SYMPOSIUM K
Molecular-Scale Electronics and Optoelectronics

April 22 – 24, 2003

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*Invited paper
TOWARD MONOMOLECULAR DIODES, TRANSISTORS, AND CIRCUITS. James Ellenbogen, Nanosystems Group, The MITRE Corporation, McLean, VA


9:00 AM *K1.2
MOLAR 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 NANOSTRUCTURES. Hongkwan Park, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA

In this presentation, I will discuss (1) the fabrication and characterization of nanometer-scale transistors that incorporate individual chemical nanostructures, including molecules, single-wall carbon nanotubes, and inorganic nanowires 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, Daifang Zhang, Xiaolu Liu, Chongwu Zhou, Univ. of Southern California, Dept. of E.E.-Electrophysics, Los Angeles, CA; J. L. Sessler, J. H. Knutson, B. J. Hwang, and P. M. Ajayan, Georgia Institute of Technology, Atlanta, GA; and Lisa A. Whitton, NASA Ames Research Center, Moffett Field, CA; and 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 been a great challenge in the device fabrication and integration. Here, we present an approach to tackle the daunting problem of molecular electronics. Our approach uses metallic nanowires 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 15 redox centers such as pyridine and NO2 groups. Our approach can be used as a simple and versatile approach for integration of molecular electronics. With the time needed, we can see a variety of applications. Our approach has great potential to be used for fast searching of molecular wire candidates and construction of integrated molecular systems.

10:45 AM *K1.5
ENGINEERING MOLECULE SURFACES INTERACTIONS FOR MOLECULAR ELECTRONICS. J.P. Bourgoin,[1,4], P. Armand,[1],[4], S. Auverry,[1], L. Capes,[1] J. Charler,[1] A. Filoramo,[1,4], M. Goffman,[1,4], A. Pahim,[1,4], J.-N. Pinaud,[1,4], L. Patrone,[1] A. Ribeyrol,[1], E. Valentin,[1], M. Wohleben[1], "CEA/DSM/DERC/QM, Saclay, FRANCE; and CNRS/CEA Molecular Electronics Laboratory, Centre de Recherche Sain-Aubin, Paris, France, "CEA/DEREC/QM, FRANCE.

During the last five years, Molecular Electronics has seen very significant advances and promises of mid-term applications. Self-assembly is generally considered as being the way to use 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) such molecule-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 relationships between the molecular structures 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 groups 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 (CNTs) can be self-assembled at predefined location on a substrate using for example a localized functionalization of the substrate by a self-assembling monolayer. The FEI 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 CNTs and that of molecules adsorbed on the CNTs on the device characteristics. Finally, I will discuss improvements of the self-assembling technique using the recognition properties of biomolecules.

11:15 AM *K1.6
UNDERSTANDING CHARGE TRANSPORT IN MOLECULAR ELECTRONICS. James Kushmerick and Bhagvanath Shashidhar, Naval Research Laboratory, Center for Bio/Molecular Science and Engineering, Washington, DC

In order for molecular electronics to become a viable technology the factors that control charge transport across a metal-molecule-metal junction need to be elucidated. We use an experimentally simple crossed-wire tunnel junction to interrogate how factors such as meta-molecule coupling, molecular structure and the choice of metal electrode influence the current-voltage characteristics of a molecular junction. Results on symmetric and asymmetric junctions demonstrate that a specific molecular core can act either as a molecular wire or a molecular rectifier depending on its coupling to the metal electrodes. Experimental measurements and theoretical calculations show that the conductance of a molecular wire can be directly related to how well its pi-conjugated backbone mimics an ideal one-dimensional metal. Finally, we will show that the conductance of a molecular junction is quantized by the number of molecules contacted.

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

1:30 PM K2.1/L2.1
ORGANIC MOLECULES ON METAL SURFACES BY HIGH RESOLUTION STM. Federico Rusu,* Y. Naito, M. Schmickel, E. Lofqvist, J. Stengs, B. Schumacher, Physikalisches Institut and L-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim, CEMES-CNRS, Toulouse, FRANCE.

*Present address: INRSE-EMT, Université du 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 unique resolving power of Scanning Tunneling Microscopy (STM) can be used to gain new information on molecular diffusion and assembly. First, we address the issue of surface diffusion. Adsorbate movement across surfaces can be followed directly by time-resolved STM movies. In the simplest picture of surface diffusion, adsorbates jump from their ground state sites to other ground state sites. Recent results suggest this is not necessarily true for complex molecules. By studying the diffusion of two related aromatic molecules, DC (C6H18) and HBBDC (C6H16No), on Cu(110), we find that their diffusion is dominated by long jumps, spanning multiple lattice spacings [1]. The HBBDC molecule has a core identical to DC, and 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 pre-designed to engineer their diffusion properties. Second, we describe the adsorption of the Lander molecule [3], (C11H18) on Cu(110) at the temperature range 100-300K. The Lander has a central polymeric wire (conducting backbone), and four “spacer legs” (3,5-di-tert-butylyphenyl) for isolation from the substrate. Lander molecules are arranged in four separate clusters by STM, which may be arranged in three different conformations. Manipulation experiments with the STM at low temperatures on isolated Lander molecules adsorbed on step edges reveal reconstruction of Cu steps [2] when removed from a step, a nanostructure appears, two atomic rows in width (corresponding to the distance between the spacer legs within the molecule). Lander molecules act as nanoscale templates, reshaping portions of step edges into chains of nanowire structures. [1] M. Scheibner, P.R. Linderoth, F. Rosel et al., Phys. Rev. Lett. 88, 156102 (2002). [2] F. Rosel et al., Science 296, 328 (2002).

1:45 PM K2.2/12.3
NANO-SCALE ORGANIC FIELD EFFECT TRANSISTORS AND SHORT CHANNEL EFFECTS. V. Wagner, Universität Würzburg, Physikalisch-Ingenieur, IP, Würzburg, GERMANY (present address: International University Bremen, School of Eng and Sci, Bremen, GERMANY); T. Backer, L. Leiben, A. Lehbi, M. Bornstein, T. Bonien, G. Schmidt, L. Molenkamp, J. Gearu, Universität Würzburg, Physikalisch-Ingenieur, IP, Würzburg, GERMANY.

Down-scaling of organic field effect transistors (OFETs) offers faster switching speeds as well as higher current capabilities at a given device area. We report on the systematic reduction of the organic channel length down to 70 nm for OFETs using quarter thionaphene (QT) as active material. Thiophene are used because of their possible high carrier mobility values. We use electron beam lithography to manufacture gold source and drain finger contacts on SiO2/n-Si substrates to fabricate OFETs within the common back gate configuration. Deviations of the standard FET characteristics (short channel effects) are expected for channel length L comparable to junction width of the electrodes and/or to the gate insulator thickness. After deposition of the organic film by UHV evaporation longchannel (L = 2 μm) devices exhibit standard characteristics at room temperature in air or nitrogen atmosphere. However, for a SiO2 gate insulator of 20 nm thickness we found degradation of the saturation regime for L < 1 μm, while on/off ratios strongly deteriorate for channel lengths of 0.5 μm or below. The effects will be discussed in comparison with short channel effects observed for inorganic devices. Furthermore, as an important result, drain current was found to increase by more than an order of magnitude for channel lengths L < 400 nm, which coincides with the average grain size in our organic layers. This indicates an important contribution of grain boundary scattering for the transport in the organic channel.

2:00 PM *K2.3/L2.3
ELECTRICAL CONDUCTANCE OF SMALL ORGANIC MOLECULES. Norton D. Long and Phaedon Avouris, IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY.

I will discuss a number of theoretical studies on carbon atomic wires and small organic molecules linking two electrodes, focusing particularly on the electrical conductance of these systems. I will consider such topics as the spatial distribution of the voltage drop in an atomic wire, the influence of a pure wire on the conductance of carbon wires of different length, the effect of impurities on conductance, and the conductance and density of electron states for a number of disubstituted benzines, as well as pyrene and biphenyl.

SESSION K3: CHARACTERIZATION AND THEORY
Chair: Massimiliano Di Ventra
Thursday, April 10, 2003, 10:00 AM - 12:00 PM
Nob Hill C/D (Marriott)

3:00 PM *K3.1
Abstract Withdrawn.

3:00 PM *K3.2
HEATING AND FLUCTUATIONS IN NANOSCALE CONDUCTORS FROM FIRST PRINCIPLES. Yu-Cheng Chen and Massimiliano Di Ventra, Virginia Polytechnic Institute and State University, Department of Physics, Blacksburg, VA.

Local heating and current fluctuations are important issues in nanoscale electronics. Both physical effects need to be small for this electronics to have practical applications as possible replacement of silicon-based technology. We present results on local heating and shot noise in atomic and molecular wires from first principle. In particular, we show that shot noise is strongly nonlinear as a function of bias and wire length and it is enhanced for very short wires due to the large contribution from the metal electrodes. We also discuss local heating in these systems. We find 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, Carillon Biomedical Institute and ACS-Petroleum Research Fund.

3:30 PM *K3.3

Transport in conjugated organic molecular films, produced by either self-assembly [SAMs] or Langmuir-Blodgett method, are of most interest for applications in 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 π-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 insulates from the electrodes by symmetric 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 in comparison 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 (SWNT/SWNT/SILICON SURFACES. Robert M. Farrell, Jr, Peter Albrecht, Joseph Lyding, University of Illinois at Urbana-Champaign, Dept of Electrical and Computer Engineering, Beckman Institute for Advanced Science and Technology, U. Illinois, and Ye Wu, Ye Wu, University of Illinois at Urbana-Champaign, Dept of Material Science and Engineering, Beckman Institute for Advanced Science and Technology, Urbana, III.

We have developed a purification process for as-produced HPSC SWNTs that combine high 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 hydrophilic 2×1 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 exfoliation of the ropes into individual SWNTs. After annealing (in a graphite crucible) we typically observe a factor of two mass reduction, which agree well with the known HPSC 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 formation 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 for 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 conduits between ICs. The work described below is part of the development of self-assembling, genetically-derived molecular arrays, essentially one-dimensional molecular crystals, to serve as a "building block" 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 nanowires are presented. Genetic sequencing of the synthesized materials confirmed the expected peptide structure. Scanning force microscopy (SFM) studies investigated the self-assembly behavior of the polypeptide materials as a function of deposition parameters on macro 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). Dimensions of the aggregates have been carried out utilizing standard molecular modeling programs to enable comparison to experimentally obtained data. In addition to commercial SFM tip deconvolution software, SFM and scanning tunneling microscopy (STM) data of polypeptide arrays on metallic substrates are also reported. Scanning tunneling spectroscopy data have been collected for identical tunneling parameters to document the electrical properties of individual genetically engineered molecules and their aggregates.

K4.6 SYNTHESIS AND MAGNETIC PROPERTIES OF NEW MANGANESE-BASED SINGLE-MOLECULE NANO-MAGNETS. Jinkweon Kim, Jiyoun Lim, Sangdon K. Giin, K. Xu, and Unit. Dept. of Chemistry, Kangju, KOREA; Jin-Mook Lim and Youngdu Do, Korea Advanced Institute of Science and Technology, Dept. of Chemistry, Daejeon, KOREA.

Single-molecule magnets (SMMs) are regarded as ultimate high-density memory devices and good candidates for qubits in quantum computer. Since the dodecamanganese cluster with the composition [Mn$_{12}$O$_2$C$_2$Mn$_{11}$]$_2$ (Mn$_{12}$ac) has been discovered as an application of electronic spin in magnets, many efforts have been made to achieve larger cluster compounds showing SMM behaviors. Recently, we have synthesized octadecamanganese cluster with the composition of [Mn$_{18}$O$_2$ (C$_2$Mn$_{17}$)]$_2$ (Mn$_{18}$ac) by treatment of a xerogel slurry of Mn(acetate)$_2$ 2H$_2$O, hemph or hept and acetic acid in methylene chloride with solid Bu$_4$N MF$_4$. X-ray crystallographic studies show that these complexes consist of mixed valent [Mn$_{18}$O$_2$ (C$_2$Mn$_{17}$)]$_2$ [Mn$_{12}$ac] core with peripheral decoration provided by eighteen acetate ligands and six hemph or hept ligands, and two terminal water molecules. The magnetic behaviors observed by SQUID magnetometry reveal these Mn$_{18}$ complexes could be regarded as new members of SMMs. Furthermore, the dodecamanganese cluster with the composition of [Mn$_{12}$O$_2$C$_2$Mn$_{11}$]$_2$ (Mn$_{12}$ac) has been synthesized from the ligand substitution reaction of Mn$_{12}$ac and thiophenacetic acid. The magnetization measurements show hysteresis loops with distinct size/structure with regular intervals. Electrochemical analysis of this complex shows four well separated redox potentials. Furthermore, molecular thin film of it was prepared successfully by dipping of Au substrate into a solution because the sulfur atoms of thiophene groups have high affinity to gold surface. These results strongly suggest that the molecular film of the SMM can be applied to the molecular quantum device. Herein, preparations and characterizations of the new Mn$_{18}$ SMM and the new S-containing Mn$_{12}$ clusters and their molecular films will be presented.

K4.7 RESISTANCE MEASUREMENTS OF CONDUCTING C60 MONOLAYERS FORMED ON NOBLE METAL FILMS. Ryo Nozaki and Iku Kanno, 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 escaping probability of C$_{60}$ molecules which favor charge transfer across C$_{60}$metal interfaces. This charge transfer effect is not particular to alkali or alkali-earth metal. Electrons can be transferred from noble metals to C$_{60}$ molecules, although the work function of noble metals is higher than those of alkali metal. In alkali fullerenes, alkali metals occupy the intersitial sites of the C$_{60}$ lattice, for the cohesive energy of alkali metal is sufficiently low. Noble metals, however, have higher cohesive energy, and cannot intercalate into the C$_{60}$ lattice to form a three-dimensional solid solution. For the case of depositing C$_{60}$ on noble metal films, therefore, the bilayer structure is formed. Electrons transfer to the adjacent monolayer of C$_{60}$ from metal atoms and make a conducting C$_{60}$ monolayer film and then etiol. SQUID resistance measurements, which enable us to see the charge transfer by the change in sheet resistance while depositing C$_{60}$ on thin noble metal films or vice versa, for the C$_{60}$/Cu bilayer structure and reported that the resistance of a conductive monolayer on a Cu underlayer was approximately 8 kΩ. In this presentation, we report on the influence of the work functions of underlayer metals on the resistances of conducting C$_{60}$ monolayers formed on noble metal (Au, Cu, Ag) underlayer by in situ resistance measurements. [1] A.F. Hebard, B.R. Ruot, 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. Further investigations are directed towards more complex, thiocarboxylic acid derivatives. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL. UCB-IC-45498 AB-8.

K4.9 THEORETICAL STUDY ON JUNCTION OF METAL PORPHYRIN FOR ULTRAFAST ELECTRON TRANSFER AS A NANOSCALE DEVICE

Toshiyuki Maeda, Nobukazu Ohashi, Yasuhisa Murakami, and Yoshiyuki Kawazoe; "Institute for Materials Research, Tohoku University, Sendai, JAPAN; Novel Materials and Structural Chemistry Division, Osaka Atomic Research Center, Mombashi, INDIA.

Recently, the molecular electronics has attracted strong attention as a "post-silicon technology" to realize a future nanoelectronics 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 studies using organic molecules in n-conjugation systems through which electrons can flow easily. By substituting different functional groups on an aromatic system it is possible to increase or decrease the n-electron density and thereby creating rectifier-type and donor-acceptor subunits. Therefore, a rectifier diode could be built by combining these two molecular subunits between two electrodes in which the current can flow from the cathode to the anode or from the anode to the cathode (253). Porphyrin possesses good electron-transporting properties due to its large easily ionized n-electron system, and a long molecular wire of fully conjugated porphyrin polymer was reported by Tsuda et al. [4]. In this study, we propose a rectifier diode can be created by combining two metal porphyrin molecules with different metal atoms to form a rectifier 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) 9451 [3] H. Mizusaki, K. Nimura, C. Majumder, and Y. Kawazoe, Comput. Mater. Sci., in press. [4] A. Tsuda and A. Osaka, Science Vol. 290 (2001) 79.

K4.10 NANOSCALE BUILDING BLOCKS AND NANOASSEMBLY OF STRUCTURE

Shyam Pratap Singh, Jiten Singh, Mihir Ozkan, University of California Riverside, Department of Chemistry, Engineering, Riverside, CA; Brooke Colburn, Cengiz Ozkan, University of California Riverside, Dept of Mechanical Engineering, Riverside, CA.


K4.11 SYNTHESIS AND CHARGE TRANSPORT PROPERTY OF DIETHYL-DERIVED 2,2'-BIPHENYRINE TRANSITION METAL COMPLEXES

Sylvia Ann, Wendy Fan, Geetha Dhindjian, Jin Han, Elocet Corp., Mountain View, CA; Jessica Koehne, M. Meyyappan, Elocet Corp., Mountain View, CA; NASA Ames Res. Ctr., Mountain View, CA; Changgu Zhou, Dept of Physics and Engineering, University of Southern California, Los Angeles, CA.

One of the goals in molecular-scale electronics is to understand the influence of structural characteristics of a molecule on its electron transport properties. Studies by Reed and Tour have shown that oligophenylethynylene containing nitro group exhibit NDR (negative differential resistance) effect and thus have potential applications as electronic switching and memory devices. The physical mechanism of the 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 oligophenylethynylene monomers using reverse Diels-Alder coupling reactions. Differing in the nature of the substituents, these molecules have different charge density on their conducting backbone. 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 nanowires containing electron deficient backbones. Furthermore, molecules containing the resonance stabilizing nitro group gave more stable and reproducible LV curves, as long as longer retention times. The results strongly indicate that the redox properties of the molecule at least partially responsible for the electron transport behavior.

K4.12 SYNTHESIS AND TRANSPORT PROPERTY STUDIES OF OLOPHENYLETHYNYLENE

Jessica Koehne, NASA Ames Research Center, Moffett Field, CA; Wendy Fan, ELOCET Corporation, Moffett Field, CA; Chao Li, University of Southern California, Los Angeles, CA; Changgu Zhou, University of Southern California, Los Angeles, CA; Jie Han, ELOCET 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 Tour have shown that oligophenylethynylene containing nitro group exhibit NDR (negative differential resistance) effect and thus have potential applications as electronic switching and memory devices. The physical mechanism of the 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 oligophenylethynylene monomers using reverse Diels-Alder coupling reactions. Differing in the nature of the substituents, these molecules have different charge density on their conducting backbone. 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 nanowires containing electron deficient backbones. Furthermore, molecules containing the resonance stabilizing nitro group gave more stable and reproducible LV curves, as long 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 TOOWARDS PREPARATION OF CONJUGATED OLO.isPlaying CONTAINING AYL THIOLS, Wendy Fan, Sylvia Ann, Jin Han, ELOCET Corp., Moffett Field, CA; Jessica Koehne, M. Meyyappan, NASA Ames Research Center, Moffett Field, CA.

Formation of self-assembled monolayers (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 witharyl thiol terminal are particularly useful because they readily self-assemble onto gold surface and allow maximum electron coupling. To date, the most successful route for preparation of such molecules is to incorporate new linkage into the conjugated systems through metal-catalyzed coupling reactions. Due to the high
reactivity of the aryl thionocarbamate, the coupling chemistry that can be employed is 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 aryl amine into thiol or thiolate in high yields. We further demonstrate the usefulness of these methods by efficient synthesis of two classes of conjugated oligomers that were previously difficult to prepare. These syntheses use a new approach in which the entire molecules were constructed with thiol/thionocarbamate groups masked in the form of halide or amine, bypassing the dilemma where the thionocarbamate is incompatible with the conditions required for preparation of the thiol of the molecule. The transformation and the synthetic approach described here offer easy access towards a wide variety of conjugated molecules with terminal aryl thiols.

SESSION K5
Chair: Jean-Philippe Bourgoin
Wednesday, April 23, 2003
Nab Hill C/D (Marriott)

8:30 AM *K5.1
THE NEAR FIELD OF AN OPTICAL TIP: PROBING IT WITH MOLECULAR OBJECTS AND USING IT FOR SINGLE OBJECT ADDRESING. A. Decrét, M. Bruin, M. Nisse, N. Chevalier, J. C. Wetl, S. Humeau, 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 this statement 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 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 analysing fluorescence images of single molecules, 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 nano-holes in a metallic 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 aluminium film with well-defined nano-holes has been deposited. We show that launching of surface plasmons into these holes allows to excite the luminescence of underlying dots. Furthermore, a technique to selectively address a single quantum dot is presented and the propagation of 2D plasmons towards a selected nano-hole, thereby permitting a well-controlled addressing of single dots located under different nano-holes. Possible applications of this control of optical processes over a single dot scale will be discussed.


9:00 AM *K5.2
CONTACT EFFECTS IN MOLECULAR JUNCTIONS. C. Daniel Frishie, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

The importance of metal-molecule interfaces in determining the current-voltage (I-V) 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 bond 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 extracted by measuring total junction resistance at different bias voltages as a function of the length of the molecules between the tip and substrate contacts, and then extrapolating resistance versus length to zero length. We find that contact resistances in molecular junctions are commensurate to the metal work function, the type of surface linker (e.g., SH vs. NC), and the bonding in the molecular backbone (i.e., conjugated vs saturated). Importantly, the work function dependence allows qualitative estimation of where the Fermi level of the junction is 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 Donhauser, Amanda Moore, Thomas Pearl, Brent Mantooth, Swraj Nandakumar, Paul Weiss, Penn State Univ, 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 test structures for appropriate function of single or bundled molecules. We use and develop scanning probe microscopes to determine both local structures and electronic properties. We have applied these to isolate molecules with electronic functions to determine the mechanisms 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 mechanism, function, and performance of the switching. We will discuss our molecule-scale measurements of these systems as well as our approaches to pattern design and creation using these methods.

10:00 AM K5.4
NEW ROUTES TO DITHIOPHOPHOSPHINE FOR FETS. Joseph Frey, Steven Proemmel, Kai Siegenthaler, Andrew B. Holmes, University of Cambridge, Mobile Laboratory, Cambridge, UNITED KINGDOM.

Dithiophosphines have recently entered 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 annihilation process based on conjugate addition of thiophosphoric esters to 2,5-diphenyl-3,4-dihydrothiophene. The procedure can be adapted to the corresponding 2,5-dicyclohexylphosphines and readily delivers full differentiation of the substituents. Using novel directed metallation procedures we have been able to prepare a range of suitably substituted dithiophosphine derivatives for Sible 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 Fermaux, Yves Chabal, and Eric Garfunkel, Rutgers - The State University, Department of Chemistry, Piscataway, NJ. Bert de Boer, David Abud-Magder, Shao Yang, Nikolai Zhitelev, and Zhenhua Bao, 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 using alkane thiol monolayers on Au [1]. In this work, scanning tunneling microscopy (STM), conductive-tip atomic force microscopy (AFM) and IR spectroscopy have been used to study a variety of organic 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 materials were examined using the procedure of conducting "wires" isolated in a lower conductivity matrix. Finally, diblock copolymers were explored for patterning both SAMs and Au (and other) top electrodes with the hope of finding new nano-fabrication methods. 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: 1. G. Poirier, Chem. Rev. 97, 1117 (1997). 2. X.D. Cole, A. Pramuk, et al., Science, 287, 571 (2000) 3. Z. Jiang et al., Phys. Rev. Lett. 88, 226801 (2002) 4. S. Dutta, W.D. Tim, et al., Phys. Rev. Lett. 79(13), 2540 (1997). 5. M. Dorgon, J. Gomez, et al., Phys. Rev. B 52(12), 9071 (1995). 6. T.D. Mamin, M.T. Cygan et al., J. Phys. Chem. B 104, 4880(2000).

11:00 AM K5.6
CHARACTERIZATION OF NANOSCALE METAL-MOLECULE-METAL JUNCTIONS. A. Eiche, B. de Boer, Z. Bao, 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 the use of a shadow mask to pattern the surface of a thin film of metal deposited on a semiconductor substrate. The top layer of the junction is then fabricated by the process of evaporation of a metal layer within the mask. The masks are made by the use of a contact or 0.5 micrometer and consist of a pattern of several tens of nanometers. The number of molecules participating in current...
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 a section. 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 TRANSMISSION X-RAY MICROSCOPY OF SELF-ASSEMBLED
MONOLAYERS OF HIGHLY CONJUGATED MOLECULES.
R. Ross, Getty, Simon Perec, Paula Hiep, and Roger French,
DuPont Central Research and Development, Wilmington, DE; Dawn
A. Bohnett, R. Tony Alvarez, Rue Shao, and Zonghao Hu, Univ.
of Pennsylvania, Dept. of Materials Science and Engineering,
Philadelphia, PA.

Scanning probe 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 alligator 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.
Viktoria Tema, Technische Universität Wien, Institut für
Mikroelektronik, Vienna, Austria; Ulrich Schönhals, Universität
Regensburg, Institut für Anorganische Chemie; Olivi Vidoni and Günter Schmid, Universität Essen, Institut für 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 Auₙ nanoclusters. Linear dependence between clustercluster 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-dithiophenylacetylene, 4,4′-dichlorobenzene, and 2,5-dithio-6-hydroxypurine have been used as bifunctional covalent linkers either in their monomeric form or in the presence of n-dimensions in 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 monodendrimer ligands as triphenylphosphate, linked only by van der Waals forces, or by using bifunctional spacers like 4,4′-dimino-1,3-diphenylthlen that interact with the clusters by ion attractions. The study of the activation energies clearly indicates that in the case of non-covalently organized nanoclusters only the cluster spacing is of relevance even if conjugated systems are used. This behaviour corresponds to an outer sphere mechanism. On the contrary, for covalently linked clusters their distances do not play a visible role. The activation energies all lie between those of the non-covalent example, however, a relation between cluster-cluster distance and activation energy is not obvious. In these cases the relation remains to an inner sphere mechanism where the transport properties of the spacer play the decisive role. These findings possibly contribute to a theory about the conductivity behaviour of organic molecules.

11:45 AM K5.9
ONE- AND TWO-DIMENSIONAL SEMICONDUCTING
NANOARCHITECTURES OBTAINED BY SELF-ASSEMBLING
PROCESSSES, Philippe Leclerc, University of Mons-Hainaut, Mons,
BELGIUM; M. Sirin, University of Mons-Hainaut, Mons, BELGIUM;
O. Henries, IRIS, UNITED KINGDOM; W.J. Fons, Durham,
Durham [UNITED KINGDOM]; F. Biscarini, CNR, Bologna, ITALY;
E.W. Meijer, Tae, Eindhoven, THE NETHERLANDS; A.C.
Grimsdale, MPL; Mainz, GERMANY; K. Ilben, MPL; Mainz,
GERMANY; J.L. Brabec, Dept. of Chemistry, Tucson, AZ, and R.
Lazzaroni, University of Mons-Hainaut, Mons, BELGIUM.

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, organic light emitting transistors, solar cells, etc.) and is primordial for potential technological applications in nanoelectronics. For instance, a clear correlation between the molecular structures, the mesoscopic structures, as shown by the film morphologies, and the optical, in particular, luminescent properties, has been recently established. Self-assembly of synthetic materials has been recently proposed as a means of fabrication of nano-devices. In this domain, the ordering of block copolymers and oligomers leads to the formation of well-organized nanostructures. We report on the observation by atomic force microscopy (AFM) of 1D and 2D nanoscale architectures obtained in the solid-state from solutions of molecularly-dispersed conjugated block copolymers or oligomers, and demonstrate that the conjugated molecules can organize into a surface over several micrometers, forming semiconductor fibrils by interlinking processes. The presence of bulky side chains or circular rings (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 molecule-surface interactions. When they present a unidimensional supermolecular organization, they are 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 Tschudin Todcor
Wednesday, Afternoon, April 30, 2003
Nob Hill A/B/C/D (Marriott)

1:30 PM K5.1/M5.1
QUANTUM TRANSPORT THEORY IN CARBON
NANOSTRUCTURES. Vincenzo Menum, William Shelton, Thomas
Zahn, Oak Ridge National Laboratory, Oak Ridge, TN; Vincenzo
Jean-Christophe Charlier, Université Catholique de Louvain,
Louvain-La-Neuve, BELGIUM; Christopher Roland, North Carolina
State University, Raleigh, NC; Jerry Bernholc, Marco Buongiorno
Nardelli, 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 nanotube based structures show a great potential for use in future nanoscale devices. However, since carbon nanotubes are found in various morphologies and dimensionalities, it is particularly important to acquire a precise understanding of the principles governing the electronic transport in all these novel systems. In this framework, we have investigated the electronic and quantum transport properties of a number of carbon nanotube based structures, including tapered (telescopic) and highly defective (Helkelettes) 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 directing the characteristics of electronic transport in these nanotube materials.

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

Electron-electron interaction in general plays a more important role in reduced dimensional systems. In this talk, we examine the influence of many-electron effects, such as quasiparticle selfenergy 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 nanoarchitectures. These calculations, which solve the Bethe-Salpelter equation of the interacting two-electron 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 to exist in both semiconducting nanotubes and even in some metallic tubes. These 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, T. Cabrín, 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 armchair 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 shown that only the armchair 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 quasimetallic zigzag tubes derived from an all numerical tight-binding model. While containing well to our numerical results and experiment, this expression shows that the band gaps in these tubes should depend sensitively on both the nearest neighbor carbon-carbon p and sigma interactions. The possible consequences of these results for the use of quasimetallic tubes as electromechanical gauges will be discussed.

4:30 PM *K6.4/3*5.4
UNUSUAL ELECTRONIC EFFECTS IN CARBON NANOSTRUCTURES: GEOMETRICAL PHASES IN GRAPHITIC CONES AND NEW BORON-BASED METALS AND SEMICONDUCTORS ON ONE DIMENSION. Vincent H. Crespi, Paul E. Lannoo, and Pielong Zhong, Department of Chemistry and Materials Science and Engineering, The Pennsylvania State University, University Park, PA.

Carbon nanostructures provide both fascinating opportunities for fundamental physics in one and two dimensions and also opportunities for electronic applications. Whereas semiconducting carbon nanotubes have a translational phase defect, carbon nanonoes have a rotational phase defect, which creates novel physical phases and profoundly modifies the global electronic properties. One impediment to practical application of carbon nanotubes has been the lack of a facile means to separate metallic tubes from semiconducting ones. I will also present new boron-based nanotubular structures, one of which is always semiconducting and the other always metallic.

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

6:00 PM *K7.1
THEORETICAL STUDY ON SINGLE CONDUCTING MOLECULAR WIRE COVERED BY MOLECULAR NANO-TUBE: APPLICATION TO CIRCUIT ELECTRONICS. Rodion V. Belashov, Hironori Sato, Amin A. Farajian, Hiroshi Masuike, Yoshisaku Kawanoe, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Despite a remarkable miniaturization trend in the semiconductor industry, in the next 10-15 years, conventional Si-based microelectronics is likely face fundamental limitations when the lengths scale below 0.10-0.05 nm. Therefore, there have been many experimental efforts, resulting in significant advances in 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 mobilities 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 encapsulated by insulating nanotube. One of the possible approaches for realization of such structure is the formation of inclusion complex in which the polymer chain located into the molecular nanotube based on cyclic cyclodextrin molecules [2,3]. Here the structural, electronic properties and current transport characteristics of different polymers covered with cyclodextrin molecules have been investigated using quantum mechanical simulations. Thus, the results of calculations showed that the structures of polythiophene in the cases of molecular nanotubular of c60 and c70 has non-planar geometry, with the electronic configuration of the optimized structure being practically same as the one in the planar conformation. Moreover, the single chain of metallic form of polyaniline can be also covered with the insulator CDs molecules nanotube. The theoretical results, in agreement with experimental data, can suggest for the application of such inclusion complexes in molecular electronics. [1] C. Joachim, J.K. Gimzewski and A. Aviram: Nature 408 (2000) 541. [2] R.V. Belashov, H. Masuike, K. Ichinoseki and Y. Kawanoe, Jpn. J. Appl. Phys. 41, (2002) 2739. [3] T. Shimomura, T. Akai, T. Abe and K. Ito, J. Chem. Phys. 116, (2002) 1733.

4:15 PM *K7.2
EFFECTS OF DYNAMICAL DISORDER ON CHARGE TRANSPORT IN DNA. G. Kakalin, K.O. Rasmussen, P. Markidis, and A.R. Bishop.

We study temperature effects on the characteristic time within which charge carriers remain spatially confined while interacting with fluctuational openings (bubbles) of double stranded DNA. Using semiclassical molecular dynamics simulations, we find that in the low temperature regime this characteristic time decreases in a power-law fashion with temperature while it remains unchanged in the high temperature limit. However, above 50-70 K the confinement time exhibits an exponential increase with temperature indicating that the polaron effects are irrelevant for conduction at elevated temperatures. Calculations of the AC conductivity of the double stranded DNA are also presented.

SESSION K8:
Chair: Serge Hunt
Thursday Morning, April 24, 2003
Neb Hill C/D (Marriott)

8:30 AM *K8.1
SIMULATIONS OF NONEQUILIBRIUM TRANSPORT IN PHENYLENE-ETHYNYLE Oligomers. Jeremy Taylor, Mada Brandbyge, and Kurt Stokbro, Microelektronik Center, Tech Univ of Denmark, Lyngby, DENMARK.

Using an ab-initio green’s function technique, as implemented in the TranSiSTa [1] package, we have carried out simulations to try to understand recent experimental data for molecular rectifiers and molecular devices displaying negative differential resistance, based on a new class of phenylene-ethynlene oligomers [2]. We have used a method to investigate the IV characteristics of an Averin-Burke type molecular diode as well as a symmetric phenylene-ethynlene olgimer [3]. The calculations reveal that the electrode coupling plays an important role, and thus an asymmetric coupling to the external electrodes is the origin of the rectification observed experimentally. A simple model is presented to calculate the diode properties as a function of coupling strength to the external electrodes [3]. These relations can rationalize several experimental results, and may be used to design molecular diodes with improved properties. Other experiments of Phenylene-ethynle with nitrile side groups [4] have shown Negative Differential Resistance. We have calculated the IV characteristics of Phenylene-ethynene oligomers with a variety of side groups, and based on these calculations we discuss the origin of the complex electrical properties of such systems. [1] M. Brandbyge, J.L. Marcos, P. Ordejón, J. Taylor, K. Stokbro, Phys. Rev. B, 65, 105401 (2002). [2] J. Chen, M.A. Reed, A.M. Rawlett, J. M. Tour, Science 286, 1550 (1999). [3] J. Taylor, M. Brandbyge, and K. Stokbro, Phys. Rev. Lett. (in press).

8:45 PM *K7.4
METALLIC PROPERTIES OF SILICON NANOWIRES. Inder P. Bhatia 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 like Al, with Si. This motivated us to investigate the electronic properties of quasi one-dimensional (1D) silicon nanowires using the pseudopotential density functional total energy method. For an infinite 1D wire, our computed value of the optimal nearest neighbor distance (\(d = 2.24\)) and the cohesive energy (3.4 eV) are both below the corresponding bulk values. The electronic structure shows partly occupied doubly degenerate \(\pi\) bands crossing the Fermi level at a point less than the middle of the zone-edge. This precludes Peierls dimensionality as an energy lowering mechanism. We therefore, allowed the nanowires to distort in a plain to find other more stable structures. We found two stable zigzag quasi 1D structures. One structure has a shallow minimum, a wide-angle \(\alpha = 117°\) zigzag structure with \(d = 2.24\). The cohesive energy of this structure is 3.8 eV, still far from the bulk value. The charge density analysis shows directional bonding among atoms. The system is metallic but the stability is questionable. The second zigzag structure, \(T\), appears more promising. It consists of nearly equilateral triangles. The cohesive energy is high (4.4 eV/atom) and the interatomic distance (2.4 A) is close to the bulk value. The charge density analysis shows that \(\pi\) and \(\sigma\) are held together by strong \(\pi\) bonds, that “flow” in a sea of delocalized \(\pi\) electrons much like free electrons from metal. From the electronic structure we estimate conductance value using the Heineberg’s uncertainty principle. Assuming that the electronic behavior will not change drastically when one goes from infinite to a finite system (and there are good reasons to rely on the abinitio) then such metallic silicon nanowires will help achieve a major integration in nanotechnology.
powerful tool for studying the coupling between tunneling electrons and molecular vibrations. Using the electromigration junction technique, we fabricated transistors where electron flow through discrete quantum states of single molecules, C60 fullerenes and its dimer C70. In C60 devices, an excited level was observed near 11 meV and multiples of 11 meV corresponding to excitations of an intercage [halo-cage] 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
Sugrapat 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 added 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, 2013
Nobel C/D (Marriott)

1:30 PM K9.1 HYBRID FABRICATE/ELECTROSTATIC SELF-ASSEMBLY OF ORGANIC POLAR MULTILAYERS FOR SECOND ORDER NONLINEAR OPTICS

Ionically self-assembled monolayer (ISAM) films have been recently shown to spontaneously assemble with a noncentrosymmetric structure that gives rise to a substantial second order nonlinear optical (NLO) response. Typically, polar ISAM films are made from covalently-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 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 vary 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 coherent 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

Biomolecular layers on semiconductor surfaces have an important potential for applications in molecular electronics, sensor development, and bio-compatible 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 even vanishingly small gap. Here, we report the synthesis using only one donor group and a single acceptor group using a sequential self-assembly process (SAM or self-assembled monolayer).

Moreover, we demonstrate experimentally and theoretically how to control the threshold voltage of these devices. We used a chemical functionalization (by conjointly modified) of the end-groups of alkyltrimethylsilane SAMs to fabricate an insulator/semiconductor (called sigma) heterostructures at a molecular level on silicon substrates. Alkyl chains comprising from 6 to 15 methylene units and we used various conjugated groups (phenyl, thiophene, anthracene, pyrene, ...). Current rectification is observed for the electronic transport through these functionalized SAMs embedded in a Si(4+/3+) gate/SAM metal junction, with rectification ratio up to the order of 35 and threshold voltages of in the range -0.3 to -0.7 V (negative voltage applied on the top electrode). Self-consistent tight binding calculations of the density of states for these systems show that the rectification occurs due to a resonant tunneling transport through the LUMO level of the conjugated group (resonance HOMO to CB of the Si n-type), while the LUMO is too high in energy to be accessible for reasonable applied positive voltages. We show that, for a given conjugated group, the threshold voltage can be slightly tuned by changing the length of the alkyl spacer. Reducing the alkyl length increases the electronic coupling between the conjugated group and the silicon substrate, thus reduces the HOMO-LUMO gap and reduces the threshold voltage.

This approach allows us to fabricate molecular rectifying diodes using an easily tunable property (threshold voltage, one of the important parameter in circuit design), and compatible with silicon nanotechnologies for future hybrid circuits.

2:30 PM K9.4

SINGLE MOLECULE LIGHT EMITTING DIODES. Ta-Hue Lee and Robert M. Dickson, Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA.

Formed as nanoscale break junctions, spatially resolved, individual Ag nanoclusters (2-8 nm atoms) have been fabricated into the first single molecule light emitting diodes. While the junctions are symmetric, the high frequency pulsed excitation (~ns) introduces polarity dependence of the electroluminescence (EL). The EL intensity under short electric pulses also shows strong dependences on pulse duration and amplitude. By the frequency dependence of material responses over the range of 10 kHz to 30 GHz, unique opportunities for greatly simplified fabrication of nanoscale electronic devices are made available. Additionally, AC-excite single Ag nanocluster EL shows strong enhancement at specific AC frequencies. EL at AC enhancements yields very stable EL spectra and significantly narrower spectra than those of the same molecules excited with DC. The strong EL enhancement at specific AC frequencies is a unique response of the nanoscale junction to very short electric fields. This nanoscale EL enhancement in the range of 10 kHz to 30 GHz opens the way toward the development of strongly light emitting diodes.

3:45 PM K9.5

SELF-ASSEMBLED MOLECULAR RECTIFYING DIODES. S. Lenz, D. Vuillaume, C. Krenzinskii, C. Delerue, Institute of Electron Physics and Nanotechnology, CNRS, Villeneuve d’Ascq, FRANCE.

Electrical transport in semiconductor nanocrystals is influenced by both Coulomb-blockade and resonant tunneling effects. Here, we present measurements of Cds nanocrystals assembled in nanometer-sized metallic or semiconductor gaps. Using a shadow-evaporation technique we are able to produce metal gaps between 3-6 nm wide. Cds nanocrystals assembled in these gaps show typical Coulomb-blockade behavior. We have also fabricated gaps of 5-20 nm between semiconductor electrodes, by selective etching of GaAs/AlAs/GaAs heterostructures. Nanocrystals assembled in these structures may exhibit negative differential resistance due to resonant tunneling between the doped semiconductor electrodes and the quantum-confined levels in the Cds surface states.

We have demonstrated successful attachment of Cds nanoparticles onto GaAs surfaces using alkylthiolates, and have characterized the resulting structures using infrared spectroscopy, optical ellipsometry, photoluminescence, and scanning tunneling microscopy.
Molecular Assemblies on Chlorinated Silicon Surfaces
Zhong Lu, Xue 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 molecular/silicon hybrid electronic and sensing devices. The molecular assemblies can be generally classified into three categories: a) thirldiolosilane or thiokysilane self-assembly on surfaces with native oxide-terminated surfaces, b) direct alkylation on Si-terminated surfaces, c) chemical reaction on halogenated surfaces. Here we 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 silicon surfaces were studied by angle measurement, ellipsometry, AFM, XPS and FTIR.

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

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: at different attachment densities resulting from various procedures can result in quite different electrical properties. Oxides of various thicknesses, ranging from 1 nm to 10 nm, were grown on silicon by rapid thermal oxidation. The resulting SAMs show the electrolyte-molecular-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 process. Furthermore, the redox voltage of the molecules 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.

Nonmetallicity in Electrochemically Fabricated Atomic Scale Metal Junctions
D. Natesan, 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 [few nm] junctions exhibit a perturbative suppression of conductance near zero bias (‘zero-bias anomaly’). 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
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Using nanotransfer printing, we have fabricated Au top electrodes for molecular junctions comprising 1-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-terminated 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 (I/V) 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 low-surface transition, while conduction in devices fabricated by conventional evaporation is dominated by direct Au-GaAs contacts even though the molecular layer was deposited in 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 position. Band alignment across the molecule-semiconductor and molecule-metal interfaces will be discussed.