

# SYMPOSIUM K

## Molecular-Scale Electronics and Optoelectronics

April 22 – 24, 2003

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### Symposium Support

Luna Innovations, Inc.

\* Invited paper

## SESSION K1: MOLECULAR DEVICES

Chair: Paul S. Weiss  
Tuesday Morning, April 22, 2003  
Nob Hill C/D (Marriott)

### 8:30 AM \*K1.1

TOWARD MONOMOLECULAR DIODES, TRANSISTORS, AND CIRCUITS. James 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 breached. That is the development of multi-device nanocircuits within single molecules. The speaker will discuss a comprehensive design strategy for achieving this goal [3-6]. The resulting integrated monomolecular logic and memory structures would provide the ultimate limit for the miniaturization of current-conducting electronic computer circuitry. References [1] G. Y. Tseng and J. C. Ellenbogen "Toward Nanocomputers," *Science*, vol. 294, 9 November 2001, pp. 1293-1294. [2] J. Markoff, "Hewlett Finds a Process to Make Chips Even Smaller," *N.Y. Times*, 9 October 2002. Available online at the URL:

<http://www.nytimes.com/2002/09/10/technology/10CHIP.html> [3] J.C. Ellenbogen and J.C. Love, "Architectures for molecular electronic computers: 1. Logic structures and an adder designed from molecular electronic diodes," *Proc. IEEE*, vol. 88, no. 3, March 2000, pp. 386-426. [4] J.C. Ellenbogen, "Monomolecular Electronic Device," U.S. Patent No. 6,339,227, issued to the MITRE Corporation, 15 January 2002. [5] J.C. Ellenbogen and J.C. Love, "Monomolecular rectifying wire and logic based thereupon," U.S. Patent No. 6,348,700, issued to the MITRE Corporation, 19 February 2002. [6] G.Y. Tseng and J.C. Ellenbogen, "Architectures for molecular electronic computers: 3. Design for a memory cell built from molecular electronic devices," Report No. MP 99W0000138, The MITRE Corporation, McLean, VA, October 1999. Unpublished MITRE report, which is to be released shortly.

### 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 NANOSTRUCTURES. Hongkun Park, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA.

In this presentation, I will discuss (1) the fabrication and characterization of nanometer-sized transistors that incorporate individual chemical nanostructures, including molecules, single-walled 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, Daihua Zhang, Xiaolei Liu, Chongwu Zhou, Univ. of Southern California, Dept. of E.E.-Electrophysics, Los Angeles, CA; Wendy Fan, Jessica Koehne, Jie Han and Meyya Meyyappan, 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 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 redox centers such as pyridine and NO<sub>2</sub> groups. Our typical devices exhibit on/off ratios around 370, retention time ~69 seconds and can be repeatedly written and read without significant degradation. Our approach has great potential to be used for fast screening of molecular wire candidates and construction of integrated molecular systems.

### 10:45 AM \*K1.5

ENGINEERING MOLECULES-SURFACES INTERACTIONS FOR

MOLECULAR ELECTRONICS. J.P. Bourgoin<sup>a,b</sup>, F. Armand<sup>a</sup>, S. Auvray<sup>b</sup>, L. Capes<sup>b</sup>, J. Charlier<sup>a</sup>, A. Filoramo<sup>b</sup>, M. Goffman<sup>a,b</sup>, S. Palacin<sup>a</sup>, J.-N. Patillon<sup>b</sup>, L. Patrone<sup>a</sup>, A. Ribayrol<sup>b</sup>, E. Valentin<sup>b</sup>, M. Werts<sup>a</sup>. <sup>a</sup>CEA/DSM/DRECAM, Saclay, FRANCE; and <sup>b</sup>Joint CEA-Motorola Molecular Electronics Laboratory, Centre de Recherche Motorola Paris, Motorola Labs, Espace Technologique Saint-Aubin and CEA Saclay, DSM/DRECAM/SCM, FRANCE.

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 being 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) molecule-surface interactions to localize the self-assembly of the molecules-including carbon nanotubes. In this lecture, I will focus on recent results developed in our group along these two axis. I will first discuss the relationship between the molecular structure 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 endgroups have been systematically compared and ii) on experiments in nanoparticles 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-assembled 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 devices 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 Ranganathan 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 metal-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

Chairs: Massimiliano Di Ventra and Junji Kido  
Tuesday Afternoon, April 22, 2003  
Salon 1-3 (Marriott)

### 1:30 PM K2.1/L2.1

ORGANIC MOLECULES ON METAL SURFACES BY HIGH RESOLUTION STM. Federico Rosei<sup>a</sup>, Y. Naitoh, M. Schunack, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, Physics Department and I-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim, CEMES CNRS, Toulouse, FRANCE. <sup>a</sup>Present address: INRS-EMT, Université du Québec, 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 yields new information on molecular diffusion and assembly. First, we address the issue of surface diffusion. Adsorbate motion across surfaces can be followed directly by time-resolved "STM movies". In the simplest picture of surface diffusion, the adsorbate jumps between 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<sub>36</sub>H<sub>18</sub>) and HtBDC (C<sub>60</sub>H<sub>66</sub>) on Cu(110), we find that their diffusion is dominated by long jumps, spanning multiple lattice spacings [1]. The HtBDC 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 [2] (C<sub>90</sub>H<sub>98</sub>) on Cu(110) by STM in the temperature range 100-300 K. The Lander has a central polyaromatic wire (conducting backbone), and four "spacer legs" (3,5-di-tert-butylphenyl) for isolation from the substrate. Lander molecules are imaged as four separate lobes 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 a restructuring 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 characteristic nanostructures. [1] M. Schunack, T.R. Linderoth, F. Rosei et al., Phys. Rev. Lett. 88, 156102 (2002). [2] F. Rosei et al., Science 296, 328 (2002).

#### 1:45 PM K2.2/L2.2

**NANO-SCALE ORGANIC FIELD EFFECT TRANSISTORS AND SHORT CHANNEL EFFECTS.** V. Wagner, Universität Würzburg, Physikalisches Institut, EP III, Würzburg, GERMANY (present address: International University Bremen, School of Eng. and Sci., Bremen, GERMANY); T. Muck, M. Leufgen, A. Lebib, M. Tormen, T. Borzenko, G. Schmidt, L. Molenkamp, J. Geurts, Universität Würzburg, Physikalisches Institut, EP III, 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 thiophene (4T) as active material. Thiophenes are used because of their possible high carrier mobility values. We use electron beam lithography to manufacture gold source and drain finger contacts on SiO<sub>2</sub>/n<sup>+</sup>-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 long channel (L > 2 μm) devices exhibit standard characteristics at room temperature in air or nitrogen atmosphere. However, for a SiO<sub>2</sub> gate insulator of 200 nm thickness we found degradation of the saturation regime for L < 1 μm, while on/off ratios strongly deteriorate for channel lengths of 400 nm 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. Lang 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 oscillatory conductance of carbon wires as a function of length, the effect of coadsorbed impurities on conductance, and the conductance and density of electron states for a number of di-substituted benzenes, as well as pyrazine and biphenyl.

#### SESSION K3: CHARACTERIZATION AND THEORY

Chair: Massimiliano Di Ventra  
Tuesday Afternoon, April 22, 2003  
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-Chang 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 principles. 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, Carilion Biomedical Institute and ACS-Petroleum Research Fund.

#### 3:30 PM \*K3.3

**ELECTRON TRANSPORT IN MOLECULAR NANOSTRUCTURES: RECTIFICATION, SWITCHING, AND HYSTERESIS.**

A.M. Bratkovsky, 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 p-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 insulated 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 conductors 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 together with current experimental situation.

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

1. P.E. Kornilovitch and A.M. Bratkovsky, Phys. Rev. B 64, 195413 (2001).
2. A.M. Bratkovsky and P.E. Kornilovitch, Phys. Rev. B (to appear); cond-mat/0204597.
3. P.E. Kornilovitch, A.M. Bratkovsky, and R.S. Williams, Phys. Rev. B (to appear); cond-mat/0206002.
4. P.E. Kornilovitch, A.M. Bratkovsky, and R.S. Williams, Phys. Rev. B, cond-mat/0206495.
5. A.S. Alexandrov, A.M. Bratkovsky and R.S. Williams, Phys. Rev. B, cond-mat/0204387 (2002).

#### SESSION K4: POSTER SESSION

Chair: Dominique Vuillaume  
Tuesday Evening, April 22, 2003  
8:00 PM  
Salon 1-7 (Marriott)

#### K4.1

Abstract Withdrawn.

#### K4.2

**NEGATIVE DIFFERENTIAL RESISTANCE IN PHENYLENE ETHYNYLENE OLIGOMERS: A QUANTUM-CHEMICAL INSIGHT.** Jerome Cornil<sup>a,b</sup>, Yasser Karzazi<sup>a</sup>, Jean-Luc Bredas<sup>a,b</sup>; <sup>a</sup>University of Mons-Hainaut, Laboratory for Chemistry of Novel Materials, Mons; <sup>b</sup>The University of Arizona, Department of Chemistry, Tucson, AZ.

The search for novel alternatives towards increased miniaturization of electronic circuits has opened the way to the emerging field of molecular electronics, whose main challenge is to design electronic components using a single molecule or self-assembled molecules. In this context, it has been demonstrated by Reed and co-workers that substituted phenylene ethynylene oligomers inserted into nanopores can be used as active elements for the fabrication of resonant tunneling diodes (RTDs), whose I/V characteristics reveal a Negative Differential Resistance (NDR) behavior (i.e., an initial raise of the current followed by a sharp decrease when the voltage is progressively increased). Several mechanisms have been proposed to explain the origin of this peak profile, relying on doping effects, rotation of electroactive substituents, current-driven geometric changes, or atoms protruding from the electrodes. In this contribution, we describe at the quantum-chemical level a new possible mechanism, based on conformational and energy level alignment effects, that accounts for the strong NDR behavior observed experimentally. The key idea is that conformers where the central ring is twisted with respect to the planes defined by the external segments can lead to resonant tunneling processes through the central ring over a very limited voltage range, and hence to a peak evolution of the transmitted current when the

voltage is progressively amplified; this is demonstrated here on a qualitative basis by analyzing the evolution of the one-electron structure of the wires upon application of a static electric field, aligned along the molecular axis, which simulates the driving voltage applied between the two electrodes in the RTD devices. [1] J. Cornil, Y. Karzazi, and J.L. Bredas, *J. Am. Chem. Soc.* 124, 3516 (2002). [2] Y. Karzazi, J. Cornil, and J.L. Bredas, *Adv. Funct. Mat.*, in press.

**K4.3**  
PURIFICATION OF SINGLE-WALL CARBON NANOTUBES (SWNTS) AND THE PREPARATION OF HIGH QUALITY 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, Urbana, IL; Wei 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 HiPCO SWNTs that combines 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 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 exfoliation 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 HiPCO 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.

**K4.4**  
INVESTIGATIONS OF THE SELF ORGANIZATION OF GENETICALLY-ENGINEERED MOLECULAR INTERCONNECTS. Narender Rana, Kenneth Bousman, Seiichiro Higashiya, Sylvana Ngo, John Welch, Robert E. Geer, Eric T. Eisenbraun, and Alain E. Kaloyeros, University at Albany, Institute for Materials, Albany, NY.

The utilization of individual molecules for digital device structures, so-called moletronics, 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 IC devices. This work describes results to date on 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 microscope investigations of the assembly of genetically engineered polypeptide beta sheets are presented. Genetic sequencing of the as-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). Dimensional analyses of the aggregates have been carried out utilizing standard molecular modeling packages to simulate expected beta-sheet conformations, in addition to commercial SFM tip deconvolution software. SFM and scanning tunneling microscopy (STM) data of polypeptide assembly on metallic substrates are also reported. Scanning tunneling spectroscopy data have been collected for intra beta-sheet tunneling to document the electrical properties of individual genetically engineered molecules and their aggregates.

**K4.5**  
SYNTHESIS AND MAGNETIC PROPERTIES OF NEW MANGANESE-BASED SINGLE-MOLECULE NANO-MAGNETS. Jinkwon Kim and Ahkelish K. Gupta, Kongju National University, Dept of Chemistry, Kongju, KOREA; Jin-Mook Lim and Youngkyu 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 dodecanuclear manganese cluster with the composition  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$  (Mn12ac) had been discovered as a single-molecule magnet, many efforts have been made to achieve larger cluster compounds showing SMM behaviors. Recently, we have synthesized octadecanuclear manganese clusters with the composition of  $[\text{Mn}_{18}\text{O}_{14}(\text{O}_2\text{CR})_{18}(\text{L})_4(\text{LH})_2(\text{H}_2\text{O})_2]$  (R = Me, Et and L = hmp; hydroxymethyl pyridine or hep; hydroxyethylpyridine) by treatment of a stirred slurry of  $\text{Mn}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ , hmpH or hepH and acetic acid in methylene chloride with solid  $\text{Bu}_4^+\text{NMnO}_4^-$ . X-ray crystallographic studies show that these complexes consist of mixed valent  $[\text{Mn}^{II}\text{Mn}^{III}(\mu_3\text{-O})_{10}(\mu_4\text{-O})_4]$  core with peripheral chelation provided by eighteen acetate ligands and six hmp<sup>-</sup> or hep<sup>-</sup> ligands, and two terminal water molecules. The magnetic behaviors observed by SQUID magnetometer reveal these Mn18 complexes could be regarded as new members of SMMs. Furthermore, The dodecanuclear manganese cluster with the composition  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_4\text{H}_4\text{S})_{16}(\text{H}_2\text{O})_4]$  has been synthesized from the ligand substitution reaction of Mn12ac and thiopheneacetic acid. The magnetization measurements show hysteresis loops with distinct staircase 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 new Mn18 SMMs and the new S-containing Mn12 clusters and their molecular films will be presented.

**K4.6**  
STM/STS ON OLIGO(PHENYLENEETHYNYLENE)MOLECULAR WIRES. Geetha Dholakia, Wendy Fan, Jessica Koehne, 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 (I-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 electronegative nitrogen, instead of a carbon in the central phenyl ring. The scanning tunnelling studies on the monolayers of these wires self assembled on Au(111) substrate show that the topography and I-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 electronegative N atom in the central phenyl ring of these wires does not significantly alter the self assembly or the transport properties.

**K4.7**  
RESISTANCE MEASUREMENTS OF CONDUCTING C<sub>60</sub> MONOLAYERS FORMED ON NOBLE METAL FILMS. Ryo Nouchi and Ikuo Kanno, Department of Nuclear Engineering, Kyoto University, Kyoto, JAPAN.

The superconductivity in alkali fullerides is caused by the low work function of alkali metals and the high electron affinity of C<sub>60</sub> molecules which favor charge transfer across C<sub>60</sub>-metal interfaces. This charge transfer effect is not particular to alkali or alkali-earth metals. Electrons can be transferred from noble metals to C<sub>60</sub> molecules, although the work functions of noble metals are higher than those of alkali metals. In alkali fullerides, alkali metals occupy the interstitial sites of the C<sub>60</sub> lattice, for the cohesive energy of alkali metals is sufficiently low. Noble metals, however, have higher cohesive energy, and cannot intercalate into the C<sub>60</sub> lattice to form a three-dimensional solid solution. For the case of depositing C<sub>60</sub> on noble metal films, therefore, the bilayer structure is formed. Electrons transfer to the adjacent monolayer of C<sub>60</sub> from metal atoms and make a conducting C<sub>60</sub> monolayer. Hebard *et al.* [1] performed *in-situ* resistance measurements, which enable us to see the charge transfer by the change in sheet resistance while depositing C<sub>60</sub> on thin noble metal films or vice versa, for the C<sub>60</sub>/Cu bilayer structure and reported that the resistance of a conducting C<sub>60</sub> 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<sub>60</sub> monolayers formed on noble metal (Au, Cu, and Ag) underlayers by *in-situ* resistance measurements. [1] A.F. Hebard, R.R. Ruel, and C.B. Eom, *Phys. Rev. B* 54, 14052 (1996).

**K4.8**  
CHARACTERIZATION OF SELF-ASSEMBLED MONOLAYERS USING NEAR EDGE X-RAY ABSORPTION SPECTROSCOPY. Trevor Willey, A.L. Vance, T. van Buuren, C. Bostedt, A.J. Nelson, L.J. Terminello, C.S. Fadley.

We have investigated methyl and carboxyl terminated alkanethiols (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 alkanethiols supposedly 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-ordering methyl-terminated alkanethiols. We have also investigated attachment and order of more complex, thioctic acid derivatives. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL UCRL-JC-143498-ABS.

#### **K4.9**

**THEORETICAL STUDY ON JUNCTION OF METAL PORPHYRIN FOR USE AS A NANOSCALE DEVICE.** Hiroshi Mizuseki<sup>a</sup>, Nobuaki Igarashi<sup>a</sup>, Rodion V. Belosludov<sup>a</sup>, Amir Farajian<sup>a</sup>, Chiranjib Majumder<sup>b</sup> and Yoshiyuki Kawazoe<sup>a</sup>; <sup>a</sup>Institute for Materials Research, Tohoku University, Sendai, JAPAN; <sup>b</sup>Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Center, Mumbai, INDIA.

Recently, the molecular electronics has attracted strong attention as a "post-silicone 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 results. Aromatic molecules have  $\pi$ -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  $\pi$ -electron density and thereby creating acceptor (p-type) and donor (n-type) molecular subunits. Therefore, a rectifier could 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 (2-3). Porphyrin possesses good electron-donating properties due to its large easily ionized  $\pi$ -electron system, and a long molecular wire of fully conjugated porphyrin polymer was reported by Tsuda *et al.* (4). In this study, we propose rectifier diode can be created by combining two metal porphyrin molecules with different metal atom. To estimate 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. Mizuseki, and Y. Kawazoe, J. Phys. Chem. A, Vol. 105 (2001) 9454. (3) H. Mizuseki, K. Niimura, C. Majumder, and Y. Kawazoe, Comput. Mater. Sci., in press. (4) A. Tsuda and A. Osuka, Science Vol. 293 (2001) 79.

#### **K4.10**

**NANOSCALE BUILDING BLOCKS AND NANOASSEMBLY OF STRUCTURES.** Sathyajith Ravindran, Mihri Ozkan, University of California Riverside, Dept of Chemical and Environmental Engineering, Riverside, CA; Brooke Colburn, Cengiz Ozkan, University of California Riverside, Dept of Mechanical Engineering, Riverside, CA.

Electronics 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 assemble nanostructures and devices. This involves the assembly of atom- and molecule-like nanostructures into functional 2-D and 3-D units. This will take advantage of the unique optical, electronic, and size-tunable properties of nanostructures and permit the use of these properties for "real" applications in a larger system (> 10 nm and < 1  $\mu$ m). Here, we demonstrate a novel technique for the fabrication of nano-assemblies of carbon nanotubes (CNT) and quantum dots (QD) (CNT-QD conjugates) for the first time using a zero length cross-linker. CNT's are primarily functionalized with carboxylic end groups by oxidation in concentrated sulfuric acid. Thiol stabilized QD's in aqueous solution with amino end groups were prepared in the laboratory. The ethylene carbodiimide coupling reaction was used to achieve the CNT-QD conjugation. Sulfo-N-Hydroxysuccinimide (sulfo-NHS) was used to enhance this coupling procedure. We present EDS and FTIR data for the chemical modification and SEM images of the first nano-building blocks. Current work includes the more complex 3-D assembly of QD's and nanotubes on Anodized Aluminum Oxide (AAO) template for

nanodevices. Potential future applications of our method include the fabrication of novel electronic and photonic devices, crystal displays and biosensors.

#### **K4.11**

**SYNTHESIS AND CHARGE TRANSPORT PROPERTY OF DITHIOL-TERMINATED 2,2'-BIPYRIDINE-TRANSITION METAL COMPLEXES.** Sylvia Asano, Wendy Fan, Geetha Dholakia, Jie Han, Eloret Corp., Mountain View, CA; Jessica Koehne, M. Meyyappan, Eloret Corp., Mountain View, CA; NASA Ames Res. Ctr., Mountain View, CA; Chongwu 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 electronic conduction behavior. Studies have shown that certain oligo(phenyleneethynylene)s containing nitro groups exhibit NDR (negative differential resistance) effect and thus have potential applications towards electronic switching and memory devices. 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 responsible. 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'-dithiol 2,2'-bipyridine and its Ru (II) and Co (II) coordination complexes. We choose the 2,2'-dipyridine 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(PHENYLENEETHYNYLENE)S.**

Jessica Koehne, NASA Ames Research Center, Moffett Field, CA; Wendy Fan, ELORET Corporation, Moffett Field, CA; Chao Li, University of Southern California, Los Angeles, CA; Chongwu 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 Tour have shown that oligo(phenyleneethynylene)s 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 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(phenyleneethynylene) analogs using repetitive Sonagashira 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 I-V curves, as well as longer retention times. The results strongly indicate that the redox properties of a molecule at least partially responsible for the electron transport behavior.

#### **K4.13**

**NEW METHODS TOWARDS PREPARATION OF CONJUGATED OLIGOMERS CONTAINING ARYL THIOLS.** Wendy Fan, Sylvia Asano, Jie Han, Eloret Corp., Moffett Field, CA; Jessica Koehne, 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, conjugated systems with aryl thiol termini 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 was to incorporate aryl thioacetate onto the conjugated systems through metal-catalyzed coupling reactions. Due to the high

reactivity of the aryl thioacetate, 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 thiol acetate in high yields. We further demonstrate the usefulness of these methods by efficient synthesis of two class of conjugated oligomers that were previously difficult to prepare. These syntheses use a new approach in which the entire molecules were constructed with thiol/thioacetate groups masked in the form of halide or amine, bypassing the dilemma where the thioacetate is incompatible with the 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 thiols.

#### SESSION K5:

Chair: Jean-Philippe Bourgoin  
Wednesday Morning, April 23, 2003  
Nob 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 ADDRESSING. A. Drezet, M. Brun, M. Nasse, N. Chevalier, J.C. Woehl, S. Huan, Laboratoire de Spectrometrie 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 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 analysing 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 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, monitoring the light polarisation allows to control 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 implications of this control of optical processes over a single dot scale will be discussed. [1] C.J. Bouwkamp, Philips Res. Rep. 5, 321 (1950) [2] E. Betzig and R.J. Chichester, Science 262, 1422 (1993) [3] C. Soennichsen et al., APL 76, 140 (2000).

#### 9:00 AM \*K5.2

CONTACT EFFECTS IN MOLECULAR JUNCTIONS. C. Daniel Frisbie, 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 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 estimated 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 plots to zero length. We find that contact resistances in molecular junctions are sensitive 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 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 Donhauser, Amanda Moore, Thomas Pearl, Brent Mantooth, Sanjini Nanayakkara, 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 serve as test structures for measurements on 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 function 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 persistence 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 DITHIENOTHIOPHENES FOR FETS. Joseph Frey, Steffen Proemmel, Kai Siegenthaler, Andrew B. Holmes, University of Cambridge, Melville Laboratory, Cambridge, UNITED KINGDOM.

Dithienothiophene 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 annelation procedure based on the conjugate addition of thioglycolic esters to 2,5-diformyl-3,4-dibromothiophene. The procedure can be adapted to the corresponding 2,5-diacylthiophenes and readily delivers full differentiation of the substituents. Using novel directed metallation procedures we have been able to prepare a range of suitably substituted dithienothiophene derivatives for Stille 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 Abusch-Magder, Shu Yang, Nikolai Zhitenev, and Zhenan 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 principals. Stimulating work involving imaging and electrical measurements has been reported over the past decade, with one focus being alkane thiol monolayers on Au(111).<sup>1, 2</sup> 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 conjugated materials were examined, permitting the study of conductive "wires" isolated in a lower conductivity matrix. Finally, diblock co-polymers 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 (1998). 2. X.D. Cui, A. Primak, et al., Science 294, 571 (2001). 3. N.B. Zhitenev, Phys. Rev. Lett. 88, 226801(2002) 4. S. Datta, W.D. Tian, et al., Phys. Rev. Lett. 79(13), 2540 (1997). 5. M. Dorogi, J. Gomez, et al., Phys. Rev. B 52(12), 9071 (1995). 6. T.D. Danbar, 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. Erbe, B. de Boer, Z. Bao, N. Zhitenev, 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 the well known metallic 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 well adjustable and on the order of several tens of nm<sup>2</sup>. 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 of the junction. We present electrical measurements 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 those features can be affected by changes in applied gate voltage.

#### 11:15 AM **K5.7**

##### SCANNING PROBE MICROSCOPY OF SELF-ASSEMBLED MONOLAYERS OF HIGHLY CONJUGATED MOLECULES.

R. Ross Getty, Simona Percec, Paula Hietpas, and Roger French, DuPont Central Research and Development, Wilmington, DE; Dawn A. Bonnell, R. Tony Alvarez, Rui Shao, and Zonghai Hu, Univ of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA.

Scanning probe microscopy was carried out on self-assembled monolayers (SAMs) of a number of new 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 Torma, Technische Universität Wien, Institute für Materialchemie; Ulrich Simon, Universität Aachen, Institute für Anorganische Chemie; Olivia Vidoni and Günter Schmid, Universität Essen, Institute 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 Au<sub>55</sub> 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 dithiols 1,5-dithionaphthaline, 4,4'-thiobis(benzenethiol), and 2,8-dithio-6-hydroxypurine have been used as bifunctional covalent linkers either in their monomeric form or, in the presence of air, dimerized 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 monodentate ligands as triphenylphosphine, linked only by van der Waals forces, or by using bifunctional spacers like 4,4'-diamino-1,2-diphenylethan that interact with the clusters by ion attractions. The study of the activation energies clearly indicates that in the case of non-covalently organized nanoparticles 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 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 reminds to an inner-sphere mechanism where the transport properties of the spacer play the decisive role. These findings possibly help to explain contradictory reports on the conductivity behaviour of organic molecules.

#### 11:45 AM **K5.9**

ONE- AND TWO-DIMENSIONAL SEMICONDUCTING NANOSTRUCTURES OBTAINED BY SELF-ASSEMBLING PROCESSES. Philippe Leclere, University of Mons-Hainaut, Mons, BELGIUM; M. Surin, University of Mons-Hainaut, Mons, BELGIUM; O. Henze, IRC, Durham (UNITED KINGDOM); W.J. Feast, IRC, Durham (UNITED KINGDOM); F. Biscarini, CNR, Bologna, ITALY; E.W. Meijer, Tue, Eindhoven, THE NETHERLANDS; A.C. Grimsdale, MPI-P, Mainz, GERMANY; K.M Ilen, MPI-P, Mainz, GERMANY; J.L. Braédas, 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, field effect transistors, solar cells, ...) 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 the 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-defined nanostructures. Here, 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-dissolved conjugated block copolymers or oligomers, and demonstrate that the conjugated molecules can organize onto a surface over lengthscales from nanometers to several microns, forming semiconducting fibrils by  $\pi$ -stacking processes. 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 molecule/surface interactions. When they are weaker, the unidimensional supramolecular organization is 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 supramolecular assemblies.

SESSION K6/M5: JOINT SESSION  
NANOTUBES AND NANOWIRES THEORY  
Chairs: George Gruner and Tchavdar Todorov  
Wednesday Afternoon, April 23, 2003  
Nob Hill A/B/C/D (Marriott)

#### 1:30 PM \***K6.1/M5.1**

QUANTUM TRANSPORT THEORY IN CARBON NANOSTRUCTURES. Vincent Meunier, William Shelton, Thomas Zacharia, Oak Ridge National Laboratory, Oak Ridge, TN; 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 nanostructures are found in various morphologies and dimensionalities, it is particularly important to acquire a precise understanding of the process 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 (Haeckelites) nanotubes, coalesced nanopeapods, as well as complex intramolecular networks 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 \***K6.2/M5.2**

MANY-ELECTRON EFFECTS AND OPTICAL RESPONSE OF CARBON NANOTUBES. Steven G. Louie, 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 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 two-particle Greens function, yield both exciton states and optical absorption spectra. 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 semiconducting nanotubes and even in some metallic tubes. These exciton states dominate the optical response of the system.

#### 2:30 PM \***K6.3/M5.3**

EFFECTS OF CURVATURE ON THE BANDGAPS OF QUASIMETALLIC CARBON NANOTUBES. C.T. White, Naval Research Laboratory, Washington, DC; J.W. Mintmire, I. Cabria, 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 tubes 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 confirmed 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 valence tight-binding model. While comparing well to our earlier numerical results and experiment, this expression shows that the band gap in these tubes should depend sensitively on both on nearest neighbor carbon-carbon pi and sigma interactions. The possible consequences of these results for the use of quasimetallic tubes as electromechanical gauges will be discussed.

### 3:30 PM \*K6.4/M5.4

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. Lammert and Peihong Zhang, Departments of Physics 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 nanocones have a rotational phase defect; this defect creates a novel geometrical phase 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 propose two new boron-based tubular structures, one of which is always semiconducting and the other always metallic.

### SESSION K7:

Chair: Tchavdar Todorov  
Wednesday Afternoon, April 23, 2003  
Nob Hill C/D (Marriott)

### 4:00 PM K7.1

THEORETICAL STUDY ON SINGLE CONDUCTING MOLECULAR WIRE COVERED BY MOLECULAR NANOTUBE: APPLICATION IN MOLECULAR ELECTRONICS.

Rodion V. Belosludov, Hiroyuki Sato, Amir A. Farajian, Hiroshi Mizuseki, Yoshiyuki Kawazoe, 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 of circuits shrink below 100 nm [1]. 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 is 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 encapsulated by insulated 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 nanotube of cross-linking  $\alpha$ -CDs and  $\beta$ -CDs has near-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 molecular 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. Belosludov, H. Mizuseki, K. Ichinoseki and Y. Kawazoe, Jpn. J. Appl. Phys. 41, (2002) 2739. [3] T. Shimomura, T. Akai, T. Abe and K. Ito, J. Chem. Phys. 116, (2002) 1753.

### 4:15 PM K7.2

EFFECTS OF DYNAMICAL DISORDER ON CHARGE TRANSPORT IN DNA. G. Kalosakas, K.O. Rasmussen, P. Maniadis, 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 and coincides with the polaronic life-time. However, above 50-70 K the confinement time exhibits an exponential *increase* with temperature indicating that polaronic effects are irrelevant for conduction at elevated temperatures. Calculations of the AC conductivity of the double stranded DNA are also presented.

### 4:30 PM K7.3

SIMULATIONS OF NON-EQUILIBRIUM TRANSPORT IN PHENYLENE-ETHYNYLENE OLIGOMERS. Jeremy Taylor, Mads Brandbyge, and Kurt Stokbro, Mikroelektronik Centret, Tech Univ of Denmark, Lyngby, DENMARK.

Using an ab-initio green's function technique, as implemented in the Transiesta [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 class of phenylene-ethynylene oligomers [2]. We have used the method to investigate the IV characteristics of an Aviram-Ratner type molecular diode as well as a symmetric phenylene-ethynylene oligomer[3]. The calculations reveal that the electrode coupling plays an important role, and that 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-ethynylene with nitro side groups[2] have shown Negative Differential Resistance. We have calculated the IV characteristics of Phenylene-ethynylene oligomers with a variety of sidegroups, and based on these calculations we discuss the origin of the complex electrical properties of such systems. [1] M. Brandbyge, J.L. Mozos, P. Ordejon, J. Taylor, K. Stokbro, Phys. Rev. B. 65, 165401 (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).

### 4:45 PM K7.4

METALLIC PROPERTIES OF SILICON NANOWIRES.

Inder P. Batra and T. Ciani, 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 inter-connects 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 ( $d = 2.2\text{\AA}$ ) 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 dimerization 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  $\alpha \approx 117^\circ$  zigzag W structure with  $d = 2.2\text{\AA}$ . The cohesive energy of the W 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 inter-atomic distance (2.4  $\text{\AA}$ ) is close to the bulk value. The charge density analysis shows that Si atoms are held together by strong  $\sigma$  bonds, that "float" in a sea of delocalized  $\pi$  electrons much like in free electron metals. From the electronic structure we estimate conductance value using the Heisenberg's uncertainty principle. Assuming that the metallic behavior will not change drastically when one goes from infinite to a finite system (and there are good reasons to be optimistic) then such metallic silicon nanowires will help achieve a major integration in nanotechnology.

### SESSION K8:

Chair: Serge Huant  
Thursday Morning, April 24, 2003  
Nob 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. Zhitenev, D. Abusch-Magder, 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. Ermakov, E. Garfunkel,

Department of Chemistry, Rutgers University, New Brunswick, NJ; M. Frank, 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 an important step towards understanding molecular-scale electronics. In order to correlate the properties of the self-assembled monolayer with the molecular structure, a series of p-conjugated mono- and dithiols have been designed and synthesized. Their self-assembled monolayer films on gold surfaces were characterized by cyclic voltammetry, grazing incidence FTIR, STM, 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 the self-assembled molecular wires will be presented.

#### 9:00 AM \*K8.2

**ELECTRONIC TRANSPORT THROUGH INDIVIDUAL ORGANIC MOLECULES.** Heiko B. Weber, M. Mayor, J. Reichert, D. Beckmann, Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Karlsruhe, GERMANY.

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 spatial symmetry, showed discrete stable conductance patterns. While the asymmetric molecule always generated asymmetric current-voltage relations (IVs), the symmetric molecules often showed symmetric IVs. This allows clearly to identify the IVs as transport through our sample molecules. The body of our data strongly suggests that each stable junction is related to current through only one single molecule, connected to both metal electrodes. Considerable differences between subsequently manipulated junctions, i.e. sample-to-sample fluctuations are attributed mainly to varying microscopic contact realisations. This is clearly demonstrated by intentionally inducing different asymmetric IVs with the symmetric molecule upon tuning the electrode 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 *trans*-Pt complex as insulating linker between delocalized  $\pi$ -electron systems on a single molecule level [3].

We further describe new experimental advances to gain more information about the molecular junction. In particular, measurements at low temperatures (T 10 K) improve the data quality considerably.

[1] J. Reichert, R. Ochs, D. Beckmann, H.B. Weber, M. Mayor, and H. v. Löhneysen, Phys. Rev. Lett. **88**, 176804 (2002).

[2] H.B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, and H. v. Löhneysen, Chem.Phys. **281**, 113 (2002).

[3] M. Mayor, C. von Hänisch, H.B. Weber, J. Reichert, and D. Beckmann, Angewandte Chemie **41**, 1183 (2002).

#### 9:30 AM K8.3

**SINGLE-ATOM TRANSISTORS.** Abhay Pasupathy, Jiwoong Park, Jonas Goldsmith, Connie Chang, J.P. Sethna, H.D. Abruna, Paul McEuen, and Daniel Ralph, Cornell University, Ithaca, NY.

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 electromigration to form nm-scale gaps in which single molecules can be attached. We have studied both 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 vibration-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 C<sub>140</sub> TRANSISTORS.** Jiwoong Park, Abhay N. Pasupathy, Connie Chang, Radoslaw Bialczak, James P. 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 electrons flow through discrete quantum states of single molecules, C<sub>70</sub> fullerene and its dimer(C<sub>140</sub>). In C<sub>140</sub> devices, an excited level was observed near 11 meV and multiples of 11meV corresponding to excitations of an intercage (ball-to-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 C<sub>140</sub> molecules.

#### 10:30 AM \*K8.5

**MOLECULAR DEVICES AND CIRCUITS.** Supryio 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, 2003

Nob Hill C/D (Marriott)

#### 1:30 PM \*K9.1

**HYBRID REACTIVE/ELECTROSTATIC SELF-ASSEMBLY OF ORGANIC POLAR MULTILAYERS FOR SECOND ORDER NONLINEAR OPTICS.** P.J. Neyman, C. Brands, J.R. Heflin, Virginia Tech, Dept of Physics, Blacksburg, VA; M.T. Guzy, R.M. Davis, K.E. Van Cott, Virginia Tech, Dept of Chemical Engineering, Blacksburg, VA; H. Wang, H.W. Gibson, Virginia Tech, Dept of Chemistry, Blacksburg, VA.

Ionically self-assembled monolayer (ISAM) films have been recently shown to spontaneously assemble with a noncentrosymmetric ordering that gives rise to a substantial second order nonlinear optical (NLO) response. Typically, polar ISAM films are made from two oppositely-charged polyelectrolytes with an ionic, conjugated NLO chromophore attached as a side-chain to one of the polymers. The  $\chi^{(2)}$  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  $\chi^{(2)}$  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  $\chi^{(2)}$  values as large as  $30 \times 10^{-9}$  esu, fifteen times that of quartz. Variation of the solution pH allows one to turn 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. Silaghi<sup>a</sup>, G. Salvan<sup>a</sup>, T.U. Kampen<sup>a</sup>, M. Friedrich<sup>a</sup>, R. Scholz<sup>a</sup>, H. Angermann<sup>b</sup>, D.R.T. Zahn<sup>a</sup>. <sup>a</sup>Institut für Physik, Technische Universität Chemnitz, Chemnitz, GERMANY; <sup>b</sup>Department of Silicon Photovoltaics, Hahn-Meitner-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.<sup>1,2</sup> Raman spectroscopy is very well

known as a non-destructive technique suitable for characterizing structural and the interfacial properties of molecular layers. Here, surface-enhanced Raman spectroscopy is used to investigate ultrathin guanine and cytosine films on silicon substrates. Very thin layers, like monolayers of guanine and its counterpart cytosine are prepared by organic molecular beam deposition (OMBD) under UHV conditions on H-terminated flat and vicinal Si(111) surfaces. Onto these biomolecular layers silver is evaporated leading to an enhancement of the Raman signal. Significant spectral changes observed in SERS spectra below  $730\text{cm}^{-1}$  in the out-of-plane region of CH, NH deformation modes are related to changes in morphology of thin cytosine layers around 1 nm compared to thick layers around 450nm. On vicinal H-Si(111) surfaces miscut  $6^\circ$  toward  $[111]$  guanine monolayers are found to be in a different molecular arrangement than on flat H-Si(111) surfaces. DFT/B3LYP calculations with the basis set LANL2DZ were carried out on silver-cytosine and silver-guanine complexes using the Gaussian '98 software package. The experimental vibrational modes observed in SERS spectra are in very good agreement with the calculated values. The donor character of guanine and the acceptor one of cytosine distinguished in SERS spectra and calculations are discussed in terms of charge transfer (CT). [1] R. Di Felice et al., "Phys. Rev. B", 65 (2001). [2] A. Calzonari et al., "Appl. Phys. Lett.", 80, 18 (2002).

### 2:15 PM K9.3

NEW BIOSENSOR STRATEGIES BASED ON LIGHT HARVESTING WATER SOLUBLE CONJUGATED POLYMERS. Brent S. Gaylord, Bin Liu, Shu Wang, Guillermo C. Bazan, Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA.

Homogeneous biosensor assays can be designed which take advantage of the optical amplification of conjugated polymers and the self-assembly characteristic of aqueous polyelectrolytes. For example, a ssDNA sequence sensor comprises an aqueous solution containing a cationic water soluble conjugated polymer such as poly(9,9-bis(6'-N,N,N-trimethylammonium)-hexyl)-fluorene phenylene) with a peptide nucleic acid (PNA) labeled with a dye (PNA-C\*). Signal transduction is controlled by hybridization of the neutral PNA-C\* probe and the negative ssDNA target, resulting in favorable electrostatic interactions between the hybrid complex and cationic polymer. Distance requirements for Förster energy transfer are thus met only when ssDNA of complementary sequence to the PNA-C\* probe is present. Signal amplification by the conjugated polymer provides fluorescein emission >25 times higher than that of the directly excited dye, allowing detection of target DNA at concentrations of 10pM using a standard fluorometer. Transduction by electrostatic interactions followed by energy transfer is a general strategy. Examples involving other biomolecular recognition events will be provided. Finally, we will probe the mechanism of biosensing, with special attention to the varying contributions of hydrophobic and electrostatic forces.

### 2:30 PM K9.4

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

Formed at nanoscale break junctions, spatially resolved, individual Ag nanoclusters (2 to 8 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 100 MHz to 3GHz, unique opportunities for greatly simplified fabrication of nanoscale electronic device are made available. Additionally, AC-excited single Ag nanocluster EL shows strong enhancement at specific AC frequencies. EL at AC enhancement frequencies yields greatly stabilized and significantly narrower spectra than those from 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 anomaly in the charge transport dynamics of the nanoscale junctions with very short pulses results from the basic electronic properties (resistance, capacitance and inductance) of the materials composing the junctions to yield resonant circuits. This novel individual Ag nanocluster EL and introduction of polarity through short pulse operation yield very useful nanoscale device properties with simple fabrication.

### 2:45 PM K9.5

SELF-ASSEMBLED MOLECULAR RECTIFYING DIODES. S. Lenfant, D. Vuillaume, C. Krzeminski, C. Delerue, Institute of Electronics Microelectronics and Nanotechnology, CNRS, Villeneuve d'Ascq, FRANCE.

Molecular rectifying diodes have been synthesized based on the Aviram and Ratner paradigm, with donor and acceptor moieties linked by a short s or even p bridge. Here we report a simplified synthesis using only one donor group and an alkyl chain using a sequential self-assembly process (SAM or self-assembled monolayer). Moreover, we demonstrate experimentally and theoretically how to control the threshold voltage for rectification in these systems. We used a chemical functionalization (by conjugated moieties) of the end-groups of alkyltrichlorosilane SAM's to fabricate insulator/semiconductor (called sigma-pi) heterostructures at a molecular level on silicon substrates. Alkyl chain lengths are comprised 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 SAM's embedded in a Si(n+ type)/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 a 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 HOMO 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-LOMO gap and reduces the threshold voltage. This approach allows us to fabricate molecular rectifying diodes owing an easily tunable property (threshold voltage, one of the important parameter in circuit design) and compatible with silicon nanotechnologies for future hybrid circuitries.

### 3:30 PM K9.6

STRUCTURE-PROPERTY STUDIES OF CONJUGATED OLIGOMERS: FROM SINGLE MOLECULES TO FILMS.

Melissa A. Summers, Michael T. Bowers, Guillermo C. Bazan, and Steven K. Buratto, Dept of Chemistry & Biochemistry, University of California, Santa Barbara, Santa Barbara, CA.

We use optical microscopy to probe the luminescence properties of oligo(phenylenevinylene) molecules with chains of five and six phenyl rings as isolated single molecules, small molecular aggregates, and bulk films. Single molecule fluorescence polarization modulation determines the relative anisotropies of single molecules within a sample. Gas-phase ion mobility experiments determine the populations of different cis-trans conformers within the same synthetic batch; correlating the statistics from the single molecule fluorescence and ion mobility experiments enables us to directly classify a single molecule's photophysical properties based on its shape. Thus, fully elongated (all trans) molecules emit with well-defined polarization anisotropy and highest peak intensity, suggesting a high emission quantum yield. When spin cast from dilute solution onto glass or polymer substrates, the oligo(phenylenevinylene) molecules tend to assemble over time into isolated aggregates with large polarization anisotropies, suggesting that these structures are comprised of elongated molecules whose dipoles are aligned. This is consistent with the herringbone packing arrangement found for similar conjugated oligomeric materials. The aggregates appear to be nucleation sites for highly ordered structures. More intricate ordering is observed for films spin cast from concentrated solutions, and spatially-resolved spectra enable us to characterize distinctive domains within these polycrystalline films.

### 3:45 PM K9.7

MOLECULAR ELECTRONICS WITH CdSe NANOCRYSTALS. E. Marx, L. Sun, S.N. Chin, H.E. Beere, D.A. Ritchie, C.J.B. Ford, N.C. Greenham, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Electrical transport in semiconductor nanocrystals is influenced by both Coulomb-blockade and resonant tunneling effects. Here, we present measurements of CdSe nanocrystals assembled in nanometer-sized metallic or semiconducting gaps. Using a shadow-evaporation technique we can reproducibly fabricate metal electrodes separated by 3 - 6 nm gaps. CdSe 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 nanocrystals. We have demonstrated successful attachment of CdSe nanocrystals onto GaAs surfaces using alkanedithiols, and have characterized the resulting structures using infrared spectroscopy, optical ellipsometry, photoluminescence, and scanning tunneling microscopy.

**4:00 PM K9.8**

**MOLECULAR ASSEMBLIES ON CHLORINATED SILICON SURFACES.** Zhiyong Li, Xuema 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) trichlorosilane or trialkoxysilane self-assembly on surfaces with native oxide (HO-terminated) surfaces, b) direct alkylation on H-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 silicon surfaces were studied by contact angle measurements, ellipsometry, AFM, XPS and FTIR.

**4:15 PM K9.9**

**FABRICATION AND CHARACTERIZATION OF REDOX-ACTIVE MONOLAYERS ON SILICON DIOXIDE FOR MEMORY APPLICATIONS.** Shyam Surthi, Qiliand Li, Guru Mathur, Srivardhan Gowda, Veena Misra, Vladimir Malinovskii, Karl-Heinz Schweikart, Lianhe Yu, Jonathan S. Lindsey, Zhiming Liu, Rajeev B. Dabke, Amir Yasserli, David F. Bocian, Werner G. Kuhr, Thomas A. Sorenson, and Robert C. Tenant.

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 test 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 capacitor with different scan rates also showed peaks due to the charging and discharging current associated with redox process. Furthermore, the redox voltages of the molecule on SiO<sub>2</sub> 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.

**4:30 PM K9.10**

**NONMETALLICITY IN ELECTROCHEMICALLY FABRICATED ATOMIC-SCALE METAL JUNCTIONS.** D. Natelson, 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", 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.

**4:45 PM K9.11**

**ELECTRICAL TRANSPORT IN Au-OCTANEDITHIOL-GaAs DIODES.** J.W.P. Hsu, Y.L. Loo<sup>†</sup>, D.V. Lang, Bell Labs, Lucent Technologies, Murray Hill, NJ; K. Raghavachari, Dept. of Chemistry, Indiana University, Bloomington, IN; <sup>†</sup>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 1,8-octanedithiol 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 (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 1,8-octanedithiol, 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.