

SYMPOSIUM J

J: Interfaces in Organic and Molecular Electronics

December 1 - 3, 2003

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* Invited paper

8:30 AM *J1.1

Transport, Switching, Devices and Circuits in Metal/Molecule/Metal Systems. R. Stanley Williams, Duncan R. Stewart, Yong Chen, Douglas A. A. Ohlberg, Jeannie Lau and Gun-Young Jung; HP Labs, Palo Alto, California.

Molecular electronics has the possibility of extending the capabilities of integrated circuits into densities not accessible to semiconductors. There have been several reports of interesting and potentially useful electrical properties of molecules, including diode characteristics and switching. However, at this time there is no universal agreement about the mechanisms responsible for these observed properties. I will present results obtained at HP Labs that examine the current transport through simple molecular monolayers and switching phenomena. Although at the time of writing this abstract these observations are not understood, we have been able to build devices and circuits based on these properties, including diodes, variable resistors, latches (signal restoration and inversion), crosspoint memories, simple programmable logic arrays, and demultiplexers coupled to memory.

9:00 AM *J1.2

Mechanism of Electron Conduction in Self-Assembled Alkanethiol Monolayer Devices. Mark Reed, Takhee Lee and Wenyong Wang; Yale University, New Haven, Connecticut.

Electron tunneling through self-assembled monolayers (SAMs) of alkanethiols is investigated using nanometer scale devices. Temperature-dependent current-voltage measurements are performed on alkanethiol SAMs to distinguish between different conduction mechanisms. Temperature-independent electron transport is observed for the first time, proving tunneling as the dominant conduction mechanism of alkanethiols, as well as exhibiting an exponential dependence of tunneling current on the molecule length. Preliminary IETS results will be presented.

9:30 AM J1.3

Temperature Dependent Tunneling through Molecular Monolayers. Duncan Stewart, Jason Blackstock, Douglas Ohlberg, Chun Ning Lau, Patricia Beck and R. Stanley Williams; Hewlett-Packard Labs, Palo Alto, California.

We characterize the electrode/organic interface of several planar electrode / Langmuir-Blodgett (LB) molecular monolayer / electrode systems via detailed electronic transport measurement and optical internal photoemission. Single-species LB monolayers of C20 and C18 carboxylic acid alkanes were sandwiched between upper and lower platinum electrodes, with active device areas of 7-200 μm^2 . Electrical current and differential conductance were measured as a function of voltage $\pm 1\text{V}$ and temperature 2-300K. Internal photoemission photocurrent was measured as a function of wavelength 300-1000 nm. The transport shows a large low-bias conductance anomaly and an anomalous exponential temperature dependence. Below 40K device characteristics were constant. Surprisingly, from 40-300K electrical current was exponential in temperature. The exponential dependence can be fit by a general vibrating tunnel barrier model, possibly associated with fluctuations in configuration of the electrode/organic interface.

10:15 AM *J1.4

Molecule/Surface Interactions: Charge Transfer, Charge Injection, Charge Flow and Charge Behavior. Mark Ratner¹, Harold Basch¹, Abraham Nitzan¹, Alex Burin¹ and Vladimiro Mujica¹; ¹Northwestern University, Evanston, Illinois; ²Northwestern University, Evanston, Illinois.

The interactions between molecules and the surfaces on which they are supported present complexities due to the fundamental problem of mixing between the continuum levels of the electrode and the discrete levels of the molecule. To analyze this problem appropriately, one needs correct quantum mechanics to describe the mixing, and sufficient experimental data to understand the behavior. At a minimum, it is necessary to deal with the electronic mixing using an appropriate non-equilibrium formulation, and with the vibronic coupling if thermal effects are to be understood. Many different situations arise, including coherent and hopping transport, dephasing behavior, image interactions, band bending effects and spin coupling. We will discuss three specific issues in particular: molecular junction transport as determined by interfacial interactions, molecular magnetism induced by metal interfaces, and mechanistic aspects of interfacial electron transport. Experimental data suggest the necessity to understand these processes at different time and length scales, both

of which will be significant in our analysis.

10:45 AM J1.5

Experimental and Theoretical Charge Transport Studies in Self-assembled Molecular Rectifying Diodes on Silicon. Christophe Delerue¹, Stephane Lenfant², Christophe Krzeminski¹, Guy Allan¹ and Dominique Vuillaume²; ¹ISEN, IEMN, LILLE, France; ²Organic Molecular Materials and Devices group, IEMN-CNRS, Villeneuve d Ascq, France.

Molecular rectifying diodes have been synthesized based on the Aviram and Ratner paradigm, with donor and acceptor moieties linked by a short σ or even π bridge. Here we report a simplified synthesis using only one donor group and an alkyl chain using a sequential self-assembly process (SAM or self-assembled monolayer). We used a chemical functionalization (by conjugated moieties) of the end-groups of alkyltrichlorosilane SAM to fabricate insulator/semiconductor (called σ - π) heterostructures at a molecular level on silicon substrates. Two chemical routes are described and compared to build these structures: a sequential two-steps method where the alkyl (6 to 15 methylene units) monolayer is first chemisorbed on the silicon surface and then the end-groups are functionalized by conjugated moieties (phenyl, thiophene, anthracene, pyrene, etc), and a direct method, where conjugated molecules substituted by functionalized alkyl spacers are chemisorbed on the surfaces. We characterized the structural properties of these SAM's by FTIR, wettability and ellipsometry before the electrical measurements. Current rectification is observed for the electronic transport through these functionalized SAM's embedded in a Si(n+)-type/ σ - π /metal junction, with rectification ratio up to about 37 and threshold voltages of in the range -0.3 to -0.9 V (negative voltage applied on a top electrode). The reference sample (the same alkyl chain monolayer without a conjugated group) does not exhibit any rectification behavior. Self-consistent tight binding calculations of the density of states for these Si/ σ - π systems show that the rectification occurs due to a resonant tunneling transport through the HOMO level of the conjugated group. The position of the HOMO with respect to the Fermi energies of the electrode is determined experimentally from the fit of a simple analytical model of the current-voltage curve and from photocurrent. A good agreement is found with our theoretical calculations for the different p end-groups. Recent attempts using acceptor end-groups to have a resonant tunneling transport through the LUMO, and thus a rectification effect for a positive voltage, will be reported at the conference. This approach allows us to fabricate molecular rectifying diodes compatible with silicon nanotechnologies for future hybrid circuitries.

11:00 AM *J1.6

Understanding electron transfer at molecule-metal junctions: a spectroscopic approach. Xiaoyang Zhu, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

Electronic interaction between a molecule and a metal surface is one of the most important and difficult problems in surface science. The recent surge of research interests in molecule-based electronic devices has necessitated a quantitative understanding of this difficult problem. In molecule-based conventional electronic devices, such as organic light emitting diodes and organic field-effect transistors, the metal-molecule interface often determines to a great extent the operation of the device. The importance of the interface only increases as device dimension shrinks, e.g., to the scale of a single molecule or a small group of molecules. This talk will take an experimentalist view and discuss recent progress in understanding electronic structure and dynamics at molecule/metal interfaces using two-photon photoemission (2PPE) spectroscopy. In this approach, the first photon excites an electron from an occupied molecular or metal state to the unoccupied state. The second photon ionizes the transiently populated state for detection. This experiment not only probes the unoccupied state in energy and momentum spaces, but also gives femtosecond resolution. The latter is particularly important because the transport of an electron across a molecule-metal interface is inherently a dynamic process in both electronic and nuclear coordinates. A time-resolved 2PPE experiment allows us to probe the rate of interfacial electron transfer, which is directly proportional to the strength of electronic coupling between a localized molecular orbital and the delocalized metal band structure. The combination of momentum and time resolution also enables the direct probe in the time domain of polaron or polaron-exciton formation in the molecular layer as well as their coupling to the metal surface. In this lecture, I will demonstrate some of the physical concepts we have learnt from 2PPE measurements in model systems. These experiments allow us to quantify the following concepts critical to the understanding of interfacial effects in molecule based electronics: (1) the alignment of unoccupied molecular orbitals to the metal Fermi level; (2) charge redistribution and the presence of interfacial dipole; (3) the formation of localized electronic states resulting from chemical bonding at the interface; (4) the strength and distance dependence of electronic

coupling between unoccupied molecular orbitals/bands and the metal substrate; (5) inter-molecular interaction and the formation of molecular conduction band, and (6) the dynamic localization of electronic excitation in the molecular layer to form a polaron or polaron-exciton. Attempts will be made to correlate the spectroscopic measurements to concepts in transport measurements and to theoretical studies.

11:30 AM J1.7

The electronic structure of oligomeric (phenylene-ethynylene) self-assembled monolayers.

Roger van Zee, Steven Robey and Christopher Zangmeister; NIST, Gaithersburg, Maryland.

Ultraviolet- and two-photon-photoemission spectroscopy have been used to study the electronic structure of self-assembled monolayers of the oligomer, di[phenylethynyl]benzenethiolate. Nanopores filled with these oligomers exhibit interesting charge-transport properties. The electronic structure is interpreted using related molecules and polymers. Near the Fermi level, occupied orbitals traceable to benzene π states are split by the C-C coupling along the backbone into density localized primarily on the ortho-carbon atoms of the phenyl rings (3.9 eV) and delocalized levels along the backbone (2 eV). These orbitals would provide the channels for hole-transport. Two unoccupied orbitals are observed, one 1.7 eV above the Fermi level and another 1.0 eV above the vacuum level. Again, these originate from unoccupied benzene-like levels localized on the carbon atoms of the phenyl ring, and would be the channels for electron transport. Hole- and electron-injection barriers are calculated using these valence level energies. The states above 5 eV binding-energy are C-C and C-H sigma-bonding states. The effects of placing an electron-withdrawing substituent on the central phenyl ring have also been investigated. Compared to the unsubstituted molecule, there is an overall shift to higher binding. The hole-injection barrier is also increased.

11:45 AM J1.8

Stochastic Switching in Molecular Wires. Ganesh K Ramachandran¹, Theresa J Hopson², Adam M Rawlett³, Larry A Nagahara⁴ and Stuart M Lindsay^{1,5}; ¹Department of Physics, Arizona State University, Tempe, Arizona; ²Molecular Imaging Inc., Tempe, Arizona; ³Army Research Labs, Aberdeen, Maryland; ⁴Physical Sciences Research Labs, Motorola, Tempe, Arizona; ⁵AZ Biodesign Institute, Arizona State University, Tempe, Arizona.

We are currently examining the underlying mechanisms that lead to stochastic switching in molecular wires, in particular, switching in molecules bonded on to Au (111) surfaces by a thiol bond (i.e. Au-S bond). We show that physical tilting alone causes a large fraction of the isolated molecules on insulating SAMs to exhibit stochastic switching. However, the strength and dynamic nature of the Au (111)-S bond adds further complexity to the switching problem. Our findings directly suggest that this dynamicity of the Au (111)-S bond contributes substantially to the observed switching effect.

SESSION J2:

Chair: David Cahen
Monday Afternoon, December 1, 2003
Back Bay D (Sheraton)

1:30 PM *J2.1

Surprising Electronic and Magnetic Properties of Closed Packed Organized Organic Layers. Ron Naaman, Itai Carmeli and Zeev Vager; Chemical Physics, Weizmann Institute, Rehovot, Israel.

It is usually assumed that the electronic properties of adsorbed molecules are not too different from that of the isolated molecules. However, simple thermodynamics teaches us that when organic molecule is chemisorbed on a metal surface a significant modification in its electronic structure must take place. We found that the adsorption of the molecules as a closed packed layer, further induces rearrangement of the charge. This rearrangement may result in new electronic and even magnetic properties.

2:00 PM *J2.2

Learning from Molecules to Understand the Electrical Properties of Molecular Junctions. Jerome Cornil^{2,1}, Yasser Karzazi² and Jean-Luc Bredas^{1,2}; ¹Department of Chemistry, The University of Arizona, Tucson, Arizona; ²Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium.

Much theoretical efforts are now devoted to the understanding of charge transport in molecular junctions in close relation to corresponding electrical measurements. The typical approach is to simulate the I/V curves of small molecules contacted by two bulk

electrodes by treating self-consistently the whole system in non-equilibrium conditions. In this context, there are some theoretical and experimental evidences that we will review pointing to the fact that the electronic structure of molecules end-capped by a sulfur atom is largely unperturbed upon adsorption on a gold surface; thus, this indicates that charge injection from the electrodes to the molecular wires and charge transport along the molecular wires are two processes that can be first addressed separately to better understand the electrical properties of molecular junctions. In this contribution, we will demonstrate through a few relevant examples that quantum-chemical calculations focusing on isolated molecular wires can prove very useful to shed light on the electrical characteristics of molecular junctions. On the one hand, we will suggest a novel mechanism to rationalize the negative differential resistance (NDR) behavior of phenylene ethynylene oligomers by simply analyzing their one-electron structure under the influence of a static electric field; the key idea is that a rotation of the central ring can induce an NDR signal by promoting at a critical field a resonant tunneling process across the central ring acting as a tunnel barrier [1]. The relevance of our approach is assessed by the validation of this model by recent I/V simulations [2]. On the other hand, we will describe the electronic structure of a large number of oligomers recently characterized by STM measurements [3] and show that the various current peaks observed in the I/V curves can be unambiguously assigned to the signature of discrete molecular levels of the wires. All together, we hope to provide convincing arguments that quantum-chemistry has a key role to play in the field of molecular electronics to help elaborating molecular junctions with desired functionalities. [1] J. Cornil, Y. Karzazi, J.L. Bredas, J. Am. Chem. Soc. 124, 3516 (2002). [2] J. Taylor, K. Stokbro, private communication. [3] F.R.F. Fan et al., J. Am. Chem. Soc. 124, 5550 (2002).

2:30 PM J2.3

Electrical Contacts to Molecules: The Contacting Process Can Dictate Device Behaviour. Hossam Haick, Jamal Ghabboun and David Cahen; Dept of Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel.

Understanding how electrical contacts to molecules, for electrical transport (and capacitance), affect electrical measurements is critical for proper interpretation of experimental data. Hybrid device structures, with non-molecular electronic materials as electrodes provide an accessible means to explore electrical transport via molecules. Most common processes for contacting molecules on solid surfaces, such as thermal evaporation or sputtering will easily damage molecules. While alternative, novel methods have been demonstrated to overcome this problem, the clear technological advantages of vacuum evaporation justify work to adapt that method for this purpose. We developed Indirect, Collision-Induced, Cooled Evaporation (ICICE). This decreases drastically the kinetic energy of the evaporated particles/atoms arriving at the surface and assures that irradiation emitted from the crucible does not reach the modified samples. Shoring has mostly been used to assess possible contacting damage to molecules. Using a series of organic molecules, chemically bound to an electrode and systematically functionalized at the other end, we find that while avoiding shorts is necessary, it is not sufficient for reliable contacts. Based on various characterizations of ICICE-made metal/molecule/ semiconductor (MMoS) junctions we find that ICICE provides intimate contacts without damaging the (1-2 nm monolayer of) molecules. We can state this because we use molecules with functional groups exposed to the incoming evaporated material, and, thus are easiest damaged. After ICICE the molecular function's effects are preserved, *prima facie* evidence for damage-free contacting. Several types of MMoS junctions were prepared. Comparing molecular effects in ICICE-prepared junctions and other soft contacting methods suggests that details of the evaporation process can completely change the resulting device characteristics. We conclude that experiments carried out with thermally evaporated contacts, even those that used cooled substrates, should be viewed with caution, also if they do not show device shorting. Supported by Israel Ministry of Science, Israel Science- and Minerva Foundations.

2:45 PM J2.4

Contact Resistance in Molecular Tunnel Junctions. Jeremy M. Beebe, Vincent B. Engelkes and C. Daniel Frisbie; Chemical Engineering/Materials Science, University of Minnesota, Minneapolis, Minnesota.

We have formed tunnel junctions in which a metal-coated AFM tip contacts an organic molecule which has been self-assembled on a metal surface. We source a voltage at the AFM tip, ground the substrate, and monitor the current that flows through the organic layer. Our results show an exponential increase in resistance with junction length, suggesting a nonresonant tunneling process. From resistance versus length plots, we are able to determine both the electron decay factor β from the slope of the graph, and also the contact resistance from its intercept. The value of the decay factor is dependent on the

HOMO-LUMO gap of the molecules, and the contact resistance depends on the type of metal-molecule bonding. We have examined varying chain lengths of alkanethiols and alkanedithiols over a series of different metals. We find that for both molecule sets, the contact resistance decreases with increasing metal work function, indicating HOMO-mediated tunneling. We also see two orders of magnitude less contact resistance in the case of the dithiol molecules, suggesting that the S-metal contact is much less resistive than a CH₃-metal contact.

3:30 PM *J2.5

Theoretical aspects of tunneling current through single molecules. Otto F. Sankey¹, Jun Li¹ and Gil Speyer²; ¹Department of Physics and Astronomy, Arizona State University, Tempe, Arizona; ²Department of Electrical Engineering, Arizona State University, Tempe, Arizona.

We will review theoretical concepts concerning coherent electron tunneling transport through molecules as applied to molecular electronic systems. Many of the basic concepts are understood, but quantitative agreement of the current with experiment is difficult to achieve. Some specific issues that will be reviewed are the alignment of the metal's Fermi level within the molecular HOMO-LUMO gap, the dependence of the current on the length of the molecule, and methods to obtain simple estimates for the conductance. We discuss the complex bandstructure approach, which gives a simple framework to understand the length dependence of the current (the exponential 'beta' factor) for some model molecules composed of fragments of infinite chains. We discuss applications to the simple chemically saturated system of alkane chains, and to the bond-alternating pi-system of carotene molecules sandwiched between gold electrodes. Theoretical results are compared to experiments. We study theoretically a model photochromic molecule which can rapidly switch from an 'off' state to an 'on' enhanced conductivity state by the application of light.

4:00 PM *J2.6

Heating in current carrying molecular junctions. Abraham Nitzan and Dvira Segal; Tel Aviv University, Tel Aviv, Israel.

A framework for estimating heating and expected temperature rise in current carrying molecular junctions is described. The approach is based on applying the Redfield approximation to a tight binding model for the molecular bridge supplemented by coupling to a phonon bath. This model, used previously to study thermal relaxation effects on electron transfer and conduction in molecular junctions, is extended and used to evaluate the fraction of available energy, i.e. of the potential drop, that is released as heat on the molecular bridge. A knowledge of the heat conduction properties of the molecular wire is needed to estimate the expected temperature rise. For this purpose we consider phononic heat transport through alkane chains connecting two thermal reservoirs. For relatively short molecules at normal temperatures we find that heat conduction is dominated by the harmonic part of the molecular force-field. In this case a Landauer-type expression for the heat conduction is obtained, in agreement with other recent studies. We find that for relatively short (1-30 carbon molecules) the length and temperature dependence of the molecular heat conduction results from the balance of three factors: (i) The molecular frequency spectrum in relation to the frequency cutoff of the thermal reservoirs, (ii) the degree of localization of the molecular normal modes and (iii) the molecule-heat reservoirs coupling. We compare the heat conduction obtained from this microscopic calculation to that estimated by considering the molecule as a cylinder characterized by a macroscopic heat conduction typical to organic solids. We find that this classical model overestimates the heat conduction of single alkane molecules by about an order of magnitude at room temperature. Implications of the present study to the problem of heating in electrically conducting molecular junctions are pointed out. References (1) D. Segal and A. Nitzan, Heating in current carrying molecular junctions, *J. Chem. Phys.* 117, 3915-3927 (2002) (2) D. Segal, A. Nitzan and P. Hanggi, Thermal conduction through molecular wires, *J. Chem. Phys.*, in press. <http://femto.tau.ac.il/~nitzan/243.pdf>

4:30 PM J2.7

The effect of permanent dipole moments of adsorbates upon I-V characteristics of a molecular tunneling junction. Masamichi Fujihira, Toshihiko Senda, Satoshi Wakamatsu, Akihiko Nakasa and Uichi Akiba; Dept. of Biomolecular Engineering, Tokyo Institute of Technology, Yokohama, Japan.

It is important to understand an interface between an organic material and a metal electrode. In the present work, we measured current-voltage (I-V) curves of self-assembled monolayers (SAMs) on Au(111) using conducting atomic force microscopy (AFM) with chemically modified Au-coated tips. This contact resulted in a bilayer junction between the Au(111) substrate covered with a SAM and the

Au-coated tip with another SAM. An alkanethiol and benzenemethanethiols with various terminal groups (-H, -CH₃, -Cl, -CF₃) were used as the adsorbates. The shapes of the I-V curves depended on the terminal groups. When terminal groups were nonpolar -H and -CH₃ the I-V curves were almost symmetric, while the I-V curves were asymmetric when terminal groups were polar -Cl and -CF₃. This phenomenon was attributed to the change in the work function of gold due to different permanent dipole moments of the terminal groups [1]. We also took electrostatic force between tip and substrate into account. Reference [1] T. Senda, S. Wakamatsu, A. Nakasa, U. Akiba, and M. Fujihira, *Ultramicroscopy*, 97, 27 (2003)

4:45 PM J2.8

Microscopic Study of Interface and Molecular "Engineering" of Electrical Transport through Individual Molecules with Metallic Contacts. Yongqiang Xue and Mark A. Ratner; Chemistry Department and Materials Research Center, Northwestern University, Evanston, Illinois.

Devices based on individual organic molecules often require attaching appropriate end groups chemically different from the molecule core in order to establish stable contact to the metallic electrodes. Single-molecule devices can therefore be considered as atomic-scale heterostructured device where the heterostructure can be introduced at the metal-molecule interface through the end groups or in the molecule core through appropriate molecular engineering techniques. A critical issue in molecular electronics research is therefore to understand and identify the different roles that the molecule core and the metal-molecule interface play in determining the transport characteristics of the molecular device. In this talk, we try to elucidate the effect on molecular transport due to chemical modification of the metal-molecule interface and the molecule core through detailed microscopic study of selected single-molecule devices using a first-principles based self-consistent matrix Green's function method. The metal-molecule interface can be "engineered" by modifying the valence structure of the end group, by modifying the electronegativity of the end group or by modifying the work function of the metals used. The molecule-core can be "engineered" by attaching selective functional side groups. In both cases, the effect on electrical transport due to molecular "engineering" will be different depending on the asymmetry of the two metal-molecule contacts. The physical picture is demonstrated by numerically calculating the charge transfer, band lineup, voltage drop and the current-voltage characteristics for each device. The results presented will provide useful guide to the prospects of device engineering through molecular design.

SESSION J3: Poster Session
Chairs: Neal Armstrong and David Cahen
Monday Evening, December 1, 2003
8:00 PM
Exhibition Hall D (Hynes)

J3.1

Negative Capacitance in Au/Copper Phthalocyanine (CuPc)/Au Investigated by Impedance Spectroscopy.

Sai Wing Tsang¹, Jian Bin Xu¹, M. S. Xu¹ and Harry H. L. Kwok²; ¹Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, Hong Kong; ²Center of Advanced Materials and Related Technology, University of Victoria, Victoria BC, V8W 3P6, British Columbia, Canada.

S. W. Tsang, J. B. Xu¹, M. S. Xu, and Harry H. L. Kwok² Department of Electronic Engineering and Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin, NT, Hong Kong ¹Corresponding Author ²Center for Advanced Materials and Related Technology, University of Victoria, Victoria BC, V8W 3P6 Canada Copper Phthalocyanine (CuPc) is a widely used organic material among organic light emitting devices (OLEDs) and organic field effect transistors (OFETs). In this presentation, we report on the frequency dependent negative capacitance measured by impedance spectroscopy in a device structure of Au/CuPc/Au. Experimentally it is found that the negative capacitance varies with different thickness of CuPc, bias voltage, and temperature. A characteristic peak is found at about 10kHz with a board (logarithm) distribution. The origin of the negative capacitance is proposed to be due to the distribution of transit times of individual carriers governed by the dispersive hole transport nature of CuPc, which is similar to the recent findings in Au/PPV/Au and Al/Alq₃/Ca [1, 2]. A transient current model is developed to fit the measured capacitance to extract the fastest and dc hole mobilities and dispersive parameters. [1] H. Martens, H. Brom, and P. Blom, *Phys. Rev. B* 60, R8489 (1999) [2] S. Berleb and W. Brutting, *Phys. Rev. Lett.* 89, 286601 (2002) This work is in part support by the Research Grants Council of Hong Kong through the Grant No. 4372/02E.

J3.2

Charge transport in DNA. Thomas Heim, Dominique Deresmes and Dominique Vuillaume; IEMN, Villeneuve d, France.

This work belongs to the field of molecular electronics. Questions about the electric conduction in DNA was firstly put in 1962 by Eley and Spivey, after the discovery of the double helix structure of DNA by Watson and Crick in 1953. Until now, no consensus has emerged about the electric properties of DNA. Charge transfers over nanometric distances have been studied in solution and are quite well understood. However, direct measurements between electrodes present various behaviors, from induced supraconductivity to insulator or semiconductor. This debate is at the basis of our work. We have studied the electronic properties of DNA deposited over different self-assembled molecular layers on silicon substrates. The first part of the study deals with the preparation of the surface and deposition of DNA. Then, conductivity of DNA is measured between electrodes built on an insulating substrate or thanks to a conducting AFM. In this last case, the AFM tip allows to image the surface and to be used as a second electrode during the electrical measurement. Two kinds of results have been obtained : insulating to conducting behaviors are observed. Resistances are spread out over at least 6 orders of magnitude, from 109 W to 1015 W, but with a lower frequency of appearance for high conductivities. Two points can be put forward to explain such a disparity : on the one hand, production of an electrical contact between the electrode and DNA, on the other hand, DNA deposition method over the surface. Formation of an electrical contact between the electrode and DNA implies some treatments which usually destroy the molecules. This contact can be improved by using piles of DNA molecules to link the evaporated electrode and the studied DNA rope. However, this method adds a high series resistance. Systematic measurements have been realized according to the distance of the AFM tip to the pile of DNA molecules, and to the estimated number of DNA strands in the rope. DNA deposition being a primordial parameter, this point is deeper studied to understand the link between DNA structure and its properties of conduction.

J3.3

In situ Detection of Protein Adsorption with Single Walled Carbon Nanotube Device. Salah Boussaad¹, Xiulan Li¹, Nongjian Tao¹, Ruth Zhang², Theresa Hopson² and Larry Nagahara²; ¹Electrical Engineering, Arizona State University, Tempe, Arizona; ²Physical Sciences Research Laboratories, Motorola Labs, Tempe, Arizona.

The ability to detect and study a single molecule represents the ultimate challenge of biosensor development and analytical chemistry. Recent progress in the fabrication of nanostructured materials and devices, such as nanoparticles, silicon nanowires, metal nanowires and carbon nanotubes has opened new avenues for us to achieve this ability. Single walled carbon nanotubes (SWNTs) are attractive for a wide range of applications, from nanoelectronics and nanomechanics to bioelectrochemistry. Biomolecules, such as DNA and proteins have been immobilized on SWNTs and the biocompatible nature of SWNTs has been recently demonstrated, which are significant steps toward biosensor applications. However, in situ detection of a small number of proteins via directly measuring the electron transport properties of a single SWNT has not been reported. We report on the detection of cytochrome c (cyt c) adsorption onto individual SWNT transistors via the changes in the electron transport properties of the transistors. The adsorption of cyt c induces a decrease in the conductance of the SWNT devices, corresponding to a few tens of molecules. We have studied the conductance vs. the potential of the SWNT with respect to a reference electrode inserted in the solution, and observed a negative shift in the conductance vs. potential plot upon protein adsorption. From the shift, we have estimated the number of the adsorbed proteins, which is similar to that from the adsorption-induced conductance decrease. The results are supported by direct atomic force microscopy (AFM) images recorded before and after the protein adsorption.

J3.4

Direct electron transfer between cytochrome c and graphite microelectrodes. Siu-Tung Yau, Physics, Hunter College of City University of New York, New York, New York.

We report the observation of enhanced electron transfer associated with Cyt c immobilized on the bare surface of graphite microelectrodes. Cyclic voltammetry shows that, due to adsorption on a particular surface of the microelectrode that promotes electron transfer, Cyt c immobilized on the microelectrodes gives rise to more electron transfer as compared to that for macroscopic electrodes (macroelectrodes). For both macroelectrodes and microelectrodes, the redox reaction of immobilized Cyt c can be switched between an 'on' state and an 'off' state by controlling the electrochemical potential. Also, the potential can be used to enhance the redox reaction in a particular direction, shifting the electron transfer from a quasi-reversible process to an irreversible one. The difference in the

chemical properties of the surface of the two kinds of electrodes results in different responses to changes the potential.

J3.5

A Simplified Test Device For The Electrical Characterization Of Metal-Molecule-Metal Junctions. Nadine Emily Gergel, Nabanita Majumdar, David Routenberg, John Bean and Lloyd Harriott; University of Virginia, Charlottesville, Virginia.

A test structure for electrical characterization of metal-molecule-metal junctions was built using simplified processing tools and procedures. This structure demonstrated efficiency by reproducing established results for long chain alkanethiols. Experimental data also suggested altered barrier characteristics for short-chain alkanethiols and identical electrical characteristics for alkanemonothiols and alkanedithiols. The test device consisted of a nanometer scale well with a gold bottom, a molecular monolayer self-assembled on the bottom of the well, and a titanium/gold top layer. This device was similar to a nanopore device previously built, but had several processing simplifications in the areas of: (1) lithography (2) evaporation conditions (3) metal deposition rate¹. The test device was used to obtain the IV characteristics of different length alkanethiols. Fitting the IV characteristics to the Simmons tunneling model² suggested that the method of electron transport was molecular tunneling. The tunneling barrier height (ϕ), the potential barrier shape (α), and the current density decay coefficient (β) were derived from this fit. The ϕ values were approximately 2.1 eV, and α values were around .54 for the longer three molecules and 0.75 for the shorter three. The β value was determined to be between 0.7 and 0.74 /Angstrom. The octanethiol and octanedithiol ϕ values were similar, suggesting that the presence or absence of the top Au-S bond did not alter the electrical behavior of the molecules. Acknowledgement: We would like to thank NSF for supporting this work. 1. C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones II and J.M. Tour, Appl. Phys. Lett. 71, 611 (1997). 2. J. G. Simmons, J. Appl. Phys. 34, 1793 (1963)

J3.6

Ultrathin Film of Oligoimide by Covalent Molecular Self-Assembly. Fengxiang Zhang and M. P. Srinivasan; Chemical and Environmental Engineering, National Univ of Singapore, Singapore, Singapore.

We report the preparation of an ultra-thin oligoimide film through molecular assembly with covalent bonding as the interlayer linkage. Pyromellitic dianhydride (PMDA) and diaminodiphenylether (DDE) were assembled alternately from their solutions in a layer-by-layer fashion on to a silicon wafer that was surface-modified with p-aminophenyltrimethoxysilane (APhS). X-ray photoelectron spectroscopy (XPS) analysis suggests that the formation of amic acids at PMDA/DDE interface is complete. Atomic force microscopy (AFM) shows morphological uniformity in the film with a surface roughness of less than 0.5 nm at each deposition. Mechanical strength of the film is assured by the interlayer covalent bond, abundant aromatics in the building units and van der Waals interaction between the oligoimide chains. The covalent molecular assembly technique together with intelligent substrate modification and material choice promises to be an attractive method for fabrication of ultra-thin robust films of nanometer thickness.

J3.7

Ultra-smooth Platinum Surfaces for Self-Assembled Monolayers and Molecular Electronic Devices. M. Saif Islam, Shun-Chi Chang, Gun-Young Jung, Yong Chen and R. Stanley Williams; Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California.

We investigate the impact of ultra-smooth platinum (Pt) surfaces on the packing and orientation of self-assembled monolayers (SAMs) and on the performance 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 0.7 nm was observed. In addition, the average height of the grains on the freshly deposited Pt surfaces is measured to be around 3 nm with a high density of more than 5nm 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. A surface planarization technique around chemical-mechanical polishing (CMP) was developed to achieve an ultra-smooth Pt surface with less than 0.1 nm RMS roughness and self-assembled monolayers of alkanethiols were grown on this smooth surface. Along with the AFM data, we will present the results of our measurements on contact angle, ellipsometry, and reflection-absorption infrared spectroscopy (RAIRS). These measurements show that the organization of self-assembled monolayers of alkanethiols on polished platinum surfaces is all-trans and well-ordered.

J3.8

STM Investigation of Benzene Adsorption on Si(001)/(111) and Ge/Si(001)/(111). Ian C. Schick, Peter Sutter, Winfried Ernst and Eli Sutter; Physics, Colorado School of Mines, Golden, Colorado.

Simple organic molecules have been studied extensively for use as molecular devices (OFETs and OLEDs). Benzene, for example, can form the basis for molecular switches with the addition of functional groups. We have adsorbed benzene to low coverage on a variety of surfaces, including Si(001)/(111) and Ge/Si(001)/(111). By applying STM to these systems, we have studied the adsorption process, as well as preferred orientation and position, for surfaces of similar chemistry but differing surface reconstruction. We have developed a novel technique, energy-filtered scanning tunneling microscopy (EF-STM), which utilizes semiconductor probe tips to achieve state-selective imaging with atomic resolution [1]. This method has the potential to selectively map given bonds in an adsorbed molecule, and may thus provide a novel pathway to spectroscopic imaging of single molecules. First results of EF-STM on adsorbed benzene will be reported. [1] P. Sutter, et al., Physical Review Letters, 90, 166101 (2003).

J3.9

Forcing the Assembly of the Building Blocks of a Molecular Wire with a Nanopatterned Cu(110) Template.

Roberto Otero Martin¹, Yoshitaka Naitoh¹, Federico Rosei¹, Ping Jiang², Andre Gourdon², Erik Laegsgaard¹, Ivan Stensgaard¹, Christian Joachim² and Flemming Besenbacher¹; ¹Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark; ²CEMES-CNRS, Toulouse, France.

Large organic molecules are promising building blocks for nanoscale molecular electronic devices, but new approaches are required to order them with atomic precision on surfaces. This goal comprises two different aspects: the adsorption sites must be arranged in a suitable pattern, and the adsorption geometry must facilitate the interconnection with the other elements of the circuit. Here we show that the nanopatterning of a Cu(110) surface with a sub-monolayer of oxygen not only creates a suitable template for the selective adsorption of two related molecular wires into ultra clean 1D nanostructures, but also can force their orientation to align along the structure. This can be considered as one step towards the parallel fabrication of long molecular wires on surfaces starting from its molecular building blocks. The template is created by exposing the clean Cu(110) surface to oxygen. Under these conditions, the surface is patterned into 1D alternating bare Cu stripes running parallel to the [001] direction, and 2x1-O reconstructed regions, consisting of Cu-O added rows aligned parallel to the [001] surface direction. Onto this template, we have deposited first the molecule known as Single Lander (SL, C90H98). It is composed of a polyaromatic hydrocarbon main board with four lateral 3,5-di-tert-butylphenyl substituents acting as spacer legs. The aromatic central board has been designed so as to act as a conductive molecular wire because of its extended pi system. On Cu(110), SL adsorbs always with its board aligned along the [1-10] crystallographic direction of the substrate, and no order is observed even at high coverage. When deposited on the periodic template obtained by the partial oxidation of Cu(110), the SL molecules adsorb exclusively on bare Cu regions, forming well ordered long molecular chains. However, the direction of the board turns out to be aligned along [1-10] and, thus, perpendicular to the direction of the chain. In order to further investigate the orientation of the molecules deposited on the substrate, we proceeded to deposit another member of the Lander molecule, the Violet Lander (VL, C108H104). The difference between the VL and SL molecules is the length of the board, being 2.5 nm long in the VL and only 1.7 nm in the SL. When deposited on Cu(110) the VL is also imaged as four lobes. On the nanotemplated surface, it only adsorbs on the bare Cu stripes. The difference now is that the direction of the board is no longer perpendicular to the direction of the stripes. Two types of orientations are most commonly found: with the board rotated 70 and 90 degrees with respect to the [1-10] direction. Therefore, we can conclude that the template not only acts by providing specific adsorption sites, but it also affects the adsorption geometry.

J3.10

Ab-Initio Simulation of the Interaction of Benzene-Thiol and Thiolate With Gold Nanoclusters. Sara Letardi and Fabrizio Cleri; Unita³ Materiali e Nuove Tecnologie, ENEA, Roma, Italy.

We studied the interaction of benzene thiol and thiolate molecules with Au nanoclusters by density-functional theory in the local-density-approximation. The core electrons are described by Troullier-Martins soft pseudopotentials, with 11 valence electrons and without relativistic correction for Au. The minimum-energy structures of RS-Au(n) and RSH-Au(n) systems, with n=1,2,3 and R the benzene, were found by conjugate-gradient relaxation. As far as the bonding geometries and bond angles, we find several similarities with

previous simulations of the adhesion of other thiolates on Au (111) surfaces. We study in detail the energetics of the adhesion of the different species, with respect to both the neutral and charged fragments. It is found that the RS (and RS-) adduct is generally the most stable. Moreover, we characterize the different states of the RS-Au(n) complex with respect to the desorbed hydrogen.

J3.11

Tripodal Thiol-Derivatized Redox-Active Self-Assembled Monolayers for Studies of Molecular Information Storage.

Lingyun Wei¹, Zhiming Liu¹, Amir A Yasser¹, Padmaja Kisari², Jonathan S Lindsey², Werner G Kuhr¹ and David F Bocian¹; ¹Chemistry department, University of California, Riverside, Riverside, California; ²chemistry department, North Carolina State University, Raleigh, North Carolina.

Recently, there have been significant advances in developing molecular-based electronic materials for use in both memory architectures and circuit elements. Our group has shown that self-assembled monolayers (SAMs) of porphyrins attached to electroactive surfaces can be used for molecular-based information storage. In this approach, the discrete redox states of the molecules in the SAMs represent stored information. The advantages of our molecular memory device include low-power consumption, high-speed circuit architecture, high-density, etc.. In this poster, a series of redox-active molecules bearing identical thiol-derivatized tripodal linkers have been investigated. The electrochemical properties of the SAMs were examined by fast scan voltammetry. The charge-storage capabilities and electron-transfer rates were studied by open circuit potential amperometry (OCPA) and swept-wave AC Voltammetry (SWAV). The electrochemical studies of the SAMs indicate that tripodal-thiol linker provides a more robust anchor than a mono-thiol. This study provides the foundation for understanding the electron-transfer properties and kinetics of diverse redox-active molecules in a controlled environment on a surface.

J3.12

Monolayers of Ferrocene and Porphyrin-chalcogens on Si(100). Novel Hybrid Molecular/Semiconductor Information Storage Media for Electronic Applications.

Amir A Yasser¹, Zhiming Liu¹, Lingyun Wei¹, Werner G Kuhr¹, Jonathan S Lindsey² and David F Bocian¹; ¹Department of Chemistry, University of California, Riverside, California; ²Department of Chemistry, North Carolina State University, Raleigh, North Carolina.

The integration of molecular materials with semiconductors offers a transition technology that may satisfy the immediate demands for increasing computational capability. Toward this goal, we report a protocol for functionalization of electroactive monolayers of ferrocene and porphyrins covalently linked to mono-crystalline Si(100) for information storage applications. Electrochemical communication with the surface immobilized redox-active molecules was achieved through anchored tethers of organo-O, S, and Se molecules thermally reacted with photolithographically patterned surfaces. Silicon microelectrodes were fabricated on p-type Si(100) with a grown oxide layer defining the active electrode area for monolayer assembly. Chemically stable hydride-terminated surfaces were obtained using an HF treatment process. Monolayer deposition was performed from either an active wet solution deposition or a dry vapor sublimation process. XPS measurements confirm the mechanism for the displacement of surface hydride species with O, S, and Se terminated ferrocene or porphyrin respectively. Cyclic voltammetry performed on the monolayers demonstrates the relative chemical stability of each molecular anchor over numerous voltage cycle scans. Modified AC voltammetric and amperometric techniques were used to probe the electron transfer kinetics and charge storage through the Si-O, Si-S, and Si-Se semiconductor interface. Collectively, the ability to prepare and survey the relative stability, and electron transfer properties of redox-active molecular monolayer media spanning O, S, and Se as tethers anchored onto Si(100) is likely to be key in development of a practical hybrid molecular/semiconductor device.

J3.13

Electrical Properties Dependence of Bisquinomethane-Based Organic Materials On Metal Electrodes. Hisato Kato, Keisuke Yamashiro, Nobuyuki Sekine, Masami Kuroda and Haruo Kawakami; Fuji Electric Corporate R&D, Ltd., Yokosuka, Kanagawa, Japan.

Dependence of electrical properties on the metal electrodes has been investigated for bisquinomethane-based (QM) organic materials. The QM materials have the electron transport properties and its lowest unoccupied molecular orbital (LUMO) level is almost the same as the work function of Al. In spite of the symmetric structure of Al/QM/Al, QM materials showed the rectifying behavior, where they were conductive in the case of the top electrode biased positive. In the rectifying behavior, the forward current was well fitted to the thermionic emission model in low voltage region and space charge

limited current in high voltage region. The barrier height estimating from the temperature dependence of the current is about 0.95eV, which agrees with the energy barrier estimating from the vacuum level shift between the bottom Al electrode and organic layer evaluated by the Kelvin method. These results indicate the rectifying behavior is derived from the interface between the bottom electrode and organic layer. With the Au top electrode, the QM materials with the high dipole moment show the switching behavior as well as the rectifying behavior. The turn-on voltage does not depend on the film thickness of organic layer. These results indicate the switching behavior is derived from the interface between organic layer and the top electrode.

J3.14

The Self Assembly Attachment of DNA Probes on GaAs and GaN Surfaces. Mohamad Al-Sheikhly¹, Aris Christou¹ and William E. Bentley²; ¹Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Chemical Engineering, University of Maryland, College Park, Maryland.

The self assembly of DNA molecules on GaAs and GaN surfaces has occurred through the hybridization reaction in a single-stranded DNA by means of near infrared irradiation. This result has been applied to the development of a gel-semiconductor DNA module for information storage. The interface chemistry has been investigated by fluorescence techniques and ESCA. The research is intended to develop procedures to replace or enhance enzyme-based hybridization reactions in sequencing applications and in the polymerase chain reaction (PCR). In achieving this goal, our approach would lead to a paradigm shift from enzymatic aqueous reactions to photo-induced surface hybridization reactions, and the use of photo-induced hybridization of surface-attached DNA probes to link them by hydrogen bonding with DNA target molecules in a gel. The approach for the development of a high-density DNA module with data storage and retrieval capability depends on the understanding of the self assembly mechanisms. A mono-layer of single-strand DNA oligonucleotides (probes) attached to the surface of a semiconductor wafer has been achieved and is presented. This strategy to move from enzyme-based reactions in aqueous solutions to reactions in a solid state would be accomplished using photo-excitation of hybridization reactions to produce double-stranded DNA suitable for information storage on a semiconductor-based module.

J3.15

Immobilization Capacities of Self-Assembled Aminosilane Films. Fengxiang Zhang and M. P. Srinivasan; Chemical and Environmental Engineering, National Univ of Singapore, Singapore, Singapore.

The primary-amine content and morphology are important factors in the use of aminosilane self-assembled films for immobilization. We investigate the effect of experimental parameters and choice of aminosilanes on these factors. In the case of 3-aminopropyltrimethoxysilane (APS), a smaller APS concentration, trace amounts of water in solvent and post-deposition curing are necessary to obtain a high primary-amine content. By optimizing the deposition conditions, we obtained uniform films with a primary-amine content of 88%, much higher than values in literature. When p-aminophenyltrimethoxysilane (AphS) was used, the primary-amine content in the film increased to 100% and the surface morphology was more uniform than that of APS film under all conditions. We also compared the immobilization capacities of the aminosilane films for pyromellitic dianhydride (PMDA). It is found that higher content of primary-amine content favors higher uptake, and AphS film yields 100% PMDA coverage.

J3.16

Influence of the Nerve Cell Growing Medium on the Electrical and Mechanical Properties of Neuron-Electrode Interfaces. Antje Reiher¹, Stephan Guenther¹, Andre Krtschil¹, Hartmut Witte¹, Ana de Lima², Thomas Voigt² and Alois Krost¹; ¹Institute of Experimental Physics, Otto-von-Guericke-University of Magdeburg, Magdeburg, Germany; ²Institute of Physiology, Otto-von-Guericke-University of Magdeburg, Magdeburg, Germany.

Neuronal networks are subject of intensive research activities like the development of artificial neural networks with application potential for information technology. Another challenge is the exploration of mechanisms for growth of and interactions within neuronal networks analyzed by electrical interfaces to semiconductor devices or electrode arrays. However, up to now there is only a sparse knowledge on the influence of the cell medium on the effects observed in the latter experiments. In this contribution, we analyzed the impact of different cell media on the electrical properties of interface structures consisting of arrays of Au-electrodes and neuron cultures prepared from cerebral cortices of embryonic rats. With respect to future stimulation experiments with electrical pulses, we studied the interaction between the culture medium and the ac- and dc- behavior as well as the

deformation of applied rectangular bias voltage pulses which were directly monitored for different frequencies in the range from 20 Hz to 1 MHz. The different physical origins, i.e. the dissociation of the cell medium as well as the impact of parasitic capacitances due to the array design, will be discussed in detail. For measurements with Ringers solution we observed regions in I-V-curves with a negative differential resistance at about 4 V caused by an irreversible destruction of the cell medium connected with a rapid foam formation on the electrode surface. A further negative differential resistance was correlated to electrolytic reactions between the medium and the electrodes, resulting in a lift-off of the latter ones. This effect was suppressed by introduction of a thin Ti interlayer between the glass substrate and the Au-electrodes allowing bias voltages up to 100 V for measurements in serum-free medium. Considering all these results, the interaction between the electrodes and the cell medium is one of the keys to successfully interface the neurons.

J3.17

Characteristics of the Pentacene Thin Film Transistor With a Gd2O3 Gate Insulator. SeongJun Kang, Kwunbum Chung, DaeSik Park, HuiJung Kim, M Noh and C. N. Whang; Institute of Physics and Applied Physics, Yonsei university, seoul, South Korea.

Pentacene is a promising material in the field of organic semiconductor. Though the mobility of a pentacene thin film transistor is comparable to that of amorphous Si-based devices, its device performance is still insufficient for achieving applicable organic semiconductor device. We used thin high-k Gd2O3 layer as a gate insulator that was grown on a heavily doped Si substrate by ionized cluster beam deposition (ICBD). The crystalline quality of Gd2O3 layer was characterized by in-situ reflection high-energy electron diffraction (RHEED). The preferentially oriented high quality pentacene thin film was prepared on the gate oxide layer by thermal evaporation in ultra-high vacuum and thin gold layer was used as an electrode. The pentacene film was characterized by using x-ray diffractometer and atomic force microscopy. We present the device properties when the SiO2 gate insulator is replaced with Gd2O3 in the pentacene thin film transistor.

J3.18

30 Nm Channel Length Organic Transistors. Yuanjia Zhang¹, Jason R Petta², Ambily Santha¹, Yulong Shen¹, Daniel C Ralph² and George G Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Physics, 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 is 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 imposes 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.

J3.19

Surface Potential Measurements of Operating Organic Field Effect Transistor Devices. Kanan Puntambekar, Paul Pesavento and C. Daniel Frisbie; Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Operating pentacene thin film field effect transistors (FETs) are being studied using Kelvin Probe Force Microscopy (KPFM) to probe the potential distribution along the conducting channel. KPFM is a direct approach to isolate and study bottlenecks to charge transport, such as contacts and grain boundaries, and to study the interplay between them in various regimes of operation: off, saturation and linear regimes. Top contact pentacene thin film transistors were used for this study. Pentacene films, ~35 nm thick, were deposited by vacuum sublimation. This was followed by thermal evaporation of gold contacts using a shadow mask with channel dimensions of W/L of 300 μm /30 μm . The typical mobility for these devices was ~0.5 cm²/Vs with on/off of ~10⁵. The conduction in these devices is believed to be in the first couple of pentacene monolayers near the organic - insulator interface, which can be probed using the KPFM technique. In the resulting surface potential distribution, potential drops at the

source and drain contacts were observed. These drops were monitored as a function of the drain and gate bias, providing a way to separate the contact and channel resistances and to obtain the contact corrected field effect mobility in pentacene. In addition, the homogeneity of the potential along the width of the channel and at the edge of the channel was studied by generating a series of surface potential maps of these devices.

J3.20

Growth Kinetics and Structure of p-Quaterphenyl Thin Films on Gold surfaces. Stefan Muellegger¹, Ingo Salzmann¹, Roland Resel¹, Gregor Hlawacek², Christian Teichert², Egbert Zojer^{1,3} and Adolf Winkler¹; ¹Institute of Solid State Physics, Graz University of Technology, Graz, Austria; ²Department of Physics, University of Leoben, Leoben, Austria; ³Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, Georgia.

We apply thermal desorption spectroscopy (TDS) to investigate the adsorption/desorption kinetics of vacuum deposited p-quaterphenyl (4P) films on single- and polycrystalline Au substrates. The 4P film morphology and its crystal structure is investigated by atomic-force microscopy (AFM), micro-channelplate low energy electron diffraction (MCP-LEED) and X-ray diffraction pole figure technique (XRD-PF), respectively. On a clean polycrystalline gold surface, Au(poly), the 4P molecules of the first monolayer are more strongly bound than the molecules within the multilayer. Two different monolayer adsorption states are found by TDS. The adsorption/desorption kinetics of the 4P monolayer is strongly influenced by the existence of a carbon pre-coverage. Such is produced in a 4P dissociation process, taking place on a clean Au(poly) at elevated substrate temperatures. The carbon coverage leads to the disappearance of the more strongly bound 4P monolayer adsorption state, found for the clean surface. On a single-crystalline Au(111) surface no pronounced 4P dissociation is observed. The desorption kinetics is very similar to the Au(poly), implying that the Au surface geometry has no significant influence on the desorption kinetics of 4P. At room temperature it is shown that 4P on Au grows in the Stranski-Krastanov mode, whereas at 93K an amorphous layer-by-layer growth mode exists. From XRD-PF measurements of 4P/Au(111) it follows that the 4P(211) plane is oriented parallel to the substrate surface. These results together with the substrate geometry yield 24 different azimuthal orientations of the 4P bulk domains. Applying MCP-LEED, we measure the surface unit cell of the 4P monolayer on Au(111). Combined with XRD-PF, the arrangement of the 4P molecules within the first layer can be solved. This work is supported by the Austrian FWF, Proj. No. P15625 and P15626.

J3.21

Crystallographic and Morphological Characterization of Tetracene and Pentacene thin Films on polycrystalline Copper surfaces. Martin Oehzelt¹, Christian Suess², Rainer Friedlein², William R. Salaneck² and Roland Resel¹; ¹Institute of Solid State Physics, Graz University of Technology, Graz, Austria; ²Dept. of Physics (IFM), Linköping University, Linköping, Sweden.

The aim of this study is to investigate the orientation and crystallinity of two oligoacenes on polycrystalline copper surfaces. The copper is sputtered on top of a Si 001 wafer and shows a fibre texture with the net plane (111) parallel to the surface. The growth of these small molecules on this Cu surface is investigated by x-ray diffraction and AFM measurements. The x-ray measurements reveal the orientation of the molecular crystals with respect to the surface as well as the homogeneity of these crystallites. From the AFM pictures the roughness of the substrate as well as the roughness of the organic thin film can be seen. A correlation between the x-ray and AFM measurements could be drawn. The organic films were grown by vapour deposition in an UHV environment. The growth of the organic film was investigated in a series of different substrate temperatures while keeping all other depositions parameter constant (source temperature, vacuum pressure,...). The resulting films show also a fibre texture with different crystallographic orientations. E.g.: pentacene shows a fibre texture with (001) net planes parallel to the surface when the substrate temperatures is 330K whereas tetracene shows a fibre texture with (200) net planes parallel to the surface when deposited at substrate temperatures of 270K. These different orientations result in standing or lying molecules, respectively. Since the mobility within these molecular systems depends crucially on their orientation a control of the texture is mandatory.

J3.22

Growth Dynamics and Morphology Studies of Pentacene Ultra-thin Films for Transistor Applications. Ricardo Ruiz^{1,2}, Alex C. Mayer², Yuanjia Zhang², Randall L. Headrick³, Alexander Y. Kazimirov⁴, James R. Engstrom⁵, Bert Nickel⁶ and George G. Malliaras^{1,2}; ¹Cornell Center for Materials Research, Cornell University, Ithaca, New York; ²Materials Science and Engineering, Cornell University, Ithaca, New York; ³Department of Physics,

University of Vermont, Burlington, Vermont; ⁴Cornell High Energy Synchrotron Source, Ithaca, New York; ⁵Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York; ⁶Department of Chemistry, Princeton University, Princeton, New Jersey.

Organic/inorganic interfaces play a crucial role in the rapidly growing field of molecular electronics. Even though huge progress has been achieved in the understanding of electronic transport in conjugated molecular materials, a complete study that relates the nucleation and growth mechanisms with charge transport properties in pentacene thin films is still missing, especially within the first few monolayers adjacent to the gate substrate where charge transport is believed to occur. Pentacene thin films were evaporated onto silicon oxide substrates and analyzed by in-situ synchrotron X-ray scattering and ex-situ atomic force microscopy (AFM). The evolution of the first monolayers was studied by monitoring the intensity of scattered X-rays at the anti-Bragg position. Layer coverages were then extracted from the X-ray intensities using a simple growth model and compared to AFM micrographs. Film evolution as a function of substrate temperature and the thermally activated surface diffusion of pentacene will also be discussed. The correlation of film growth and film morphology on device performance was also studied. Thin film transistors with a channel length, $L \sim 25 \mu\text{m}$, were fabricated with these films for electrical characterization showing a field effect hole mobility of $0.1 \text{ cm}^2/(\text{V}\cdot\text{sec})$. Film morphology in nano-scale transistors ($L \sim 30\text{-}100\text{nm}$) will also be presented.

J3.23

Abstract Withdrawn

J3.24

Conjugated Network Ultrathin Films of Polythiophene Precursor and Thiophene Co-monomers Investigated by EC-SPS. Akira Baba^{1,2}, Ken Onishi², Rigoberto Advincula² and Wolfgang Knoll¹; ¹Max-Planck-Institute for Polymer Research, Mainz, Germany; ²Chemistry, University of Houston, Houston, Texas.

Poly(N-vinylcarbazole) (PVK), which exhibit interesting optical/electrochemical properties has been extensively studied because of their possible application as light emitting diode materials, polymer battery materials, and applications in various electrochromic devices. Recently, we have reported the conversion of "precursor polymers" to form modified conjugated polymer network films on conducting surfaces. With the interest in identifying precursor polymer architectures, PVK was investigated, having a polyvinyl polymer backbone and a capacity for secondary polymerization (and cross-linking) through the carbazole units. In this study, PVK was electrochemically cross-linked to form a conjugated polycarbazole network and deposited on conducting electrode surfaces. In order to understand the electrodeposition process, the electropolymerization process was investigated in situ combining electrochemical-surface plasmon resonance spectroscopy (EC-SPS) and electrochemical quartz crystal microbalance (EQCM). Furthermore, the morphology observed under atomic force microscopy (AFM) correlated with the in-situ EC-SPS evanescent optical properties and EQCM acoustic properties.

J3.25

Variation in the Electrical Characteristics of Al/Polythiophene Interfaces Due to Preparation Conditions and Aging. Velda Goldberg¹, Michael Kaplan¹, Leonard Soltzberg¹,

Joseph Genevich¹, Shari Benson¹, Alison Bergeron¹, Emily Coombs¹, Casey Gifford¹, Erica Gunn¹, Amanda Hagar¹, Colleen Harty¹, Andrea Higdon¹, Diana Ouellette¹, Eleana Pham¹, Lisa Torgersen¹ and George Malliaras²; ¹Chemistry and Physics Departments, Simmons College, Boston, Massachusetts; ²Materials Science and Engineering Department, Cornell University, Ithaca, New York.

Current vs voltage and current vs time were monitored for devices consisting of layers of Al/polythiophene/Al on glass. The Al layers were deposited by vacuum evaporation, and the polythiophene layers were spin-coated. The effect of ambient environment was studied. The temperature of the substrate during vacuum deposition was also varied and correlated with the electrical characteristics of the devices. Changes in the chain lengths and the surface roughness of the polythiophene were investigated through MALDI-TOF mass spectrometry and scanning probe analysis, respectively. Using UV and infrared spectroscopy (transmittance and reflectance modes), we compared changes in the polythiophene layer due to prolonged exposure to the ambient environment with the foregoing observations.

J3.26

Deposition of High Molecular Weight Organic Materials in an Ultra High Vacuum Environment. Niels Dam, Chris Braunagel, Brian Doran, Martin M Beerbom, Yusuf Emirov and Rudy Schlaf; Department of Electrical Engineering, Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida.

We have successfully been able to deposit a number of high molecular weight organic macromolecules directly from solution in an ultra high vacuum (UHV) environment using the electrospray (ES) method. The thin films prepared by this method are largely contamination free and hence enable photoemission spectroscopy measurements of fundamental electronic and structural properties of interfaces important to organic and molecular electronics. While low molecular weight organic molecules can be deposited using thermal deposition methods, most high molecular weight materials cannot due to their thermal fragility. This largely prevented clean in situ preparation of such systems in the past. To circumvent these problems, and to enable detailed surface scientific studies on macromolecular materials, we developed an ES system capable of depositing such materials in an UHV chamber. Another intriguing aspect of using ES as a deposition method is the potential to prepare multilayered depositions of different high molecular weight organic materials without the interference of intersolubility problems as are frequently encountered when using other thin film deposition methods such as spin coating. We will present data from initial experiments on the well-known electroluminescent polymer Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV)]. Additional data from experiments designed to assess the viability of the ES method for such applications will be presented. In these step-by-step ES deposition of the low molecular weight material tris (8-hydroxyquinolinato) gallium (Gaq₃) has been compared to previously performed measurements on in situ evaporated Gaq₃ thin films. We will also discuss some of the experimental parameters influencing the morphology of the depositions and hence the electronic and structural properties of the films.

J3.27

Abstract Withdrawn

J3.28

Desorption of Water from Crystalline Vinylidene Fluoride-Trifluoroethylene Polymer Surfaces. Luis Gabriel Rosa, Christina Othon, Stephen Ducharme and Peter Dowben; Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, Nebraska.

We report on water desorption crystalline copolymer thin films of vinylidene fluoride (80%) with trifluoroethylene (20%) (PVDF-TrFE). Ultra-high vacuum angle-resolved thermal desorption studies of water from PVDF-TrFE has identified several distinct thermal desorption peaks at about 200 K and 380 K, with ice desorbing (at high coverages) at about 200 K. While the origin of the desorption peaks have not yet been conclusively been identified, the multiplicity of desorption peaks in the region of 380 K, suggests that dipole-dipole coupling, between adsorbed water and this crystalline ferroelectric polymer, influences the heats of desorption. The bulk ferroelectric transition has been identified to occur in the region of 360 K, even in films as thin a few molecular monolayers [1]. We believe that this water adsorption affects the film capacitance and conductance increase linearly with water absorbed throughout the polymer film, not just in the electrodes or at the interfaces. As the water evaporates, the capacitance relaxes exponentially as the water desorbs. [1] A.V. Bune, V.M. Fridkin, S. Ducharme, L.M. Blinov, S.P. Palto, A.V. Sorokin, S.G. Yudin, and A. Zlatkin, Nature 391, 874 (1998)

J3.29

Electronic structure of doped hexadecafluoro-zinc-phthalocyanine thin film. Kaname Kanai¹, Eiji Kawabe¹, Toshio Nishi¹, Heiko Peisert², Tadanobu Ikame¹, Martin Knupfer² and Kazuhiko Seki^{1,3}; ¹Nagoya university, NAGOYA, Japan; ²IFW, Dresden, Germany; ³RCMS, Nagoya university, Nagoya, Japan.

Hexadecafluoro-zinc-phthalocyanine (F16ZnPc) is one of the potential candidates both for effective p-type dopant of organic dye film and electron transport material due to its strong electron affinity. Moreover, the robust C-F bond promises to give the thermal- and chemical-stability of F16ZnPc molecule, which are desired attributes for the applications to the electric devices. In this work we focused on the n-doping effects on the F16ZnPc thin film with inorganic and organic dopants, respectively. In addition, we studied the energy level alignment at the organic/organic heterojunction between zinc-phthalocyanine (ZnPc) and F16ZnPc. The effect of doping with potassium on F16ZnPc thin film was investigated by probing the electronic structure by ultraviolet-photoemission spectroscopy (UPS). The small structure springs up within the energy gap of the pristine F16ZnPc film as increasing the potassium doping level. The dependence of the valence band structures on the potassium concentration revealed a clear limit to effective charge transfer from potassium atom to F16ZnPc molecules. The higher level doping than about 4 potassium atoms per an F16ZnPc molecule no longer make any effect of charge transfer. We also found the potassium doping breaks the C-F bonds of F16ZnPc molecule and generates potassium

fluoride even at low doping level. We fabricated the organic/organic heterojunction by forming the F16ZnPc overlayer upon a ZnPc film. The energy level alignment at the interface was investigated by x-ray photoemission spectroscopy and UPS. The work-function gradually increases as depositing F16ZnPc molecule onto the ZnPc film and reaches a value 0.9 eV higher than that of the ZnPc film. The shift of 0.9 eV is exceptionally large as compared with other organic/organic heterojunctions, consistently with the reported value.[1] At present we suppose the chemical interaction between ZnPc and F16ZnPc at the interface leads the large interfacial dipole layer. On the other hand, the topmost part of the occupied energy bands derived from the HOMOs of ZnPc and F16ZnPc, shows complicated behavior at the interface. The typical way of the energy level alignment for the pn junction familiar to the inorganic semiconductor wasn't observed in this case. Finally, we will present the results of the F16ZnPc film doped with tetrathianaphthacene (TTN) molecule, an organic molecular n-dopant. TTN was chosen because of its low ionization energy of about 4.4 eV.[2] [1] D. Schlettwein, et al., Chem. Phys., 285, 103 (2002), [2] N. Sato, et al., J. Chem. Soc., Faraday Trans. 2, 77, 1621 (1981).

J3.30

Magnetic Resonance Force Microscopy: A New Tool for Subsurface Characterization. Sean R. Garner¹, Seppe Kuehn², Jahan Dawlaty², Tse Nga Ng², Neil Jenkins² and John A. Marohn²; ¹Physics, Cornell University, Ithaca, New York; ²Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Magnetic resonance force microscopy (MRFM) is a technique in which magnetic resonance is detected as a deflection of a microcantilever. Originally proposed as a strategy to achieve three-dimensional imaging at the atomic scale, MRFM offers huge benefits to materials research in general, and to organic electronics in particular, as there is currently no technique which can be used to study the morphology of a conducting organic material at the buried interface in a device. We have made large advances in the core technology of the technique, ultrasensitive cantilevers, and have used these cantilevers to demonstrate a new method of MRFM in which the signal is a shift in the cantilever's mechanical resonance frequency. This method, we will show, makes a much wider range of materials available to MRFM and offers a clear technical route to single-spin sensitivity.

J3.31

Interface of water soluble conducting polymer and substrate. Swanand S. Vaidya and Jaewu Choi; Department of Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

We studied a water soluble thiophene polymer, sodium poly[2-(3-thienyl)ethoxy-4-butylsulfonate] which is a technologically important organic material and is a good candidate for biosensors, chemical sensors and optoelectronic devices. In particular, we investigated the interface of these polymer molecules with diverse substrate materials ranging from semiconductors to metals. High work function materials as a substrate were chosen such as Si, Cu, Al, and Au. Electronic and molecular structures were studied using scanning tunneling microscope. The Schottky barrier formation and chemical interaction between substrate and polymer were also studied using X-ray photoemission spectroscopy (XPS). Transport properties and space charge formation at the interface were studied by an impedance analyzer. The study results indicate that the water-soluble polymer could be a good candidate for electronic devices.

J3.32

Adsorption of Sexithiophene on Clean and Potassium-Dosed Aluminum Surfaces. Heejuon Ahn, Sandip K Sengupta and James Edward Whitten; Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts.

Sexithiophene is finding important organic device applications, including light-emitting diodes (LEDs) and field-effect transistors (FETs). Aluminum is commonly used as an electrode material, and understanding the nature of the sexithiophene-aluminum interface is important for optimizing device performance. Salaneck, Bredas and coworkers [1] have experimentally and theoretically studied the interface obtained when aluminum is thermally deposited on oligo- and polythiophene films. Their results demonstrate donation of electron density from aluminum to the thiophene rings, as evidenced by low binding energy components in the C 1s and S 2p X-ray photoelectron spectra and aluminum-induced changes in the valence spectra of the organic layers. We have observed similar evidence of strong bonding in a variety of studies of aluminum deposited on thiophene monomer and aliphatic substituted polythiophenes [2,3]. It is interesting to consider the opposite approach in which the organic layer is deposited on the metal surface. These types of studies are complementary to aluminum deposition on the organic film since they interrogate how the organic layer interacts with bulk metal. In the

present work, the adsorption of sexithiophene in ultrahigh vacuum on clean and potassium-dosed Al(111) at 130 K has been studied by X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). Sexithiophene interacts weakly with the clean Al(111) surface, as evidenced by minimal changes in its valence electronic spectrum in progressing from monolayer to multilayer films, a relatively small work function decrease, and an absence of low binding energy components in the XPS spectra. Small amounts of coadsorbed potassium, however, have been found to cause the appearance of a new peak in the valence spectrum of sexithiophene (at approximately 0.7 eV below the Fermi level). This potassium-induced peak likely originates from the filling of previously unoccupied electronic states of sexithiophene prior to its adsorption on the electron-rich alkali-metal dosed surface. Comparison experiments have also been performed in which potassium has been deposited on sexithiophene films. [1] W.R. Salaneck, S. Stafstrom and J.L. Bredas, *Conjugated Polymer Surfaces and Interfaces* (Cambridge University Press, Cambridge, 1996). [2] S.K. Sengupta, H. Ahn and J.E. Whitten, *Surf. Sci.* 520 (2002) 207. [3] H.Y. Seung and J.E. Whitten, *Synth. Met.* 114 (2000) 305.

J3.33

Charge Injection In Doped Organic Semiconductors.

Ahmad Reza Hosseini, Yulong Shen, Man Hoi Wong and George G Malliaras; Materials Science and Engineering, Cornell University, Ithaca, New York.

A study has been done to understand the dependence of injection on the degree of doping of an organic semiconductor. A model organic semiconductor, tetra-methyl triphenyl diamine doped polycarbonate (PC:TMTDP) was used for these experiments. By substituting TMTDP molecules with a TMTDP+SbF₆⁻ salt, the degree of doping in the organic semiconductor was systematically varied. Charge injection was achieved through various interdigitated electrodes of varying separation to yield its dependence on degree of doping, electric field, and junction length. This provides a better understanding of how doping, and electrode spacing affect device performance.

J3.34

Interface Dipoles and Graded Doping of Multilayer OLEDs by Organic Molecules.

Christopher Williams, Jose Gutierrez, Andrew Washington, Sergey Li, John P. Ferraris and Anvar Zakhidov; Chemistry, Nanotech Institute, Univ. of Texas at Dallas, Richardson, Texas.

Choosing organic acceptors, specially synthesized to selectively match their LUMO energy level within the barrier at the interface with injection electrodes, one can create interfacial charge transfer dipole layers. Such ID layers should lower the barrier and increase injection currents. Using a high precision computer controlled vacuum co-deposition set-up the asymmetric charge transfer interface dipoles and graded doping of organic layers by molecular acceptors (home synthesized Fn-TCNQ, n=1-4, with gradually changed electron affinity) is achieved. Monitoring the deposition rate for each organic material allows to create functionally graded doping, with a desired dopant concentration profile: e.g. thin monolayer of weak acceptor F2-TCNQ at the outer interface with hole injection electrodes, then heavily F4-TCNQ doped layer (p+) with concentration in the range of 2-5 %, followed by lightly doped p region (at 0.2-1% range). Similar profiles are being checked for several organic donor dopant. This functional gradients of doping allowed to achieve several goals: increase injection by interfacial dipoles and lower interface barriers, and enhance conductivity of hole transport (HTL: TPD, NPB) and electron transport layers. The I-V curves are significantly improved compared with undoped multilayer systems and demonstrate the decreased threshold and operating voltages of OLEDs with both low molecular and polymer (of home synthesized BEH-PPV polymer) emissive layers.

J3.35

Naturally-formed graded junctions for organic light-emitting diodes. Yan Shao and Yang Yang; MSE, UCLA, Los Angeles, California.

In this presentation, we report that the naturally-formed graded junctions for organic light-emitting diodes (OLEDs). The junctions are fabricated using single thermal evaporation boat loaded with uniformly mixed charge transport and light-emitting materials. Upon heating, material sublimated sequentially according to their melting temperatures forming the gradient junction. Two kinds of graded structures, sharp and shallow graded junctions, can be formed based on the thermal property of the selected materials. It was concluded that structural properties of the graded multifunctional layers are strongly dependent on the nature of the thermal properties of the mixed organic materials. The naturally-formed graded junction OLEDs have shown excellent performance in both brightness and lifetime compared with heterojunction devices.

J3.36

Plasma Treatment of the Cathode-Alq3 Interface in OLEDs: Effect on Adhesion and Performance. H. Michelle Grandin, Keith Griffiths and Peter R Norton; Chemistry, University of Western Ontario, London, Ontario, Canada.

The adhesion and sticking of a Mg:Ag cathode to the tris-(8-hydroxy-quinoline) aluminum (Alq3) in organic-light emitting devices (OLEDs) can be greatly enhanced by a remote plasma treatment of the Alq3 layer using either air or N₂ prior to metal deposition. The increased adhesion results from the introduction of new functional groups into the organic layer as observed by X-ray photoelectron spectroscopy (XPS). The storage life of the plasma treated devices in air without any capping treatment, as judged by a visible deterioration of the cathode, was increased by approximately three to four times compared to untreated OLEDs. Current-voltage characteristics and EL efficiency, however, were shown to deteriorate for devices incorporating either an air or a N₂ plasma treated Alq3 layer. For OLEDs subjected to short treatment times with an N₂ plasma, only a very slight increase in the turn-on voltage, of about 0.2 volts, was observed. An investigation of black spot formation revealed that an air plasma treatment resulted in a five-fold decrease in the time required for 50% of the device to become non-emissive. N₂ treated devices on the other hand, developed black spots at a comparable rate to the non-treated devices. Thus, a short N₂ plasma treatment of the Alq3 layer prior to metal deposition improves the adhesion at the interface thereby reducing the oxidation and degradation of the device through exposure to ambient conditions, particularly in storage.

J3.37

Surface Morphology Investigations of Conjugated Polyrotaxane Based Blends for LECs: A Supramolecular Approach to Organic Electronics.

Paolo Samori¹, Laura Sardone^{2,1}, Franco Cacialli^{3,4}, Joanne S Wilson⁴, Anna Maria Petrozza^{3,4}, David G Bucknall⁵, Charlotte Williams⁵, Harry L. Anderson⁶ and Giovanni Marletta²; ¹CNR, Bologna, Italy; ²Chemistry, University of Catania, Catania, Italy; ³Physics and Astronomy, University College, London, United Kingdom; ⁴Physics, University of Cambridge, Cambridge, United Kingdom; ⁵Materials, University of Oxford, Oxford, United Kingdom; ⁶Chemistry, University of Oxford, Oxford, United Kingdom.

Marrying the supramolecular approach with organic electronics is a new route to fabricate devices with increased performance [1]. Tailoring of interfacial as well as of intermolecular interactions is necessary for the development of prototype molecular wires [2,3] and is instrumental in acquiring a better understanding of the factors controlling the performance of devices such as light-emitting diodes, LEDs [4,5]. We focused our attention on a new class of supramolecular architectures, based on cyclodextrin-threaded conjugated polyrotaxanes [1,6], and looked at the surface morphology of blends of poly(4,4-diphenylenevinylene), PDV, based rotaxanes with poly(ethylene oxide), PEO. These are especially relevant for the understanding of light-emitting electrochemical cells (LECs) that we have recently characterised, and that show significant increase of both the photoluminescence and electroluminescence efficiency [7]. Investigations on the self-assembly of the blend at surfaces were performed varying systematically the substrate, the method of deposition (spin-coating and drop casting), the thickness of film and the composition of the polymer blends. Complementary information on the self-organization has been obtained by means of secondary ion mass spectroscopy (SIMS). In addition to the dependence of surface structure and phase separation on the relative concentration of the components, we find that the phase separation between the different components is particularly evident where we use an organic-solvent soluble rotaxane, that we have recently developed [8]. [1] F. Cacialli et al. *Nature Materials* 2002, 1, 160-164. [2] G.K. Ramachandran et al. *Science* 2003, 300, 1413-1415. [3] D. Cahen et al. *Adv. Mater.* 2002, 14, 789-798. [4] R.H. Friend et al. *Nature* 1999, 397, 121-128. [5] Q. Pei et al. *Science* 1995, 269, 1086-1088. [6] P. N. Taylor et al. *Angew. Chem. Int. Ed.* 2000, 39, 3456. [7] J.S. Wilson et al. unpublished. [8] C.C. Williams et al. unpublished.

J3.38

AC conductivity model for polymer light-emitting diodes. Rodrigo Fernando Bianchi, Lucas F Santos and Roberto M Faria; Instituto de Fisica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, SP, Brazil.

Alternating conductivity, $\sigma(f) = \sigma'(f) + i\sigma''(f)$, measurements of (Au or ITO)/poly[(2-methoxy-5-hexyloxy)-p-phenylenevinylene]/(Au or Al) samples were carried out at room temperature under vacuum. The conductivity of (Au or ITO)/polymer/Au devices obeyed a quasi-universal behavior in a log-log graphics: while $\sigma''(f)$ increases linearly with f in the whole frequency range, $\sigma'(f)$ is frequency independent at low frequencies, and obeys the relation $\sigma'(f) \propto f^{\beta}$ (n

~ 1) in the domain of higher frequencies. It is the typical behavior of disordered material, where the electrode influence is neglected. However, some additional influence of the interface was observed to occur when Al was used as electrode. Current density vs. voltage confirmed these evidences. A simple model was developed to represent the conductivity of such diodes, where the polymer bulk is attributed to obey the random free energy barrier model, while the interface polymer/Al the Davidson-Cole dielectric relaxation theory. This model made possible to distinguish between bulk from polymer/Al interface contributions to the alternating conductivity. It was also shown that bulk properties already exist in a polymer thin film, and the influence of polymer/Al interface is of the order of 50 nm.

J3.39

Abstract Withdrawn

J3.40

Filled and empty molecular levels, single particle gap, and exciton binding energy in polyfluorenes. Jaehyung Hwang and Antoine Kahn; Electrical Engineering, Princeton University, Princeton, New Jersey.

Poly[(9,9-dihexyfluorenyl-2,7-diyl)-alt-co-(N,N'-diphenyl)-N,N'di(butylphenyl)-1,4-(diamino-benzene)] (PFO derivative), one of the derivatives of PFO, is known to be a good candidate for polymer-based light emitting diodes. Mapping out the electronic energy levels of this and other similar polymers is important for estimating their interface energetics. We focus here on the occupied and unoccupied electronic states of this material investigated with ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES). The polymer film is spun in a nitrogen box from a 0.3wt% xylene solution on ITO substrates and dried at 80 °C. Measurements are performed in ultra high vacuum. Films investigated so far are exposed to ambient atmosphere for a very short time (< 3 minutes). Measurements on films not exposed to air will be performed and reported as well. Highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) are measured via UPS and IPES, respectively. The ionization energy and electron affinity, measured as the energy difference between vacuum level and the onset of the filled and empty states, were found equal to 5.3 eV and 1.8 eV, respectively. The transport gap, or single particle gap, is measured as the energy difference between the centroids of the LUMO and HOMO peaks, corrected for surface vs. bulk polarization and for vibrational energy, following the methodology applied to molecular films [1]. The single particle gap represents the energy difference between the positive and negative polaron levels. The optical gap is measured at the edge of the absorption spectrum, and represents the minimum energy to create an exciton. From the difference between these two gaps, we estimate the exciton binding energy. On the films investigated here, and applying the correction used for poly(9,9-dioctylfluorene) [2], we find a single particle gap of 3.4 eV. Using the optical gap of 2.85eV, and assuming that the chain length of the polymer is long enough to saturate the exciton energy [3], we obtain an exciton binding energy of 0.55 ± 0.4 eV. This value is compatible with those reported for similar polymer systems, and close to expectations based on results for films of stacked overlapping small molecules, such as perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) [1]. This study of electron energy levels will constitute an important reference for further investigations of interface energetics and electrical doping of this materials. 1. I. G. Hill, A. Kahn, Z. G. Soos and R. A. Pascal, Chem. Phys. Lett. 327, 181 (2000) 2. M. K. Fung, W. Gao, A. Kahn, C. S. Lee and S. T. Lee, to be published. 3. E. M. Conwell, Synth. Met., 83, 101 (1996)

J3.41

A study of charge transport of a conducting polymer hybrid/metal parallel interface to indium phosphide.

Frank Eugene Jones^{1,3} and Mark C Lonergan^{2,3}; ¹Physics, University of Oregon, Eugene, Oregon; ²Chemistry, University of Oregon, Eugene, Oregon; ³Material Science Institute, University of Oregon, Eugene, Oregon.

The focus of this contribution is electronic transport across nanostructured semiconductor interfaces. Nanostructure has emerged as an important explanation of anomalous transport behavior at traditional semiconductor interfaces, and it may be important at many organic semiconductor interfaces that exhibit similarly anomalous transport behavior. Studying nanostructured interfaces will also give insight into weaving molecular and nanoscale materials into microelectronic devices. The specific system in this study is a parallel contact to indium phosphide (InP) with both a low-barrier metal and a high-barrier poly(pyrrole) phosphomolybdate hybrid polymer (PMH). In terms of electronic conduction, the two contacts may or may not interact in controlling charge transport across the interface. The level of interaction is based on the relative size of the two contact regions and differences in barrier height between

independent contacts. The size of the metal contact is defined and controlled lithographically, from a macroscopic contact down to nanoscale lines. PMH was chosen as a second parallel contact for two reasons. First, the PMH — n-type InP interface is well-modeled by classic thermionic emission near room temperature, with a large barrier height (0.78 eV by capacitance-voltage measurements) compared to metal — InP interfaces. Second, the barrier height on any single PMH — n-InP interface can be controlled by manipulating the electrode potential of the PMH, thus changing the forward bias current by orders of magnitude. Therefore, the PMH barrier can be tuned in order to control the relative difference in barrier between the two contacts. The electrical measurements from these parallel contacts are compared to the theoretical predictions, including the voltage-dependence of large interactions. Finally, the consequences of these results for charge transport descriptions for devices ranging from macroscopic to the nanoscale are considered.

J3.42

Interface Modification of ITO Thin Films: Organic

Photovoltaic Cells. Adam Simmonds¹, Chet Carter¹, Carrie Donley¹, Michael Brumbach¹, Seunghyup Yoo², Benoit Domercq², Bernard Kippelen² and Neal Armstrong¹; ¹Chemistry, University of Arizona, Tucson, Arizona; ²Optical Sciences, University of Arizona, Tucson, Arizona.

While showing promising results, the performance of thin layer organic photovoltaic (PV) cells continue to suffer from chemical incompatibilities at the electrode interfaces. The basic PV platform we use to investigate these interfaces involves a transparent indium tin oxide (ITO) anode with a vacuum deposited copper phthalocyanine/C60 system acting as the hole and electron transport layers respectively. The surface of as-received ITO films, and those cleaned by various solution and plasma-etching processes, are unavoidably hydrolyzed to In(OH)3-like and InOOH-like surface species. Our current study involves the modification of the ITO surface through the chemisorption of small carboxylic acid substituted organic molecules, such as ferrocene dicarboxylic acid and 3-thiophene acetic acid to the oxide surface. We also present our initial results of an electrochemically grown conducting polymer layer as a precursor to the organic thin film deposition. Our preliminary data shows that these modifications appear to enhance the chemical compatibility between the polar ITO and the subsequent non-polar organic layers. The increase in surface wettability results in enhanced photovoltaic performance as observed through higher power conversion efficiency and a lower series resistance in the functional photovoltaic devices.

J3.43

Electrochemical Treatment of Tin-doped Indium Oxide for Improvement of Hole Injection Efficiency. Zhaohong Huang¹,

Xianting Zeng¹, E T Kang² and Y H Fuh³; ¹Surface Technology Group, Singapore Institute of Manufacturing Technology, Singapore, Singapore; ²Chemical Engineering, National University of Singapore, Singapore, Singapore; ³Mechanical Engineering, National University of Singapore, Singapore, Singapore.

Tin-doped indium oxide (ITO) is commonly used as a transparent, hole-injecting electrode material in organic light-emitting diodes (OLEDs) for its good transparency and low resistivity. For most polymers, however, the HOMO of polymer lies more than 5 eV below vacuum. A significant energy barrier to hole injection into polymer, combined with surface contamination, is then expected to be responsible for an increase in the turn-on voltage of the devices. To overcome this problem, many ITO surface treatment techniques have been developed to improve the hole injection efficiency, among which oxygen plasma treatment demonstrated the best effectiveness. In this paper, a new method of ITO surface treatment for enhancement of hole injection from anode to active polymer layer is reported. The ITO film was electrochemically treated in an electrolyte under a low current. The surface energy and I-V characteristics of ITO/polymer/metal devices were measured. The results showed that the surface energy of ITO, especially the polar component, was significantly increased and the turn-on voltages of devices were reduced. More importantly, compared with oxygen plasma treatment, the electrochemically treated ITO surface is more stable in ambient atmosphere. The highly active oxygen released during the electrochemical treatment leads to the decontamination and possibly the higher work function of ITO surface. The high polarity and stability are possibly resulted from the formation of hydrogen bonding and its isolation of ambient contaminants. As a result, a better electronic contact between ITO and polymer is expected, leading to improved hole injection. It is suggested that the electrochemical approach be effective for improvement enhanced performance of polymeric light-emitting devices, especially in presence of the water soluble PEDOT layer as the hole injection layer.

8:30 AM *J4.1

Chirality and electron tunneling in solution and at surfaces.

David N. Beratan, Michael R. Goldsmith, LeRoy Guy Holman, Jianping Lin and Misha Galperin; Chemistry, Duke University, Durham, North Carolina.

A theoretical perspective will be used to compare some of the expected chiro-optical and transport properties of molecules in contact with metals or semiconductors with their characteristics in homogeneous solution. The computation of optical rotation angles will be described for self-assembled structures and for adsorbates on clusters. Tunneling currents mediated by conformationally disordered molecules and open shell adsorbates will also be discussed.

9:00 AM *J4.2

Characterization of Nanotransfer-Printed Electrical Contacts in Au/Alkanedithiol/GaAs Diodes.

Yueh-Lin Loo^{1,3}, John A. Rogers^{2,3}, Julia W.P. Hsu³ and David V. Lang⁴; ¹Chemical Engineering, University of Texas at Austin, Austin, Texas; ²Materials Science, University of Illinois, Urbana-Champaign, Illinois; ³Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; ⁴Agere Systems, Murray Hill, New Jersey.

We have developed a non-invasive technique for establishing efficient electrical contacts to alkanedithiol molecular layers on semiconductor surfaces at room temperature. Using nanotransfer printing (nTP), we have been able to directly transfer thin layers of patterned gold films onto a molecular layer of 1,8-octanedithiol that is deposited on the surface of an n+ GaAs (100) wafer. Printing relies on the presence of S-Ga and S-As bonds on the substrate surface, and the formation of Au-S bonds when a Au-coated stamp is brought into intimate physical contact with the molecules. Nanotransfer printing is purely additive in operation and occurs readily at ambient conditions. These features have eliminated the need for direct evaporation of Au contacts on the molecules. The transferred Au patterns are mechanically robust; they easily pass Scotch tape adhesion tests. Electrical experiments - current-voltage, capacitance-voltage and internal photoemission measurements - conducted on these nTP-generated two-terminal devices show that electrical transport occurs through the insulating molecular layer. Specifically, we observe low current levels (< 10 nA/cm²) and high barrier heights (0.82-0.91V) in the current-voltage measurements. Further, the exponential energy dependence in the photoresponse yield indicates transport through disordered materials. These measurements contrast drastically with experiments conducted on Au/alkanedithiol/GaAs diodes whose Au electrical contacts are not fabricated by nTP, rather by direct evaporation of Au through a shadow mask. In fact, the current-voltage and internal photoemission characteristics of diodes with evaporated contacts are not significantly different from those of Au/GaAs diodes without alkanedithiol molecules. This observation strongly suggests that electrical conduction through diodes whose electrical contacts consist of evaporated Au pads is dominated by direct Au-GaAs contact.

9:30 AM J4.3

Characterization of Molecular Monolayers on Template-stripped Pt and Au for use in Molecular Electronic Devices.

Jason J Blackstock^{1,2}, Zhiyong Li², Duncan R. Stewart², R. Stanley Williams² and Mark R. Freeman¹; ¹Physics, University of Alberta, Edmonton, Alberta, Canada; ²Hewlett-Packard Labs, Palo Alto, California.

Ultra-flat electrode surfaces may be a critical component in the fabrication of reproducible molecular electronic devices. We report physical characterization of ultra-flat template-stripped platinum and gold surfaces, including physical characterization of various length alkanethiol monolayers (C6 to C22) prepared on these surfaces. For the bare template-stripped metal surfaces, optical constant measurements, atomic force microscopy (AFM), X-ray diffraction and low-energy electron diffraction (LEED) revealed near-atomic scale flatness over micron length scales, as well as information regarding the atomic ordering of the metal atoms. The alkanethiol self-assembled monolayers grown on these surfaces were studied with contact angle, ellipsometry, reflection-absorption infrared spectroscopy (RAIRS) and AFM, and the results were compared against films prepared on as-deposited platinum and gold surfaces. The high flatness of the template stripped surfaces was found to influence the packing behavior of alkanethiols, inducing better observable ordering for several intermediate chain lengths. Finally, electrical measurements of the alkanethiol monolayers were obtained using a conductive probe AFM, and correlations with the physical studies of the molecular films and underlying metal surfaces are examined.

9:45 AM J4.4

Heterojunction and Photoconductive Nature of Electromigration Induced Nanoscale Break Junctions.

Tae-Hee Lee, Jose I Gonzalez and Robert M Dickson; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Nanoscale metallic electrode pairs fabricated through electromigration have been used by numerous groups in molecular-scale electronics research. We have utilized these common methods to fabricate nanoscale silver and gold heterojunctions. Formed junctions show strong single molecular electroluminescence (EL) from metallic nanoclusters with strong polarity dependence. These broken junctions are found to be heterojunctions with different amounts of oxygen on either side of the junction as determined through photoluminescence and energy dispersive spectroscopy. This heterojunction nature yields not only single molecule light emitting diode behavior of the EL, but also a strong diode behavior in the electric current without additional materials within the nanogap. The junctions also show asymmetric photoconductivity - only one side of the junction is fluorescent, and therefore only one side of the junction yields photoconductivity. Thus, these commonly employed and easily fabricated electromigration-induced nanogap junctions are naturally heterojunctions and can be directly utilized as useful nanoscale electronic device components. Diode-diode logic gates were also implemented through direct electrical writing of multiple connected nanogaps.

10:30 AM *J4.5

Measuring and Controlling Molecular-Scale Properties for Single Molecular Devices.

Paul S Weiss, Chemistry & Physics, Pennsylvania State University, University Park, Pennsylvania.

We use intermolecular interactions to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements on single or bundled molecules. We use and develop scanning probe microscopes to determine local structures as well as the electronic and other local properties. We have applied these to isolated molecules with electronic and electromechanical function to determine the mechanisms of function, and the relationships between molecular structure, environment, connection, coupling, and function. We have demonstrated that single molecules can function as multistate electronic switches, and have determined important aspects of the mechanism, function, and persistence of switching. We will discuss the origins of switching and the relevant aspects of the molecular structure and environment required.

11:00 AM *J4.6

Understanding Charge Transport in Molecular Electronics.

James G. Kushmerick, Center for Bio/Molecular Science and Engineering, 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. Results on junctions with symmetric and asymmetric metal-molecule contacts demonstrate that a specific molecular core can act either as a molecular wire or a molecular rectifier depending on its coupling to the metal electrodes. 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 extent 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 π -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 π -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 the molecular junction will also be presented.

11:30 AM J4.7

Electron transport through conjugated organic molecules.

Ganesh K Ramachandran¹, Stuart M Lindsay¹, Li Jun¹, John K Tomfohr¹, Sankey F Otto¹, Yuichi Terazono², Thomas A Moore², Ana L Moore², Devens Gust² and Larry A Nagahara³; ¹Department of Physics, Arizona State University, Tempe, Arizona; ²Department of Chemistry, Arizona State University, Tempe, Arizona; ³Physical Sciences Research Labs, Motorola Labs, Tempe, Arizona.

We present here our electrical characterization studies of metal-molecule-metal junctions studied with a conducting AFM. In the case of the long chain carotene(dithiol), the I-V curves are relatively insensitive to contact probe force and cluster around integer

multiples of a fundamental curve, suggesting that members of the smallest set correspond to data obtained from a single molecule. First principles calculations based on tunnel transport yield results that are remarkably close (within a factor of 4) to the measured data. It appears that electron tunneling dominates transport even in this 3-nm-long molecule. The carotenoid is a better conductor than a saturated n-alkane of equivalent length by a very large factor and is significantly more conductive than 2,5-di(phenylethynyl-4'-thioacetyl)benzene, another candidate "molecular wire".

11:45 AM J4.8

Electrochemical Gate Controlled Electron Transport in Molecular Junctions. Bingqian Xu, Xiaoyin Xiao and NJ Tao; Electrical Engineering, Arizona State, Tempe, Arizona.

We have measured the current-voltage characteristics of several small molecules (e.g., alkane chains and heterocyclic molecules) attached to two Au electrodes. The molecules have either two thiol groups or heterocyclic rings on two ends that can attach to Au electrodes via S-gold or N-Au bindings. For a given molecule, a considerable amount of variations in the conductance is observed from one junction to another, which likely reflects the difference in the molecule-Au contact geometries. Conductance histogram obtained from over thousands of measurements shows a well defined peak, corresponding to a thermodynamically favorable contact geometry. We have studied the electron transport by controlling the potential of the Au electrodes with respect to a reference electrode inserted in the electrolyte. This electrochemical gate control does not significantly change the conductance of the studied molecules within the potential window. The lower limit of the window is chosen to avoid the desorption of the molecules from the Au electrodes, and the upper limit is determined by the oxidation of the Au electrodes at positive potentials.

SESSION J5:

Chair: Masamichi Fujihira
Tuesday Afternoon, December 2, 2003
Back Bay D (Sheraton)

1:30 PM *J5.1

An Ab initio Study of Interfaces for Molecular Electronics. Jorge M Seminario, Electrical Engineering, University of South Carolina, Columbia, South Carolina.

A systematic evaluation of metal-molecule and semiconductor-molecule interfaces is performed to determine optimal device behavior for molecular electronic devices. The study focuses on the physical, chemical, and electrical interface characteristics where the effects of the molecule and the contact atoms in its neighborhood as well as the effects of the extended and continuum nature of the contacts are considered through the use of molecular and extended ab initio procedures interconnected to account for the interfacial characteristics.

2:00 PM *J5.2

Experimental Studies of Electron Tunneling and its Dependence on Chemical Composition. David H Waldeck, University of Pittsburgh, Pittsburgh, Pennsylvania.

We report on electron tunneling studies through molecules imbedded in self-assembled monolayer films. Studies have been performed using both electrochemical measurements of electron transfer rate constants and conductive AFM measurement of i-V curves. Comparisons between the two methods are drawn. These studies investigate how the chemical composition of the molecules and the structure of the films influence the tunneling probabilities.

2:30 PM *J5.3

Redox Sites Confined in a Nanometer Gap Junction. Maria Rampi¹ and George M Whitesides²; ¹Dipartimento di Chimica, University of Ferrara, Ferrara, Italy; ²Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

We report a series of studies of electron transfer processes carried out in an electrical systems, that is measuring the current flowing through molecules sandwiched between two electrodes. The junctions are based on Hg electrodes: Hg-SAM//SAM-M, where SAM is a self assembled monolayer organized at the metal surfaces and M is a metal (Au, Ag, Hg). The junctions are easy to assemble (because the mercury electrode is compliant) and they are compatible with SAMs incorporating organic groups having a range of structures. Junction 1 where SAM(1) is formed by molecules of different length and different structure, allows for correlating electrical properties and molecular structure [1]. In junction 2, by changing X and Y it is possible to

perform different interactions connecting the two metal electrodes: it is possible to compare electron transfer rate through covalent bonds, H bonds and van der Waals interactions [2]. In junction 3, different redox sites behave as ultimate quantum dots [3,4]. [1] R. E. Holmlin, R. Haag, R. F. Ismagilov, M. A. Rampi, G. M. Whitesides, J. Am. Chem. Soc. 2001,123, 5075. [2] R. E. Holmlin, R. Haag, R. F. Ismagilov, V. Mujica, M. A. Ratner, M. A. Rampi, G. M. Whitesides, Angew. Chem. Int. Engl. Ed. 2001,40, 2316. [3] M. L. Chabinyc, X. Chen, R. E. Holmlin, H. Jacobs, H. Skulason, C. D. Frisbie, V. Mujica, M. A. Ratner, M. A. Rampi, G. M. Whitesides J. Am. Chem. Soc. 2002, 124, 11730. [4] M.A Rampi, G.M. Whitesides, Chem. Phys.2002, 281, 373.

3:30 PM *J5.4

Electron Transfer through Non-Covalent Contacts in Tunneling Junctions. Slawomir Sek^{1,2}, Roger York², Krzysztof Slowinski^{2,3} and Marcin Majda¹; ¹Department of Chemistry, University of California at Berkeley, Berkeley, California; ²Department of Chemistry and Biochemistry, California State University, Long Beach, California; ³Current address: Global Research Center, General Electric Co, Niskayuna, New York.

We describe electron transfer (ET) through monolayers and bilayers of alkanethiols self-assembled in the Me-Hg (Me=Hg, Ag, Au) tunneling junctions. Potentiodynamic, current transient, and impedance methods were used to measure both the capacitance and tunneling currents. The following are the main conclusions derived from our tunneling measurements: (1) Plots of the logarithm of the tunneling current vs. the total number of carbon atoms in each junction yield identical tunneling coefficients (1 per methylene group) [1, 2]. (2) Tunneling current recorded for a bilayer of 1-octanethiol or 1-nonanethiol is ca. 2-fold larger than a corresponding tunneling current recorded for monolayers of 1-hexadecanethiol or 1-octadecanethiol, respectively. This result is explained in terms of weak electronic coupling across the noncovalent molecule/electrode interface [2]. (3) The largely all-trans structure of the bilayers becomes disordered with time as a result of the van der Waals and coulombic forces squeezing the junction. This leads to a diminished electronic coupling between electrodes [3]. (4) ET through a two-component bilayer containing shorter (nonanethiol) and longer (hexadecanethiol) components is less efficient than ET through a single-component bilayer. This result is rationalized in terms of a diminished electronic coupling through the van der Waals contacts [4]. (5) Asymmetric I/V curves with respect to the polarity of the voltage bias were observed in the Hg-Au junctions containing bilayers of alkanethiols of different chain length [5]. (6) Conductivity of Ag-S-Cn-SH/Hg junctions is substantially larger if the sulfur atom is covalently bonded to the mercury surface [6]. References: [1] R. York, P. Nguyen, K. Slowinski JACS, 2003, 125, 5948 [3] K. Slowinski, M.Majda J. Electroanal.Chem., 2000, 491, 139 [4] R. York, K. Slowinski J. Electroanal.Chem., 2003, WEB ED [5] M.Galperin, A.Nitzan, S.Sek, M.Majda J. Electroanal.Chem., 2003, WEB ED [6] S.Sek, K.Slowinski - 2003, submitted

4:00 PM J5.5

Ab Initio Study of Quantum Capacitance of Nanotube/Metal and Nanotube/Nanotube Junctions. Pawel Pomorski^{1,2}, Lars Pastewka¹, Christopher Martin Roland¹, Hong Guo² and Jian Wang³; ¹Physics, NC State University, Raleigh, North Carolina; ²Physics, McGill University, Montreal, Quebec, Canada; ³Physics, The University of Hong Kong, Hong Kong, Hong Kong.

From general considerations, it has been theoretically predicted and experimentally verified that the capacitance of molecular-scale conductors show distinct non-classical behavior. Currently, there is little understanding of the capacitive issues for nanotube systems, even though these determine the ability of nanotubes to charge and store charge for scanning probe and memory device applications. Using a recently developed nonequilibrium Greens function approach combined with large-scale density functional calculations, we have investigated capacitive issues for a variety of prototypical nanotube configurations, including: (i) nested nanotubes; (ii) the insertion of one nanotube into another; (iii) two metallic nanotubes with a conductance gap; and (iv) a nanotube interacting with a flat metallic Al surface. In all cases, the capacitive matrix elements show considerable deviations from the classical behavior due to the quantum corrections, which may be analyzed in terms of the finite density of states of the nanotube. The implications of the nanotube capacitance for memory devices and capacitive scanning of surfaces will also be discussed.

4:15 PM J5.6

Electron Transport in Metal-Molecule-Metal Junctions: A Transiesta Study of the Adsorption Site Dependence of Metal-Molecule Contacts. Anton Grigoriev¹, Goran Wendin¹, Zeljko Crljen² and Kurt Stokbro³; ¹MC2, Chalmers University of

Technology, Gothenburg, Sweden; ²Theoretical Physics Division, Institut Ruder Boskovic, Zagreb, Croatia; ³Mikroelektronik Centret, Technical University of Denmark, Lyngby, Denmark.

Using ab initio methods applied to molecular electronics, we investigate structure and electron transport properties of metal-molecule-metal systems where sulphur-containing molecules are connected through "alligator clip" interfaces to two Au(111) surfaces. We have chosen sulphur, thiol, methylthiolate, dithiolbenzene (DTB) and oligo(n-phenylene vinylenes) (OPVn), n=3-5 with protected thiol termini, on Au(111) surface as model systems. The metal-molecule contact interface is of great importance and determines the order-of-magnitude of the conductivity, but the importance of the binding site and the sensitivity of IVCs are not known. In addition to flat surfaces we also consider surface defects like vacancies that can promote molecular adsorption at specific sites, different from the flat surface configuration. In addition, possible isomerisation of the molecules is considered. In our recent work [1], it was found, that the structure of adsorbed molecules depends on coverage, and that the metal-molecular interface can not always be modelled as a simple atomic contact (e.g., another adsorbate atom could be close to the bridging atom). This implies that determining the structure of molecular contacts in the sandwiched system is a tremendous task. Therefore, in the the present transport studies we start by testing reasonably simple examples, with special care taken to reproduce the gold surface and the gold bulk substrate. The recently developed Transiesta density functional non-equilibrium Green's function method [2] is used for the transport calculations. An important outcome of this research will be to establish reliable models for metal-molecular interfaces, needed for transport calculation. Although the jellium model for contacts is not accepted as sufficiently accurate, the degree of accuracy needed for modelling metal bulk contacts and metal surface is not known. Work is in progress to clarify the structure of the metal-molecular interface and its transport properties in molecular multiterminal devices. We will present results for bias-dependent transmission spectra and IVCs for DTB and OPVn for different adsorption sites and contact groups. We expect the results of this study to be useful for developing realistic descriptions of transport through the interface, important for preliminary design of new devices. [1] S. Mankefors, A. Grigoriev and G. Wendin, Molecular alligator clips: a theoretical study of S, Se and S-H adsorption on Au(111), Nanotechnology 14, 849 (2003). [2] Mads Brandbyge, Jose-Luis Mozos, Pablo Ordejon, Jeremy Taylor, and Kurt Stokbro Density functional method for nonequilibrium electron transport, Phys. Rev., B. 65 165401 (2002).

4:30 PM J5.7

Electrical measurements of oligoazomethine-doped planar tunnel junctions. Al-Amin Dhirani, Jose Amado Magbanua Dinglasan and Aly Shivji; Dept. of Chemistry, University of Toronto, Toronto, Ontario, Canada.

Electrical properties of planar aluminum/aluminum oxide/silver tunnel junctions modified with phenyl-based azomethine oligomers were investigated. Normalized differential conductance of the junctions increases with oligomer length. At a bias of 2 V, junctions doped with azomethines with three phenyl rings exhibit normalized differential conductances that are on average more than an order of magnitude greater than those of unmodified oxide junctions. Conductances of junctions modified with azomethines increase more rapidly with temperature than those of plain oxide junctions. Our results are consistent with a model in which both increased conjugated length of the sandwiched organic layer and a molecule/metal interface lead to a lowering of the barrier profile outside the aluminum oxide tunnel region.

4:45 PM J5.8

Voltage-driven Changes in Molecule-metal Contact Yield Negative Differential Resistance at Room Temperature. Adi Salomon, Rina Arad-Yellin, Abraham Shanzer and David Cahen; Dept of Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel.

We demonstrate molecule-controlled devices based on metal-semiconductor junctions, which exhibit Negative Differential Resistance (NDR) at room temperature. Such device has a peak to valley ratio (PVR) of 5 and NDR of -2 Ohm/cm². The active component is a self-assembled monolayer containing a cyclic di-sulfide terminal which, adsorbed on a Hg electrode, can undergo a redox reaction in the dry state (the other electrode is Si or GaAs). This reduction process, which takes place during the voltage scan, leads to changes in the metal-molecule contact, which, in turn, result in a huge decrease in the current with increasing voltage. In contrast to the NDR that we obtained in earlier studies¹, this effect is stable, that is, it is repeatable over more than 20 scans without any reduction in the current or in the effect. The stability of the system is due to a new molecular design with end-substituted C₁₄ alkyl chains. The added

alkyl chain results in a much better organized monolayer than with the original molecules (without alkyl chains), one that has sufficient van der Waals interactions to maintain the molecules' orientation also after disulfide reduction. Moreover, after the NDR effect diminishes after applying high forward bias (Hg negative), the system recovers, itself and the effect reappears, something that we interpret as reorganization of the molecular orientation. Reference: ¹ Y. Selzer, A. Salomon, J. Ghabboun, and D. Cahen, Angew. Chem. B **105**, 12011(2001)

SESSION J6:

Chair: Neal Armstrong
Wednesday Morning, December 3, 2003
Back Bay D (Sheraton)

8:30 AM *J6.1

Schottky Barriers and Metal-Molecule Interfaces.

Raymond T. Tung, Physics, Brooklyn College, Brooklyn, New York.

Due to the apparent similarities between the organic molecule-metal interfaces and the semiconductor-metal interfaces, many concepts and theories presently used to describe and model the electronic transport properties at metal-organic interfaces have been borrowed straight from the Schottky barrier literature. Perhaps unbeknownst to the organic materials community, the Schottky barrier height field has also been going through some slow yet steady modifications of its own, even concerning its most basic concepts. In this presentation we briefly review concepts, old and new, on the formation mechanism of the Schottky barrier height at metal-semiconductor interfaces. We first examine the formation of interface dipole, which is necessary to account for the Fermi level pinning phenomenon, and the various problems associated with the traditional view of interface dipole, namely, through an exchange of charge between the metal and some fixed interface states. These are then contrasted with the latest way to consider interface dipole formation, through interface bonding and with the help of a method traditionally used by molecular chemists. Not only is this latest approach more in accord with the thermodynamics of interfaces, but also it gives better agreement with the experimentally observed Fermi level pinning phenomenon. These results point to the importance of correctly handling the chemistry at semiconductor interfaces in order to understand their electronic properties. We then comment on how the latest view of Schottky barrier formation can be applied to the metal-molecular interfaces. Some specific differences between the two types of interface are also pointed out.

9:00 AM *J6.2

How to Make Ohmic Contacts to Organic Semiconductors.

George Malliaras, Materials Science, Cornell University, Ithaca, New York.

The process of charge injection plays an important role in organic semiconductor devices. We studied the behavior of metal contacts with a host-guest organic semiconductor using a variety of techniques. These studies helped determine the dependence of the charge injection efficiency on parameters such as the mobility of the organic semiconductor, its carrier density (doping level) and thickness, and the energy barrier at the interface. We describe a theory that explains the experimental results and discuss similarities and differences with contacts of inorganic semiconductors. The implications of our findings on the performance of organic light emitting diodes and thin film transistors will be discussed and guidelines for forming ohmic contacts will be presented.

9:30 AM J6.3

Nanoscale Charge Injection Tuning at Indium-Tin-Oxide Anode-Organic Interface in Organic Light-Emitting Diodes.

Qinglan Huang^{1,2} and Tobin J Marks^{1,2}; ¹Chemistry, Northwestern University, Evanston, Illinois; ²Materials Research Center, Northwestern University, Evanston, Illinois.

Physical and chemical phenomena at electrode-organic interfaces are crucial to understand charge injection/transport/recombination properties of organic light-emitting diodes and are directly related to device performance and degradation. To elucidate interfacial effects, a mechanistic study conducted precisely at nanoscale interfaces is required. A self-assembly approach has been developed for this purpose, which utilizes self-limited chemisorption of silyltriarylamine molecules at tin-doped indium oxide (ITO) anode surface hydroxide groups. A conformal and thermally/mechanically robust ultra-thin layer with nanoscale thickness control can be coated on ITO electrodes via this simple and reproducible method. A series of silyltriarylamines are designed and coated on ITO anodes followed by OLED fabrication. These devices exhibit very different hole current density vs. voltage characteristics that can be directly correlated with

interfacial chemical structure variation. Systematically adjusting the chemical structures of the silyltriarylamine absorbates reveals that charge injection is very sensitive to the absorbate ionization potential, anode-adsorbate spacing, and adsorbate interactions. These correlations can be used to tune charge injection in varied OLED device structures and yield dramatic performance improvement over bare ITO-based devices. Very bright and efficient ($\sim 70,000$ cd/m² and $\sim 2.5\%$ forward external quantum efficiency) tris (8-hydroxyquinolinato) aluminum (III) (Alq₃)-based OLEDs have thereby been fabricated. Compared to widely used photoelectron spectroscopy to study the ITO anode-organic interface, the present method reveals strong chemical structure effects existing in this nanoscale region which have not been detected before. This molecular level approach therefore offers novel interfacial charge injection tunability and enriches the fundamental understanding of charge injection processes across electrode-organic interfaces in organic semiconductor devices.

9:45 AM J6.4

Modification of the Indium Tin Oxide/Organic Thin Film Interface: Solution Electrochemical Probes of Changes in Electronic Properties, and Correlation with Performance Changes in Simple OLED Structures. Chet Carter¹, Carrie Donley¹, Michael Brumbach¹, Benoit Domercq², Adam Simmons¹, Bernard Kippelen² and Neal Armstrong¹, ¹Department of Chemistry, University of Arizona, Tucson, Arizona; ²Optical Sciences, University of Arizona, Tucson, Arizona.

Simple solution and plasma etching procedures have been developed by a number of research groups to change the surface chemistry of indium-tin oxide (ITO) and related TCO anode surfaces, to increase work function, decrease contaminant levels, and enhance overall device performance. Recent work from our group, however, suggests that hydrolysis of the ITO surface can contribute to a significant coverage of electronically inactive sites on the ITO surface, and that at most ca. 40% of a monolayer of electronically active ITO may result. Solution electrochemical probes (the one-electron oxidation of ferrocene in acetonitrile) are shown to be a sensitive indicator of the extent of electroactivity of the modified ITO surface, and that one can easily monitor changes in the electron transfer rates of such a probe molecule as a function of various surface pretreatments. Not surprisingly ITO surfaces which have been air or O₂-plasma etched, followed by addition of spin-cast conductive polymer films, show at least a 100x increase in k_{ET} versus the untreated ITO surface. We have recently seen, however, that even better performance can be obtained from the ITO anode if small molecule modifiers are allowed to chemisorb to the ITO surface, before addition of the conductive polymer film. Changes in device performance were characterized for simple vacuum deposited ITO/MODIFIER/PEDOT: PSS/TPD/Alq₃/Mg:Ag OLEDs. The presence of the small molecule modifier allows space charge limited currents to be realized at much lower voltages, turn-on voltages to be reduced by 100mV, and device efficiencies nearly double that of unmodified devices. These results suggest that, even though electron injection and transport are considered to be the major limitations to OLED device efficiency, considerable gains are still to be made with anodes whose surface compositions have been tailored to optimize electron transfer rates. Similar enhancements in organic PV cell performance have been noted, the subject of the companion paper in this symposium.

10:30 AM *J6.5

High-Performance Organic Light Emitting Diodes With Laminated Gold Electrodes. Julia W. P. Hsu¹, Tae-woo Lee¹, Jana Zaumseil¹, Zhenan Bao¹ and John A. Rogers², ¹Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; ²MSE Department, UIUC, Urbana, Illinois.

The nature of the interface between an organic semiconductor and a metal electrode is critical to the performance of organic electronic and optoelectronic devices. Conventionally, devices are built by depositing bottom electrode, organic active layer, and top electrode sequentially. This approach inevitably leads to evaporating metal onto the organic materials. Furthermore, because of the chemical and mechanical fragility of organic materials, conventional lithography techniques are not applicable to pattern the top electrodes. In this talk, I will discuss our efforts in building organic light emitting diodes (OLEDs) by soft contact lamination (SCL). In SCL, the OLEDs are made in two separate steps: (1) the electroluminescence (EL) organic material (MEH-PPV and polyfluorene derivatives) is spin-cast onto of ITO bottom electrode, and (2) the top Au contact is deposited on an elastomeric (PDMS) stamp, not on the organic layer. The device is completed by laminating the Au coated PDMS stamp on the EL coated ITO substrate. The process is reversible, i.e., the Au electrode can be peeled off the organic without visible changes. We found the quantum efficiency (QE) of such SCL devices to be 10 to 100 fold higher than that of conventional devices with evaporated Au electrodes. In fact, the QE of the SCL devices with Au electrodes is

also higher than conventional ITO/MEH-PPV/Au devices with a lower work function metal (Au). Using a film of MEH-PPV blended with organic salts, we obtain a maximum external efficiency of 2.5 % ph/el at 3.4 V. To better understand the difference in QE between the two types of devices, we perform photoluminescence (PL) experiments on ~ 10 -nm thick MEH-PPV films with an evaporated or a laminated Au layer. PL results indicate that evaporation of Au causes disruption of the p-p conjugation in the polymer. Since the metal electrode is fabricated separately from the active organic EL layer in SCL devices, we are able to pattern the Au electrode using soft lithography techniques. We have achieved nano-line OLEDs with ~ 150 nm wide Au electrodes.

11:00 AM *J6.6

Impact of electrical doping on molecular level alignment at metal-organic and organic-organic heterojunctions.

Antoine Kahn and Weiyang Gao; Princeton University, Princeton, New Jersey.

Molecular level alignment at metal-organic (MO) and organic-organic (OO) semiconductor heterojunctions defines charge injection into and transport through multi-layer organic devices. Considerable work has been devoted to the energetics of MO interfaces, somewhat less to molecular level alignment at OO interfaces. Breakdown of vacuum level alignment is generally observed at MO interfaces. A variety of mechanisms have been identified, e.g. chemical bonds across the interface, occupation of interface states and modification of substrate surface electronic structure, which lead to charge transfer and formation of an interface dipole barrier [1]. On the other hand, vacuum level alignment prevails at a majority of OO interfaces, consistent with weaker intermolecular interactions and absence of free charges at interfaces between wide gap materials [1]. We focus here on the impact of electrical doping on the energetics of these interfaces. Using direct and inverse photoemission spectroscopy (UPS, XPS, IPES), we demonstrate [2] that doping at MO interfaces between Au and ZnPc or α -NPD p-doped with the strong electron acceptor F₄-TCNQ induces a depletion region in the organic film, but does not alter the molecular level alignment at the interface, consistent with strong metal-organic molecular level anchoring. We then investigate a number of OO interfaces between electron transport layers (ETL) (CBP, BCP, Alq₃) and hole transport layers (HTL) (ZnPc, α -NPD) as a function of p-doping in the HTL [3]. The first important result is that, unlike MO interfaces, OO interfaces exhibit a systematic shift in molecular level alignment upon doping the HTL. The shift is accompanied by the formation of an interface dipole, the size of which depends on the constituents of the heterojunction. The second key result is that the position of the HOMO of the undoped ETL remains fixed with respect to the Fermi level (EF) and independent of the HTL when the HTL is doped. This observation suggests that the introduction via doping of charges and/or electronic states at the interface in the gap of the HTL and ETL results in pinning of EF at or near a specific energy level, tentatively related to the charge neutrality level of the organic material. The notion of charge neutrality level, and its relevance and applicability to MO and OO interface level alignment, is discussed. 1. A. Kahn, N. Koch and W. Gao, Journal of Polymer Science, Polymer Physics (June 2003) 2. W. Gao and A. Kahn, Organic Electronics 3, 53 (2002) and J. Appl. Phys. (July 1, 2003) 3. W. Gao and A. Kahn., Appl. Phys. Lett. (June 30, 2003)

11:30 AM *J6.7

Energetics and Complexation at Organic-Metal Interfaces.

Kazuhiko Seki^{1,2}, Y. Morikawa³, Y. Sakurai⁴, T. Yokoyama⁴, D. Yoshimura¹, H. Ishii⁵ and K. Kanai⁴, ¹Res. Cent. for Mat. Science, Nagoya University, Nagoya, Japan; ²Adv. Res. Inst., Nagoya University, Nagoya, Japan; ³Natl. Inst. Adv. Inc. Sci. Tech., Tsukuba, Japan; ⁴Chemistry, Nagoya University, Nagoya, Japan; ⁵Res. Inst. Electrocommun, Tohoku University, Sendai, Japan.

The organic-metal interfaces have attracted much attention in relation to the organic and molecular-scale electronics. We have been studying electronic structure and various phenomena at interfaces by various surface scientific tools such as UPS, XPS, MAES, LEED, IRRAS, NEXAFS, and Kelvin probe, and here we will report on our recent progress. The alkane/metal interface offers a unique combination of metals and a molecule with very deep HOMO [1] and very high LUMO (even above the vacuum level) [2]. Although the absence of charge-transfer was thus expected, recent experimental and theoretical studies reported the occurrence of electron transfer [3,4]. Our own theoretical studies by DFT method [5] also indicated some mixing of the molecular unoccupied orbitals with the occupied levels, of metals, and the results quantitatively explained the observed CH softening and the work function change. Metal deposition on organic layer can often lead to charge-transfer (CT) and chemical reaction. There was theoretical prediction that alkali metal deposition on Alq₃ leads to CT complex with the conversion of Alq₃ from the stable meridional isomer to facial isomer [1], which should work as an electron trap [6]. Since UPS can not distinguish these isomers, we

studied the K deposition on Alq3 by IRRAS and Raman spectroscopy, with theoretical simulations [7]. The results showed that Alq3 in the complex remains in the meridional form without isomer conversion. Studies were also carried out for deposition of metals on Alq3 by NEXAFS, including the detailed analysis of Alq3 spectra [8] and for K deposition on hexadecafluoro Zn phthalocyanine (F16ZnPc) by UPS etc. [9]. The importance of the existence of bare charge in the energetics of organic electronic devices will also be discussed. Work supported by NEDO International Collaboration and Grant-in-Aid for Creative Science Research from MEXT, Japan. [1] D. Yoshimura et al., Phys. Rev., B60, 9046 (1999) and references therein. [2] N. Ueno et al., Phys. Rev., B34, 6386 (1986). [3] K. A. Fossler et al., J. Chem. Phys., 118, 5115 (2003) and references therein. [4] H. Oestrom et al., J. Chem. Phys., 118, 3782 (2003). [5] Y. Morikawa et al., unpublished. [6] A. Curioni et al., Chem. Phys. Lett., 294, 263 (1998). [7] Y. Sakurai et al., unpublished. [8] T. Yokoyama et al., unpublished. [9] K. Kanai et al., presentation at the present session.

SESSION J7:

Chair: Dan Frisbie

Wednesday Afternoon, December 3, 2003

Back Bay D (Sheraton)

1:30 PM J7.1

Charge Carrier Tunneling and Effects of Anode Properties on Device Performance in Multilayer Organic Photodetectors. Jiangeng Xue^{1,2} and Stephen R. Forrest^{1,2}; ¹Center for Photonics and Optoelectronic Materials (POEM), Princeton University, Princeton, New Jersey; ²Dept of Electrical Engineering, Princeton University, Princeton, New Jersey.

The broad absorption spectra, high absorption coefficients, and low indices of refraction, as well as the chemists' ability to tailor the electronic and optoelectronic properties, make organic materials of particular interest for applications to photodetection and solar energy conversion. Multilayer organic photodetectors with external quantum efficiencies of 75% in the visible spectrum and bandwidths approaching 450 MHz have been demonstrated using an ultrathin alternating multilayer stack as the optically active region [P. Peumans, V. Bulovic, and S. R. Forrest, Appl. Phys. Lett. 76, 3855 (2000)]. Investigations of carrier transport in such devices are important to our understanding of carrier transport in organic materials in general, and to provide insight leading to further device performance improvements. By measuring the temperature dependence of the external quantum efficiency of multilayer organic photodetectors whose individual layers in the active region are ≤ 30 Å thick, we find an activation energy of ≤ 0.1 eV, which suggests that the photogenerated carriers tunnel through potential barriers formed by the energy level offsets in the multilayer stack. From the temperature and voltage dependencies of the dark current, we also find that the tunneling injection of electrons from the indium-tin-oxide (ITO) anode into the organic active region dominates the dark current at $T \geq 200$ K, which can be described using a semi-classical tunneling model. While no apparent correlation between the anode surface morphology and the dark current was observed, treating the anode in oxygen plasma or UV ozone to increase the anode work function dramatically lowers the dark current with only a slight decrease in quantum efficiency. The effect of anode work function on the dark current can be explained by our tunneling model.

1:45 PM J7.2

Charge transport through organic single crystals using elastomeric transistor stamps. Vikram Sundar¹, Jana Zaumseil¹, Robert Willett¹, Vitaly Podzorov², Michael Gershenson² and John A. Rogers³; ¹Lucent Technologies, Bell Laboratories, Murray Hill, New Jersey; ²physics and astronomy, rutgers university, new brunswick, New Jersey; ³material science and engineering, University of Illinois, urbana champagne, Urbana, Illinois.

Recent interest in science and emerging applications of electro-active organic and bio-organic materials motivates research into non-invasive methods for forming high resolution electrical contacts on these classes of soft molecular materials. Many of the lithographic techniques that were developed for traditional microelectronic systems require processing protocols that are too severe for these organics. We have developed new, elastomeric stamps that contain embedded gate electrodes as well as source-drain electrodes patterned on them. Such transistor stamps allow the growth of organic semiconductors to be decoupled from their characterization and subsequent incorporation into devices. This procedure provides a powerful tool for studying the physics of charge transport in pristine yet chemically fragile organic single crystals. We present results for the temperature-dependent hole transport through single crystals of rubrene as well as a detailed characterization of the composite devices.

2:00 PM J7.3

Dielectric Dependent Contact Resistance in Organic Thin Film Transistors. Michael Lefenfeld¹, Graciela Blanchet¹, Curtis Fincher¹ and John A. Rogers²; ¹Central Research & Development, DuPont, Wilmington, Delaware; ²Materials Science & Engineering, University of Illinois, Urbana/Champaign, Illinois.

This work describes the properties of pentacene transistors with printed conducting polymer electrodes and gate dielectric layers fabricated from different polymer materials. The conducting polymer, dinonylnaphthalene sulfonic acid doped polyaniline (DNNSA-PANI), contained several weight percent of single walled carbon nanotubes (SWNT) to improve its conductivity. Pentacene served as the p-type organic semiconductor. We have studied a family of styrenic polymer dielectrics ranging from mildly acidic to basic in nature. The morphological structures of the pentacene grains were nearly indistinguishable with the different dielectric surfaces. While the mobility across the thin semiconductor film depended weakly on the dielectric material, our results show that the contact resistance varied greatly due to the chemical properties of the dielectric. Thin film transistor performance not only relied on short channel length, but also on the contact resistance at the electrode interface. Good electrical performance of these printed devices requires low resistance contacts at the triple interface between the printed source/drain electrodes, the dielectric, and the pentacene. The results suggest that the barrier to charge injection did not solely depend on the electrode/semiconductor interface, but was also influenced by the chemical interactions at the dielectric/electrode and dielectric/semiconductor interfaces. A better comprehension of material interactions at the triple interface and their effect on the contact resistance will be needed to achieve deeper understanding of device performance.

2:15 PM J7.4

Electrostatic Field at The Pentacene SiO2 Interface.

Liwei Chen¹, R. Ludeke², A. G. Schrott², C. R. Kagan² and L. E. Brus¹; ¹Columbia University, New York, New York; ²IBM T.J.Watson Research Center, Yorktown Heights, New York.

The electrical properties of the gate-channel interface play a crucial role in determining the transport properties of pentacene Thin Film Transistors (TFTs). We have used Electric Force and Kelvin Probe Microscopy to directly probe the electrostatic properties of monolayer islands of pentacene deposited on SiO₂ gate oxides. The single layer islands, which occasionally exhibited multilayer features, were thermally deposited in an ultra-high vacuum (UHV) of 5x10⁻⁹ torr onto n+ silicon wafers with a 25nm thick thermal oxide. The samples were imaged with an UHV atomic force microscope equipped with an electric force module. The pentacene islands were 0.5V higher in electrostatic potential than the silicon dioxide background. This vacuum level shift defines the energy level alignment at the pentacene-silicon dioxide interface. The electric force images showed a dependence on bias voltage between the AFM tip and the sample. When the sample was negatively biased, the electric field between the tip and the sample polarized the pentacene monolayer islands so that the field of the induced dipole opposed the static interface field. Consequently the image contrast vanished and even reversed at higher negative bias. Additional electrostatic contrast was observed between a multi-layer pentacene island and the underlying pentacene monolayer. This indicates that the multi-layers screens the static interface field and suggests that the interface dipole is an intrinsic property of the oxide-pentacene monolayer interface.

2:30 PM J7.5

Surface potential variation in a molecularly doped polymer system observed by ultrasensitive electric force microscopy. William Richard Silveira, Erik Muller, Neil Jenkins, Brian To and John Marohn; Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

We are trying to gain a more microscopic understanding of metal/organic charge injection by making careful and quantitative electric force microscopy (EFM) measurements. To date, models of charge injection have mainly been tested by following the behavior of devices as a function of voltage and temperature. Since organic conductors are often unavoidably disordered, one might worry that bulk characterization techniques are not well suited for testing microscopic theories. We have used variable temperature electric force microscopy to study and image the surface potential in films of the hopping conductor triphenyldiamine-doped polycarbonate (TPD-PC), a molecularly doped polymer system used in xerography. In 100 nm thick films with a surface roughness less than 1 nm, we find a 60-80 mV variation in surface potential on a 100-200 nm length scale. We have varied substrates, degree of dipole doping, film thickness, TPD concentration, and temperature. The data tentatively supports the conclusion that the observed surface potential arises from a spatial

inhomogeneity in an underlying charge transfer dipole layer formed at the buried interface between TPD-PC and gold. This means that, even in this model system, charge injection is a far more complicated process than has been assumed. We have incorporated ultra-soft silicon microcantilevers into our microscope to dramatically increase sensitivity. We find that the resonance frequency and quality factor of the cantilevers are a very sensitive function of voltage, distance, and the underlying sample. Such electromechanical dissipation measurements hold promise for quantifying and imaging in-plane conductivity in thin organic films.

2:45 PM J7.6

Characterization of Pentacene Thin Films by Field Effect Transistor Measurement with Micro Four-Point Probe.

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Field effect transistor (FET) measurements using metal-insulator-semiconductor (MIS) structures with patterned source and drain electrodes are widely employed to estimate carrier mobility of organic thin films. However, 'carrier mobility' obtained by such a method is not always an intrinsic physical quantity at the semiconductor/insulator interface but extrinsic showing the overall device performance. Extrinsic mobilities often include the influence of nonlinear contact resistances at metal/semiconductor contacts, modulation of the contact resistances by gate voltage and degradation of the organic material due to, for example, heat during the top metal deposition. In this research, we have therefore adopted micro four-point probe (MFPP) [CAPRES A/S, <http://www.capres.com/>] as source, drain and sensing electrodes for FET measurements. The intrinsic electrical properties at the semiconductor/insulator interface could be extracted by this method. MFPP-FET measurements of pentacene films, grown by molecular beam deposition on oxidized silicon substrates, were performed in high vacuum. The results showed that the nonlinear I-V characteristics due to the metal/semiconductor contact were effectively removed. Moreover, the estimated mobilities by MFPP-FET were invariably higher than those by conventional top-contact FET measurements performed with the same films, which is probably because the deterioration of organic films by the top metal deposition has been eliminated. A positive correlation between the mobility and subthreshold slope was also observed although they usually have a negative correlation. Deviation of the mobilities and threshold voltages in the polycrystalline film is one of the possible causes of this correlation.

3:30 PM J7.7

Real-time optical monitoring of molecular thin film growth by reflectance anisotropy spectroscopy.

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In organic molecular beam deposition (OMBD), the film growth is usually monitored by a quartz oscillator (or microbalance) or by electron techniques, such as reflection high energy electron diffraction, well developed and established as control tools for molecular beam epitaxy. However, these methods suffer major drawbacks: the calibration procedure and the limited information it can give, for the microbalance; their destructiveness, particularly serious for organic molecular materials characterized by softer intra- and inter-molecular bonds with respect to inorganic materials, for the diffraction techniques. Optical techniques, e.g. ellipsometry and reflectance anisotropy spectroscopy (RAS), solve these problems, contemporarily giving a measure of the film thickness and important insights on its optical and structural properties. Among them, RAS [1,2] is the one providing straightforwardly interpreted results, both on the solid state structure and electronic properties, being in addition very sensitive, non destructive, and easily assembled. In organic materials, the anisotropy related to the molecular structure itself or to any supermolecular organization, up to the crystal structure of molecular crystals, makes RAS particularly useful. A linearly polarized light beam, with polarization modulated between two orthogonal directions, is directed to the substrate through a strain-free window and the reflected light is collected in real time during the film growth. When collected at a fixed wavelength, properly chosen for each particular material, the RAS signal is a sensitive measure of the increasing film thickness, while the complete RAS spectra collected at different growth stages give a monitoring tool for the electronic properties of the first layers. In this paper, RAS is demonstrated to be extremely sensitive and powerful for real time and in situ monitoring of the Ultra-High-Vacuum (UHV) growth of thin sexithiophene (6T) films on organic crystal substrates by OMBD. This material/substrate system exhibits a relevant anisotropy, which makes RAS sensitive down to 1/50 monolayer. At about 3.35 eV the characteristic response

of 6T is observed to increase with the film thickness and to vary slightly in spectral position and lineshape for thicknesses above 2 monolayers. As a consequence, the kinetics of the process (growth and further structural modifications of the layer) can be followed during deposition. References [1] B.G. Frederick, J.R. Power, R.J. Cole, C.C. Perry, Q. Chen, S. Haq, Th. Bertrams, N.V. Richardson, P. Weightman, Phys. Rev. Lett. 80, 4470 (1998). [2] D.E. Aspnes, IEEE J. Quantum Electronics 25, 1056 (1989).

3:45 PM J7.8

Low Energy Electron Microscopy Studies of Thin Film Pentacene Growth.

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The growth of pentacene (Pn) thin films on insulating, semiconducting, and metallic substrates provides a simple and interesting model system to study the interaction of a simple aromatic molecule with a wide range of substrate materials. In this contribution we will present comprehensive results on the growth of Pn on Si, metal decorated Si, Au, Bi, and SiO₂ and Al₂O₃ surfaces. We find that in each case the details of thin film growth are substantially different. The Pn molecular layers are oriented with the molecular axis roughly normal to the surface on insulators. On Si, an initial Pn layer reacts covalently with the substrates, but subsequent layers grow again as on oxides. With increasing Au coverage on Si(111), the molecular orientation changes from roughly normal to in-plane, resulting in a dramatic change of the growth mode, from layer-by-layer to islanded. On pure Au, the molecular orientation is in-plane as well. A typical Pn thin film transistor is fabricated by overgrowing Au source and drain contact deposited on top of a gate insulator with a thin Pn layer. Since the Pn crystal orientation changes drastically from the Au electrodes onto the gate insulator, large angle grain boundaries negatively affect device performance. Remarkably, Bi(001) provides a (semi)metallic substrate on which Pn is found to grow epitaxially, i.e. the Pn molecules are oriented roughly normal to the surface, and the in-plane lattice structure aligns itself to the Bi(001) lattice, even in the first layer of Pn film growth. Apparently, the Pn growth mode is determined by a competition between the interaction strength between Pn molecules in the film, and between Pn molecules and the substrate. Weak substrate-Pn interactions lead to the desired layer-by-layer growth mode, but this gets disrupted with increasing Pn-substrate interaction strength. Thus, careful substrate engineering may provide a pathway to the fabrication of high quality, single crystal TFT's with optimum performance characteristics.

4:00 PM J7.9

Deposition of pentacene on silicon surfaces: A computational study.

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Over the last few years, great strides have been made in the use of organic molecules as the building blocks of novel electronic devices. However, the performance of organic thin films is strongly affected by the choice of organic compound, substrate surface, and deposition conditions. Here we report multi-lengthscale simulations to understand the effect of the first adsorbed layer on the growth mechanism of subsequent layers of pentacene. Our studies provide atomistic insight into the nature of the interaction between pentacene molecules and various silicon-based substrates. The chemical bonding interactions of the pentacene molecule on the Si (100)-(2x1) surface is investigated using a combination of tight-binding simulations and ab initio Gaussian calculations. A broad range of adsorption energies and preferred adsorption configurations are determined which confirm the strong monolayer adsorption observed previously in experimental STM images. Using Gaussian, we also studied the weaker intra-molecular van der Waals interactions between pairs of pentacene molecules as a function of orientation and interactions with various substrates including silicon surfaces passivated with either cyclopentene molecules or silicon dioxide. We find the interaction of the pentacene molecules with the substrates to be extremely weak, weaker than the pentacene-pentacene interactions, confirming that the passivation of the silicon surface nullifies the strong attractive effect of the surface. These binding energies are subsequently used in a mesoscopic scale study of the layer-by-layer deposition of organic thin films in a lattice-based Kinetic Monte Carlo simulation, providing information unattainable by experimentation and which can lead to improved device characteristics. Here we approximate the pentacene thin film growth process as two-site dimer deposition on a square lattice substrate. The effect of the varying local environment is provided by incorporating the results of the ab initio simulations into the energetic biasing factors of the kinetic constants.

4:15 PM **J7.10**

Self-organised polymer field-effect transistors. Lay-Lay Chua, Peter Ho, Henning Sirringhaus and Richard Friend; Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

The fabrication of defect-free ultrathin polymer gate dielectric layers which show a high-quality interface with the semiconductor is a key challenge in organic field-effect transistors (FETs). In order to lower the FET operation voltages for practical devices and to improve their lifetimes, current activity has been directed at reduction of device dimensions. Both the channel length and gate dielectric thickness have to be scaled down together. As the source-drain channel length is reduced to 1 micron and less, electrostatic considerations require the gate dielectric thickness to scale into the sub-100-nm regime. The ultrathin polymer dielectric film to be used has to be pinhole free. Furthermore the dielectric-semiconductor interface needs to be smooth and be devoid of localization potential to avoid charge carrier trapping. The task is not trivial. Here, we report a novel approach to simultaneously address all these issues by harnessing the spontaneous surface-directed self-organization of a ternary solvent-dielectric-semiconductor system. We show that this can produce conformal dielectric-semiconductor bilayer structures in which the interface quality is good enough to observe field-effect transistor action. We have investigated systematically the thermodynamic phase diagram of the ternary solvent-dielectric-semiconductor system and the kinetics of the formation of the semiconductor-dielectric active interface. The buried interface roughness (and structure) can be imaged in real space by atomic force microscopy, in contrast to most other systems which require recourse to k-space scattering methods. The intrinsic width of the polymer-polymer interface and capillary wave contributions are deduced to be remarkably small owing to a large unfavorable interaction parameter at the Flory-Huggins level. The interaction parameter was determined experimentally from the ternary phase diagram. The polymer-polymer interface produced is locally stable, and the process of controlled interface formation is surprisingly robust when the phase trajectory of the system is properly controlled. The interfacial roughness deduced from these measurements will be correlated with measurements of the field-effect mobility of transistor devices with a dielectric thickness down to 50 nm. Diagnostics top-gate FETs using an amorphous fluorene-triarylamine copolymer active layer were fabricated. 3-micron channel devices with the 50-nm polymer gate dielectric show good saturation characteristics with gate and drain operation voltages < 20 V, saturation current \sim few μ A, gate dielectric leakage < 10 nA, and gate dielectric breakdown strength > 3 MV/cm.

4:30 PM **J7.11**

Interfacial Structure in Semiconducting Polymer Devices.

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The development of electronic devices that use semiconducting polymers as their active materials has been one of the most exciting developments in polymer physics in recent years. One of the major driving forces for these developments has been the realization that, while the performance of plastic electronics may not match that of conventional, inorganic semiconductors, the applicability of cheap, large area processing techniques may open up entirely new markets made possible by considerably lower costs. As plastic electronics approaches market, attention needs to be focused more and more on the way different processing routes can be used to optimise performance. Devices will increasingly be made from blends or multilayers, and in these the control of the structure of interfaces will be of particular significance. Developing an understanding of the factors that control the structure of interfaces in semiconducting polymer devices will become increasingly important. This understanding will need to draw on the extensive knowledge of interfaces in conventional synthetic polymers. We examine some of the interfacial issues that are likely to be important in polymeric electronic devices and report some recent experimental results. The work presented here will focus on the characterisation of the structure of interfaces involving conjugated polymers and other polymeric materials. In particular, we will describe measurements of the width of the interface between polyfluorene-based polymers and i) polymer dielectrics [1] and ii) other polyfluorene-based conjugated polymers [2]. These measurements will be made by neutron reflectivity, utilising deuterated materials to give contrast across the interfaces. The nature of these two types of interface has great significance in the behaviour of polymer field-effect transistors and light-emitting diodes/photo-voltaic cells respectively, and the motivation for our studies is to link structural and morphological studies directly to the performance of these devices. To this end, we will also discuss experiments in which polymer-based devices will be specifically fabricated to have different interfacial widths, to see the effect on the electronic and optoelectronic properties of these devices. [1] A neutron reflectometry study of the interface between poly(9,9-dioctylfluorene)

and poly(methylmethacrylate). Higgins, A. M. et al. Appl. Phys. Lett. (2002) 81 4949-4951. [2] Interfacial structure in semiconducting polymer devices. Higgins, A. M. et al. J. Mater. Chem. (2003) 13,1.

4:45 PM **J7.12**

Nanoscale Polymer Field-Effect Chemical Sensors.

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There is a need to develop sensors with very small active areas for sensing a variety of chemical and biological agents. Nanoscale conjugated polymer field-effect devices are a promising way to realize such sensors. In this work, regioregular poly(3-hexylthiophene) is utilized as the active semiconductor in bottom contact FET's with channel lengths below 10 nm. For comparison purposes, larger area devices were also fabricated. To suppress spreading current effects, we employed a pair of guarding electrodes at the two sides of the channel. The dependence of chemical sensing responses on channel lengths has been investigated. The chemical sensing responses on both of the currents collected from the drain and side-guarding electrodes were measured simultaneously. The sensing mechanism for nanoscale channels is different from that of larger micron sized devices. In larger devices, sensing is related to grain boundary effects whereas in very small geometry devices, the sensor response is markedly different for the same analyte. The reasons for this and the possible mechanisms will be discussed. The role of the interface between semiconductor and insulator and that of contacts will be discussed.