

**SYMPOSIUM T**  
**Molecular Electronics**

April 13 - 15, 2004

**Chairs**

**Cherie R. Kagan**

IBM T. J. Watson Research Center  
P.O. Box 218  
1101 Kitchawan Rd., Rte. 134  
Yorktown Heights, NY 10598  
914-945-3003

**Marcel Mayor**

Institut fuer Nanotechnologie  
Forschungszentrum Karlsruhe GmbH  
Postfach 3640  
Karlsruhe, D-76021 Germany  
49-7247-82-6392

\* Invited paper

**8:30 AM \*T1.1**

**Carbon Nanotube Macromolecular Electronics.** Hongjie Dai, Stanford Univ, Stanford, California.

This talk will present our latest research in carbon nanotube electronic properties and devices. The content will include ohmic contact, ballistic electron transport in both metallic and semiconducting nanotubes, pushing the performance limit of nanotube field effect transistors, and the scaling properties of both metallic and semiconducting nanotubes.

**9:00 AM \*T1.2**

**Carbon Nanotube Electronics and Photonics.** Phaedon Avouris, IBM T.J. Watson Research Center, Yorktown Heights, New York.

I will present results of transport and spectroscopic experiments and theoretical calculations to address such issues as the nature of the switching in nanotube transistors, the nanotube-metal electrode interaction, the resulting charge transfer and the role of the ambient environment on the transport properties. I will also discuss how these findings can be utilized to control the characteristics of nanotube field-effect transistors. Carbon nanotubes are direct gap materials and their one-dimensional character has important implications for their electro-optical properties. I will show that an ambipolar nanotube field-effect transistor device can act as a single molecule electrically-driven light source. I will present electroluminescence spectra, polarization data, quantum yields and the dependence of light intensity on drain and gate bias that prove that the light is generated through radiative recombination of electrons and holes in the nanotube channel. The reverse process of current generation through IR laser irradiation of a single nanotube FETs will also be demonstrated. Resonant photoconductivity spectra from individual nanotubes will be compared with experimental absorption spectra and theoretical calculations on nanotube exciton states.

**9:30 AM T1.3**

**Tunable Charge Transport Across a Metal to Carbon Nanotube Junction.** Sujit Kumar Biswas<sup>1</sup>, Robert Vajtai<sup>2,3</sup>, Yung Joon Jung<sup>2</sup>, Leo Schowalter<sup>1</sup> and Pulickel Ajayan<sup>1</sup>; <sup>1</sup>Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; <sup>3</sup>Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

Junctions play a major role in determining the conductive properties of a circuit consisting of nanotubes and metal electrodes. The band structure of the nanotubes and the metal electrodes, coupled with the environment result in the unique current voltage characteristics. We have made use of conductive tip atomic force microscopy to study individual nanotube circuits. Through combination of scanning potential and current spectroscopy, and using the principle of transmission line model, we have isolated the contributions to the resistivity along the nanotube from that of the junctions. The contact potential between the nanotubes and the metal electrodes are found to depend on the specific metal used, and the environment. Atmospheric gases, chemical treatment, and substrate characteristics on which the circuit is fabricated strongly affect the resistance of these junctions. We believe that the adsorbents perturb the work function difference between the nanotube and metal causing these changes. This phenomenon can be used to tune the contact resistance, making it possible to identify recipes for different modes of current injection into the nanotubes. We can also consider the variations as a possible chemical sensor. Multiple nanotubes on a substrate form a complex network, with many junctions. Charge transport through the interface between molecules is expected to be associated with a very high resistance. We have found that appreciable current can be made to flow from one nanotube to another, which is in physical contact. The associated resistance is comparable to that of metal junctions, and can be analyzed similarly. The nanotube to nanotube junction properties can be varied with electrostatic fields set up using a back gate contact to the conductive substrate, and by altering the chemical environment.

**9:45 AM T1.4**

**Modeling of Carbon Nanotube Schottky Barrier in Gaseous Environment.** Toshishige Yamada, NASA Ames Research Center, Moffett Field, California.

A model is proposed for the lower Schottky barrier for hole transport in air than in vacuum at a metallic electrode - semiconducting carbon nanotube (CNT) junction observed in the experiment [R. Martel et al., Phys. Rev. Lett. 87, 256805 (2001)]. We consider the electrostatics

of a transition region between the electrode and the CNT in the presence (air) or absence (vacuum) of oxygen molecules, where an appreciable potential can drop. The oxygen molecules are negatively charged because of their large electronegativity, and counter positive charges appear in both the electrode and the CNT to shield the oxygen charge under a closed circuit condition. The oxygen charge increases the potential drop in the transition region and leads to a lower Schottky barrier for hole transport. The Schottky barrier difference in air and in vacuum is large when a CNT depletion mode is involved, while the difference is negligible when only a CNT accumulation mode is involved. The mechanism prevails in both p- and n-CNTs, and the model consistently explains the key experimental findings. The model can be extended to the Schottky barrier modulation due to other gases.

**10:30 AM \*T1.5**

**Electrochemistry With Individual Single-Walled Carbon Nanotubes.** Jing Kong, I. Heller, H.A. Heering, K. Williams, S.G. Lemay and C. Dekker; Department of Nanoscience, Delft University of Technology, Delft, Netherlands.

Single-walled carbon nanotubes (SWNT) are seamless cylinders of sp<sup>2</sup> carbon, with diameters of 0.7-2 nm and lengths of 0.1-10 μm. Depending on chirality, SWNT are either metallic or semiconducting. SWNT can be derivatized with proteins and oligonucleotides by amide chemistry. The goal of this work is to use metallic SWNT as electrochemical nanoprobe for biomolecules. Nanotubes on a surface are contacted by nanolithography and insulated by a layer of resist with windows to partially expose them. To test the electrochemical properties of such SWNT electrodes, the devices are immersed in solutions of ferrocene derivatives, and the current is measured as function of the applied potential difference between the nanotube and a Ag/AgCl reference electrode. The results show that the SWNT is acting as an ideal, nanoscopic carbon electrode. This opens the exciting possibility to study individual biomolecules, tethered to a nanotube electrode.

**11:00 AM T1.6**

**Engineering of NT electronic properties by symmetry breaking: Application for molecular devices.** Slava V Rotkin, Beckman Institute, UIUC, Urbana, Illinois.

Nanotube (NT) materials are very promising for use in molecular electronic devices, in particular in field effect transistors (FETs). For the FET applications semiconductor NTs are used nowadays, because a metallic conductance is thought to prevent the penetration of the electric field except for extremely short distances, too short to achieve device function. We propose a new approach to control electronic transport in metallic one dimensional systems, for example, NTs or nanowires by use of the inhomogeneous electric field induced by a highly localized gate such as an STM tip, nanotube tip or metallic nano-interconnect. The highly localized gate induces a high electric field in a narrow region. This inhomogeneous electric fields lead to the opening of a band gap in carbon nanotubes due to the symmetry breaking. We also study symmetry breaking due to effect of the substrate and variation of NT materials properties following the symmetry breaking. Even a simplest spatial variation of the band gap resulted from the (spatial modulated) pattern and subsequent lowering of the symmetry can be used for molecular switch applications. We discuss also possibilities for engineering of NT smart material which will have better control of electronic properties and higher functionality than a simple lithographic circuit.

**11:15 AM T1.7**

**Fabrication of vertical cross junctions for hybrid molecular diode arrays.** Erik Dujardin<sup>1,2</sup>, Vincent Derycke<sup>1</sup>, Marcello Goffman<sup>1</sup> and Jean-Philippe Bourgoin<sup>1</sup>; <sup>1</sup>Service de Chimie Moleculaire, CEA / Saclay, Gif-sur-Yvette, France; <sup>2</sup>NanoScience Group, CNRS - CEMES UPR 8011, TOULOUSE, France.

Hybrid-molecular electronics is one actively explored alternative to the CMOS-based technology. In this approach, the active part of the device is composed of a limited number of functional molecules but the connections are conventionally fabricated by nanolithography techniques. Among various potential architectures, the vertical cross junction architecture presents several technological assets: it is compatible with the deposition of molecules organized in self-assembled monolayers, well adapted to implement a molecular equivalent of semiconductor resonant tunneling diode arrays and it can be extrapolated to very high integration level (> 10<sup>11</sup> devices / cm<sup>2</sup>) and to small numbers of molecules per device (~ 400). We will report on the fabrication process of vertical crossbar devices which address critical issues such as pinhole defect formation when the top electrode is evaporated or precise deposition of pre-synthesized nanowires when these are used as top electrode material. Indeed, we will show how a chemically reactive pattern can be used to direct the deposition of carbon nanotube (CNT) so that they are suspended over

a bottom metallic electrode functionalized with molecules. Using this technique, we will show how switches based on CNT can be prepared, the characteristics of which depend on the geometry of the arrangement. In addition first measurements on molecules will be shown.

#### 11:30 AM **T1.8**

**Large-scale fabrication of carbon nanotube-based circuit structures via self-assembly strategy.** Seunghun Hong<sup>1</sup>, Saleem Rao<sup>2</sup> and Ling Huang<sup>2</sup>; <sup>1</sup>Physics, Seoul National University, Seoul, South Korea; <sup>2</sup>Physics, Florida State University, Tallahassee, Florida.

Carbon nanotube-based nanoelectronic devices, such as transistors and sensors, can be much smaller and more versatile than conventional microelectronic chips, but a lack of massive assembly method of such devices has been holding back their practical applications. Inspired by biomolecular self-assembly processes, we have created chemically functionalized patterns on a surface, to which pre-grown nanotubes in solution can align themselves in huge numbers [1]. This method allows wafer-scale fabrication of millions of carbon-nanotube circuits with single-nanotube precision, and may enable massive production of nanotube-based devices. [1] Nature 425, 36 (2003).

#### 11:45 AM **T1.9**

**Atomic-scale Topographic and Electronic Characterization of Single-walled Carbon Nanotubes on Silicon Surfaces.** Peter Michael Albrecht and Joseph W Lyding; Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

An ultrahigh-vacuum scanning tunneling microscope (UHV-STM) is used to elucidate the electrical and mechanical properties of individual single-walled carbon nanotubes (SWNTs) and to ascertain their atomistic interactions with silicon surfaces. Atomically-resolved topographic imaging, combined with local density of states (LDOS) information inferred from spatially-selective dI/dV tunneling spectroscopy, make the UHV-STM an ideal instrument for correlating SWNT physical features with the associated electronic signatures. We employ a novel in situ dry deposition technique to generate an atomically pristine interface between SWNTs and silicon [1]. This solid-phase deposition process, whereby HiPco SWNTs are transferred to the substrate in UHV by direct mechanical contact, circumvents several undesirable consequences often encountered with solution-based schemes, including unintentional doping of SWNTs by charged species and residual substrate contamination by nonvolatile adsorbates. Results to be presented include UHV-STM topographic and current images showing simultaneous atomic resolution of SWNTs and the proximal H-passivated Si(100). Furthermore, tunneling spectroscopy reveals specific electronic features unique to semiconducting and metallic SWNTs, respectively. The theoretically-predicted constant tunneling conductance (I/V) about the Fermi level for an isolated armchair metallic SWNT is measured to be invariant to the presence of a supporting substrate with a semiconducting gap > 1 eV. All of our experiments to date suggest that the UHV dry deposition scheme results in the transfer of predominantly isolated SWNTs, rather than cumbersome SWNT ropes or catalyst particles, to the silicon surface. This fortuitous outcome sets the stage for sensitive electronic measurements that are unperturbed by tube-tube interactions arising within a bundle. We will also demonstrate how the STM tip can be implemented to cut and precisely manipulate SWNTs. A H-terminated Si(100) surface lends itself to lithographic patterning via the controlled desorption of H by the STM tip [2]. One can exploit the chemical contrast between the highly reactive Si dangling bonds and the relatively inert H-passivated background to engineer the local environment at an arbitrary position along the SWNT. Lastly, the dry transfer technique is generalizable to the deposition of sensitive and/or nonvolatile molecules and nanoparticles onto a wide range of surfaces that are incompatible with ambient exposure [3]. The ultimate goal of our experimental effort is the nanofabrication of hybrid SWNT-Si devices and circuits leveraging these two unique electronic materials synergistically. [1] P. M. Albrecht and J. W. Lyding, Appl. Phys. Lett. (in press). [2] J. W. Lyding et al., Appl. Phys. Lett. 64, 2010 (1994). [3] L. B. Ruppalt, W. Ye, P. M. Albrecht, and J. W. Lyding (unpublished).

SESSION T2: Molecular Self-Assemblies  
Chair: Marcel Mayor  
Tuesday Afternoon, April 13, 2004  
Room 3008 (Moscone West)

#### 1:30 PM **\*T2.1**

**Creating Molecular Electronic Materials through Self-Assembly.** Colin Peter Nuckolls, <sup>1</sup>Chemistry, Columbia University, New York, New York; <sup>2</sup>Nanoscience Center, Columbia University, New York, New York.

This presentation will explore methods to design, synthesize, and assemble electronic materials on molecular length-scales. One of the new chemical systems that is to be presented self-organizes into one-dimensional assemblies that are only a single molecule wide but microns in length. Efforts are aimed at devising methods to measure the electrical transport and electrostrictive properties of these systems. A second chemical system presented forms self-assembled monolayers whose constituent molecules orient their path of conjugation perpendicular to the metallic surface. From these monolayers, scanned probe microscopy and nanoscale electrode fabrication are being used in concert with further chemical assembly to create molecular electronic test structures.

#### 2:00 PM **T2.2**

**Self-Assemblies with Nanoscale Ordering for Molecular Electronics.** Alex K.-Y. Jen, Hong Ma, Kyoung-Soo Kim, Mun-Sik Kang, Seok-Ho Kang, Melvin T Zin, Hadi Zareie and Mehmet Sarikaya; Materials Science and Engineering, University of Washington, Seattle, Washington.

It is ideal to obtain highly-ordered and stable self-assembled monolayers (SAMs) with nanoscale features for exploring the charge injection/transport mechanisms in molecular electronics. Recently, several series of fused-ring aromatic self-assembling molecules have been designed and synthesized to have a variable molecular geometry through different molecular architectures,  $\omega$ -functional groups and hydrogen bonding moieties. We have found controlled self-assemblies of these molecules as crystalline arrays on gold substrates at room temperature. The size, shape, orientation and ordered assemblies of molecular wires can be engineered through a delicate interplay of the intermolecular  $\pi$ - $\pi$  stacking and chemisorptive substrate-linker interactions. In particular, the molecule based on a fused-aromatic, anthracene or pyrene, forms an ordered two-dimensionally stacked array. Through scanning tunneling spectroscopy, we demonstrate changes in electronic behavior of single molecules that form into superlattices. We have also designed and synthesized a novel functional hybrid molecule by taking advantage of the excellent physical and chemical properties of C60 and nanoscale ordering of anthryl-based SAMs. The SAM of this molecule exhibits stable and highly ordered two-dimensional arrays that form an oblique lattice at room temperature. The self-assemblies have also shown both reversible electrochemical peaks and very interesting electronic properties such as a potential negative differential resistance (NDR) effect.

#### 2:15 PM **T2.3**

**$\alpha,\omega$ -Bis(thioacyl)oligophenylenevinylene Chromophores From Thioanisole Precursors.** Dwight S. Seferos<sup>1</sup>, David A. Banach<sup>2</sup>, Norma A. Alcantar<sup>4</sup>, Jacob N. Israelachvili<sup>3</sup>, James G. Kushmerick<sup>5</sup> and Guillermo C. Bazan<sup>1,2</sup>; <sup>1</sup>Department of Chemistry and Biochemistry, UCSB, Santa Barbara, California; <sup>2</sup>Department of Materials, UCSB, Santa Barbara, California; <sup>3</sup>Department of Chemical Engineering, UCSB, Santa Barbara, California; <sup>4</sup>Department of Chemical Engineering, USF, Tampa, Florida; <sup>5</sup>Center for Bio/Molecular Science, NRL, Washington, DC, District of Columbia.

Dithiol conjugated oligomers are important surface modifying reagents, and provide a platform for assembling molecular-scale junctions and devices. In this work we demonstrate that the selective cleavage of arylmethyl thioethers provides a convenient protocol for the synthesis of all-E isomers of  $\alpha,\omega$ -bis(thioacyl)oligophenylenevinylene molecules (OPVs). The arylmethyl thioether is tolerant of Wittig and Heck-type reactions for forming OPV structures and can be converted to the S-acyl group by treatment with sodium thiomethoxide and acetyl chloride. The thermal conditions of this deprotection/reprotection step concurrently isomerize the conjugated chromophore to the all-E isomer, regardless of the stereochemistry of the starting olefins. This synthetic approach is demonstrated for a variety of linear and [2.2]paracyclophane containing OPVs, which have been characterized by both electrochemical and spectroscopic techniques. Additionally, the self-assembly of these S-acyl terminated OPVs on gold surfaces is demonstrated. Monolayers containing these molecules were characterized by water contact angle measurements, ellipsometry, and X-ray photoelectron spectroscopy. The molecular structure of the [2.2]paracyclophane containing chromophores can serve to study how a well-defined through-space delocalized unit influences electronic communication between a pair of electroactive organic units. To examine this unique property we take advantage of the S-acyl group incorporated within the molecular structure, and its ability to self-assemble on gold surfaces, to fabricate and test molecular junctions in a cross-wire test bed.

#### 2:30 PM **T2.4**

**Supramolecular Self-Assembly and Magnetic Property Study of Metalloporphyrin in Langmuir and Langmuir-Blodgett Films.** Yuhua Ni and Qun Huo; Polymers & Coatings, North Dakota

State University, Fargo, North Dakota.

The self-assembly and supramolecular engineering of porphyrins into ordered arrays have recently attracted much interests because of their promising application potentials in molecular and electronic devices, spintronics, energy harvesting and storage, catalysis, and sensor development. One of our current research interests is to develop ferromagnetic organic thin film materials for spintronics applications. Metal complexes of organic porphyrins are well-known organic paramagnetic materials. It has been reported that these paramagnetic materials could become ferro- or ferrimagnetic materials when aligned in ordered structures. Triaminotriazines are known to form highly ordered linear supramolecular self-assembly through complementary hydrogen bonding with barbituric acid molecules at the air-water interface. We recently have reported the synthesis of a novel porphyrin molecule, 2Por-TAZ, with two porphyrin macrocycles attached to a triaminotriazine head group. Further surface chemistry study, spectroscopic and microscopic characterizations have shown that this molecule formed a highly ordered linear supramolecular self-assembly with barbituric acid in Langmuir and Langmuir-Blodgett films. The long linear hydrogen bonding network domain structures were clearly observed in the images obtained from Atomic Force Microscopy. Metal complexes of 2Por-TAZ with its Co<sup>2+</sup> and Fe<sup>3+</sup> metal and their Langmuir and Langmuir-Blodgett films were also prepared and studied. The magnetic responses of these thin film materials were characterized by magnetic force microscopy and SQUID experiments. Detailed results obtained from these studies will be discussed in the presentation.

### 3:15 PM T2.5

**Self-Assembled Metal-Diisocyanide Mono- and Multilayer Films.** Sally A Swanson, Richard McClain, Katherine S Lovejoy, Jeremy S Hamilton and J Campbell Scott; IBM Almaden Research Center, San Jose, California.

In order to promote electron injection from metal electrodes into conjugated organic molecules we have studied the formation of self-assembled monolayers (SAMs) of the double-ended diisocyanides; 1,4-phenylenediisocyanide, 2,3,5,6-tetramethyl-1,4-phenylenediisocyanide, 4,4'-biphenyldiisocyanide (BPDI), 3,5,3',5'-tetramethyl-4,4'-biphenyldiisocyanide, and 4,4'-p-terphenyldiisocyanide; on gold and palladium substrates. The films were characterized using variable angle and spectroscopic ellipsometry and polarization-modulation infrared reflection-absorption spectroscopy. The SAMs of BPDI can be used to prepare multilayer thin films consisting of alternating organic and metal complex layers. In some cases, the metal complex promotes polymerization instead of the desired monolayer formation as indicated by film thickness and IR data.

### 3:30 PM T2.6

**Organic field-effect transistors solution processed from liquid crystalline phthalocyanines.** Wei Xia<sup>1</sup>, Carrie L Donley<sup>1</sup>, Britt A Minch<sup>1</sup>, Samir K Sherian<sup>2</sup>, David Mathine<sup>2</sup> and Neal R. Armstrong<sup>1</sup>; <sup>1</sup>chemistry, University of Arizona, Tucson, Arizona; <sup>2</sup>Optical Science Center, University of Arizona, Tucson, Arizona.

We have recently introduced a series of side-chain-substituted phthalocyanines (Pc – benzyl-terminated ethylene oxide side chains) which form liquid crystalline (LC) mesophases and self-organize into exceptionally coherent columnar aggregates. High optical and electrical anisotropies are observed in thin films of these materials (conductivity and field-effect mobilities are much higher along the Pc column axis vs. across the Pc column axis). Initial d.c. conductivity studies done on Langmuir-Blodgett (LB) films with interdigitated microelectrodes (IME) showed conductivity anisotropies of ca. 50 when measured over a ten to hundred micron length scale. Anisotropy in conductivity as high as 1000 was observed at the sub-micron length scale with conductive probe AFM (CP-AFM). Organic field-effect transistors (OFETs) fabricated with LB films of these materials demonstrated current anisotropies up to 30 in the saturation region. The device characteristics were strongly dependent upon the contact of Pc material with the source/drain electrodes and the coherence within these Pc aggregates. New generation LC-Pcs are introduced here which are easier to process, having a more discrete K<sup>+</sup>/LC transition, and in some cases a clear melting transition. OFETs fabricated with solution-cast films showed a threshold voltage close to 0V and on/off ratio of ca. 1000. Large crystalline sites were generated as a result of vacuum annealing at temperature above the melting point of this material. Recent research will be presented where chemical modification strategies for both the gate oxide and the source/drain contacts are compared to optimize the electronic properties of these materials.

### 3:45 PM \*T2.7

**Nanoscale Self-Assembly of Functional Organic Molecules at**

**the Liquid/Metal Interface.** Denis Fichou<sup>1,2</sup>, Alexandr Marchenko<sup>1,2</sup> and Nathalie Katsonis<sup>1,2</sup>; <sup>1</sup>DSM/DRECAM/SPCSI, CEA-Saclay, Gif-sur-Yvette, France; <sup>2</sup>UMR 7611 CNRS-UPMC, Paris 6 University, Paris, France.

Molecular self-assemblies on atomically flat surfaces (gold, graphite, etc) are governed by molecule-molecule and molecule-substrate interactions. Both types of interactions strongly depend on the shape and chemical nature of the molecules. One simple way to investigate molecular self-assemblies is to generate and observe them in situ at a liquid/solid interface by means of scanning tunneling microscopy (STM) and spectroscopy (STS). In this technique, the liquid acts both as the deposition medium for selected molecules and as the dielectric medium for STM tunnel currents. We report here on the growth, nanostructure and local I/V properties (STS) of molecular self-assemblies formed at the n-tetradecane/Au(111) interface by various series of conjugated molecules having either a linear, planar or spherical shape. In particular, we recently discovered that a series of linear polyunsaturated trimethylsilyl-acetylenes (TMSA) derivatives self-assemble on gold. These TMSA molecules stand upright on the surface, forming an hexagonal close-packed lattice commensurate with the Au(111) substrate along the <112> direction [1,2]. The vertical position and high stability of TMSA monolayers on gold are appropriate to STS measurements, giving access to transport properties along single molecular wires [3]. Beside, we report on the in-situ growth, nanostructure and nano-manipulation of self-assemblies formed by (sub)-monolayers of C<sub>60</sub> and C<sub>70</sub> fullerenes adsorbed at the n-tetradecane/Au(111) interface [4]. Finally, molecular resolution STM reveals that 2D-molecules like alkoxy-substituted triphenylenes self-assemble in different geometries depending on the length of their alkoxy substituents [5]. In particular, we observed that for a specific alkoxy chain length, triphenylene molecules associate in dimers (or pairs) to form linear rows.

1. A. Marchenko, N. Katsonis, D. Fichou, C. Aubert, and M. Malacria, *J. Am. Chem. Soc.* 2002, 124, 9998. 2. N. Katsonis, A. Marchenko, S. Taillemite, D. Fichou, G. Chouraqi, C. Aubert, M. Malacria, *Chem. Eur. J.* 2003, 11, 2573. 3. E.G. Petrov, N. Katsonis, A. Marchenko, and D. Fichou, *Phys. Rev. B* submitted. 4. Katsonis, N.; Marchenko, A.; Fichou, D. J. *Photochem. Photobiol. A: Chem.* 2003, 158, 101. 5. Katsonis, N.; Marchenko, A.; Fichou, D., *J. Am. Chem. Soc.* 2003, ASAP Web 16-Oct-2003.

### 4:15 PM \*T2.8

**Single Molecule Conductance by STM.** N.A. Pradhan, N. Liu, G.V. Nazin, X.H. Qiu and W. Ho; Department of Physics and Astronomy and Department of Chemistry, University of California-Irvine, Irvine, California.

The strong influence of the immediate environment on molecular electronic properties and transport is demonstrated. In one case, a scanning tunneling microscope (STM) is used to study the conductance of single C<sub>60</sub> molecules in isolation and in monolayers adsorbed on an ultrathin alumina film grown on a NiAl(110) surface. The differential conductance (dI/dV) spectra display a series of equally spaced features, attributed to the vibronic states of the molecules. The details of the spectra show the influence of molecular orientation and environment on the differential conductance. The local effects of alkali metal impurities were also studied in an effort to gain further understanding of the origin of the electron-phonon coupling in alkali fulleride superconductivity. In another approach, the STM was used to construct and observe the differential conductance of a metal-molecule-metal bridge. The local density of states of this structure was visualized by spatially resolved electronic spectroscopy and tuned by varying the number of metal atoms in the bridge by STM tip manipulation. This artificial bridge elucidates the nature of the contacts between the molecule and the metal in this junction. These experiments serve to highlight the role of the local environment in the spatially resolved conductance of molecules and provide the basic understanding that may play a significant role in the emerging field of molecular electronics.

### 4:45 PM T2.9

**Self Assembly and Tunneling Spectroscopy of Self Assembled Monolayers.** Geetha R Dholakia, James Williams, Robert Zeches and M Meyyappan; Center for Nanotechnology, ELORET/NASA Ames Research Center, Moffett Field, California.

Self assembled monolayers of organic molecules are of potential interest for molecular electronic devices. We study the self assembly and electronic transport of different types of SAMs by scanning tunneling microscopy and spectroscopy. It is important to understand the transport mechanisms through these monolayers and currently there are only a few temperature dependent transport studies. Whether the nature of electronic transport through the SAMs is by tunneling or by activated transport depends on the both the magnitude of the HOMO-LUMO gap and the length of the molecule. We perform temperature dependent scanning tunneling spectroscopic

studies on alkanethiol self assembled monolayers. The I-Vs on dodecanethiol SAMs do not show a marked temperature dependence from 300K-150K, indicating that the transport through this SAM is by tunneling. These results will be compared with that of alkanethiols of different lengths and also with other types of SAMs.

SESSION T3: Electronics of Molecular Self-Assemblies  
Chair: Cherie R. Kagan  
Wednesday Morning, April 14, 2004  
Room 3008 (Moscone West)

**8:30 AM \*T3.1**

**Mechanisms for current rectification by molecular junctions.**  
Abraham Nitzan, Tel Aviv University, Tel Aviv, 69978, Israel.

Current rectification is obviously associated with some form of symmetry breaking. This talk will focus on three scenarios of current rectification by molecular conductors. First, the asymmetric response of the electrostatic potential along a biased molecule in structurally asymmetric junctions(1); second, electron pumping by an external time-periodic potential interacting with an asymmetric molecular chain(2) and third, the asymmetric conduction of heat by non-linear molecular oscillators(3). (1) M. Galperin, A. Nitzan, S. Sek and M. Majda, *J. Electroanalytical Chem.* 550/551, 337 (2003) (2) J. Lehmann, S. Kohler, P. Hanggi and A. Nitzan, *Phys. Lett.* 88, 1 (2002); *J. Chem. Phys.* 118, 3283 (2002) (3) D. Segal and A. Nitzan, to be published

**9:00 AM T3.2**

**Theory of molecular-assembled single-electron devices.**  
Yongqiang Xue and Mark A. Ratner; Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois.

The advancement of the fabrication process using self-assembly or biodirected-assembly technique with molecular recognition has made devices based on single and assembled nanoparticles attractive candidates in applications including single-electronics, novel biosensors and nanophotonic devices. For the nanoparticle-based single-electron devices, the transfer of single electron is achieved by tunneling through the linker molecule connecting the nanoparticles to the electrodes and to each other, where the tunneling barrier is induced by the energy mismatch of the molecular levels relative to the metal Fermi-level. In addition, charge transfer between the linker molecule and the metals will lead to an intrinsic background charge even in the absence of charged impurities and gate voltages, which may affect significantly the current-voltage characteristics. Depending on the conductance of the molecular bridge and the size of the nanoparticle, interesting quantum mechanical effects such as co-tunneling and quantum-size effects may further complicate the analysis of such molecular-assembled single-electron devices. In this talk, we present a microscopic theory of single-electron tunneling through molecular-assembled metallic nanoparticles, which combines the Coulomb Blockade effect with a microscopic description of the electronic processes in the molecular tunnel junctions. We demonstrate the variety of transport characteristics that can be obtained through "engineering" of the metal-molecule interaction. We also consider the possibility of incorporating mechanical degree of freedom into such molecular-assembled single-electron devices through mechanical modulation of one of the tunnel junctions.

**9:15 AM T3.3**

**Effect of molecular self-assembly on charge transport characteristics of molecular wires.** Yong-Hoon Kim, Seung Soon Jang and William A. Goddard; Materials and Process Simulation Center, California Institute of Technology, Pasadena, California.

We report a multi-scale computational study of structures and current-voltage (I-V) characteristics of single and self-assembled monolayer (SAM) bi-phenyl-dithiol (BPDT) molecular wires sandwiched between Au(111) electrodes. We prepare SAM device models together with corresponding single molecular wires suspended in the vacuum gap and surrounded by alkanethiol molecules by force-field (FF) and density-functional theory (DFT) calculations. I-V characteristics of the devices are calculated by the non-equilibrium Green's function (NEGF) method and compared in a consistent manner. We find that changes in intra molecular structures such as the phenyl ring rotation and the molecular tilting has much larger effects on I-V characteristics than the inter-molecular band formation, and conclude that the major albeit indirect role of molecular self-assembly on device characteristics is stabilization of specific single-molecule conformations. Examining the correlation between structure and I-V characteristics, the BPDT SAM is claimed as a poor device component and better device candidates will be proposed.

**9:30 AM \*T3.4**

**Molecular Conduction.** Supriyo Datta, Electrical & Computer Engineering, Purdue University, West Lafayette, Indiana.

In this talk I will review our understanding of electrical conduction through individual molecules stressing the factors that influence the current-voltage characteristics, namely, the location of the equilibrium Fermi energy, the coupling to the contacts and the effects of electron charging. I will then present a simple model that can be used to incorporate the relevant physics and illustrate it with several examples including silicon-based molecular devices that exhibit negative differential resistance (NDR). Experimental evidence for such effects has recently been reported by Mark Hersam et.al. (*Nano Letters*, Jan.2004).

**10:30 AM \*T3.5**

**Single Molecule Electronics on Silicon.** Mark C Hersam, Materials Science and Engineering, Northwestern University, Evanston, Illinois.

In recent years, substantial progress has been made in the emerging field of molecular electronics. In particular, metal-molecule-metal junctions have been widely studied. In this paper, charge transport through molecule-semiconductor junctions is considered. The presence of the energy band gap in semiconductors provides opportunities for resonant tunneling through individual molecules, leading to interesting effects such as negative differential resistance (NDR). Furthermore, by doping the substrate, the majority charge carrier can be tailored, thus allowing asymmetry to be intentionally designed into the current-voltage characteristic. Through judicious choice of the molecular species, the bias voltage of the NDR can also be controlled. By demonstrating these effects on the Si(100) surface, semiconductor-based molecular electronic devices have the potential of being directly interfaced to conventional silicon integrated circuit technology. The ultra-high vacuum scanning tunneling microscope (STM) allows individual molecules to be imaged, addressed, and manipulated on semiconducting surfaces with atomic resolution at room temperature. This paper considers three different molecules on the Si(100) surface: styrene, cyclopentene, and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). In all cases, STM current-voltage characteristics on individual molecules mounted on degenerately n-type Si(100) show multiple NDR events at negative sample bias. On the other hand, at positive sample bias, the current-voltage characteristics do not show NDR, although a discontinuity in the differential conductance is observed. When the Si(100) substrate is changed to degenerate p-type doping, multiple NDR events are observed at positive sample bias while the discontinuity in the differential conductance occurs at negative sample bias. These empirical observations can be qualitatively explained by considering the energy band diagram for a semiconductor-molecule-metal junction. This paper will conclude by describing recent efforts to quantify and understand the critical parameters that dictate charge transport through individual molecules on silicon.

**11:00 AM T3.6**

**Organic molecules adsorption on Si{100}: role of surface defects studied by a semiempirical orbital method.**  
Anna Maria Mazzone, Istituto IMM, CNR, Bologna, Italy.

It is known that the silicon surface is spontaneously defective. Nominally flat surfaces contain trains of monoatomic steps which act as preferential sink for dopants, surfactants and chemical etchants. The purpose of this study is to get insight into the interactions of steps on the Si(100) surface with organic molecules of the simplest composition. The study is divided into two parts. The first part illustrates preferred adsorption sites and the step-molecule bonding. The possibility of a functionalization of a surface containing steps is also analyzed. This study is performed using a molecular orbital method with a semiempirical hamiltonian. In the second part the thermal and electrical conductivity of the systems studied in the first part is analyzed using the Kubo theory.

**11:15 AM T3.7**

**30 Nm Channel Length Organic Transistors.** Yuanjia Zhang<sup>1</sup>, Jason R. Petta<sup>2</sup>, Daniel C. Ralph<sup>2</sup> and George G. Malliaras<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Physics, Cornell University, Ithaca, New York.

The use of organic thin film transistors OTFTs has raised a large interest in emerging electronic technologies where large area coverage and low cost are required. The current delivered by the TFT is inversely proportional to the channel length L of TFT, and that motivated studies of OTFTs with submicron channel lengths. Past work has shown the characteristics of the TFTs to degrade when L is below 100nm, due to either poor charge injection at metal/organic semiconductor interface [1] or "punch-through" effect [2]. To explore

whether those effects impose the inherent limitation in the performance of nanoscale organic transistors, we combined state-of-the-art e-beam lithography with organic semiconductor deposition techniques to fabricate organic field-effect transistors with channel lengths down to 30 nm. The current-voltage characteristics of the devices exhibited the behavior expected for p-channel TFTs and scaled gracefully with channel length and width. These 30 nm channel length organic transistors allowed the studies of charge transport in organic semiconductors at the nanometer length scale. [1] E. L. Granstrom, C. D. Frisbie, J. Phys. Chem. B 1999, 103, 8842. [2] M.D. Austin, S.Y. Chou, Appl. Phys. Lett. 2002, 81, 4431.

#### 11:30 AM T3.8

**10 nm Channel Length Pentacene and Oligothiophene Organic Transistors.** Josephine Bea Lee<sup>1</sup>, Paul C Chang<sup>1</sup>, Amanda R Murphy<sup>3</sup>, Jean M J Frechet<sup>3</sup>, J Alexander Liddle<sup>2</sup> and Vivek Subramanian<sup>1</sup>; <sup>1</sup>Department of Electrical Engineering and Computer Science, University of California, Berkeley, California; <sup>2</sup>Center for X-Ray Optics, Lawrence Berkeley National Laboratory, Berkeley, California; <sup>3</sup>Department of Chemistry, University of California, Berkeley, California.

Currently, there is great interest in scaling organic thin film transistors (OTFTs) to nanoscale channel lengths in order to probe the intrinsic behavior of organic materials and as part of the drive towards high performance organic devices. With certain organic semiconductors exhibiting thin film charge mobilities at or exceeding mobilities measured in their bulk single crystalline form, the conduction mechanisms for these materials is no longer clear. Since these thin films are polycrystalline in nature, charge transport is suspected to be defect-driven. Nanoscale OTFTs, which can be fabricated with completely defect-free active areas, would greatly enhance the current understanding of conduction mechanisms in organic semiconductors. Devices scaled to dimensions approaching the conjugation lengths in organic molecules also open the possibility of new transport regimes with enhanced charge mobility. However, attempts to scale OTFTs channel lengths below 100nm have been met with a number of difficulties. Here, we report on the scaling of OTFTs to 10 nm channel lengths and discuss the issues that become significant at these dimensions, such as contact resistance and limits posed by electrostatics. We have fabricated 10 nm channel length organic thin-film transistors (OTFTs) from pentacene, dihexyl sexithiophene, and several novel oligothiophenes. These devices represent the smallest OTFTs reported to date. Gold electrodes were formed using e-beam lithography and lift-off techniques. Thin films of various organic semiconductors were then deposited by vacuum evaporation, spin casting, or dip casting to form bottom-contact, back-gated devices. As the channel length was scaled, short channel effects such as V<sub>t</sub>-rolloff and increased off-state leakage were observed. The impact of contact resistance also became increasingly significant. Nanoscale devices consistently exhibited lower FET mobilities and worse on/off current ratios than identically processed micron-sized devices, likely due to the growth dynamics of the thin-film organic layer in the nanogaps. This study is a significant step towards optimization of the deeply scaled OTFT.

#### 11:45 AM T3.9

**From Electron Transfers to Electric Currents: Light-induced in-plane Currents in Monomolecular Films.**

Vladimir Burtman<sup>1,2</sup>, Andrew Pakulev<sup>2</sup> and Dimitry Zaslavsky<sup>2</sup>; <sup>1</sup>Physics Dept., Univ. of Utah, SLC, Utah; <sup>2</sup>Chemistry Department, University of Illinois at Urbana-Champaign, Urbana, Illinois.

The world of the in-plane currents in monomolecular films has been unexplored; having ultimately thin cross-sections, monolayers a priori did not seem to be prospective research avenue for the needs of electronics. However, we find that (i) monomolecular films of 1,4,5,8-naphthalene tetracarboxylic diimide (NTCDI) can be photo-chemically populated with positive charges via ejection of electrons into the semi-conducting base and (ii) these charges can travel within the film as far as several millimeters within microseconds. We show that this long-range charge migration requires a sufficiently dense packing of the film to permit electron transfer between the covalently immobilized molecules. Such density was achieved by chemo-sorption of the vaporized precursor and manifested itself as an additional broad asymmetric "aggregation" absorbency band. This in-plane "fluidity" of charge-carriers allows small-sized cathodes to harvest charges generated in remote areas and thus can be utilized in numerous applications.

SESSION T4: Transport in Molecular Junctions I  
Chair: Marcel Mayor  
Wednesday Afternoon, April 14, 2004  
Room 3008 (Moscone West)

#### 1:30 PM \*T4.1

**Measurement of Electron Transport Properties of a Single Molecule Junction.** NJ Tao, B.Q. Xu and X.Y. Xiao; Electrical Engineering, Arizona State, Tempe, Arizona.

We have studied electron transport properties of N-alkanedithiol chains and conjugated molecules covalently bonded to gold electrodes by repeatedly creating a large number of molecular junctions. For each molecule, a large variation in the conductance is observed from one junction to another, which reflects the difference in the molecule-Au contact geometries. However, the conductance histogram obtained from thousands of measurements shows pronounced peaks at integer multiple of a fundamental conductance value, which is used to identify the conductance of a single molecule. The conductance of N-alkanedithiols can be described by  $G = G_0 \exp(-\beta n)$ , where  $G_0 = 2e^2/h$  and  $\beta = 1.0$  per carbon atom. When one of the C-C bonds in the chain is replaced with peptide bond, the conductance changes considerably. The dependence of the conductance of the conjugate molecules on the molecule length is much slower than that of alkanedithiol molecules. We have also studied electron transport by controlling the potential of the gold electrodes with respect to a reference electrode inserted in the electrolyte.

#### 2:00 PM T4.2

**Electrical Transport in Au-Alkanedithiol-GaAs Junctions.** Julia W. P. Hsu<sup>1</sup>, Ken W. West<sup>2</sup>, David V. Lang<sup>2</sup>, Mat D. Halls<sup>3</sup>, Krishnan Raghavachari<sup>3</sup> and Yueh-lin Loo<sup>4</sup>; <sup>1</sup>Sandia National Laboratories, Albuquerque, New Mexico; <sup>2</sup>Lucent Technologies, Murray Hill, New Jersey; <sup>3</sup>Indiana University, Bloomington, Indiana; <sup>4</sup>University of Texas - Austin, Austin, Texas.

Molecular junctions composed of alkanedithiol chemically bonded to Au and GaAs electrodes were made by nanotransfer printing. Electrical shorting between electrodes is minimized in these printed junctions. Furthermore, the chemical bonding that facilitates the printing process ensures the current path through the entire length of the molecules. Current-voltage (I-V), capacitance-voltage (C-V) and internal photoemission (IPE) experiments were performed to study the transport properties of these junctions. Experimental results were compared with electronic structure calculations. C-V results indicate excess negative charges at the molecular-GaAs interface. This is in agreement with calculations in which more negative charges are localized on S when it is bonded to Ga than to Au. This contact asymmetry is the primary reason behind the I-V asymmetry at low bias. It is also consistent with the observation that the shape of I-V curves is the same for n type GaAs and p type GaAs. However, the current levels of the molecular junctions made on p-GaAs are many orders of magnitude higher, suggesting transport is predominating hole conduction through molecular occupied levels. Calculations also show the presence of occupied levels ~1 eV below the Fermi energy that overlaps alkane backbone and Au/GaAs electrodes. Furthermore, this is supported by the observed high yield in photocurrent measurements when the photon energy (E) is above the GaAs band gap. When E is below the GaAs band gap, we observed an exponential IPE dependence. Exponential E dependence in IPE yield signifies exponential distribution of density of states, which could result from the presence of disordered materials or high fields. By varying the doping levels of GaAs, we separate out the contribution due to the molecular layer from that of GaAs Franz-Keldysh effect. An exponential IPE yield with a characteristic energy of 70 meV can be attributed to the molecular layer. Band alignment across the molecule-semiconductor and molecule-metal interfaces will be discussed.

#### 2:15 PM T4.3

**High-Quality Alkanethiol Bilayer Molecular Junctions on Gold Substrates.** John D Le, Curtis C Mead and Richard A Kiehl; Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

The electrical characteristics of alkanethiol bilayer molecular junctions formed on gold substrates are reported over a wide range in methylene chain length. The Hg-SC<sub>n</sub> // C<sub>n</sub>S-Au junctions are formed by bringing into contact a C<sub>n</sub>SH self-assembled monolayer (SAM) on the surface of a Hg drop with another alkanethiol SAM on the surface of a Au substrate. The currents are measured up to the junction breakdown voltages for both bias polarities for chain lengths corresponding to n = 6, 8, 10, 12, 14, 18. This range includes both long molecules, which are difficult to characterize due to their low current levels, as well as short molecules, which present characterization difficulties due to their poorer junction stability,<sup>1</sup> especially in the case of SAM on the Hg-drop electrodes. The observed dependence of the current on bias voltage and junction thickness are consistent with tunneling over a ten order-of-magnitude range in current. The variation in breakdown voltage with junction thickness is well-behaved and corresponds to a breakdown field of  $6 \times 10^6$  V/cm, which is significantly higher than previously reported for

bilayers on Au substrates.<sup>1</sup> The breakdown voltage is found to exhibit a bias polarity dependence that decreases with molecular length. In general, the electrical characteristics for the wide range of junctions presented here are greatly improved compared to previous results for similar bilayers on Au substrates and are comparable to the best results achieved for bilayers on Ag substrates.<sup>1,2</sup> Possible explanations for the improved characteristics observed in this study are discussed.

<sup>1</sup> R. Haag et al., J. Am. Chem. Soc. **121** (34), 7895 (1999). <sup>2</sup> R. E. Holmlin et al., J. Am. Chem. Soc. **123** (21), 5075 (2001).

#### 2:30 PM \*T4.4

##### Conductance Properties of Single-Molecule Junctions.

Heiko B. Weber, Marcel Mayor, Mark Elbing, Rolf Ochs and Jan Wurfel; Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

We have performed conductance measurements with a self-assembled metal-molecule-metal junction [1] both at room temperature and low temperatures. The gap between the electrodes could be adapted in situ to the molecule's length employing the mechanically controlled break junction technique. Part of our research is focussing on the correlation between molecular structure and electronic properties. As an example, molecules divided in two conjugated sections were designed and synthesized. By fluoridizing one of the two segments, the functionality of a diode was targeted. Indeed the measurements result in diode-like IV-characteristics with an on-off ratio of approx 5. Different mechanisms how asymmetries may arise are considered. Further attention is paid to the interaction of single-molecule junctions with light. [1] J. Reichert, R. Ochs, D. Beckmann, H.B. Weber, M. Mayor, and H. v. Lohneysen, Phys. Rev. Lett. {88}, 176804 (2002).

#### 3:30 PM \*T4.5

##### Understanding Charge Transport in Metal-Molecule-Metal Junctions.

James G. Kushmerick, Naval Research Laboratory, Washington, District of Columbia.

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. By tuning the coupling at the two metal-molecule interfaces-through the use of different attachment chemistries and metal electrodes-we are able to control the amount of current rectification. Experimental measurements and theoretical calculations demonstrate that the conductance of a molecular wire can be directly related to how well it's  $\pi$ -conjugated backbone mimics an ideal one-dimensional metal. Finally, we will show that the conductance of a molecular junction scales with the number of molecules contacted, and that the  $\pi$ -systems of molecular wires in a self-assembled monolayer are not strongly coupled. Initial results demonstrating the utility of in situ vibrational spectroscopy to characterize molecular junctions will also be presented.

#### 4:00 PM T4.6

##### Measuring Electrical Properties from Single Molecules to Moletronic Devices.

Jayne Carol Garno<sup>1</sup>, Christina A. Hacker<sup>2</sup>, Christopher D. Zangmeister<sup>3</sup>, Carlos Gonzales<sup>4</sup>, Lee J. Richter<sup>1</sup>, Roger D van Zee<sup>3</sup>, Curt A. Richter<sup>2</sup> and James D. Batteas<sup>1</sup>; <sup>1</sup>Surface & Microanalysis Sciences Division, NIST, Gaithersburg, Maryland; <sup>2</sup>Semiconductor Electronics Division, NIST, Gaithersburg, Maryland; <sup>3</sup>Process Measurements Division, NIST, Gaithersburg, Maryland; <sup>4</sup>Physical and Chemical Properties Division, NIST, Gaithersburg, Maryland.

Developing theoretical models to understand and predict electron transport in metal-molecule-metal junctions is a significant challenge, with direct potential benefits to technology. Advancement of molecular electronics-based systems requires the ability to achieve reliable and precise measurements of conductance and charge transport in molecular electronic test structures. A combination of modeling, spectroscopy, and scanned probe approaches are applied in a concerted effort to correlate theoretical studies with molecular level measurements of conduction, as well as measurements with device-level prototype structures. As the electrical behavior of molecules depends on the structure, organization and orientation of molecules within films on conductive surfaces, studies with self-assembled monolayers (SAMs) are a key element of our research endeavor. Initial efforts have focused on current-voltage measurements for test structures scaling sizes from small ensembles of tens to thousands of molecules for n-alkanethiol and substituted SAMs. To evaluate ensemble size effects in the organization of molecules on surfaces and associated transport properties, SAMs are embedded in structural wells of varied dimensions. Using surfaces of Au(111), we conducted a series of UHV experiments measuring electron transport for alkanethiols (such as dodecanethiol) with different molecular orientations. Also, AFM-based nanofabrication is used to construct

engineered test arrays which consist of an alkanethiol matrix with candidate wire molecules such as oligo (phenylene-ethynylene) thiolates (OPEs). We are also investigating changes in electrical behavior induced by chemical modifications of OPEs. AFM and STM investigations of current-voltage measurements for a monofluorinated molecular wire SAM (F-OPE) show an increased rectifying behavior in comparison to the unsubstituted OPE. Studies of alkanethiols and OPE SAMs are models for measuring and predicting the electrical response of molecules.

#### 4:15 PM T4.7

**Interfaces in Molecular-Scale Electronics: From organic molecules to carbon nanotubes.** Yongqiang Xue and Mark A. Ratner; Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois.

It is now widely accepted that the nature of the contact to the measurement electrodes plays a significant if not dominant role in determining the transport characteristics of any molecular-scale electronic devices. Questions are then raised if such interface effects can be tuned to advantage through improvement in the device fabrication processes or appropriate molecular design techniques. For devices based on organic molecules, the contacts are often made through appropriate end groups chemically different from the molecule core. For devices based on carbon nanotubes, the contacts can be made either through end-bonding the nanotube onto the electrodes or by embedding the nanotube end deeply within the electrodes. Regardless of the dimensionality and size of the molecular nanostructures, the effects of the contact on the device transport characteristics are determined through the interfacial charge transfer and the corresponding formation of interfacial potential barriers. In this talk, we present a unified theoretical framework for studying interface effects in arbitrary molecular-scale devices, which combines Green's function theory of quantum transport with atomistic description of the interface electronic structure in the real space. We discuss the insights obtained from such atomistic modeling for understanding the interface effects in devices based on individual organic molecules, finite-size carbon nanotubes, and long carbon nanotubes in the limit of 1-D quantum wires. Both linear and nonlinear transport characteristics will be discussed.

#### 4:30 PM T4.8

**Charge transport in DNA probed by Conducting AFM and EFM.** Dominique Vuillaume, Thomas Heim and Dominique Deresmes; CNRS-IEMN, Villeneuve d Ascq, France.

We studied the electrical conductivity of DNA samples as function of the number of DNA molecules in the ropes. We performed a systematic study of the distance-dependent behavior of the CT in DNA versus the size of the DNA samples: from DNA polymers, bundles and ropes to few single molecules. In that latter case, the CT behavior was correlated with the flattened conformation of the DNA molecule as observed by topographic TM(tapping mode)-AFM. We showed that the insulating gap (no current at low voltage) increases from 1-2 V for bundles and large ropes to 4-7 V for few DNA molecules. From the distance dependent variation of the current, a unique hopping distance of 3 nm is calculated (polaron-hopping model) independently of the number of DNA in the sample. The highly resistive behavior of the single DNA is correlated with its flattened conformation (measured by TM-AFM) on the surface (reduced thickness, 0.5-1.5 nm, compared to its nominal value, 2 nm). Contactless measurements were also used. We have injected charges locally in the DNA from the C-AFM tip. The charge distribution along the DNA molecule after injections at various voltages and time durations was investigated by EFM. We showed that on elongated DNA, the charges stay localized at their injection point, while charges are delocalized few micrometers along the DNA in non-elongated molecules. This long distance delocalization implies some conducting properties in that latter case. This results demonstrates possible long distance charge transfer in undistorted and contactless DNA molecules.

#### 4:45 PM T4.9

**Implications of space charge limited transport for BEEM studies on metal-organic interfaces.** Cedric Troadec, Linda Kunardi and Natarajan Chandrasekhar; Institute of Materials Research and Engineering, Singapore, Singapore.

Interfaces between metals and organics/semiconductors exhibit a Schottky barrier. Ballistic electron emission microscopy is a technique to determine the magnitude of this barrier, potentially with nanometer resolution. The carriers injected from a STM tip, travel ballistically through the top metal electrode and are collected at the bottom of the organic/semiconductor layer. Due to the large differences in mobilities of the carriers in the metal and the organic, transport of injected carriers is limited by space charge effects in the organic. In this work, we will discuss the implications for space charge limited transport on measurement of the Schottky barrier with

experimental results.

SESSION T5: Poster Session: Molecular Electronics  
Poster Session  
Chairs: Cherie R. Kagan and Marcel Mayor  
Wednesday Evening, April 14, 2004  
8:00 PM  
Salons 8-9 (Marriott)

### T5.1

**Synthesis and Electrochemical Properties of Polyphenylene bearing nitroxide radicals as an Electrode Active Material.** Masahiro Suguro, Shigeyuki Iwasa, Jiro Iriyama, Kentaro Nakahara, Yukiko Morioka and Masaharu Satoh; Environment and Material Research Laboratories, NEC Corporation, Kawasaki, Kanagawa, Japan.

Polyradicals are known to be oxidized and reduced electrochemically. We reported the redox processes would be suitable for a reaction of cathode active materials in rechargeable batteries. The use of organic materials as an active material in cathodes appears promising to design environmentally friendly, high energy-density rechargeable batteries. We synthesized poly[1-(N-t-butyl nitroxyl)-3,5-phenylene] (PBNP), which has the possibility of high energy-density. The ESR spectrum of PBNP consist of a single line. The g value is 2.010, which is characteristic of nitroxyl radicals. A coin-type cell fabricated with the polyradical as cathode active material has demonstrated the reversible charge and discharge curves. The voltage plateau of 3.6 V vs Li/Li+ for charge and 3.4 V vs Li/Li+ for discharge have been observed. These results indicate the possibility of PBNP for active material of organic radical battery. Here, we will present syntheses and fundamental properties of PBNP and the battery.

### T5.2

**Biomimetic Molecular Muscles.** Yi Liu<sup>1,2</sup>, Amar H Flood<sup>1,2</sup>, Paul Bonvallet<sup>1,2</sup>, Tony J Huang<sup>3</sup>, Scott C Vignon<sup>1,2</sup>, Sergei Magonov<sup>4</sup>, Marko Baller<sup>4</sup>, Chih-Ming Ho<sup>3</sup> and J Fraser Stoddart<sup>1,2</sup>; <sup>1</sup>California NanoSystems Institute, Los Angeles, California; <sup>2</sup>Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California; <sup>3</sup>Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California; <sup>4</sup>Veeco Metrology Group, Santa Barbara, California.

Switchable [2]rotaxanes have been likened to linear molecular motors.<sup>1</sup> These compounds are composed of ring and dumbbell-shaped components that are interlocked with each other, in which the ring's linear mechanical movements along the dumbbell component can be precisely controlled. These mechanical movements have been utilized as the working electromechanical mechanism in rotaxane-based electronic devices.<sup>2</sup> More recently, attention has been focused on harnessing the mechanical movements as the actuating mechanism in novel nanoelectromechanical systems (NEMS). It is for this purpose that switchable artificial motor-molecules have been designed to perform extension and contraction movements, showing a unique form of biomimicry akin to biological muscle fibers. In this presentation, we outline (1) the design of a family of switchable artificial motor-molecules, (2) their modular synthesis, (3) the demonstration of controllable molecular movements in solution, (4) the self-assembly of those molecules on surfaces, and (5) their application in a NEMS device. A variety of molecular muscle compounds have been designed and prepared. A linear [3]rotaxane, which has two rings encircling the dumbbell component, has been designed as a biomimetic molecular muscle capable of electrically-controlled contraction and extension. Disulfide tethers have been covalently attached to both of the ring components in the [3]rotaxane for the purposes of self-assembly onto a gold surface. A [2]daisy-chain constitution, based on similar molecular recognition interactions, has been designed as an alternative biomimetic muscle motif. In addition, a smaller, self-complexing motor-molecule has been designed for self-assembly onto a gold surface for the purpose of producing a controllable functional surface. The chemical and electrochemical controllable machine-like movements of the two ring components in the [3]rotaxane are demonstrated by various techniques in solution. These results indicate a contraction and extension of the inter-ring distance to be a dramatic 3.5 nm, 44 percent of the overall molecular length. It has been shown subsequently that the [3]rotaxanes self-organize into large areas of regular superstructures on the surface of highly-ordered pyrolytic graphite (HOPG). Lastly, the surface-bound [3]rotaxane has been integrated into a NEMS device. The preliminary results indicate that the cooperative contraction and extension motion in the surface-bound muscle molecules can exert sufficient force to bend a cantilever beam that is much larger (  $\mu\text{m}$ ) than the molecule's individual sizes. We thank DARPA biomolecular motor program for financial support. 1. Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew.Chem.Int.Ed.* **2000**, *39*, 3349. 2. Luo, Y.; Collier, C. P.; Jeppesen, J. O.; Nielsen, K.

A.; DeIonno, E.; Ho, G.; Perkins, J.; Tseng, H. R.; Yamamoto, T.; Stoddart, J. F.; Heath, J. R. *ChemPhysChem* **2002**, *3*, 519.

### T5.3

**Cruciform javascript:window.opener.insertText("π");-systems for Molecular Electronics Applications.** Jennifer E. Klare, George S Tulevski and Colin Nuckolls; Chemistry, Columbia University, New York, New York.

The majority of molecular-scale electronic devices using junctions defined by monolayers, scanned probes, electromigrated junctions, and nanoscale crossed wires require a well-formed and densely packed monolayer with a path of conjugation perpendicular to a metallic substrate. This orientation is difficult to achieve in linear aromatic monolayers because the interaction between molecules is weak. A general and modular synthesis of cruciform 1,4-bisoxazoles has been developed in order to create a library of conjugated compounds for molecular electronics devices. The synthesis of this new class of rigid molecules is contingent upon an unprecedented double Staudinger cyclization. Surface spectroscopy and scanned probed experiments reveal that these molecules form ordered, self-assembled monolayers on metal and metal-oxide surfaces. The molecules are forced into an upright position, causing the path of conjugation to be normal to the surface plane, as a result of the bulky phenyl substituents that are forced out of the aromatic plane. In situ chemical reactions on the monolayer results in the extension of the conjugation length and offers an efficient method to alter the monolayer. For example, an aldehyde terminated monolayer immersed in an amine solution results in the formation of an imine dimer. These ongoing studies could allow for the connection of two closely spaced monolayer-coated electrodes with a conductive bridge. These studies are the focus of electron transport measurements in electromigration junctions, nanogap devices, and scanned probed experiments.

### T5.4

**Degradation studies of blended layer polymer light emitting devices.** Nicholas E Widdowson<sup>1</sup>, Michael C Petty<sup>1</sup>, Christopher Pearson<sup>1</sup>, Changsheng Wang<sup>2</sup> and Martin R Bryce<sup>2</sup>; <sup>1</sup>Centre for Molecular and Nanoscale Electronics and School of Engineering, University of Durham, Durham, United Kingdom; <sup>2</sup>Centre for Molecular and Nanoscale Electronics and Department of Chemistry, University of Durham, Durham, United Kingdom.

The degradation mechanisms in organic polymer electroluminescent devices in which the active layer is a blend of a polymer and an electron transport compound have been studied. The polymer layer was poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) while the electron transport material was 2,5-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl] pyridine (PDPyDP). The mixture (20:80 PDPyDP:MEH-PPV by weight) was deposited from solution by spin-coating. The anode and cathode consisted of indium tin oxide (ITO) and thermally evaporated aluminium, respectively. The light output of the as-deposited devices decayed rapidly to zero over a period of several hours. This was accompanied by a photodegradation of the polymer and delamination of the aluminium cathode. We suggest that this is the result of attack by water vapour and oxygen in the atmosphere. The effects of various encapsulation techniques, i.e. surrounding the devices in either nitrogen, dry air, vacuum or epoxy resin, on the device performance and operating lifetime were investigated. Encapsulation in either dry nitrogen or in an epoxy resin considerably enhanced the operating lifetime and the devices could be operated continuously for several days. However, a further degradation mechanism, associated with the ITO anode was also noted in these structures. This resulted in a significant increase in roughness of the ITO surfaces. It is suggested that this can produce localised short-circuits in the device. Although these can heal themselves, the active area of the device is reduced.

### T5.5

**Abstract Withdrawn**

### T5.6

**Assessment of stability in polysilanes.** Asha Sharma<sup>1</sup>, U. Lourderaj<sup>2</sup>, . Deepak<sup>1</sup>, N. Satyamurthy<sup>2</sup> and Monica Katiyar<sup>1</sup>; <sup>1</sup>Materials and Metallurgical Engineering & Samtel Centre for Display Technology, Indian Institute of Technology, Kanpur, UP, India; <sup>2</sup>Chemistry, Indian Institute of Technology, Kanpur, UP, India.

Polysilanes are Si-backbone polymers with organic substituents attached to the main chain. These are quasi one-dimensional materials with delocalized sigma electrons along the polymer chain, exhibiting photoluminescence in the UV or NUV region. They can be used as active sources for electroluminescence(EL) devices mainly suitable for blue emission. We have examined four polysilanes, namely, polydi-n-butylsilane(PDBS), polydi-n-hexylsilane (PDHS), polymethylphenylsilane (PMPS) and poly[bis(p-butylphenyl)silane](PBPS), which have been reported in [1]



as active materials in LEDs. Among these, PBPS LED shows the greatest durability of the device at room temperature and NUV-EL is observed continuously for over 12 hours. For PDBS, PDHS and PMPS either room temperature EL is not observable or the device life time is very short. Understanding the factors influencing the stability of PBPS in comparison to other reported polysilanes would help design polymers that are better. The four polysilanes mentioned above differ primarily in the nature of the substituents attached to the main chain. Therefore, attempts have been made to determine the instability of PDBS, PDHS and PMPS LEDs in comparison to the PBPS based LED by evaluating the effect of the substituents and the conformational changes in these polysilanes. Ab initio (CIS/6-31g\*) and semi-empirical (AM1/PECI = 8) calculations have been carried out to ascertain the relative stabilities of the different electronic states. Potential energy curves plotted as a function of the Si-Si bond distance reveal that the first excited singlet ( $S_1$ ) state is stable for all the four polysilanes investigated. However the lowest triplet ( $T_1$ ) state is repulsive, leading to the dissociation of the molecule. The dissociation of the triplet ( $T_1$ ) state seems to be preceded by an intersystem crossing between the  $S_1$  and  $T_3$ ,  $T_2$  states, mediated by vibronic coupling. The relative stability of the four polysilanes is correlated to the energy differences between the different triplet states. References: [1] Suzuki et al., IEEE Journal of Selected Topics in Quantum Electronics, Vol. 4, No.1, 1998, p. 129

### T5.7

**Efficient electroluminescence of europium complex based organic light emitting diodes.** Tobias W. Canzler and Junji Kido; Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan.

The spectrally broad emission of most organic molecules makes it difficult to achieve high color purity as required for full color display application. Lanthanide ions, however, exhibit spectrally narrow emission, due to the well shielded intra-atomic transitions within the 4f shell. Europium complexes, which exhibit a dominant photoluminescence peak at 612 nm, corresponding to the  ${}^5D_0 - {}^7F_2$  transition in  $\text{Eu}^{3+}$  ions, are hence promising materials for red EL devices. We use tris(dibenzoylmethane) mono(4,7-diphenylphenathroline) europium(III) ( $\text{Eu}(\text{DBM})_3\text{BPhen}$ ) to fabricate red-light emitting devices. A simple two-layer device, consisting of N,N'-Diphenyl-N,N'-di(m-tolyl)-benzidine (TPD) as hole transport layer and  $\text{Eu}(\text{DBM})_3\text{BPhen}$  as electron transport / emission layer exhibits efficient emission at low currents. We attain peak external quantum and power efficiencies of 4% and 4lm/W, respectively. By co-evaporation of the Eu complex with various host materials we achieve efficient electroluminescence also at higher currents. For high driving currents we observe slight changes in the emission spectrum by a relative increase of emission from the  ${}^5D_1$  state relative to the dominant  ${}^5D_0$  emission.

### T5.8

**Interface Formation in K doped poly(dialkoxy-p-phenylene-vinylene) Light-Emitting Diodes.** Hans Gommans<sup>1</sup>, A W Denier van der Gon<sup>1</sup>, G G Andersson<sup>2</sup>, L J van IJendoorn<sup>1</sup>, R M T Pijper<sup>1</sup> and H H Brongersma<sup>1</sup>; <sup>1</sup>Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; <sup>2</sup>Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Germany.

Al / K / MDMO-PPV / ITO LED structures manufactured by physical vapor deposition of K onto the emissive polymer layer have been characterized by electroluminescence (EL) and ion spectroscopy. EL measurements clearly demonstrate a K-concentration dependent behavior: varying the deposited K areal density in the sub-monolayer regime from  $3.9 \times 10^{12}$  to  $1.2 \times 10^{14}$  atoms  $\text{cm}^{-2}$  the external efficiency rises from 0.01 to 1.2 cd  $\text{A}^{-1}$ . The observed increase in built-in potential can at most partially account for this effect. Low Energy Ion Spectroscopy (LEIS) probes the elemental composition of the topmost atomic layer: the mass of the surface atoms is determined from analysis of the kinetic energy of elastically backscattered noble gas ions, while efficient neutralization of the ions ensures the surface sensitivity. In the set-up, the kinetic energy of ions scattered by 145 degrees was analyzed and detected by a double toroidal analyzer and position sensitive detector and allowed for a detection limit of 100 ppm in the case of K. By measuring the time of flight (TOF) of the charged plus neutralized noble gas ions, we were able to study the composition in deeper layers with Neutral Impact Collision Ion Scattering Spectroscopy (NICISS). A complete absence of K at the polymer outermost surface layer is observed. As the K deposition is clearly below the critical density that limits the charge transfer process typical for alkali /  $\pi$ -conjugated systems, bulk diffusion is not impeded by cluster formation. Consequently, diffusion profiles were derived with a characteristic decay length as large as 62 Angstrom. These profiles were modeled using a Fickian diffusion model with an irreversible first order trapping reaction that may stem from confinement of the electron at a conjugated segment. This

demonstrates that evaporation of low work function metals onto organic systems should not be depicted as simple stacking process. We propose that the enhanced electroluminescence with sub monolayer K deposition is attributed to the shift of the recombination zone away from the Al cathode, which is demonstrated to prevail over the known non-radiative exciton dissociation mechanism due to the formation of gap-states. This shift in the recombination zone can be either due to an improved balance in carrier density or the presence of radiative recombination centers in the interfacial layer.

### T5.9

**Organic Field Effect Transistors with PMMA/TA2O5 as Gate Dielectric.** Anne-Laure Deman and Jacques P. Tardý; LEOM, ECL, Ecully, France.

We report in this study on the fabrication of organic field effect transistors with a gate dielectric made of Ta2O5 covered with a thin PMMA film. In a MOSFET, the charge in the channel is proportional to the product of the voltage by the dielectric capacitance. Thus, a high dielectric constant oxide as Ta2O5 would help in lowering the operating voltage of the transistor as demonstrated in recent work (C. Bartic et al., Organic Electronics 3 (2002) 65). However, as many high-k materials, Ta2O5 is somewhat leaky. Furthermore the electronic properties of its surface are ill defined which could be detrimental to a good transistor behavior in accumulation type devices where the charge transport takes place within the first monolayers of semiconductor. That implies that the interface between the gate dielectric and the organic semiconductor is of a prime importance. Organic-organic interfaces are recognized to be far better than organic-inorganic ones. However, polymer dielectric have a low dielectric constant. In order to combine the respective advantages of Ta2O5 and of the polymer, a gate dielectric consisting of a Ta2O5 film covered with a PMMA film was reported in this study. Ta2O5 thin film is deposited on highly doped silicon by electron beam evaporation in presence of an oxygen partial pressure on a substrate kept at near room temperature. After deposition, Ta2O5 is annealed in oxygen at temperature ranging between 120 and 600 C. Unannealed films were also checked. Films were characterized by ellipsometry and admittance spectrometry. Transistors have been processed with bare Ta2O5 either annealed or not. The semiconductor used was pentacene in a top contact geometry with gold source and drain electrode. For devices with bilayer gate dielectric, PMMA was spun on Ta2O5 to a thickness between 15 and 250 nm with the rest of the device being unchanged. Operating voltage as low as -1.5V were obtained with 120 nm thick Ta2O5. We point out the influence of annealing which leads to a better saturation characteristics and also to a decrease of gate leakage. The measured mobility is about 0.02  $\text{cm}^2/\text{V} \cdot \text{s}$ . Upon deposition of PMMA overlayer, the operating voltage increases (up to 20V for 250 nm PMMA) but the output characteristics do not exhibit any gate leakage. The mobility increases to 0.25  $\text{cm}^2/\text{V} \cdot \text{s}$  on non purified pentacene and on devices characterized in room atmosphere. With annealed Ta2O5, the on/off ratio is 1. 105 and the voltage swing 1.2 V/decade. Work is in progress to evaluate other polymers onto Ta2O5, and comparative results will be presented.

### T5.10

**Small polarons in dry DNA.** Helio Chacham<sup>1</sup>, Simone Silva Alexandre<sup>1,3</sup>, Jose Soler<sup>3</sup> and Emilio Artacho<sup>2</sup>; <sup>1</sup>Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil; <sup>2</sup>Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom; <sup>3</sup>Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, Madrid, Spain.

The phenomenon of charge transport in DNA has been attracting attention of both biologists and physicists. From the biology side, there are evidences that charge injection can be associated to damage, mutation, and repair processes in DNA. From the physical sciences side, recent developments in nanotechnology now allow the measurement of currents through single DNA molecules in dried samples, which depict semiconductor behavior. Several mechanisms have been proposed for charge migration and transport in DNA. In that respect, detailed electrical transport measurements through DNA molecules containing identical base pairs (poly(dA)-poly(dT) and poly(dG)-poly(dC)) have been recently reported by Yoo et al [1]. These results fit extremely well a model in which the conduction is due to small polaron motion. In particular, these results indicate that the I-V characteristic of poly(dG)-poly(dC) DNA above 200 K is consistent with a small polaron hopping regime with an activation energy of 0.12 eV. In this work [2] we investigate the polaron formation in dry DNA by applying ab initio calculations to both neutral and charged fragments of dry poly(dG)-poly(dC). Our calculations show that the hole polaron in dry poly(dG)-poly(dC) DNA is a clear case of small polaron. This is verified by four basic properties: (i) the small variation of the polaron binding energy as a function of the DNA fragment size, for small fragment sizes, which is an indication of polaron localization; (ii) the fact that the width of

the uppermost valence band is an order of magnitude smaller than the polaron binding energy; (iii) the explicit localization of the hole wavefunction for the largest considered fragment (four base pairs), indicated by the fact that about half of the norm of the hole is localized on a single guanine site; (iv) the localization of structural deformations at the nucleotides where the hole is concentrated. Our calculations also give a polaron binding energy of 0.30 eV. This allows us to estimate a hopping activation energy of 0.15 eV, which compares well with the experimental value [1] of 0.12 eV. [1] K. H. Yoo et al, Phys. Rev. Lett. 87, 198102 (2001). [2] S. S. Alexandre, E. Artacho, J. M. Soler, and H. Chacham, Phys. Rev. Lett. 91, 108105 (2003).

#### **T5.11**

**Low-Dimensional Nano-Structures of C<sub>60</sub> Ultrathin Films by Re-Evaporation Method.** Hiroki Okuyama, Akane Kinjo, Yoshimasa Nagayama, Nobuyuki Iwata and Hiroshi Yamamoto; College of Science and Technol., Nihon University, Funabashi, Chiba, Japan.

Recently, nanoscale electronic devices have attracted much attention from the points of low power consumption and high integration. C<sub>60</sub> is a hopeful candidate for the nanoscale devices fabricated by a bottom-up method. C<sub>60</sub> is available for a functional molecule because of its high symmetry, and its diameter is about 0.7nm. C<sub>60</sub> molecules make strong bonds with metals rather than themselves. This characteristic is applied to prepare the C<sub>60</sub> monolayers only onto metals. Then C<sub>60</sub> molecules which didn't adsorb to metals can be re-evaporated after deposition. In this work, we used MgO(110) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) as the substrates of which surfaces forms step-terrace structures. And we chose Au as metal layers of the specific sites of C<sub>60</sub>. We tried to prepare one-dimensional Au layers by using diffusion barriers of steps on single crystal substrates. Successively C<sub>60</sub> monolayers were prepared on the specific substrate by a re-evaporation method. The substrates were annealed at 1000°C, 12h. The Au films were evaporated on the substrates at 600°C from an effusion cell of 1300°C, and immediately annealed for 30min at the temperature. The C<sub>60</sub> were deposited on the Au ultrathin films at 190°C for 10min and then annealed at 350°C for 30min. The films were evaluated by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). From results of AFM measurements, the surfaces of annealed MgO(110) substrates formed one dimensional alignments of step-terrace structures with the terrace widths of 20-80nm. This is due to the cleavage at {100} plane of MgO single crystals. The surfaces of annealed Al<sub>2</sub>O<sub>3</sub>(0001) substrates formed uniform parallel steps with the height of 0.21nm and terraces with the width of 80nm. The steps and terraces structures existed in the length larger than 5 $\mu$ m. Those morphologies are suitable to prepare the one-dimensional nano-structures of C<sub>60</sub>/Au. The AFM images insisted that Au particles aligned one dimensionally along the steps of substrates. After the deposition of C<sub>60</sub> onto the specific substrates, the average height of the particles rose up by about 0.8nm than that of Au particles. This value is same as the C<sub>60</sub> diameter. Since the tail of XPS C 1s peak extended to the higher binding energy side, the electronic states of C<sub>60</sub> may be metallic-like due to charges transferred from Au. The results of AFM and XPS indicated that C<sub>60</sub> monolayers on Au nano-structures were realized by the re-evaporation method developed in this work.

#### **T5.12**

**Highly conjugated meso-to-meso ethyne-bridged porphyrin oligomers with enhanced intra- and intermolecular communication for solid-state devices.** Paul R. Frail<sup>1</sup>, Kimihiro Susumu<sup>1</sup>, Paul J. Angiolillo<sup>3</sup>, Jay M. Kikkawa<sup>2</sup> and Michael J. Therien<sup>1</sup>; <sup>1</sup>Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>Physics, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>3</sup>Physics, Saint Joseph's University, Philadelphia, Pennsylvania.

Two new series of soluble (porphyrinato)zinc oligomers that feature a highly conjugated meso-to-meso ethyne linkage topology have been synthesized; these species exhibit exceptional ground and excited state properties. One series of these conjugated oligomers possesses peripheral aryl groups at the macrocycle's 10,20 positions; these aryl groups, which lie orthogonal to the porphyrin plane, feature substituents (3,3-dimethyl-1-butoxy and 9-methoxy-1,4,7-trioxanonyl) that dramatically enhance solubility. The second series does not have macrocycle meso aryl substituents; solubilizing, sterically unencumbered alkyl chains instead allow for van der Waals porphyrin-to-porphyrin interplanar contact distances. The electronic properties of these oligomers were investigated in solution and in the solid state. Comparison of key physical properties, as well as the magnitude and intermolecular electronic interactions, will be discussed.

#### **T5.13**

**Three-Dimensional Inhomogeneities In The Conductivity Of PEDOT/PSS.** Martijn Kemerink<sup>1</sup>, Salvatore Timpanaro<sup>2</sup>, Margreet

de Kok<sup>2</sup>, Eric Meulenkamp<sup>2</sup>, Fred Touwslager<sup>2</sup> and Rene Janssen<sup>1,3</sup>; <sup>1</sup>Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; <sup>2</sup>Philips Research Laboratories, Eindhoven, Netherlands; <sup>3</sup>Chemical Engineering, Eindhoven University of Technology, Eindhoven, Netherlands.

PEDOT-PSS (poly(3,4-ethylenedioxythiophene stabilized with poly(4-styrenesulfonic acid))) is a transparent and conductive dispersion that is widely used as anti-static and as electrode material in organic semiconductor devices like LEDs and photo-voltaic cells. One of its strengths is that smooth films can easily be spin-cast from watery solutions. However, for applications it is very important that also the electrical properties show little lateral variations within a film. So far, this issue has not been addressed. We have used scanning-tunneling microscopy and spectroscopy to study the conductive properties of a 1:1 PEDOT-PSS blend in all spatial dimensions. Extensive use is made of the fact that the metallic STM tip can penetrate the soft organic material without damage to the tip. In particular, I-z spectroscopy, in which the tip-sample current under constant bias is measured as a function of depth, yields detailed information about the conductivity as a function of z. By taking I-z curves on a lateral grid, a three dimensional conductivity map is obtained. Despite the seemingly destructive nature of such experiments, reproducible conductivity images are obtained. In addition, z-V spectroscopy, in which the bias is ramped with the feedback system active, and conventional I-V spectroscopy are performed. Combination of the experimental results with a three-dimensional numerical model shows that these films are covered with a 5-20 nm thick layer of relatively low conductivity. The conductivity in this layer can be an order of magnitude less than in the underlying bulk, which is attributed to a reduced PEDOT content in the top layer. The latter assignment is in agreement with recent photo-emission experiments. Also deeper in the layer, considerable variations in conductivity occur as a function of depth, with a typical length scale of 10 nm. In the lateral directions, both short-range and long-range variations in the conductivity are observed. The former are identified as grains in topographic STM images and have a minimum size of 20-30 nm, which is in excellent agreement with the particle size in solution of 18-30 nm. The latter, long range variations, occur on a length scale of hundreds of nanometers and translate into conductivity variations of about one order of magnitude. Surprisingly, qualitative differences are found between I-V characteristics measured at different spots. Depending on position, either linear or quadratic curves are obtained. The former is what is expected for an ohmic medium, the latter is generally assumed to be indicative of space charge limited conduction. This would indicate that either the PEDOT is inhomogeneously doped, or that the PSS is inhomogeneously distributed over the sample. When the tip is in contact with such a region, this domain limits the current, and thus determines the I-V curve.

#### **T5.14**

**Substitution And Preparation Effects On The Morphology Of PPV.** Martijn Kemerink<sup>1</sup>, Jeroen van Duren<sup>2</sup>, Albert van Breemen<sup>3</sup>, Herman Schoo<sup>3</sup> and Rene Janssen<sup>1,2</sup>; <sup>1</sup>Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; <sup>2</sup>Chemical Engineering, Eindhoven University of Technology, Eindhoven, Netherlands; <sup>3</sup>TNO Industrial Technology, Eindhoven, Netherlands.

It is known that morphology plays a crucial role in determining the electrical and optical properties of conjugated polymers. In turn, the morphology can be influenced by numerous parameters. We present a systematic study to the morphology of spin-cast films of poly(p-phenylene vinylene) derivatives as a function of substitution, concentration, annealing, and solvent. Using a recently developed method, we are able to resolve both individual molecules and aggregates at the surface of arbitrarily thick films by AFM. This ability allows monitoring subtle morphological changes, that are invisible by other means, including conventional AFM and STM. The most marked result is the difference between symmetric and asymmetric PPVs. The latter tend to self-aggregate into circular conformations with a 10-15 nm diameter. In contrast, the former tend to align the conjugated backbones of neighbouring chains, giving rise to relatively straight conformations and the formation of inter-chain aggregates. Inter-chain aggregation at the film surface is not observed for asymmetrical non-regio-regular (rr) PPVs. Strong aggregation was observed for an asymmetrical rr-PPV, proving the importance of configurational disorder for the morphology in the solid state. Heating the films for about 1 hr above T<sub>g</sub> causes only relatively small rearrangements in the molecular morphology. However, these rearrangements, occurring on a length scale of at most tens of nm, have profound effects on the (self-)aggregation, which is sensitive to changes in position and orientation on a sub-nm scale. In general, both inter-chain aggregation (for symmetric polymers) and intra-chain self-aggregation (for asymmetric polymers) are promoted by annealing. In contrast to claims based on indirect proof in literature, no straightening of coiled-up chains is observed after annealing. No

significant difference between annealing in either an inert atmosphere or in a saturated solvent vapour is found. Increasing the polymer concentration from 1 to 5 mg/ml does not seem to give any appreciable changes in the surface morphology of asymmetric PPVs. For symmetrical PPVs aggregation is promoted. For one asymmetric polymer (MDMO-PPV) different solvents are used. Contra-intuitively, self-aggregation into circular conformations was observed for good solvents, but not for a relatively bad one, which yields a more extended network-like morphology. The larger inter-chain overlap in this case predicts an enhanced carrier mobility, which is indeed observed. The reduced self-aggregation suggests that inter-chain aggregates are either already present in solution or solvent-promoted during spincasting. In either case, these results are a direct proof that the used solvent affects the film morphology via influence on chain conformations. Finally, the results are compared to molecular dynamics calculations which, amongst others, confirm the stability of self-aggregates, and their tendency to form on asymmetric PPVs.

#### **T5.15**

##### **Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using NEXAFS.**

Trevor M Willey<sup>1,2</sup>, Andrew L. Vance<sup>1</sup>, Tony van Buuren<sup>1</sup>, C.

Bostedt<sup>1</sup>, B. R. Hart<sup>1</sup>, R. W. Meulenberg<sup>1</sup>, A. J. Nelson<sup>1</sup>, L. J. Terminello<sup>1</sup> and C. S. Fadley<sup>3,2</sup>; <sup>1</sup>Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; <sup>2</sup>Physics, University of California, Davis, Davis, California; <sup>3</sup>Materials Sciences, Lawrence Berkeley National Laboratory, Berkeley, California.

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on Au(111) have become increasingly important to achieve surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful in functionalizing surfaces for surface attachment and immobilization of proteins, DNA, viruses, as well as using the charged state of the endgroups in switchable surfaces. We are also using such functionalization in surface attached interlocking molecules to attempt to induce and measure reorientation (switching) within interlocking molecules. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH<sub>2</sub>)<sub>15</sub>COOH) a long-chain molecule with strong chain-chain interactions and thioctic acid (S<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>2</sub>)<sub>4</sub>COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO<sup>-</sup> vs. COOH.) In addition, we will present preliminary results using functional groups in switching interlocking molecules on surfaces. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL; also W-DE-AC03-76SF00098 at the ALS at LBNL, DE-AC03-76SF00515 at the SSRL at SLAC.

#### **T5.16**

##### **Structural characterization of polymer thin film transistors.**

Ni Zhao<sup>1</sup>, Gianluigi Botton<sup>1</sup>, Shiping Zhu<sup>1</sup>, Beng Ong<sup>2</sup> and Yiliang Wu<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; <sup>2</sup>Xerox Research Center of Canada, Mississauga, Ontario, Canada.

The performance of polymer thin film transistors (TFTs) crucially depends on the structural properties of the channel semiconductor layer and its interfaces. Despite extensive studies on the structural characterization of polymer TFTs, reports of direct visualization of the microstructures in the active channel layers and their interfaces have been rare. We have investigated the morphological and structural properties of the polymer semiconductor layer and its interfaces in TFT devices using transmission electron microscope (TEM), atomic force microscope (AFM) and X-ray diffraction (XRD), and have correlated these properties to TFT performance. Highly ordered structures in the semiconductor polymer layer, which are responsible for high field-effect mobility, have been observed. We have also exploited energy-filtered TEM to provide information on the structure and chemical composition of the materials used as component of the TFT and the assembled device. We will describe our direct observation of nano-size domains, the chemical analysis, and the cross-section structural imaging of polymer TFTs. Our success in obtaining a direct visualization for the first time of the ultra-thin self-assembled monolayer (SAM) between polymer and dielectric layer (SiO<sub>2</sub>) with the combination of energy filtered imaging and elemental mapping will be presented.

#### **T5.17**

##### **Electronic processes and exciton decay dynamics at organic semiconductor donor-acceptor interfaces.** Linus Lu, JiSeon Kim and Richard H Friend; Physics (Optoelectronics Group), University of Cambridge, Cambridge, United Kingdom.

We have studied different length-scale organic semiconductor heterojunctions based on blends and random copolymers of conjugated polyfluorene materials;

poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB/Donor) and poly(9,9-dioctyl-fluorene-co-benzothiadiazole) (F8BT/Acceptor). In these materials, organic heterojunction starts with predominant micron-scale in the blends and ends with

molecular-scale segregation in the copolymers. At these different length-scale organic heterojunctions, we have explored the molecular-scale electronic processes such as charge-carrier injection, transport, recombination, and dissociation processes, through a combination of electrical, optical, and spectroscopic measurements at various device structures such as Light Emitting Diodes (LEDs) and Photovoltaics (PVs). Our results show that the molecular-scale electronic processes within these materials are quite different when these processes occur at the heterojunctions with different length-scales. For example, in the LEDs, the copolymer exhibits a much constant electroluminescence quantum efficiency through high electric field, whereas the blend shows initial high efficiency at low electric field but drastically decay as an electric field increases. In the PVs, the copolymer shows different short-circuit photocurrent action spectra compared to the blend, without changing the maximum peak external quantum efficiency of the short-circuit photocurrent.

However, there is a very little difference in electron and hole mobility in copolymer and blend. In this report, we also present a photophysics study of exciton decay dynamics in these systems, based on the observations we made from time-correlated single-photon counting (TCSPC) experiments on both films and diluted solutions. We will discuss the role and implication of organic semiconductor heterojunctions, especially across the donor-acceptor interface in the copolymer, for organic semiconductor devices. We have initially identified a new intra-chain state/species found in this copolymer system previously absent in samples of both the homopolymers and the blend. This intra-chain exciton has a unique and distinctive decay dynamics and contribute to efficient electron-hole capture in light-emitting diodes and charge dissociation in photovoltaics (PVs) incorporating the copolymer as the active material.

#### **T5.18**

##### **Negative Capacitance Phenomenon in Organic and Polymeric Light-Emitting Diodes: a Recombination-Dependent Event.**

Fernando A. Castro<sup>1,2</sup>, Paulo R. Bueno<sup>1</sup>, Lucas F. Santos<sup>2</sup>, Roberto M. Faria<sup>2</sup>, Libero Zuppiroli<sup>3</sup>, Frank A. Nuesch<sup>3</sup> and Carlos F.O. Graef<sup>1</sup>; <sup>1</sup>DFM - FFCLRP, Universidade de Sao Paulo, Ribeirao Preto, Sao Paulo, Brazil; <sup>2</sup>DFCM - IFSC, Universidade de Sao Paulo, Sao Carlos, Sao Paulo, Brazil; <sup>3</sup>LOMM, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Organic semiconductors either based on molecular or macromolecular materials have attracted much attention for their potential applications as active materials in electronic and optoelectronic devices. However, the basic physical phenomena involved in charge injection, transport and recombination in such kind of devices are not understood up to this moment, despite of the great progress achieved in the last decade. A good approach to study injection, transport and recombination features involved in PLEDs and OLEDs is to use impedance (admittance) spectroscopy (IS), taking advantage of the fact that it is a frequency-resolutive technique. Here we have used IS technique to discuss about the evidences that negative capacitance phenomenon arises in PLEDs and OLEDs just when the recombination process is present, so that they are related to each other. The negative capacitance is observed in a variety of conditions and systems, representing one of the less clearly understood dielectric phenomena. Accordingly, there are few reports on negative capacitance in pure electronic devices and the physical origin of this phenomenon is far from been understood. Our goal in this work is to demonstrate that this negative capacitance phenomenon is related to the recombination process in organic electroluminescent devices. We report the appearance of negative capacitance in tris-8-hydroxyquinoline-aluminum (Alq<sub>3</sub>) and poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) based LEDs, depending on dc forward bias conditions leading to recombination. In ITO/CuPc/NPD/Alq<sub>3</sub>/LiF/Al LED we observe a capacitance increase as we start increasing the forward bias. However for bias higher than 2 V (when recombination starts to take place), the capacitance starts to decrease and becomes strongly negative. On reverse bias no negative capacitance is observed. Similar results are observed for MEH-PPV, although the first capacitance increase in forward bias is not seen. In hole-only and electron-only organic diodes based on these active materials no negative capacitance phenomenon is observed.

### **T5.19**

**Fabrication of N-electrode nano-junctions for mono-molecular electronics interconnects** [1]. Olivier Cacciolati<sup>1</sup>, Christian Joachim<sup>1</sup>, Jean-Paul Martinez<sup>2</sup>, Franck Carcenac<sup>2</sup> and Erik Dujardin<sup>1</sup>; <sup>1</sup>NanoScience Group, CNRS - CEMES UPR 8011, TOULOUSE, France; <sup>2</sup>LAAS, CNRS, Toulouse, France.

So far, the CMOS-based microelectronics technology has been able to keep up with the miniaturization and integration challenges thanks to numerous scientific and technological innovations. However, the foreseeable physical limitations of the current semiconductor industry could be reached within the next decade. The idea that a few (or even one) molecules could be embedded between electrodes and perform basic functions of digital electronics was suggested in the 70s and has now been implemented in a number of different so-called hybrid-molecular devices. Nevertheless, the fabrication of complex circuits out of individual components remains challenging. A second approach is mono-molecular electronics, in which a single molecule integrates several elementary functions and the required interconnections. Computation is achieved by interfacing the molecules with N input/output [2]. Following this second approach, we will present a new e-beam nanolithography process developed to fabricate N-electrodes nano-junctions for the electrical interconnection of a mono-molecular circuit having N input/output,  $N > 4$ . The fabricated electrodes of the junction have a width below 20 nm and are buried but with an upper surface coplanar with the SiO<sub>2</sub> surface. For  $N = 5$  and  $N = 20$ , such electrodes can be positioned on a circle of a diameter below 40 nm and 200 nm respectively. An interconnection roadmap for molecular electronics will also be discussed to put this new process in perspective with the different possible ways of interconnecting a mono-molecular circuit via atomic wires, nanotubes or metallic nanowires. [1] O. Cacciolati, C. Joachim, J.P. Martinez, F. Carcenac, in press. [2] C. Joachim, J. K. Gimzewski, A. Aviram, Nature, 2000, 408, 541-548.

### **T5.20**

**Preliminary Nanocalorimetry Study of Self-Assembled Monolayers on Planar Layers and Nanoparticles of Au on SiNx Substrates.** Z S Zhang<sup>1</sup>, M Yu Efremov<sup>1</sup>, O M Wilson<sup>2</sup>, E A Olson<sup>1</sup>, M Zhang<sup>1</sup>, P V Braun<sup>1</sup> and L H Allen<sup>1</sup>; <sup>1</sup>Materials science and engineering, U. of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>2</sup>Chemistry, Texas A&M University, College Station, Texas.

We present a new technique for characterizing thermal properties of SAMs which are chemisorbed onto isolated gold nanoparticles as well as continuous gold planar layers on SiNx. The Au films are deposited on a SiNx substrate, the growth of SAMs is performed by immersing the substrate into an alkanethiol solution. The amount of material sampled (20 picomole) is typically below the sensitivity limits of conventional calorimetry. However, the nanocalorimetry technique (1,2) – which has recently been used to observe glass transition in 1-3 nm thick films of polymers (3) and melting in 0.2 nm thick films of metals (4) – has higher sensitivity (less than 1 nJ/K) and allows us to study the order/disorder phase transition and desorption of SAMs. We envision this technique to be useful in characterizing SAMs formed on both planar (2-D) and particle (3-D) surfaces in a systematic manner. (1) M.Yu. Efremov, E.A. Olson, M. Zhang, F. Schiettekatte, Z.S. Zhang, and L.H. Allen, Rev. Sci. Instrum. (2004), in press. (2) E.A. Olson, M.Yu. Efremov, M. Zhang, Z.S. Zhang, and L.H. Allen, J. MEMS 12 (2003) p.355. (3) M.Yu. Efremov, E.A. Olson, M. Zhang, Z.S. Zhang, and L.H. Allen, Phys. Rev. Lett. 91 (2003) p.085703. (4) M.Yu. Efremov, F. Schiettekatte, M. Zhang, E.A. Olson, A.T. Kwan, R.S. Berry, and L.H. Allen, Phys. Rev. Lett. 85 (2000) p.3560.

### **T5.21**

**Nanoscale Patterning of Organic and Molecular Electron Devices through Radiation-induced Film Modification.** Brian Alexander Mattis, Yunan Pei and Vivek Subramanian; Electrical Engineering, University of California, Berkeley, Berkeley, California.

Molecular electron devices have recently gained significant attention, with particular applications in ultra-dense memories and computational circuits. To date, all demonstrations of ultra-dense molecular circuits have used blanket organic layers, resulting in the potential for crosstalk between adjacent devices. Furthermore, such demonstrations have either used silicon-based addressing circuitry, or hardwired off-chip addressing. Clearly, on-chip, on-pitch addressing is a crucial need for ultra-dense molecular electronics. However, to increase device density to nanoscale dimensions, it has become essential to develop a patterning technology that can electrically isolate devices from one-another at dimensions far below those obtainable via the shadow-masking typically used in organic layer deposition. Here, the direct patterning of organic semiconducting films utilizing electron-beam lithography has proven to modify the molecular structures, resulting in drastic changes in the film's

electrical characteristics. By testing the exposure of OTFT device channels, electron doses as low as  $10\mu\text{C}/\text{cm}^2$  can reduce both mobility and on-current to 10% of their original values. These effects have also shown high contrast, as only slight changes in applied dosage can have a significant electrical impact, which is important when considering the inevitable beam-spreading and the resulting unintentional exposure occurring as electrons bombard the organic film surface. Current organic materials under investigation include poly(3-hexylthiophene) and pentacene, which were chosen for their high mobility and wide-spread usage in the research community. Both materials show excellent contrast and, in conjunction with this technology, allow for the fabrication of densely packed transistor arrays with extremely low inter-device currents. Such transistor arrays may be used to provide on-pitch addressing for molecular crosspoint array memories.

### **T5.22**

**A New Method of Fabricating Nano-sized Gap Electrodes.** Chan Woo Park, Sang-Ouk Ryu, Sang-Hee Ko Park, Han Young Yu, Ung Hwan Pi and Sung-Yool Choi; Basic Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon, South Korea.

We have fabricated a pair of metal electrodes with a nano-sized gap to characterize the electrical properties of a single molecule for the application in molecular electronic devices. A physical width of the nano-sized gap is crucial for characterization of molecules and has to be comparable to the length of a molecule. In the previous techniques of fabricating nano-gap electrodes, for example, the mechanical break-junction, electrochemical deposition, and electromigration methods, the overall processes are complicated and the size, shape, and location of nano-gaps cannot be easily controlled in a reproducible manner. In this paper, a new method of forming nano-gap electrodes using a thin sacrificial layer is described. This method consists of the formation of the first metal electrode with vertical sidewalls and the deposition of a thin conformal film as a sacrificial layer followed by the deposition of the second metal layer, which results in a pair of metal electrode regions with the sacrificial layer between them. The thickness of the sacrificial layer itself works as a gap between the two electrode regions after a highly selective etching process. In this new method, the gap is located exactly at the edges of the first metal electrode and the width of the gap can be easily controlled by adjusting the thickness of the sacrificial layer. Using atomic-layer-deposited thin films as sacrificial layers, we fabricated several Au/Pt electrode pairs with gaps of a few nms reproducibly.

### **T5.23**

**Conductance Measurements on Different Phases of Dodecanethiol Self-Assembled Monolayer.** Ung Hwan Pi, Chan Woo Park, Sang-Ouk Ryu, Han Young Yu and Sung-Yool Choi; Basic Research Lab., ETRI, Daejeon, South Korea.

We report the effect of the order of molecules on the tunneling currents through the molecular films. A self-assembled monolayer (SAM) of dodecanethiol was deposited on Au(111)/mica substrate followed by annealing in UHV condition. Scanning tunneling microscope (STM) imaging reveals the formation of three different phases, a high density one with  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure, a low density one with well-ordered stripe structure, and a disordered mixed one. Current-voltage characteristics were measured on each phase of different structures by using scanning tunneling spectroscopy. The current voltage curves measured on disordered phase were less reproducible than those measured on the well ordered phases. This shows that the ordering of the molecules is very important in stable measurement of the electrical properties of the molecular films.

### **T5.24**

**Electrical properties of bamboo-shaped multiwalled carbon nanotubes.** Jae Won Jang<sup>1</sup>, Cheol Eui Lee<sup>1</sup>, Tae Jae Lee<sup>2</sup>, Seung Chul Lyu<sup>2</sup> and Cheol Jin Lee<sup>2</sup>; <sup>1</sup>Physics, Korea Univ., Seoul, South Korea; <sup>2</sup>Nanotechnology, Hanyang Univ., Seoul, South Korea.

The bamboo-shaped multiwalled carbon nanotubes (BS-MWNTs) have been reported in various forms, such as arc-discharge evaporation of graphite, catalytic pyrolysis of hydrocarbons at high temperature, thermal chemical vapor deposition on catalytic film deposited substrates, and nitrogen-containing CNTs (CN<sub>x</sub> nanotubes). Their growth mechanism and properties of BS-MWNTs have been of great interest. In this work, we have studied the electrical properties of BS-MWNTs. The temperature-dependent resistivity measurements were carried out on BS-MWNTs vertically grown on cobalt catalyst deposited Al<sub>2</sub>O<sub>3</sub>/Ti substrates and iron catalyst deposited SiO<sub>2</sub>/Ti substrates at 750 - 950 °C by thermal chemical vapor deposition. Besides, the electrical properties of individual BS-MWNTs with 2- $\mu\text{m}$  size Ti/Au/Ti electrodes were measured. For the bulk BS-MWNTs, a heterogeneous model, compromising quasi 1-D metal terms and the fluctuation-induced tunneling through thin barriers between metallic

regions, was introduced to explain the conduction mechanism of bulk sample. As a result, the inter-sheet conduction has been found to be a decisive factor of the conduction mechanism. The electrical properties of individual BS-MWNTs were investigated in relation to the compartment structure in the BS-MWNTs.

#### **T5.25**

**Acidochromism of Fluorescent Distyrylbenzenes containing Pyridine Rings.** Heiner Detert, Institut fuer Organische Chemie, Johannes Gutenberg-Universitaet, Mainz, Germany.

A series of C<sub>2</sub>-symmetrical aza- analogous 1,4-distyrylbenzenes has been synthesised via twofold PO-activated olefinations or Heck reactions. Pyridine, pyrimidine and quinoline were used as terminal rings, furthermore, the 2,5-positions of the central benzene ring were substituted with H, alkoxy, or alkylsulfonyl groups. All compounds were freely soluble and strongly fluorescent. Whereas the electronic spectra of the pyridine and pyrimidine chromophores were very similar to those of the parent compound 1,4-distyrylbenzene, the spectra of the former were strongly altered in the presence of trifluoroacetic acid. Depending on the concentration of acid, protonation of the ground state and/or the excited state caused bathochromic shifts of the absorption and the emission spectra accompanied by reductions of the fluorescence efficiencies.

#### **T5.26**

**Abstract Withdrawn**

#### **T5.27**

**Logic gates with novel molecular rectifier having Donor-sigma-Acceptor-SAC molecule for molecular electronics.** hyoyoung Lee, Do-Hyun Kim, Eun-ju Lee and Taehyoung Zyung; ETRI, Taejon, South Korea.

Molecular electronics, a new technology based on molecules and molecular-scale components, is getting an interesting topic as the miniaturization of solid-state silicon circuitry is edging closer and closer to fundamental limits, especially for the circuit density and the cost of chip-manufacturing facilities. It has been proposed that molecular electronics may provide moderate computational power, high-density memory and logic devices in an extremely small, low-power format that will not require high cost fabrication facilities. For the realization of logic gates with diode array device, a stable molecular rectifier consisting of self-assembled monolayer (SAM) on the metal electrode has been required. Here, we report the synthesis and characterization of novel electron donor-sigma-acceptor-thiol acetate molecule including reduction and oxidation potentials of CV data and the characterization for the formation of single monolayer by SAM. In addition, we also report molecular rectifying properties with CP-AFM and metal-molecule-metal (MMM)-type device. Finally, the array device fabrication and performance of molecular logic gates will be presented.

#### **T5.28**

**Abstract Withdrawn**

#### **T5.29**

**Resistivity Anomaly Observed at Interfaces of C60 Derivatives Self-Assembly Monolayer /Ultrathin Au Films.** Hirohi Yamamoto, Nobuyuki Iwata and Yoshiki Shimizu; College of Sci. & Technol., Nihon University, Funabashi, Chiba, Japan.

The exotic electric conducting properties, for example a room temperature superconductivity have been expected at interfaces of organic molecule monolayer /metallic ultrathin film. The purposes of this work are to prepare such the interface and to examine its conducting properties. Self-assembly monolayers of C60 derivatives, C60-O-C8SH, (C60-SAM) were accumulated on ultrathin Au films which were deposited on MgO (100) single crystal substrates. The surface morphologies of the specimens were observed and analyzed by AFM. Since the surfaces of pre-annealed MgO were atomically flat and revealed step-terrace structures, the ultrathin Au films were deposited along the edges of the steps with the length of a few micro-meters. As the result of the characteristic nano-structure of the Au films, the C60-SAM adsorbed on them showed also one-dimensional alignments with the width of few tens nm. When temperature dependences of the resistivity of the C60-SAM/ultrathin Au film were measured by a four probe technique, the Au electrodes were simultaneously deposited during the preparation of the Au ultrathin films through the metal masks in which the distance between the holes was 0.19mm. Some of the specimens revealed the temperature dependences of resistivity deviated from metallic linear dependences on temperature and/or anomalous changes of resistivity in the temperature range of 150 - 250K.

#### **T5.30**

**Fabrication and Conduction mechanism of the metal-SAM-metal containing Phenylene ethynylene groups.** Do-Hyun Kim<sup>1,3</sup>, Hyoyoung Lee<sup>1</sup>, Chung-Kun Song<sup>3</sup>, Eun-ju Lee<sup>1</sup>, Changjin Lee<sup>2</sup>, Yongku Kang<sup>2</sup> and Taehyoung Zyung<sup>1</sup>; <sup>1</sup>Basic Research Division, ETRI, Daejeon, South Korea; <sup>2</sup>KRICT, Daejeon, South Korea; <sup>3</sup>Dept. of Electrical & Electronics & Computer Eng, Dong-A Univ., Busan, South Korea.

As microelectronics devices approach their technological and physical limits, molecule electronics, i. e., the information technology at the molecule-scale, becomes more and more investigated and envisioned as a promising candidate for the nanoelectronics of the future. To this respect, synthesized molecules on solid substrates is a powerful 'bottom-up' approach (Langmuir-Blodgett(LB) and Self-Assembled(SA) method) for the fabrication of devices for molecular-scale electronics. For the molecular devices it is the most difficult task to attach nano-size metal contacts on the active molecule. Several ways have been suggested. But, these methods are complicated and required expensive fabrication cost. In addition, to measure the electronic transport through an organic monolayer, we need a test device as simple as possible. In this presentation we fabricated an array of molecular devices with a simple vertical metal-molecule-metal (MMM) junction. Especially, SiO<sub>2</sub> or SiN<sub>x</sub> insulating layer was employed in order to prevent the electrical short circuit between bottom and top contacts. And to contain the molecules inside, the nanopores were formed in insulating layer by RIE. The molecular devices produced diode-like characteristics and they produced a good yield only with 4% of short circuits, reflecting a possible application to characterize unknown molecules and fabricate a molecular system. Also, we report measurements on through-bond electronic transport properties of phenylene ethylene based molecule-metal junctions. Nanoscale metal-molecule-metal junctions with single monolayer of self-assembled phenylene ethylene were analyzed with variable temperature conductance measurements to determine the dominant electronic transport mechanisms.

#### **T5.31**

**Measuring and Engineering the Conductivities of tris-(8-hydroxyquinoline) Aluminum.** S.K. So, S.C. Tse and H.H. Fong; Physics, Hong Kong Baptist University, Hong Kong, China.

The electron mobility of *tris*-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) is intentionally altered by means of doping. Transient electroluminescence (EL) is then employed to measure the electron mobility of doped Alq<sub>3</sub>. The transient EL sample has a structure of ITO/TPD/undoped Alq<sub>3</sub>/doped Alq<sub>3</sub>/cathode. Intrinsic electron mobility of Alq<sub>3</sub> can be evaluated for the thick film devices and the results are in excellent agreement with independent time-of-flight measurements on non-dispersive transient. Mobilities of C540, DCM, and BPhen doped-Alq<sub>3</sub> are measured. The electron mobility is reduced by almost one order of magnitude after doping C540 while DCM doped-Alq<sub>3</sub> exhibits much lower electron mobility. The decrease in mobility can be attributed to scattering or trapping of carriers as they traverse through the doped layer. However, the electron mobility is enhanced in BPhen doped-Alq<sub>3</sub>. It is expected that by combining Alq<sub>3</sub> and BPhen at the right composition, the conductivity and the stability of the "alloy" will be optimized. Reference: [1] S.C. Tse, H.H. Fong, and S.K. So, *J. Appl. Phys.* **94**, 2033 (2003). [2] H.H. Fong, K.C. Lun, and S.K. So, *Jpn. J. Appl. Phys., Part 2*, **41**, L1122 (2002)

#### **T5.32**

**Atomic Resolution STM Study of Single-Walled Carbon Nanotubes on GaAs(110).** Laura Ruppalt, Peter M. Albrecht and Joseph W. Lyding; Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Carbon nanotubes, because of their unique blend of robust electronic and material properties and inherent nanoscale-dimensionality, could form the fundamental building block of the next generation of electronic devices<sup>1</sup>. Additionally, reports of the photo-conductive<sup>2</sup> and -absorptive<sup>3</sup> properties of these structures raise the possibility of nanotube-based optoelectronic devices. However, before such devices can be fully realized and the materials properties of nanotubes fully exploited, a more thorough understanding of nanotube properties and their interactions with technologically relevant substrates must be achieved. To that end, we have deposited and obtained atomic resolution scanning tunneling microscopy (STM) images of single walled carbon nanotubes (SWNT) on the cleaved GaAs (110) surface in ultra-high vacuum (UHV). The cleaved III-V substrate is well suited to surface interaction studies due to the absence of surface states within the bandgap. Additionally, the semiconducting III-V materials form the basis of most current optoelectronic devices and may play an important role in the development of nanotube-based photonic devices. In our study, SWNT's were deposited in-situ via a dry-contact procedure previously demonstrated on the hydrogen passivated Si (100) surface<sup>4</sup>. Subsequent STM images reveal evidence

of a fairly high density of nanotubes, similar to that seen on Si, with no indication of tube or substrate perturbation due to the deposition process. These results suggest the successful extension of this in-situ dry-contact deposition technique to more general substrates, a step that would greatly facilitate further UHV STM investigations of nanotube interactions with surfaces incompatible with solution-based ex-situ deposition procedures. Both topographic and current images provide simultaneous atomic resolution of the SWNT's and the underlying substrate. Individual tube chirality can be identified and theoretical band gap predictions calculated. Spectroscopic data reveal nanotube bandgaps in the semiconducting range, with electronic features distinguishable within the GaAs substrate bandgap. Further studies of SWNT's on the cleaved GaAs surface, as well as investigations of carbon nanotubes coupled to more complex III-V heterostructures, will also be reported. <sup>1</sup>J. Appenzeller, R. Martel, V. Derycke, M. Radosavljevic, S. Wind, D. Neumayer, Ph. Avouris, *Micro. Engin.* **64**, 391-97 (2002). <sup>2</sup>M. Freitag, Y. Martin, J.A. Misewich, R. Martel, Ph. Avouris, *NanoLetters* **3** 1067-71 (2003). <sup>3</sup>H. Kataura, et. al., *Synthetic Metals*, **103**, 2555-2558 (1999) <sup>4</sup>P.M. Albrecht, R.M. Farrell, W. Ye, and J.W. Lyding, Conference Proceedings, Third IEEE Conference on Nanotechnology 2003, 327-30 (2003).

### T5.33

**Ultrathin Polymer Film Capacitor Composed of Relaxor-Ferroelectric Fluoropolymer Langmuir-Blodgett Films.** Cheng Huang<sup>1</sup>, Q.D. Shen<sup>2</sup> and Q.M. Zhang<sup>1</sup>; <sup>1</sup>Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Department of Polymer Science and Engineering, Nanjing University, Nanjing, Jiangsu, China.

Polymer film capacitors are widely used in electronics. However, compared with ceramics, the dielectric constant of polymers is small and the volume of the polymer film capacitor is large. Improving the dielectric constant and reducing the film thickness of capacitor have two points of merit, that is, large value of capacitance and smaller size of capacitor. Smaller size of capacitors is recently required for miniaturizing cellular phones and portable computers. Furthermore, molecular size capacitor will be need for nanotechnology. Recently we have developed processible and high-performance poly(vinylidene fluoride-trifluoroethylene) based electroactive fluoropolymer which possess a relatively high room-temperature dielectric constant (60), one order of magnitude higher than that of current dielectric polymer materials. The high-dielectric-constant fluoropolymer ultrathin film might be a good candidate for an ultrathin polymer film capacitor. To achieve ultrathin film capacitor and molecular size capacitor, the Langmuir-Blodgett (LB) technique was carried out on the silicon wafer. In this paper, the capacitor properties of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer, P(VDF-TrFE-CFE), Langmuir-Blodgett films were investigated as a function of number of layers with dielectric and current-voltage measurements. The breakdown electric field of the LB films was also measured with the number of layers. The results gave us an idea for constructing molecular thin film capacitors using the relaxor-ferroelectric fluoropolymer materials. Compared with our previous results from the spin-cast polymer ultrathin films, by using the LB technique, thin film thickness can be precisely controlled by the thickness of monolayer (nanometer level) and the number of deposited layers; thus, we can make an ultrathin polymer film capacitor at a molecular level.

### T5.34

**Effect of tertiary butyl substitution on the charge transport of aromatic hydrocarbon based organic semiconductors.** H.H. Fong, K.L. Tong and S.K. So; Physics, Hong Kong Baptist University, Hong Kong, Hong Kong.

Aromatic hydrocarbon based organic compounds (e.g. anthracene, naphthalene, and pentacene) have demonstrated importance in organic light-emitting diodes because of its high luminance efficiency and superior stability. In device application, tertiary butyl (*t*-butyl) substitution is practically used to prevent re-crystallization of organic transporters and fluorescence quenching of organic emitters. Therefore, it is worth to investigate the effect of *t*-butyl substitution on these hydrocarbon-based complexes. As a demonstration, the charge transport of rubrene (5,6,11,12-tetraphenylnaphthalene or RB), and a new rubrene-based complex, tetra(*t*-butyl)-rubrene [2,8-di(*t*-butyl)-5,11-di[4-(*t*-butyl)phenyl]-6,12-diphenylnaphthalene or TBRB], were examined in form of amorphous films as functions of electric field and temperature by means of time-of-flight technique. It was found that both materials exhibited *p*-type conduction. By *abinitio* calculations, results suggest that the hole conduction is contributed by the central naphthalene moiety. At room temperature, the hole mobility  $\mu_h$  for RB is  $7.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  whereas  $\mu_h$  for the more bulky TBRB is about  $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The microscopic conduction mechanism in both materials can be modeled

by the Gaussian disorder model (GDM) in which hopping conduction occurs through a manifold of sites with energetic and positional disorder. The energetic disorder in RB and TBRB is almost identical and is about 78 meV in each case, and is mainly controlled by Van der Waals interaction. Indeed, the *t*-butyl groups in TBRB induce large fluctuations in the spatial separation among TBRB molecules and result in an increase in the positional disorder from 2.7 to 3.1, and hence a reduction in the hole mobility. With sufficient high mobility in amorphous state, RB can be blended into the polycarbonate (PC) in order to engineer the mobility such that RB:PC is able to establish potential applications in polymeric transistors.

### T5.35

**Electrically Detected Magnetic Resonance applied to Alq3 based light emitting diodes.** George Barbosa Silva<sup>1</sup>, Carlos

Frederico de Oliveira Graeff<sup>1</sup>, Fernando A. Castro<sup>1</sup>, Frank Nuesch<sup>2</sup> and Libero Zuppiroli<sup>2</sup>; <sup>1</sup>DFM-FFCLRP, USP, Ribeirao Preto, Sao Paulo, Brazil; <sup>2</sup>LOMM-IMX, EPFL, Lausanne, Switzerland.

Organic semiconductor devices based on molecular material have attracted much attention for their potential application as active materials in electronic and optoelectronic devices. Amongst the molecular organic semiconductors, tris(8-hydroxy-quinolate) aluminum (Alq3) is a promising material for light emitting devices. Despite the great progress achieved in the understanding of devices operation in the last two decades, the detailed description of processes such as injection, transport and recombination is still lacking. In this work we use electrically detected magnetic resonance (EDMR) to provide microscopic insight in these phenomena. We demonstrate that this sensitive technique can be used to study processes such as carrier transport and recombination in real devices. For this study we used homopolar and bipolar device architectures based on Alq3 such as ITO/CuPc/ $\alpha$ -NPD/Alq3/LiF/Al (bipolar), ITO/Alq3/ $\alpha$ -NPD/Ag (hole-only) and Al/LiF/Alq3/LiF/Al (electron-only). All devices were fabricated by vapor deposition in high vacuum. For the EDMR experiments the samples were contacted and sealed inside a quartz tube in order to avoid air induced degradation. The fabrication and encapsulation occurred without exposure to ambient atmosphere. In an EDMR experiment, microwave-induced changes in the conductivity are measured as the sample is subjected to a swept dc magnetic field. The measurements were done using a X-Band (9 GHz) and a K-Band (24 GHz) spectrometer at room temperature. In the case of bipolar devices, the EDMR signal is only observed in forward bias and when the diodes starts to emit light. This signal is quenching, in other words the conductivity decreases when the system is brought into resonance, typically  $10^{-5}$  in amplitude and composed of two lines. The first component has a linewidth of 16 G and a g-factor that decreases from 2.0046 to 2.0041, as the forward bias increases from 3 to 8 V. The second component has a g-factor of 2.0035 and linewidth that increases from 20 to 35 G as the bias voltage increases. The EDMR signal observed is assigned to spin dependent exciton formation. The first component is attributed to cations, while the second to anions. The EDMR signatures of cations and anions are corroborated by measurements in hole-only and electron-only devices where spin dependent hopping processes were observed.

### T5.36

**Carbon Nanotube T-junctions: Formation, Characterization and Transport Properties.** Po-Wen Chiu, Jean-Michel Benoit, Ursula Dettlaff and Siegmund Roth; MPI for solid state research, Stuttgart, Germany.

Intermolecular carbon nanotube junctions were formed by coupling chemically functionalized nanotubes with molecular linkers. An end-to-side or end-to-end heterojunction were formed by reacting chloride terminated nanotubes with aliphatic diamine. The chemically modified nanotubes were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy and transport measurements. The optical measurement results reveal that the attached chemical functional groups can behave as either an electron donor or acceptor, and facilitate charge transfer with the nanotube host. The charge transport in individual T-junctions will also be discussed in detail.

### T5.37

**Oligoacenes. Theoretical Prediction of an Open Shell Ground State and a Constant, Semiconductor Type HOMO-LUMO Gap.** Michael Bendikov, Hieu M Duong, Kyle Starkey, Emily A Carter, Kendall N Houk and Fred Wudl; Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California.

Oligoacenes have attracted wide interest from both theoretical and experimental scientists. Pentacene has received much attention in the very recent past due to its unusually high charge-carrier mobility as the active semiconducting material in field-effect transistors. Despite considerable interest, homologs higher than hexacene remain to be fully characterized. A thorough understanding of electronic properties in large oligoacenes ends with pentacene. In this paper, we will

present our results using density functional theory (DFT) and complete active space self-consistent field (CASSCF) methods that strongly support the intriguing finding that even small (heptacene and higher) oligoacenes exhibit a significantly high biradical character and a constant non-zero semiconductor type HOMO-LUMO gap. We were somewhat curious to find that at the RB3LYP/6-31G(d) level of theory, the wavefunction for as small an oligoacene as hexacene (and all longer oligoacenes) becomes unstable. Re-optimization of the wavefunction, using the unrestricted broken symmetry B3LYP method (UB3LYP), leads to a biradical singlet ground state. In contrast to the common view that acenes are closed shell systems; these results, to the best of our knowledge, offer the first theoretical prediction for biradical character in the ground state of oligoacenes. For heptacene, at the B3LYP/6-31G(d) level of theory the open shell singlet is 2.7 kcal/mol more stable than the closed shell state and the spin contamination is small ( $\langle S^2 \rangle = 0.80$ ). However, these values increased with respect to the number of benzenoid units. The relative energy of the triplet state (using the same level of theory) for decacene is 4.7 kcal/mol lower than the closed shell singlet state, however, it is still 5.8 kcal/mol higher than the open shell singlet state. Similar results were obtained with BLYP, PW91 and BPW91 functionals. Triplet structures are always higher in energy than open shell singlet structures, but the triplet is more stable than closed shell singlet for nonacene. Hence, our calculations predict that oligoacenes will maintain a ground state singlet even above hexacene-octacene. CASSCF calculations are in agreement with DFT results. The data presented here, in contrast to the literature, predict a non-zero HOMO-LUMO gap (1.8 eV), similar to that of hexacene, thus experimentally known oligoacenes are near the limit of the calculated HOMO-LUMO gap. Moreover, longer acenes are anticipated to exhibit biradical character. This might be a reason for their high reactivity and reported difficulty in isolation. Any design of electronic devices based on the higher oligoacenes will require that attention be paid to the theoretical results given above.

### T5.38

**Conjugated polymer wires for nano-scale field effect transistors.** Hyunsik Moon<sup>1</sup>, Woong Sang Jahng<sup>2</sup>, Xing Cheng<sup>3</sup>, L. Jay Guo<sup>3,1</sup> and M. David Curtis<sup>2,1</sup>; <sup>1</sup>Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Chemistry, University of Michigan, Ann Arbor, Michigan; <sup>3</sup>Electrical engineering and computer science, University of Michigan, Ann Arbor, Michigan.

Organic semiconductors can be described as molecular assemblies in which conjugated molecules are held together by weak van der Waals type force. The weak intermolecular interactions lead to the potential limitation of the performance of organic field effect transistors because of substantial electron-phonon scattering at room temperature. One of two strategies for higher field effect mobility is to design organic semiconductors with strong intermolecular interactions among nearest neighbor molecules. The stronger interaction would result in stiffer crystalline structures, facilitating charge carrier transport. The other is to explore alternative conduction mechanisms and device structures. This would involve a molecular wire of rigid-rod conjugated polymers, the two ends of which are covalently bonded to source and drain electrodes. Carrier transport takes place through a single polymer chain which would be bridged between two electrodes. Mobility along the long axis of polyacetylene was reported to be as high as 1000 cm<sup>2</sup>/Vs which is comparable to that in crystalline silicon. For the realization of this device, there are two big challenges. Firstly, a polymer with functional groups should be synthesized so that the functional groups might be self assembled onto the electrodes to make good contacts. Secondly, transistor channel length has to be reduced from micro size to nano size to fit the length of the single polymer chain. In this work, we designed and prepared polyphenylene ethynyls (PPEs) with thioacetate groups at the polymer chain ends, and fabricated nano-scale field effect transistor. The Heck-Cassar-Sonogashira-Hagihara reaction, the Pd-catalyzed coupling of aromatic alkynes and aromatic iodides in tetrahydrofuran/ amine solvent, yielded PPEs with reactive iodo terminal groups. Subsequent coupling reaction between the PPEs and a compound containing the thioacetate groups produced the target polymer. The synthesized polymer was self assembled onto the devices with a nano channel which was prepared by E-beam lithography. We will present molecular design, synthesis, self-assembly and device properties.

### T5.39

**Monte Carlo modelling of charge transport in polymer photovoltaic materials.** Jenny Nelson<sup>1</sup>, Amanda J Chatten<sup>1</sup>, Stelios A Choulis<sup>1</sup> and James R Durrant<sup>2</sup>; <sup>1</sup>Physics, Imperial College London, London, United Kingdom; <sup>2</sup>Chemistry, Imperial College London, London, United Kingdom.

Understanding the mechanism of charge transport in single polymer materials and blends is critical to the development of improved organic solar cells and other molecular electronic devices. Transport in

organic electronic materials is traditionally evaluated within frameworks such as the Gaussian Disorder Model and its variants [1,2] where the field and temperature dependence of charge mobility are used to quantify the degree of energetic and configurational disorder in the charge transport matrix. Although useful for comparative studies, these models are unhelpful for identifying the microscopic transport mechanism or for relating the charge transport properties to the chemical or physical structure of the materials. Moreover, they have as yet been applied only to single component systems and do not allow for the impact of geometry on transport in two-component blends. We have developed Monte Carlo models of polaron transport in organic films that allow for more than one component material, and for alternative microscopic models for the intermolecular hole transfer rate, as well as for correlations in the site energies, which may result from dipolar or torsional interactions [2]. We apply the models to simulate the results of time-of flight mobility measurements in a range of homopolymers and blends. We show that geometric effects on transport in two component systems lead to characteristics typical of dispersive transport even using non-dispersive components. We find that a small-polaron hopping rate is more appropriate than the commonly used "symmetric" and Miller-Abrahams charge transfer expressions in the limit of ordered materials, and we argue that that both polaronic effects and disorder must be incorporated to describe transport in the general case. A complementary probe of charge transport is provided by transient absorption spectroscopy, where the population of polaronic species is monitored optically following photoexcitation. Unlike time-of-flight mobility studies, transient absorption probes transport in the low-field diffusion-limited regime, and in certain conditions the dynamics are dominated by polaron diffusion in a single component [3]. We have previously shown that the rates of transport and recombination in the same material system, respectively measured by ToF and transient absorption, can be correlated experimentally [4]. In this paper we extend our Monte Carlo transport model to the low field regime and in order to explain the observed behaviour with a single transport model. [1] H.Baessler, Phys. Status Solidi (b) 175, 15 (1993). [2] S. V. Novikov et al., Phys. Rev. Lett. 81, 4472 (1998); Z.G.Yu et al., Phys. Rev. Lett. 84, 721 (2000). [3] J.Nelson, Phys. Rev. B 67, 155209, (2003); I.Montanari et al., Appl. Phys. Lett. 81, 3001 (2002) [4] S.A. Choulis et al., Appl. Phys. Lett. (in press)

### T5.40

**High Efficiency Polymer LEDs through Barrier-Free Electron-Hole Capture at Heterojunctions.**

Arne Claudio Mordeani<sup>1</sup>, Ji-Seon Kim<sup>1</sup>, Anoop S. Dhoot<sup>1</sup>, Carlos Silva<sup>1</sup>, Neil C. Greenham<sup>2</sup>, Craig Murphy<sup>2</sup>, Ellen Moons<sup>2</sup>, Salvatore Cina<sup>2</sup>, Jeremy Burroughes<sup>2</sup> and Richard H. Friend<sup>1</sup>; <sup>1</sup>Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Cambridge Display Technology, Cambridge, United Kingdom.

We report a novel, "barrier-free" route for electron-hole capture and recombination at conjugated polymer heterojunctions. This mechanism enables us to fabricate polymer light-emitting diodes of excellent electroluminescence efficiencies (above 19 lm/W), very low turn-on voltages (below 2 V) and high stability under operation (many thousand hours at room temperature). We fabricated "distributed heterojunction" structures by de-mixing of hole-accepting and electron-accepting derivatives of polyfluorene during spin-coating from common solution. The "type II" heterojunction between the two polymers promotes the formation of localised interface states with significant charge-transfer character, termed exciplex states. Time- and temperature-resolved spectroscopic data clearly shows their presence in three different, blue-, green- and red-emitting polymer blends. With respect to the bulk excitons, the exciplexes are red-shifted (between 140 and 360 meV) and their radiative lifetime is strongly increased (between 55 and 120 ns at low temperatures). The excellent device characteristics are achieved because the electron-hole capture at the heterojunction occurs directly into the exciplex without prior injection of one of the charges into the opposite polymer. This barrier-free process is possible because the exciplex has significant charge transfer character and therefore direct overlap with the charge-separated state. We show that the exciplex state can subsequently be thermally excited away from the heterojunction towards the bulk exciton (activation energies between 100 and 250 meV). Due to the long lifetime of the exciplex this process can be highly efficient resulting in efficient bulk exciton electroluminescence. We present time-, temperature- and electric field-dependent photoluminescence and transient absorption data as well as low-temperature electroluminescence from different device structures to show that barrier-free capture and thermally activated exciplex-exciton energy transfer occur in all three polymer blends investigated. The devices discussed here utilise tailored molecular interactions for electronic functionality, and therefore represent a good example for molecular electronics.

#### **T5.41**

##### **Alignment and Photopolymerization of Difunctional Liquid Crystalline Mesogens.** Sang-Hyon Paek<sup>1</sup>, Jemin Yeoun<sup>1</sup> and Ji

Young Chang<sup>2</sup>; <sup>1</sup>Institute of Natural Sciences, Kyung Hee University, Yongin, Kyungki-Do, South Korea; <sup>2</sup>School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

The effective and simplest method to improve viewing angles of liquid crystal display (LCD) is to use compensation films; especially, the films consisting of disk-like (discotic) liquid crystalline polymers (LCPs) are currently employed for TFT-LCDs. The optimal performance of the compensation films requires a specific (in-plane and out-of-plane) arrangement of constituent molecules. The research and development of these films are of great importance in the new technology of advanced materials as well as in the LCD industrial technology. The film technology requires the synthesis and alignment of LCPs and the optical simulation to induce optimal compensation. For the basic and fundamental studies for application of LCPs to the compensation films, the synthesis and photopolymerization of rod-like (calamitic) LCs, the control of alignment of the polymer, and analysis of the photoreaction, polymerization, and the optical properties of the resultant LCPs have been carried out. The two photopolymerizable LC monomers have been employed; one (LCM1) has an acrylate terminal and the core incorporating a diacetylene group, which can allow the selective photopolymerization, while the other (LCM2) does two acrylates as both of terminals. The uniform alignment of the calamitic LC monomers has been achieved using the rubbed polyimide layers and then photopolymerization of the uniformly aligned LCs has been carried out in the nematic phase at various conditions. The studies of DSC and XRD show that LCM1 and LCM2 are nematic in the range of -20 to 75°C and 45 to 115°C, respectively. LCM1 has been selectively photopolymerized at room temperature by irradiation of 254 nm or 365 nm UV light. The former has induced topochemical polymerization of diacetylene groups but the polymerization accompanied removal of the LC phase and thus the uniform alignment. On the other hand, the latter has allowed the photo-initiated polymerization of acrylate groups with keeping the alignment uniformity, resulting in formation of a uniformly aligned LCP. The LCP has then been crosslinked by the topochemical polymerization of diacetylenes. The crosslinked LCP film has showed some uniformity in the alignment and considerable rigidity. In the case of LCM2, the polymerization has been done by irradiation of 365 nm UV light at various environments. As two acrylate groups exist in the both terminals, the resultant LCP has a network structure, resulting in formation of a rigid film for proper polymerization conditions. The polymerization and the properties of the polymerized LCP film are affected by polymerization conditions, while the uniform alignment after polymerization has been observed for all the cases. The study suggests that the polymerization of the LC monomer with both photoreactive terminals, with control of the alignment and polymerization conditions, can induce the LCP film suitable (applicable) to the compensation film.

#### **T5.42**

##### **Chemical-Mechanically Polished Ultra-Smooth Platinum Surfaces for High Yield in Molecular Electronic Devices.**

M. Saif Islam<sup>1</sup>, Shun-Chi Chang<sup>1</sup>, Gun-Young Jung<sup>1</sup>, Chun Ning Lau<sup>1</sup>, Duncan R. Stewart<sup>1</sup>, Doug A. A. Ohlberg<sup>1</sup>, Yong Chen<sup>2</sup>, Shih-Yuan wang<sup>1</sup> and R. Stanley Williams<sup>1</sup>; <sup>1</sup>Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California; <sup>2</sup>School of Engineering and Applied Science, University of California, Los Angeles, Los Angeles, California.

We investigate the impact of Chemical Mechanically Polished (CMP) ultra-smooth platinum (Pt) surfaces on packing and orientation of self-assembled monolayers (SAMs) and on the yield of molecular electronic devices. A large number of measurements were carried out in order to investigate the surface roughness of freshly deposited Pt films using atomic force microscopy (AFM) and a root-mean square (RMS) roughness of 7 Å was observed. In addition, the average height of the grains on the freshly deposited Pt surfaces is measured to be around 30 Å with a high density of more than 50 Å high grain clusters. The height of the grains is larger than that of molecules and it is believed to be a potential cause of device shorting in molecular electronic devices. Although considerable milestone has been reached in the development of manufacturable fabrication process, this critical issue of high density of "shorted" and in some cases "open-circuit" devices has raised a strong concern. We developed and applied a CMP process to achieve ultra-smooth Pt electrode surfaces with less than 1 Å RMS roughness and grew two different types of molecular monolayers, i.e. SAMs of alkoxy-naphthalene thiols and Langmuir-Blodgett (LB) monolayers of eicosanoic acid on polished Pt electrodes defined by optical lithography. Using AFM, contact angle measurements, ellipsometry and reflection-absorption infrared spectroscopy (RAIRS), we observed a dramatic improvement in the packing and orientation of both types of monolayer. A shadow mask was used to delineate the top electrode with Ti metal. We

observed an impressive 100% device yield in the molecular devices made of LB monolayer with device sizes varying from 1000 nm x 5000 nm to as big as 20,000 nm x 5,000 nm. After the "burn-in" step, the molecular devices were found to switches with similar characteristic as were reported by several research groups. Previously more than 50% of the devices with such sizes would short. On the other hand, around 35% of the devices we tested with SAM monolayer of alkoxy-naphthalene thiols molecules demonstrated a diode-like I-V characteristic signifying a remarkable improvement in the device yield given that all of our previous yields with SAMs were less than 5% even when electrodes with extremely narrow dimension were used. Our results indicate that all-trans and well-ordered molecular mono-layers on CMP metal surface can go a long way to solve the existing yield issue of molecular devices making it a strong candidate for future ultra-high density functional nano-electronic circuits.

#### **T5.43**

##### **A Novel Field Effect Transistor using Platinum Nanowires made from Single Wall Carbon Nanotubes.** Shaoxin Lu, Kousik Sivakumar and Balaji Panchapakesan; Department of Electrical Engineering, University of Delaware, Newark, Delaware.

In this paper, we show a new technique of using carbon nanotubes as templates for platinum nanowire formation, and the subsequent electrophoretic self assembly of nanowires between pairs of gold electrodes to form a pt-nanowire field effect transistor. Single wall carbon nanotubes of 1.5-10 nm diameter and 2 micron length were grown using methane based chemical vapor deposition using iron nanoparticles as catalyst material. Following growth, the nanotubes are suspended in a solution of iso-propanol, and 200 µg dihydrogen hexachloroplatinate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) was added to the solution containing nanotubes and agitated at 70 °C for 4 hours. Under the influence of heat and ultrasonic agitation, the platinum nanoparticles were observed to uniformly coat the surface of the carbon nanotubes, thereby forming nanowires of 30 nm to 100 nm in diameter. The nanowires formed were then electrophoretically self-assembled between pair of gold electrodes that were distanced about 2 microns apart on an oxide coated silicon wafer at a DC voltage of 3.5 V. Following electrophoretic self-assembly, the sample was then heated to 200 °C on a hotplate for 10 minutes to allow the evaporation of solvents completely and also to aid in intimate contact between the platinum nanowire and gold electrodes. The sample was then placed in a probe station attached to a curve tracer to obtain the current-voltage characteristics of the nanowire. The two gold electrodes were used as source and drain and the silicon as a back gate for measuring the transistor characteristics. When the gate voltage was changed from -5V to 7V, the source-drain current dropped from 650 nA to 240 nA for source to drain voltage of 4 V. The channel resistance changed almost three times with the changing gate voltage essentially showing field effect characteristics. These results show the promise of building functional electronic materials on carbon nanotubes for nanoelectronics and sensing applications.

#### **T5.44**

##### **Structural study of nitrogen-doping effects in bamboo-shaped multiwalled carbon nanotubes.** Jae Won Jang<sup>1</sup>, Cheol Eui Lee<sup>1</sup>, Seung Chul Lyu<sup>2</sup>, Tae Jae Lee<sup>2</sup> and Cheol Jin Lee<sup>2</sup>; <sup>1</sup>Physics, Korea Univ., Seoul, South Korea; <sup>2</sup>Nanotechnology, Hanyang Univ., Seoul, South Korea.

We have investigated nitrogen doping effects on the structure and crystallinity of bamboo-shaped multiwalled carbon nanotubes (BS-MWNTs) by means of x-ray photoemission spectroscopy (XPS) and transmission electron microscopy (TEM). By controlling the NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> flow ratio during the chemical vapor deposition, the nitrogen concentrations of 0.4% to 2.4% were obtained. According to the XPS measurements, increasing nitrogen concentration gave rise to an increase of the N - sp<sup>3</sup> C bonds as well as deterioration of the crystallinity of the BS-MWNTs. Besides, the N - sp<sup>3</sup> C bonds were found to prevail over the N - sp<sup>2</sup> C bonds above 5% nitrogen concentration. At higher nitrogen concentrations, the BS-MWNTs showed shorter compartment distances, presumably due to the suppressed surface diffusion of carbon on the catalyst particles.

#### **T5.45**

##### **The effect of interfacial states in the electrical characteristics of organic MIS structures.** Ignacio Torres, Eiji Itoh and Martin Taylor; School of Informatics, University of Wales, Bangor, Bangor, United Kingdom.

We have carried a detailed study of both DC and AC electrical characteristics of metal-insulator-semiconductor structures with different organic and inorganic dielectrics (polyimide, poly-silsesquioxane and silicon dioxide) where the semiconductor is a film of poly(3-hexylthiophene) (P3HT) typically between 200 nm and 300 nm thick prepared by spin-coating from a chloroform solution before and after P3HT purification. Contact to the P3HT is via a



vacuum-deposited gold film. The admittance characteristics reveal the presence of interfacial states at the dielectric-semiconductor interface. We have performed a detailed analysis of those states based on equivalent circuits models and propose that they could be responsible for the recently reported instability problems in organic TFTs. We have also performed a study on the change in the electrical characteristics after the sample has been biased for prolonged periods of time at different temperatures. Capacitance-voltage measurements show that instability problems occur not only in the accumulation regime but also in the depletion regime. We have found that light with band-gap wavelength rapidly restores the initial characteristics. Our results suggests that interfacial traps present at the dielectric-semiconductor interface and at the dielectric itself play an important role in the operation of organic semiconductor devices by trapping both majority and minority carriers and are responsible for the electrical instability found in TFTs.

#### **T5.46**

##### **Electron transport in short macromolecular nanotubes.**

Ali Javey and Hongjie Dai; Stanford, Stanford, California.

Electron transport and phonon scattering in metallic carbon nanotubes are explored as a function of length. The mean free paths for acoustic and optical phonon scatterings are estimated to be 300 and 15 nm respectively. Transport through short macromolecular (10 nm) nanotubes is, therefore, found to be free of any significant scattering and thus essentially ballistic at both the low and high bias voltage limits. High currents of up to 120  $\mu$ A can flow through an individual short nanotube.

#### **T5.47**

##### **The memory effect of a quaterthiophene field effect transistor with a polarizable gate dielectric.**

Narayanan Unni K.N., Jean-Michel Nunzi, Sylvie Dabos Seignon and Remi de Bettignies; Laboratory POMA, University of Angers, Angers, France.

The nonvolatile transistor memory element is an interesting topic in organic electronics. In this case a memory cell consists of only one device where the stored information is written as a gate insulator polarization by a gate voltage pulse and read by the channel conductance control with channel voltage pulse without destruction of the stored information. Therefore such transistor could be the base of nonvolatile non destructively readable computer memory of extremely high density. In the present work we have fabricated organic field effect transistors with quaterthiophene as the active material and poly(vinylidene fluoride-trifluoroethylene) as the gate insulator. The device exhibits memory effect because of the ferroelectric properties of the gate. The effect of using another insulating layer of lower dielectric constant as a buffer layer between the ferroelectric polymer and the semiconductor is also discussed.

SESSION T6: Transport in Molecular Junctions II

Chair: Cherie R. Kagan

Thursday Morning, April 15, 2004

Room 3008 (Moscone West)

#### **8:30 AM \*T6.1**

##### **Electrical Transport Properties of Nanoscale Molecular Junctions.**

Theresa S Mayer<sup>1</sup>, Lintao Cai<sup>1</sup>, Yoram Selzer<sup>2</sup>, Marco Cabassi<sup>1</sup>, Thomas Mallouk<sup>2</sup> and David Allara<sup>2</sup>; <sup>1</sup>Department of Electrical Engineering, Penn State University, University Park, Pennsylvania; <sup>2</sup>Department of Chemistry, Penn State University, University Park, Pennsylvania.

Designing molecular devices that exhibit desired electronic properties requires a fundamental understanding of conduction in molecular junctions. Progress toward this goal has been hindered by the complexity of fabricating robust and reliable metal-molecule junctions and in identifying the nature of the as-fabricated molecular junction. This presentation will compare temperature dependent electrical transport measurements and inelastic tunneling spectra collected from three different nanoscale molecular junction testbeds that incorporate dithiolated molecular wire molecules coupled to Au- or Pd-metal electrodes. The testbeds include individual molecules spanning planar nanogaps introduced by Au electromigration, and self-assembled monolayers inserted within or at the intersection of crossing 30-nm diameter Pd- or Au-metal nanowires. The results of these measurements is beginning to provide insight into the role of factors such as molecular structure, endgroups, contacts, and collective effects in metal-molecule junction transport properties.

#### **9:00 AM \*T6.2**

##### **Molecular features that govern resonant tunneling behaviors.**

Christopher Gorman, Chemistry, North Carolina State University, Raleigh, North Carolina.

We will show how structurally simple, electroactive self-assembled monolayers can give rise to negative differential resistance. We will then show how chemical interactions can modify the characteristics of this behavior. These interactions include chemically well-defined lithographic patterning and reversible, non-covalent assembly, disassembly and modulation of the junction.

#### **9:30 AM T6.3**

##### **Multilevel Molecular Memory.**

Chao Li, Wendy Fan and Chongwu Zhou; USC, LA, California.

Multilevel Molecular Memory Chao Li,<sup>1</sup> Wendy Fan,<sup>2</sup> Bo Lei,<sup>1</sup> Daihua Zhang,<sup>1</sup> Song Han,<sup>1</sup> Tao Tang,<sup>1</sup> Xiaolei Liu,<sup>1</sup> Zuqin Liu,<sup>1</sup> Sylvia Asano,<sup>2</sup> M. Meyyapan,<sup>3</sup> Jie Han,<sup>2</sup> Chongwu Zhou <sup>1a</sup> Abstract Multilevel molecular memory was proposed and demonstrated for nonvolatile data storage up to three bits (eight levels) per cell, in contrast to the standard one-bit-per-cell (two levels) technology. In the demonstration, charges were precisely placed at up to eight discrete levels in redox active molecules self-assembled on a single-crystal semiconducting nanowire field effect transistor. Gate voltage pulses and current sensing were used for writing and reading operations, respectively. Charge storage stability was tested up to retention of 600 hours, as compared to the longest retention of a few hours previously reported for one-bit-per-cell molecular memories. Comparison between silicon and molecular devices shows that multilevel molecular memory enables low-power, ultra-dense and high-performance nonvolatile data storage to go beyond the silicon technology scaling limit. 1. Dept. of E.E.-Electrophysics, University of Southern California, Los Angeles, CA 90089, USA. 2. Eloret Corporation, MS 229-1, NASA Ames Research Center, Moffett Field, CA 94035, USA. 3. MS 229-1, NASA Ames Research Center, Moffett Field, CA 94035, USA. a. To whom correspondence should be addressed: chongwuz@usc.edu

#### **9:45 AM T6.4**

##### **Scanned Probe Imaging of Nanoscale Switching Centers in Metal/Molecule/Metal structures.**

Chun Ning lau<sup>1</sup>, Duncan Stewart<sup>1</sup>, R. Stanley Williams<sup>1</sup> and Marc Bockrath<sup>2</sup>; <sup>1</sup>Hewlett-Packard Labs, Palo Alto, California; <sup>2</sup>Applied Physics, California Institute of Technology, Pasadena, California.

Molecular conductance switching has been experimentally observed in a number of different systems using a wide variety of molecules. Understanding the switching mechanisms, which remain controversial to date, is essential for design and fabrication of functional nanoscale switches. Here We describe a new switching mechanism revealed by a novel scanned-probe technique that yields an image of the mechano-electrical response of a Pt/stearic acid/Ti structure device. Such a device switches reversibly between "on" and "off" states with unusually high on/off ratio(105) under appropriate bias voltages. However, because stearic acids have a simple molecular structure and are electrical insulators, previously proposed switching mechanisms such as molecular conformational changes are not likely to account for switching in our system. Using our technique, a single switching center, characterized by a single nanoscale conductance peak, appeared (disappeared) in the scanned probe image when the device was switched "on" ("off"). The quantitative agreement between our results and a simple model demonstrate that conductance switching in our molecular structures arises from the formation and dissolution of individual nanoscale filaments through the molecular layer. This work has important implications for the optimization of molecule-based switching devices for use in nanoelectronics.

#### **10:30 AM \*T6.5**

##### **Gating of Small Organic Molecules.**

Norton D Lang, IBM Research, Yorktown Heights, New York.

I will discuss theoretical studies on small organic molecules linking two electrodes, focusing on changes in conductance due to a gate potential. Issues such as what aspects of the electronic structure of the molecule make it more or less sensitive to the presence of the gate will be explored.

#### **11:00 AM \*T6.6**

##### **Electron Transport in Single Molecule Transistors.**

Jiwoong Park, <sup>1</sup>Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York; <sup>2</sup>Rowland Institute at Harvard, Cambridge, Massachusetts.

The possibility of using single molecules as active elements of electronic devices offers a variety of scientific and technological opportunities. In this talk, we discuss transistors where electrons flow through discrete quantum states of a single molecule. First, we will describe molecules where current flows through one cobalt atom surrounded by two insulating terpyridyl ligands. Depending on the length of the insulating part of the molecules, two different behaviors are observed: Coulomb blockade for a longer molecule and the Kondo

effect for a shorter molecule. We will also discuss measurements of the C<sub>60</sub> fullerene and C<sub>70</sub> dimer (C<sub>140</sub>). In C<sub>140</sub> devices, the transport measurements are affected by an interstage stretching vibrational mode that has an energy of 11 meV. We make comparisons between the observed tunneling rates and those expected from the Franck-Condon model.

**11:30 AM T6.7**

**The Kondo Effect in C<sub>60</sub> Single-Molecule Transistors.**

Douglas Natelson<sup>1,2</sup> and Lam H. Yu<sup>1</sup>; <sup>1</sup>Physics and Astronomy, Rice University, Houston, Texas; <sup>2</sup>Electrical and Computer Engineering, Rice University, Houston, Texas.

We have used an electromigration technique to fabricate C<sub>60</sub>-based single-molecule transistors. We describe in detail the process statistics and the protocols used to infer the successful formation of a single-molecule transistor. At low temperatures each transistor acts as a single-electron device in the Coulomb blockade regime. In several devices we observe conductance features characteristic of the Kondo effect, a coherent many-body state comprising an unpaired spin on the molecule coupled by exchange to the conduction electrons of the leads. The inferred Kondo temperature can significantly exceed 100 K. Signatures of molecular vibrational modes are also observed in the Kondo regime.

**11:45 AM T6.8**

**Phenyldithiol-based Molecular Transistors with Strong Gate Effects.**

Hiroshi Inokawa, Hiroshi Nakashima, Kazuaki Furukawa, Kenji Yamazaki, Junzo Hayashi, Yasuo Takahashi and Keiichi Torimitsu; NTT Basic Research Laboratories, Atsugi, Kanagawa Pref., Japan.

We introduced a new method to efficiently fabricate Au nano-gaps, in which length and width of suspended masks were systematically varied to obtain gaps of 1 nm directly, and contacts that could be converted to nano-gaps later by break-junction technique. These gaps were made on a 20-nm-thick gate SiO<sub>2</sub> that could reliably apply electric field of +/- 3 MV/cm. 4,4'-terphenyldithiol SAM was deposited from a solution under an inert-gas atmosphere to bridge the gaps. The nano-gap devices showed noisy Id-Vgs characteristics at room temperature, but they became stable and exhibited peaks as the temperature decreases. At 30 K, more than 40 % of devices showed Id-Vgs with on/off ratios larger than 10 at Vds = 0.1 V, and some had ratios of more than 1000. A group of devices having "on" current around 1 nA displayed large on/off ratios and clear Coulomb diamonds with conductance gaps of up to 0.6 V. This presumably indicates that the number of molecules involved in these devices is small, and the molecular conductance is of the order of 10 nS. Single-electron charging is not generally considered to play a major role in electrical conduction through Au-terminated phenyldithiols [1]. However, in view of the reported conductance values much lower than the quantum conductance (e<sup>2</sup>/h) and the Coulomb blockade effects observed in slightly larger molecules [2,3], the present results could be rationalized. [1] Y. Xue and M.A. Ratner, Phys. Rev. B **68**, 115406 (2003). [2] J. Park, et al., Nature **417**, 722 (2002). [3] S. Kubatkin, et al., Nature **425**, 698 (2003).