic force microscopy (AFM) and IR spectroscopy have been used to study a variety of self-assembled monolayers (SAMs) of aromatic thiols. SAMs were deposited on flat Au surfaces and examined for both structural and electrical behavior. Metallization on top of the SAM was also accomplished using several methods, and then characterized. SAMs consisting of mixed contacted layers were also examined for their ability to conduct and examine the study of directions of current by the study of nanostructures. The results of these studies are useful in understanding the properties of small organic molecules and monolayers which may find use in future electronic devices. References: I. G. Poirier, Chem. Rev. 97, 1117 (1997). 2. X.D. Cai, A. Pranak, et al., Science, 287, 657 (2000). 3. A. Pranak, et al., Phys. Rev. Lett. 88, 228601(2002) 4. S. Datta, W.D. Xin, et al., Phys. Rev. Lett. 79, 2540 (1997). 5. M. Dorogi, J. Gomez, et al., Phys. Rev. B 82 (2010), 9701 (1995). 6. T.D. Dinh, M.Y. Cygan, et al., J. Phys. Chem. B 104, 4880 (2000).

11:00 AM *K5.6*

**CHARACTERIZATION OF NANO-SCALE METAL-MOLECULE-MOLECULE JUNCTIONS**

A. Erbic, B. de Boer, B. Zhao, N. Zhitelev, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

A new approach to fabrication and characterization of nanoscale metal-molecule-metal junctions is developed. The technique is based on shadow stencil mask evaporation similar to that known for metal Single Electron Transistor fabrication. The mask is defined by electron beam lithography in direct contact with the substrate. The active area of the junction is written with the shadow of the mask and the contact size is approximately tens of nm. The number of molecules participating in current flow
transport can be controlled by monitoring the conductance during the final evaporation. The design of the structure includes a metallic gate in close vicinity to the organic material. We report on the observation of various types of molecules controlling external conditions. Distinct features are found in the I-V characteristics at low temperatures indicating that single or few molecules are contacted. Some of these features can be affected by changes in applied gate voltage.

11:15 AM K5.5

Scanning electrochemical microscopy was carried out on self-assembled monolayers (SAMs) of highly conjugated molecules that could function as electron conducting pathways. Surface potentials and tunneling currents were measured under ambient conditions and the effects of electron active substituents and different anilin ligand clips were examined. The SAMs were obtained by flooding or by micro-contact printing using soft stamping. The SAMs were characterized by ellipsometry. The relationship between observed measurements and molecular properties is explored.

11:30 AM K5.8
CHARGE TRANSFER MECHANISMS BETWEEN GOLD CLUSTERS. Victoria Tomas, Technische Universitat Wien, Institute fur Materialwissenschaften, Universitaetsstrasse 12, A-1060 Vienna, Austria; Anja Rehagen, Institut fuer Anorganische Chemie; Olavin Vidoni and Guntar Schmidt, Universitat Essen, Institute fur Anorganische Chemie, GERMANY.

Electron transfer processes in complex chemistry are usually described by Taube’s “outer sphere” and “inner sphere” mechanisms. A behaviour, similar to these electron transfer mechanisms in complex chemistry, can be observed for charge transfer transport between ligand protected Au16 nanoclusters. Linear dependence between cluster-cluster distance and activation energy for electron transfer is observed if non-covalent linkage exists. However, covalently linked clusters interact independent of the distance. Rather the activation energy depends on the electronic nature of the linking molecules. The dithiol 1,5-dithio-2-propylene, 4,4’-dichlorobenzenethiol, and 2,8-dithio-6-hydroxypureine have been used as bifunctional covalent linkers either in their monomeric form or in the presence of aminated via S-S bonds and so increasing the distance between the clusters and leading to the cluster networks. Non-covalent cluster networks are formed either by pellets of clusters with monodendritic ligands in trimethylphosphine, linked only by van der Waals forces, or by using bifunctional spacers like 4,4’-diamino-1,3-diphenylethane that interact with the clusters by ion attractions. The study of the activation energies clearly indicates that in the case of non-covalently linked clusters only the cluster spacing is of relevant even if coagulated systems are used. This behaviour corresponds to an outer sphere mechanism. On the contrary, for covalently linked clusters their distance do not play a visible role. The activation energies all lie below those of the non-covalent examples; however, a relation between cluster-cluster distance and activation energy is not obvious. In those cases the relation remains to an inner sphere mechanism where the transport properties of the spacer play the decisive role. These behaviour possibly contributed to the recent reports on the conductivity behaviour of organic molecules.

11:45 AM K5.9

The solid-state properties of organic electronic materials are determined not only by those of individual molecules but also by those of ensembles of molecules. The ability to control the architectures of these ensembles is thus essential in optimising the properties of conjugated materials for use in electronic devices (light emitting diodes, transistors, solar cells, and so on) and is essential for potential technological applications in nanoelectronics. For instance, a clear correlation between the molecular structure, the mesoscopic structures, as shown by the film morphologies, and the optical, in particular, electrical properties, has been recently established. Self-assembly of synthetic materials has been recently proposed as a means of fabrication of nanodevices. In this domain, the ordering of block copolymers and oligomers leads to the formation of well-ordered nanorods. In this work, we report on the observation of atomic force microscopy (AFM) of 1D and 2D nanoscale architectures obtained by self-assembly of molecularly-disordered and ordered block copolymers or oligomers, and demonstrate that the different molecular arrangements can coexist and co-orient into a surface over hundreds of microns, forming semiconducting fibrils of different chirality. The presence of bulky side chains or chiral centers (located either along the non-conjugated segment or on a substituent of the conjugated segment) are also drastically affecting the final morphology. It appears that the formation of fibrils is predominant only when the molecular interactions are stronger than the molecular surfaces interactions. When they are reversed, randomly unidimensional supermolecular organizations are prevented and non-organized or 2D morphologies (like crepes or tiles) dominate. These facts strongly suggest that the nature of the surface is one key parameter governing the formation of the supermolecular assemblies.

SESSION K5/M5: JOINT SESSION
NANOTUBES AND NANOWIRES THEORY

Chairs: George Gruner and Tiejun Todorov
Wednesday, April 3, 2003
Nob Hill A/B/C/D (Marriott)

1:30 PM K5.1/M5.1
QUANTUM TRANSFER THEORY IN CARBON NANOSTRUCTURES. Vincenzo Muenier, William Shelton, Thomas Zacharia, Oak Ridge National Laboratory, Oak Ridge, TN; and Jean-Christophe Charlier, Universite catholique de Louvain, Louvain-la-Neuve, BELGIUM; Christopher Roland, North Carolina State University, Raleigh, NC; Jerry Bemmhol; Marco Bucagniero; Ngoc-Hung, Oak Ridge National Laboratory, Oak Ridge, TN, and North Carolina State University, Raleigh, NC.

It has been shown both experimentally and theoretically that carbon nanotubes and nanowires based systems show a great potential for use in future nanoscale devices. However, since carbon nanoscale systems are found in various morphologies and dimensions, it is particularly important to acquire a precise understanding of the processes governing the electronic transport in these novel systems. In this framework, we have investigated the electronic transport properties of a number of carbon nanotube based structures, including tapered (telescopic) and highly defective (Helkellites) nanotubes, coalesced nanowires, as well as complex intranetworks comprised of up to four carbon nanotubes. In addition, we will discuss the critical role played by the metallic contacts in driving the characteristics of the electronic transport in these nanoscale materials.

2:00 PM K5.2/M5.2
MANY-ELECTRON EFFECTS AND OPTICAL RESPONSE OF CARBON NANOTUBES. Robert G. Gordon, Dept of Physics, University of California at Berkeley, and Lawrence Berkeley National Laboratory, Berkeley, CA.

Electron-electron interaction is a more important role in reduced dimensional systems. In this talk, we examine the influence of many-electron effects, such as quasiparticle self-energy and electron-hole interaction (or excitonic) effects, on the optical response of carbon nanotubes. Recent advances in theory and computational methodology have allowed the first-principles calculation of these effects in the optical spectra of many systems including solids, surfaces, and nanostructures. These calculations, which solve the Bethe-Salpeter equation of the interacting quasiparticle Greens function, yield both exciton states and optical absorption spectrum. Our results show that, indeed, many-electron effects can change qualitatively the absorption spectrum of carbon nanotubes. Exciton states with large binding energies are predicted in low dimensional systems, even in some metallic tubes. These exciton states dominate the optical response of the system.

2:30 PM K5.3/M5.3
EFFECTS OF CURVATURE ON THE BANDGAPS OF QUASIMETALLIC CARBON NANOTUBES. C. T. White, Naval Research Laboratory, Washington, DC; J. W. Mintmire, J. C. Cabot, Department of Physics, Oklahoma State University, Stillwater, OK.

Extended single-walled carbon nanotubes can be grouped based on the graphene sheet model as either semiconducting or metallic. However, within the subset of ‘metallic’ tubes only the wide ones should be truly metallic due to symmetry with the remaining quasimetallic tubes having small band gaps that depend on the chiral angle and vary as the inverse square of the nanotube radius. Also, within this set of metallic and quasimetallic tube theory predicts
that the zigzag and armchair tubes yield the upper and lower limits for the band gap for a given tube radius. Recently, experimental results have indicated that some of the zigzag tubes are truly metallic, while the zigzag tubes do have gaps that vary as the inverse square of the nanotube radius. We present an approximate analytic expression for the band gaps of the quasi-metallic zigzag tubes derived from an all-atom tight-binding model. While comparing well to our numerical results and experiment, this expression shows that the band gap in these tubes should depend sensitively on both the nearest neighbor carbon-carbon interaction and the diameter. The possible consequences of these results for the use of quasi-metallic tubes as electromechanical devices will be discussed.

SESSION K7:
Chair: Tchandor Todorov
Wednesday Afternoon, April 23, 2003
Nab Hill C/D (Marriott)

4:00 PM K7.1
THEORETICAL STUDY ON SINGLE CONDUCTING MOLECULAR WIRES COVERED BY MOLECULAR NANO TUBE: APPLICATION TO electron TRANSPORT ELECTRONICS.
Rudenk V. Belosludov, Hiroshi Sato, Amir Faraj, Hiroshi Masuiko, Yoshihiko Kawano.
Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Despite a remarkable miniaturization trend in the semiconductor industry, in the next 15-15 years, conventional Si-based microelectronics is likely face fundamental limitations when the length scale is reduced below 10 nm. Therefore, there have been many experimental and theoretical efforts, resulting in significant advances in the fabrication of molecular wires, diodes and two-terminal electrical switches made from single molecules. For application to molecular wire the conducting polymers are one of the attractive materials. However, the carrier mobility is limited by structural disorder of conducting polymer and hence, in metallic state, it limits the electrical conductivity. Therefore, it would be better if the long molecules were composed of insulating nanotubes. One of the possible approaches for realization of such structure is the formation of inclusion complex in which the polymer chain is inserted in the nanotube, based on cyclic cycloexdextrin molecules. Here the structural, electronic properties and current transport characteristics of different polymers covered with cycloexdextrin molecules have been investigated using quantum mechanical simulations. Thus, the results of calculations showed that the structures of polyethylene in the cases of molecular nanotubes of CD and CDs and nanotubes of pseudocamphors have nanotube geometry, with the electronic configuration of the optimized structure being practically same as the one in the phase-conformation. Moreover, the single chain of metallic form of polynioline can be also covered with the insulator CDs molecular nanotubes. The theoretical results, in agreement with experimental data, can suggest for the application of such inclusion complexes in molecular electronics.

4:45 PM K7.4
METALLIC PROPERTIES OF SILICON NANOWIRES.
Inder P. Batra and T. Chen, Department of Physics, University of Illinois at Chicago, Chicago, IL.

In our drive towards a truly integrated silicon nanotechnology environment, it may be desirable to replace metallic interconnects of the order of 100-1000 nm in length with nanoscale wires having a diameter of 1-10 nm. This can be achieved by addressing two questions. The first question is whether such wires can be made with the necessary metal required for interconnects. The second question is whether such wires can be made using standard silicon foundry processes. It is remarkable that both the questions can be answered positively.

SESSION K8:
Chair: Sergei Hurst
Thursday Morning, April 24, 2003
Nab Hill C/D (Marriott)

8:30 AM K8.1
SYNTHESIS, CHARACTERIZATION, AND ELECTRICAL MEASUREMENTS OF SELF-ASSEMBLED MOLECULAR WIRES.
Z. Bao, B. de Boer, A. Erbe, N. Zehren, D. Abraham, Bell Laboratories, Lucent Technologies, Murray Hill, NJ; H. Meng, D.F. Perepichka, Department of Chemistry, University of California at Los Angeles, Los Angeles, CA; W. Jiang, A. Ermenkov, E. Garfinkel,
Department of Chemistry, Rutgers University, New Brunswick, NJ; M Prank, Y.J. Chabal, Agere Systems, Berkeley Heights, NJ; Z. Liu, K. Chin, New Jersey Institute of Technology, Newark, NJ.

The synthesis and characterization of self-assembled monolayer and multilayer molecular arrays which serve as the active layer in electronic devices is a very important and developing area of molecular electronics. In order to correlate the properties of the self-assembled monolayer with the molecular structure, a series of p-conjugated mono- and dilithih compounds have been synthesized and characterized. Their self-assembled monolayer films on gold surfaces were characterized by cyclic voltammetry, grazing incidence FTIR, STMs, contact angle and ellipsometry measurements. The effect of metal contacts on the chemical structure and molecular orientation of the monolayer as well as the electrical behavior measured by STM will be discussed. Finally, nano-scale devices enabled by self-assembled molecular wires will be presented.

9:00 AM *K8.2

We have performed conductance measurements with a self-assembled metal/molecule/metal junction [1]. The gap between the electrodes could be adapted in situ to the molecule's length employing the mechanically controlled break junction technique. The organic sample molecules were designed to form a stable chemical bridge between the electrodes. Both molecules, which differed essentially by their chemical composition, showed discrete stable conductance patterns. While the symmetric molecule always generated symmetric current-voltage relations (IVs), the asymmetric molecules often showed symmetric IVs. This allows to clearly identify the IVs as transport through our sample molecules. The body of our data strongly suggests that the intermolecular distance is related to the current through only one single molecule, connected to both metal electrodes. Considerable differences between subsequently manufactured junctions, i.e. sample-to-sample fluctuations are attributed mainly to varying microscopic contact realizations. This is clearly demonstrated by intentionally inducing different asymmetric IVs with the symmetric molecule using the electronic distance. The observed phenomena are compared with theoretical investigations [2].

A further molecule, designed to have an additional strong tunnel barrier in the middle, indeed has much higher resistance values. The IV can be well described by formula for insulating materials up to voltages as high as 6 V. This indicates the potential of a nano-Si-Pt complex as insulating linker between delocalized π-electron systems on a single molecule level [3].


9:30 AM K8.3

We describe the fabrication and measurement of single-molecule transistors in which electrons flow via transition-metal atoms coupled to electrodes by organic linkers. The devices are made by using electroplating to form nm-scale gaps in which single molecules can be inserted. We report both metal and organic molecules containing a single transition metal atom and molecules containing two metal atoms coupled together by an organic bridge. By varying the length of the organic tethers, we can modify the properties of the transistor. Molecules with long tethers exhibit Coulomb-blockade characteristics and variation-assisted tunneling. Molecules with shorter linkers show Kondo physics with Kondo temperatures varying from less than 1K to more than 50 K.

9:45 AM K8.4
CURRENT ENHANCEMENT BY AN INTERCAGE VIBRATIONAL MODE IN SINGLE-MOLECULE TRANSISTORS. Jieqing Peng, Ahlby Pasquetti, Connie Zhang, Brendan Binkskier, James F. Sethna, Daniel C. Ralph, and Paul L. McEuen, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY; Alexander V. Soldatov, Dept. of Physics, Harvard University, Cambridge, MA.

Electron transport measurements in a single-molecule regime offer a powerful tool for studying the coupling between tunneling electrons and molecular vibrations. Using the electromigration junction technique, we fabricated transistors where electron flow through a discrete quantum states of single molecules, C60 fullerene and its dimer (C100). In C60 devices, an excited level was observed near 11 meV and multiples of 11 meV corresponding to excitations of an intercage (ball-ball) vibrational mode. We observe a large current increase when this mode is excited, indicating a strong coupling between the electronic and mechanical degrees of freedom in C60 molecules.

10:30 AM *K8.5
MOLECULAR DEVICES AND CIRCUITS. Supriyo Datta, Institute for Nanoelectronics and Computing, and the School of Electrical & Computer Engineering, Purdue University, West Lafayette, IN.

In this talk we will first review our understanding of electrical conduction through individual molecules, stressing the distinction between two- and three-terminal devices. We will then (1) discuss the prospect for three-terminal devices based on conformational changes, pointing out the fundamental limits imposed by thermal fluctuations; (2) draw attention to the possibility of silicon-based devices that exhibit negative differential resistance (NDR) which could be used to provide novel functionality for conventional devices and (3) propose a scheme for implementing large scale functional circuits based on molecular assemblies.

SESSION K9: OPTOELECTRONICS AND HYBRID TECHNOLOGIES
Chair: Heiko B. Weber
Thursday Afternoon, April 24, 2008
Nob Hill C/D (Merritt)

1:30 PM K9.1

Ionically self-assembled monolayer (ISAM) films have been recently shown to spontaneously assemble with a noncentrosymmetric order that gives rise to a substantial second order nonlinear optical (NLO) response. Typically, polar ISAM films are made from oppositely-charged polyelectrolytes with an ionic, conjugated NLO chromophore attached as a side-chain to one of the polymers. The χ(2) value of such a system is diminished due to competing dipole alignment at opposing ends of each polyelectrolyte layer and by randomized chromophore orientation within thicker layers. Significant enhancements in χ(2) have been achieved by replacing the NLO-active polyelectrolyte with a monomeric chromophore that has a reactive functionality and ionic moieties on opposite ends of the molecule. The growth of multilayers through alternating mechanisms of covalent coupling and electrostatic adsorption results in highly polar chromophore ordering with χ(2) values as large as 30x10^-12 esu, fifteen times that of quartz. Variation of the solution pH allows one to tune the reactive coupling on and off, verifying the important role of the alternating adsorption mechanisms in producing a film with bulk polar order. Quadratic growth of the second harmonic generation (SHG) intensity with the number of layers demonstrates that the bulk polar order exists through large (>50) numbers of bilayers. Since the solution cells, aqueous solutions, and glass substrates are all amorphous and exhibit negligible SHG, in situ SHG measurements allow real-time measurement of the growth of a single, polar monolayer onto the substrate from the solution. These measurements demonstrate that the covalent formation of the chromophore monolayer is complete in less than two minutes, allowing for relatively rapid buildup of thick multilayer films.

2:00 PM K9.2
OPTICAL PROPERTIES OF BIOMOLECULAR LAYERS ON SILICON SURFACES. S.D. Siislu, G. Salmen*, T.U. Kumpen†, M. Friedrich*, R. Scholz*, H. Angermann*, D.R.T. Zahn*. Institut für Physik, Technische Universität Chemnitz, Chemnitz, GERMANY; Department of Silicon Photonics, Helm-Meier-Institut, Berlin, GERMANY.

Biomolecular layers on semiconductor surfaces have an important potential for applications in molecular electronics, sensor development, and biocompatible implants. Among biomolecular systems, DNA bases are particularly interesting in view of achieving conductive molecular nanowires.1, 2 Human spectroscopy is very well
Molecular rectifying diodes have been synthesized based on the Aviram and Ratner paradigm, with donor and acceptor moieties linked by a short or a conjugated bridge. Here we report on self-assembled monolayers of alkanethiol chains on gold surfaces and the formation of thin monolayers on silicon substrates. The thiol groups on the surface are chemically functionalized to carry hydrogen atoms. This results in a chemical functionalization by conjugated molecules of the end groups of alkylthiols. 

Moreover, we demonstrate experimentally and theoretically how to control and detect the threshold voltage of these self-assembled monolayers. We used a chemical functionalization by conjugated molecules of the end groups of alkylthiols to fabricate an electronic device that can be used as a rectifier. The rectifier is based on a thin film of silicon dioxide. The device consists of a silicon substrate with a thin film of silicon dioxide on top. The silicon dioxide is patterned into a network of nanowires. The nanowires are contacted by gold electrodes. The gold electrodes are connected to external circuits. The rectifier is operated at a bias voltage of 0.1 V. We observe a rectifying behavior with a rectification ratio of 100. The rectifier can be switched between a low and a high current state by applying a voltage pulse. This behavior is explained by the presence of a Schottky barrier at the gold-silicon dioxide interface. The Schottky barrier is formed by the gold electrodes and the silicon dioxide. The voltage pulse causes a thermal emission of electrons from the gold electrodes into the silicon dioxide. The electrons then tunnel through the Schottky barrier and into the nanowires. This results in a current flow through the nanowires. The rectifier is switching between a high and a low current state by applying a voltage pulse. This behavior is explained by the presence of a Schottky barrier at the gold-silicon dioxide interface. The Schottky barrier is formed by the gold electrodes and the silicon dioxide. The voltage pulse causes a thermal emission of electrons from the gold electrodes into the silicon dioxide. The electrons then tunnel through the Schottky barrier and into the nanowires. This results in a current flow through the nanowires. The rectifier is switching between a high and a low current state by applying a voltage pulse. This behavior is explained by the presence of a Schottky barrier at the gold-silicon dioxide interface. The Schottky barrier is formed by the gold electrodes and the silicon dioxide. The voltage pulse causes a thermal emission of electrons from the gold electrodes into the silicon dioxide. The electrons then tunnel through the Schottky barrier and into the nanowires. This results in a current flow through the nanowires.

We demonstrated the potential of self-assembled monolayers for the fabrication of electronic devices. The rectifier is a promising device for future electronic applications due to its compactness and low power consumption.
Molecular Assemblies on Chlorinated Silicon Surfaces

Zhong Li, Xuemei Li, Ted Kamins, Yong Chen, R. Stanley Williams, Hewlett-Packard Laboratories, Palo Alto, CA.

The assemblies of molecules on silicon surfaces are of interest to a number of research fields, such as adhesion control, surface passivation, soft lithography, and molecule/silicon hybrid electronic and sensing devices. The molecular assemblies can be generally classified into three categories: a) thiol/mercapto or thiolato organosilyl self-assembled monolayers with native organosilyl (O-terminated) surfaces, b) direct alkylation on O-terminated surfaces, c) chemical reaction on halogenated surfaces. Here we will present a novel method to form chlorinated silicon surfaces. A high temperature treatment method was developed to provide atomically smooth surfaces and generate Cl-terminated surfaces at the same time. The self-assembly of functional molecules via covalent bonding onto these chlorinated surfaces were studied by contact angle measurements, ellipsometry, AFM, XPS and FTIR.

Fabrication and Characterization of Redox-Active Monolayers on Silicon Dioxide For Memory Applications

Shyam Srushti, Qiuhong Li, Guru Mathur, Srinivasa Gowda, Venita Miers, Vladimir Malinowski, Karl Heinz Schwieger, Liming Yu, Jonathan S. Lindsey, Zuming Liu, Rajeev B. Doble, Amir Yossi, David F. Bocian, Werner G. Kehr, Thomas A. Sorensen, and Robert C. Tennes

Our approach towards molecular-scale electronics focuses on hybrid silicon-molecular devices wherein redox-active molecules are incorporated into silicon-based devices. We have successfully fabricated capacitors by forming self-assembled monolayers (SAMs) of redox-active ferrocene and porphyrin molecules with appropriate linkers on silicon dioxide using recently developed surface derivatization methods. Surface derivatization was found to be a critical step; as different attachment densities resulting from various procedures can result in quite different electrical properties. Oxides of various thicknesses, ranging from 1 nm to 3 nm, were grown on silicon by rapid thermal oxidation. The resulting SAM structures of electrolyte-molecule-oxide-silicon (EMOS) capacitors were characterized using conventional capacitance and conductance techniques. The presence of distinct capacitance and conductance peaks associated with oxidation and reduction of the monolayers at low gate voltages indicated discrete electron storage states for these capacitors, suggesting their feasibility in memory devices. Cyclic voltammetry of the EMOS capacitors with different scan rates also showed peaks due to the charging and discharging current associated with redox processes. Furthermore, the redox voltages of the molecule on SiO2 can be tuned by controlling the oxide thickness. This work also shows that hybrid-silicon EMOS structures are very useful tools for characterizing molecular SAMs. Due to the molecular scalability and low-power operation, molecular-silicon hybrid devices may be strong candidates for next generation electronic devices.

Non-Metallicity in Electrochemically Fabricated Atomic-Scale Metal Junctions

D. Nuttman, L. H. Yu, Rice University, Dept. of Physics and Astronomy, Houston, TX.

Electrochemical methods have been proposed as a means of fabricating nm-spaced electrodes for molecular electronics investigations. We report conductance measurements of atomic-scale Au junctions grown by electrodeposition onto lithographically defined electrodes. At low temperatures large fawm junctions exhibit a perturbative suppression of conductance near zero bias (so-called "zero bias anomaly", ZBA). As junction size is reduced to the atomic scale, this ZBA approaches 100% suppression. We present evidence that our junctions are truly atomic scale in cross-section, and that the ZBA is due to the onset of a nonmetallic density of states in the electrodeposited Au when constrained to atomic dimensions. We discuss implications of this result for fabricating molecular electronic test structures.

Electrical Transport in Au-Octanethiol-GaAs Diodes

J. W. Hsu, Y. L. Lo, D. V. Lang, Bell Labs, Lucent Technologies, Murray Hill, NJ, R. Hageaard, Dept. of Chemistry, Indiana University, Bloomington, IN, Current address: Dept. of Chemical Engineering, University of Texas-Austin, Austin, TX.

Using nanotransfer printing, we have fabricated Au top electrodes for molecular junctions comprising 18-octanethiol on n+ GaAs substrates. These printed junctions are mechanically robust with reproducible electrical properties. Unlike devices in which Au contacts are fabricated by direct evaporation onto dithiol coated n+ GaAs (evaporated junctions), these printed diodes contain no electrical shorts between the top and bottom contacts. To understand the nature of the electrical contact in these molecular junctions, we have performed current-voltage (IV) and photoresponse experiments. The current levels in the printed junctions are five orders of magnitude lower than the evaporated junctions. Results from quantitative analysis and photoresponse measurements with above-GaAs-bandgap excitation indicate that small effective area is not the primary reason for the observed low current levels in the printed junctions.

Furthermore, the energy (E) dependence of the photoresponse yield with below-bandgap excitation for the printed junctions is different from that for the evaporated junctions. The evaporated junctions show a quadratic E dependence characteristic of metal-semiconductor Schottky barriers; the measured barrier height of 0.7 V is consistent with Au-GaAs contacts. In contrast, the photoresponse yield of the printed junctions depends exponentially on E, signifying electron emission from disordered material. Thus, fundamentally different transport mechanisms are at work depending on the fabrication of the contacts. Our results imply that electrical transport in printed devices occurs primarily through 18-octanethiol, while conduction in devices fabricated by conventional evaporation is dominated by direct Au/GaAs contacts even though the molecular layer was deposited the same way in both cases. To understand the experimentally observed transport behavior in the printed diodes, electronic structure calculations are performed to obtain the molecular electronic level positions. Band alignment across the molecule-semiconductor and molecule-metal interfaces will be discussed.

4:30 P.M. 30.10

4:45 P.M. 30.11