SYMPOSIUM J

J: Interfaces in Organic and Molecular Electronics

December 1 - 3, 2003

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*Invited paper
of which will be significant in our analysis.

10:45 AM *11.5 Experimental and Theoretical Charge Transport Studies in Self-Assembled Molecular Rectifying Diodes on Silicon
Christophe Derene,1 Stephanie Lefrant,1 Christophe Krezmiński,1 Guy Alhaj1 and Dominique Vuillaume,2 1ESRF, EIMN, LILIE, France; 2Organic Molecules and Devices group, EIMN-CNRS, Villeurbanne d'Asq, France

Molecular rectifying diodes have been synthesized based on the A0rvin and Ruter 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 SAM or self-assembled monolayer approach. We used a chemical functionalization (by conjugated moieties) of the end-groups of alkylchirorosilane SAM to fabricate insulator/semiconductor (called σ-π) heterostructures at a molecular level of silicon substrates. Two or three devices were described and compared to build these structures: a sequential two-stage method wherein the alkyl (6 to 16 methylene units) monolayer is first chemosorbed 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 spacer are chemosorbed on the surfaces. We characterized the structural properties of these SAM’s by FTIR, weightability and ellipsometry before the electrical measurements. Current rectification is observed for the electronic transport through these functionalized SAM’s embedded in a Si(111)-type $\pm \frac{\pi}{2}$ mesas, with rectification ratio up to about 301 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 those σ-π systems show that rectification occurs due to a resonant tunneling transport through the HOMO level of the conjugated group. The position of the Fermi level 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 circuits.

11:00 AM *11.6 Understanding electron transfer at molecule-metal junctions: a spectroscopic approach
Xingyong 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 interest 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 electrode interface often determines the growth behavior 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 molecular interfacial space 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-creation formation in the molecular layer as well as their coupling to the metal surface. In this presentation, I will demonstrate some of the physical concepts we have learned from 2PPE measurements in model systems. These experiments allow us to quantify the following concepts: structural to electronic, and electronic to electronic, 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 dipoles; (3) the formation of localized electronic states resulting from the charge transfer at the interface; (4) the strength and distance dependence of electron
coupling between unoccupied molecular orbitals and the metal substrate; (5) intermolecular interaction and the formation of molecular complexes, and (6) nonadiabatic 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 11.7
The electronic structure of oligomeric (phenylethynyl) self-assembled monolayers.
Roger van Zee, Steven Obeey 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, diphenylethynylbenzenedithiol. 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 pi states are split by the C-C coupling along the backbone into density localized primarily on the ortho-carbon atoms of the phenyl rings (3.4 eV) and delocalized levels along the backbone (2 eV). These orbitals would provide the channel for hole-transport. Two unoccupied orbitals are observed, one 1.7 eV above the Fermi level and another 1 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 channel 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 sigmabonding 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 11.8
Stochastic Switching in Molecular Wires. Ganesh K Ramanatharam* 1, Theresa J. Hopson2, Adam M. Harlee 1, Lenny A. Nagahara 1 and Stuart M. Lindsay 1, 3, Department of Physics, Arizona State University, Tempe, Arizona; 2Molecular Imaging Inc., Tempe, Arizona; 3Army Research Labs, Aberdeen, Maryland.

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 tiling 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 12
Chair: David Cohen
Monday Afternoon, December 1, 2003
Back Bay D (Sheraton)

1:30 PM #12.1

It is usually assumed that the electronic properties of adsorbed molecules are not too different from that of the isolated molecules. However, simple thermodynamic techniques teach us that when organic molecules are heated in 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 reorganization of the charge. This reorganization may result in new electronic and even magnetic properties.

2:00 PM #12.2
Learning from Molecules to Understand the Electrical Properties of Molecular Junctions. Jerome Corral 1, 2, Yasser Kamratu 2 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 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 on solid-state molecular wires can prove very useful to shed light on the electronic characteristialistics of molecular junctions. On the one hand, we will suggest a novel mechanism to rationalize the negative differential resistance (NDR) behavior of phenylene ethynyl 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; on the other hand, we will study the electronic structure of a large number of oligomers recently characterized by STM measurements 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.

2:30 PM #12.3

Understanding how electrical contacts to molecules, for electrical transport (and capacitance), affect electrical measurements is critical for the 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 (ICCE). This decreases dramatically 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. Scanning has mostly been used to assess possible contacting devices on molecules. Using a series of organic molecules with different properties, we bound to an electrode and systematically functionally characterized at the other end, that while avoiding shorts is necessary, it is not sufficient for reliable contacts. Based on various characteristics of ICCE, we deduced metal/molecule/metal/semiconductor (MMoM) junctions we find that ICCE 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 not damaged. After ICCE the molecular function’s effects are preserved, primary evidence for damage-free contacting. Several types of MMoM junctions were prepared. Comparing molecular effects in ICCE-prepared junctions and other soft contacting methods suggest 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 coated 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 #12.4
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 reverse resistance versus length plots, we are able to determine both the electron decay factor, r, from the slope of the graph, and make the contact resistance from its intercept. The value of the decay factor is dependent on the
3:30 PM #12.5
Theoretical aspects of tunneling current through single molecules. Otto F. Sankey, 1 Jun Li, 1 and Gil Speyer, 2 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 electronics 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 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 band structure approach, which gives a simple framework to understand the length dependence of the current (the exponential ‘bet’ factor) for some model molecules composed of fragments of infinite chains. We discuss applications to the simple chemically saturated systems of allene chains, and to the bond alternating p-system of acetylene molecules sandwiched between gold electrodes. Theoretical results are compared to experiments. We study theoretically a model photonic molecular which can rapidly switch from an ‘off’ state to an ‘on’ enhanced conductivity state by the application of light.

4:00 PM #12.6
Heating in current carrying molecular junctions. Abraham Nitzan and Dov Reum, 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 allene 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 molecule conduction results from the balance of these 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 reservoir coupling terms. 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 allene 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. Huang, Thermal conduction through molecular wires J. Chem. Phys. in press.

**SESSION 33: Poster Session**

Chairs: Neal Armstrong and David Cohen

Monday Evening, December 1, 2008

8:00 PM

Exhibition Hall D (Hyatt)

**J3.1 Negative Capacitance in Au/Copper Phtalocyanine (CuPc)/Au Investigated by Impedance Spectroscopy.** Shu-Wing Tsang 1, Juo Bin Xu 1, M. S. Xu 1 and Harry H. L. Kwok 2; 1Electronic Engineering, The Chinese University of 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. Xu 1 [1], M. S. Xu, and Harry H. L. Kwok 2 [2] Department of Electronic Engineering and Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin, NT, Hong Kong; [1] Corresponding Author [2] 2Center for Advanced Materials and Related Technology, University of Victoria, Victoria BC, V8W 3P6 Canada Copper Phtalocyanine (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 dependence 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 1 kHz with a broad (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 confirmed in the recent findings in Au/BV/Al and Au/AlGaN/Cs [1, 2]. A transient current model is developed to fit the measured capacitance to extract the fastest and slowest mobilities and dispersive parameter. [1] H. Matsumoto, H. H. L. Kwok, and P. Blom, Phys. Rev. B 60, R8889 (1999) [2] S. Berbec and W. Brütting, Phys. Rev. Lett. 89, 286601 (2002). This work is in part supported by the Research Grants Council of Hong Kong through the Grant No. 4372/02E.
13.2 Charge transport in DNA. Thomas Hein, Dominique Deserens and Dominique Vailliam; JEMM, Villeneuve d’A, France.

This work belongs to the field of molecular electronics. Questions about the electric conduction in DNA was first put in 1982 by Eley and Spirov, after the discovery of the 12-base DNA structure of DNA by Watson and Crick in 1953. Until now, no consensus has emerged about the electric properties of DNA. Charge transfer over nanometric distances have been studied in solution and are quite well understood. Direct measurement of charge transfer between oligomers using various techniques, from induced superconductivity to insulator or semiconductor. This debate is at the heart of our work. We have studied the electrical properties of DNA exposed to different self-assembled molecular layers on silicon substrates. The first part of the study deals with the preparation of the silicon substrate and the 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 tip allows to image the surface and be used as a second electrode during the electrical measurement. Two kinds of results have been obtained: insulating to conducting behavior are observed. Resistances are spread out over at least 6 orders of magnitude, from 108 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 several layers of DNA to link the two electrodes used for the studied DNA sample. However, this method adds a high series resistance. Systematic measurements have been realized according to the distance of the AFM tip to the p-decade of DNA molecules, and to the estimated number of DNA strands adsorbed on the surface. DNA deposition ratio being a primary parameter, this point is deeper studied to understand the link between DNA structure and its properties of conduction.

13.3 In situ Detection of Protein Adsorption with Single Walled Carbon Nanotube Device. Salah Bousnina1, Xiuhua Li, Nongjian Tao2, Ruth Zhang2, Theresa Hopson2 and Larry Nguyen2.

6Electronic Science Research Laboratories, Motorola Labs, Tempe, Arizona.

The ability to detect and study a single molecule represents the ultimate challenge of biochips and bioelectronics. Recent progress in the fabrication of nanostructured materials and devices, such as nanoparticles, silicon nanowires, metal nanowires and carbon nanotubes has opened new venues for us to achieve this ability. Single wall carbon nanotubes (SWNTs) are attractive for a wide range of applications, from nanoelectronics and nanomechanics to bioelectronics. Molecules, such as DNA and proteins have been immobilized on SWNTs and the biocompatibility of SWNTs has been demonstrated recently, which are significant steps toward bioelectronics applications. However, in situ detection of a small number of proteins via direct measuring the electronic transport properties of a single SWNT has 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 percent. 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.

13.4 Direct electron transfer between cytochrome c and graphite microelectrodes. Sin-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 macroelectrodes (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, 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 in the potential.

13.5 A Simplified Test Device For The Electrical Characterization Of Metal-Molecule-Metal Junctions. Navine Emily Gergel, Natasha Majumdar, David Renzenberg, John Breen and Lloyd Herrick; University of Virginia, Charlottesville, Virginia.

A test structure for electrical characterization of metal-molecule-metal junctions was built using fabrication tools that are not available in other laboratories.

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 alkanethiols 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 nanoscale device, but had several processing simplifications in the areas of: (1) lithography (2) evaporation conditions (3) metal deposition rate. The test device was used to obtain the IV characteristics of different length alkanethiols.

Fitting the IV characteristics to the Simmons tunneling model suggested that the method of electron transport was molecular tunneling. The tunneling barrier height (β), the potential barrier shape (α), and the current density decay coefficient (β) were derived from this fit. The β 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 at room-temperature. The model and current density of the fit were similar, suggesting that the presence of the bottom contact is not the main problem in this type of electronic devices. A film of sulfur 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. Grunwald, M. A. Reed, L. Jones II and J. M. Tour, Appl. Phys. Lett. 71, 61 (1997). 2 J. G. Simmons, J. Appl. Phys. 34, 1738 (1963).

13.6 Ultrathin Film of Oligothiols by Covalent Molecular Self-Assembly. Pengfeng Zhang and M. P. Grzybowski; Chemical and Environmental Engineering, National Univ of Singapore, Singapore, Singapore.

We report the preparation of an ultrathin oligothiol film through molecular assembly with covalent bonding as the interlayer linkage. Pyrromellitic dianhydride (PMDA) and dianisidine (DDE) were assembled alternately from solutions in a low-vapor pressure solvent to form a thin film on silicon wafer that was surface-modified with p-nitromethylphenylthiols (APHT). 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 assayed by the interlayer covalent bond, abundant amic acids in the building blocks in between the oligothiol chains. The covalent molecular assembly technique together with intelligent substrate modification and material choice promises to be an attractive method for fabrication of ultrathin robust films of nanometer thickness.


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 lower than 5 nm. It is suggested that 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 plasma-oxidation technique has been used to improve the surface roughness of Pt surfaces with less than 0.1 nm RMS roughness. All self-assembled monolayers of alkanethiols were grown on the clean smooth surface. Along with the AFM data, we 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 platinum surface is all-trans and well-ordered.
13.8 STM Investigation of Benzene Adsorption on Si(001)/(111) and Ge(001)/(111) 
Ian C. Schack-Traum, 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(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 atomic-selective imaging with atomic resolution [1]. This method has the potential to selectively map nnb dip bonds in an adsorbed molecule, and may thus provide a novel means to spectroscopically imaging of single molecules. First results of EF-STM are to be published in the near future. [1] P. Sutter, et al., Physical Review Letters, 90, 166101 (2003).

13.9 Forcing the Assembly of the Building Blocks of a Molecular Wire with a Nanopatterned Cu(110) Template.
Roberto Otero Martin, Yoshitaka Naitoh, Federico Rosi, Ping Jiang, Andre Gourjon, Erik LeungNgai, Ivan Steeghoudt, Christian Joachim and Flemming Besenbacher, 1 Department 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 how 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 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, C9H9O8). It is composed of a polyaromatic hydrocarbon main chain with four internal 3,6-di-tert-butylphenyl substituents acting as spacers legs. The aromatic central bond 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 bond aligned along the [1-10] crystallographic direction of the substrate, and no other 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 bond turns out to be aligned along [1-10] and, thus, perpendicular to the dimension of the chain. In order to further investigate the orientation of the molecules deposited on the substrate, we proceeded to deposit another another molecule, the Single Lander II (SL II, C18H18O9). The difference between the VL and SL molecules is the length of the bond; 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 lines. On the nanopatterned surface, it only adsorbs on the bare Cu stripes. The difference now is that the direction of the bond is no longer perpendicular to the direction of the stripes. Two types of orientations are most commonly found: with the bond 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.

Sara Letardi and Fabrizio Cleri, Unità Matter e Nanotecnologie, ENEA, Roma, Italy.

We studied the interaction of benzene thiol and thiokol molecules with Au using a many-body 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 RISA(n) systems on Au are 1.25, 2.5 and 3.8 on Au(111). The benzene, were found by conjugated-gradient relaxation. As far as the bonding geometries and bond angles, we find several similarities with previous simulations of the adsorption of other thiols on Au(111) surfaces. We study in detail the energetics of the adsorption of the different species, with respect to both the neutral and charged fragments. It is found that the RS (and RS-) adsorption is generally the most stable. Moreover, we characterize the different states of the RS-Au(n) complex with respect to the desorbed hydrogen.

13.11 Tripeptide Thiol-Derivatized Redox-Active Self-Assembled Monolayers for Studies of Molecular Information Storage.
Liming Wei, Zhiming Liu, Jonathan S Lindsey 2, Werner G Kuhr1 and David F Bocian3, 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 circuitry. To this end, self-assembled monolayers (SAMs) of porphyrins attached to electrode 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 paper, a series of redox-active molecules bearing identical thiol-derivatized tripeptide 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 sweep-wave AC Voltammetry (SAV). The electrochemical studies of the SAMs indicate that the tripeptide linker provides a more robust anchor than a mono-thiol. This study provides the foundation for understanding the electron-transfer processes and kinetics of diverse redox-active molecules in a controlled environment on a surface.

13.12 Monolayers of Ferrocene and Porphyrin-chelagens on Si(100). Novel Hybrid Molecular/Semiconductor Information Storage Media for Electronic Applications. Amir A Yasser 1, Liming Liu, Zhiming Liu, Liming Wei, Werner G Kuhr1 and David F Bocian3, 1Department of Chemistry, University of California, Riverside, Riverside, California, 2Department of Chemistry, North Carolina State University, Raleigh, North Carolina.

The integration of molecular materials with semiconductors offers a promising technology that might 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 monocrystalline 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 gold photoangiographically patterned surfaces. Silicon microelectronics were fabricated on p-type Si[111] 5×5 with a chalcogenide layer defining the active silicon area for monolayer assembly. Chemically hydride-terminated surfaces were obtained using an HF treatment process. Monolayer deposition was performed from an electroactive solution deposition or a dry vapor sublimation process. XPS measurements confirm the mechanism for the displacement of surface hydride tethers 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 reliable 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.


Dependence of electrical properties on the metal electrodes has been investigated for bisquinolines-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 is near the energy barrier obtained from the experimental 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. While the Al electrode is exposed to the air, 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, Mohamed Al-Sheikhly 1, Aria Christou 1 and William E. Bentley 2, 1 Materials Science and Engineering, University of Maryland, College Park, Maryland; 2 Chemical 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 self-assembled DNA probes to link them by hydrogen bonding with DNA target molecules n 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 multi-layer of single-stranded 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 an organic 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**


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 3aminopropyltrimethoxysilane (APS), a smaller APS concentration, trace amounts of hydrazine, and appropriate pH condition 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 3-aminopropyltrimethoxysilane (APTMS) 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 examined the immobilization capacities of the aminosilane films toward bovine serum albumin (BSA). It is found that higher content of primary-amine content favors higher uptake, and APS film yields 100% PMDA coverage.

**J3.16**

Influence of the Nerve Cell Growing Medium on the Electrical and Mechanical Properties of Neuron-Electrode Interfaces, Anjie Reiter 1, Stephan Guenther 1, Andre Krutsch 1, Hartmut Wietel 1, Anna de Lima 2, Thomas Voigt 3 and Alois Kress 1, 1 Institute of Experimental Physics, Otto-von-Guericke University of Magdeburg, Magdeburg, Germany; 2 Institute of Physiologic, 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 and interactions within neuronal networks analyzed by electrical interphases 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 experimentally. In the present 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 in- and off-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 kHz. The different physiological responses 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 Ringer 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 rise 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 one. This 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 Ga2O3 Gate Insulator, Seongjun Kung, Kwanbum Chang, 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 thick-film, flexible, or wearable semiconductor device. We used thin high-k Ga2O3 layer as a gate insulator that was grown on a heavily doped Si substrate by ionized cluster beam deposition (ICBD). The crystalline quality of Ga2O3 layer was characterized by 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 thin film transistor was fabricated using a stylus electron microprobe and a diffractometer and atomic force microscopy. We present the device properties when the SiO2 gate insulator is replaced with Ga2O3 in the pentacene thin film transistor.

**J3.18**

30 nm Channel Length Organic Transistors, Yuenja Zhang 1, Jason R Petta 2, Amably Samtha 3, Yulong Shen 4, Daniel C Ralph 2 and George G Malliaras 2; 1 Materials Science and Engineering, Cornell University, Ithaca, New York; 2 Physics, Cornell University, Ithaca, New York.

The use of organic thin film transistors OTFTs has raised a large interest in emerging electronic technologies where large area coverage and low cost is required. The current delivered by the TFT is inversely proportional to the channel length L of TFT, and thus motivated studies of OTFTs with submicron channel lengths. Past work has shown the channel length dependence of the ON current is below 100 nm, due to either poor charge injection at metal/organic semiconductor interface [1] or ‘‘punch-through’’ effect [2]. To explore whether these effects imposes a limit on the performance of amorphous organic transistors, we combined structural data by scanning electron microscopy with scanning electron microscopy data from organic semiconductor deposition techniques to fabricate organic field-effect transistors with channel widths down to 30 nm. The current-channel length dependencies of the transistors exhibited the behavior characterized for traditional channel TFTs and was scaled gracefully with channel length and width. These 30 nm channel length organic transistors allowed the study of charge transport in organic semiconductors at the nanometer length scale. [1] E. L. Gornetstrom, C. D. Frickie, 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, Ksenia Pustembeke, Paul Pescetto and C. Daniel Frabie; Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, 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 bottlenecked 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 are 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. The typical mobility for these devices was ~0.3 cm2/Vs with a threshold voltage of ~1 V. 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 resistance from the resistance of the device.

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 Muellegger, Ingo Salzmann, Roland Resel, Gert Brommer, Christian Reichert, Egebret Zojer, and Adolf Winkler.

We apply thermal desorption spectroscopy (TDS) to investigate the adsorption/desorption kinetics of vacuum-deposited p-quat-phenyl (4P) films on single- and polycrystalline Au substrates. The 4P film morphology and its crystal structure is investigated by atomic force microscopy (AFM), microchannel plate low electron energy 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-cover. 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).

The presence of such a significant amount of carbon on the substrates may affect the kinetic measurements of 4P/Au(111) if follows that the 4P(211) plane is oriented parallel to the substrate surface. These results together with the substrate geometry yield different orientational states of the 4P bulk domains. Applying MCP-LEED, we measure the surface unit cell of the 4P film on Au(111). Compared with XRD-PF, the arrangement of the 4P molecules within the first layer is different. This work is supported by the Austrian FWF, Project No. P 15625 and P15626.

**J3.21**

**Crystalllographic and Morphological Characterization of Tetraene and Pentacene Thin Films on Polycrystalline Copper Surfaces:** Martin Oelchle, Christian Stens, Rainer Siegel.

The aim of this study is to investigate the orientation and crystallinity of two oligoacenes on polycrystalline copper surfaces. The copper is spotted on top of a Si (100) wafer and shows a fibre texture with the [211] direction parallel to the substrate. The growth of the small molecules on this Cu surface is investigated by x-ray diffraction and AFM measurements. The x-ray measurements reveal the orientation of the crystalline molecules with respect to the surface as well as the appearance of the crystallographic phases. 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 deposition parameters 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 330 K whereas tetraene shows a fibre texture with (201) net planes parallel to the surface when deposited at substrate temperatures of 270 K. 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**


Cornell Center for Materials Research, Cornell University, Ithaca, New York; Materials Science and Engineering, Cornell University, Ithaca, New York; Department of Physics, University of Vermont, Burlington, Vermont; Cornell High Energy Synchrotron Source, Ithaca, New York; Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York; Department 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. The evolution of the 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=25 μm, were fabricated with these films for electrical characterization showing a field effect hole mobility of 0.1 cm²/V·sec. Film morphology in nano-scale transistors (L=38-100nm) will also be presented.

**J3.23**

**Abstract Withdrawn**

**J3.24**

**Conjugated Network Ultrathin Films of Polythiophene Precursor and Triphenylene Monomers Investigated by EELS-SPS, Akira Baba, Ken Kitayama, Kenji Koshiji, and Wolfgang Knoll.**

**Max-Planck-Institute for Polymer Research, Mainz, Germany; Chemistry, University of Houston, Houston, Texas.**

Poly(N-vinylcarbazole) (PVK), which exhibit interesting optical/photoreactive 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-polymer" to form modified conjugated polymer network films on conducting surfaces. With the interest in identifying precursor polymer architecture, 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 poly-carbazole network and deposited on conducting electrode surfaces. In order to understand the electrodeposition process, the electropolymerization process was investigated in situ combining electrochemically-surface plasmon resonance spectroscopy (EELS-SPS) and electrochemical quartz crystal microbalance (EQCM). Furthermore, the morphology observed under atomic force microscopy (AFM) was correlated with EQCM, EELS-SPS, and EQCM acoustic properties.

**J3.25**

**Variation in the Electrical Characteristics of Al/Polythiophene Interfaces Due to Preparation Conditions and Aging:** Veldt Grieb, Michael Kuhal, Leonard Schrager, Joseph Genevich, Shari Benson, Alison Bergeron, Emily Coombs, Casey Gifted, Eric Gum, Armanda Haug, Colleen Harty, Andrew Higdon, Dinae Ouellette, Eleana Plam, Lisa Trepp, and George Malliaras.

**Chemistry and Physics Departments, Simmons College, Boston, Massachusetts; Materials 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 polythiophene. Changes in the chain lengths and the surface roughness of the polythiophene were investigated using electron diffraction 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 Braunske, Brian Dorn, Martin M Beerboth, Yusuf Emur, and Rudy Schifl.

**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 oligomers onto the substrate by direct electron beam evaporation in a high vacuum (UHV) environment using the electron-beam (EB) method. This allows the free rotation of the molecules during deposition, which is important for the growth of thin films and the formation of nanomaterials. In addition to the growth of high-quality nanomaterials, the method is also suitable for the design of devices and processes. We are currently studying the interplay of these factors to achieve better control over the nucleation and growth processes. Furthermore, we are investigating the influence of the growth conditions and substrate properties on the structural and electronic properties of the films. This work is supported by the National Science Foundation and the Office of Naval Research.

\[ \text{[Total Text Reference]} \]
present work, the adsorption of selenium onto a high vacuum on clean and polished-doped Al(111) at 130 K has been studied by X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). Selenium 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, but a small work function change does occur, and an absence of low energy components in the XPS spectrum. Small amounts of adsorbed selenium, however, have been found to cause the appearance of a new peak in the valence spectrum of selenium (at approximately 0.2 eV below the Fermi level). This increase in the work function results from the filling of previously unoccupied electronic states of selenium to its adsorption on the electron-rich alkali-doped metal surface. Comparison experiments have also been performed in which selenium has been deposited on selenium films. [1] W.R. Salmecke, S. Stuhrmann, and J.L. Bredas, Conjugated Polymer Surfaces and Interfaces (Cambridge University Press, Cambridge, 1996). [2] S.K. Seo, J. Alkan and J.E. Whitten, Surf. Sci. 520 (2003) 287. [3] R.Y. Seung and J.E. Whitten, Synth. Met. 114 (2000) 315.

13.33 Charge Injection In Doped Organic Semiconductors, Ahmad Reza Hasemi, Xueling Shen, Min Hoi Wong and George M. Malliaris; Materials Science and Engineering, Cornell University, Ithaca, New York.

A study has been done to understand the dependence of injection in the degree of doping of an organic semiconductor. A model organic semiconductor, tetra-methyl tricyanovinyl doped polyfluorene (PTMCD-PDF) was used for these experiments. By substituting TMTTF molecules with a TMTTF-S3F 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 degree of doping, degree of field, and junction length. This provides a better understanding of the doping and the degree doping affect device performance.

13.34 Interface Dipoles and Graded Doping of Multilayer OLEDs by Organic Molecules, Christopher Williams, Jose Gutierrez, Andrew Washington, Sergey Li, John P. Ferraro and Amra Zhakirov; 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 interface change transfer dipole layers. Such ID layers should lower the barrier and increase injection currents. Using a high precision computer controlled vacuum codeposition set-up the symmetric change transfer interface dipoles and graded doping of organic layers by molecular acceptors (home synthesized F5-TCNQ, n=1-4, with gradually changed electron affinity) is achieved. Monitoring the deposition rate for each organic material on its own would lead to functional grading, with electrode foam concentration profile: e.g. thin monolayer of weak acceptor P2-TCNQ, then at the outer interface with ion injection electrodes, then heavily P6-TCNQ doped layer (p+) with concentration in the range of 2.5 %, followed by lightly doped p region (0.5% range). Similar profiles are being checked for several organic donor dopant. This functional gradients of doping allowed to achieve several goals: increase injection by interface dipoles and lower interface barriers, and enhance conductivity of hole transport (HTL, TPD, DPP) and electron transport layers. The L-V curves are significantly improved compared with undoped multilayer systems and demonstrate the decrease threshold and operating voltages of OLEDs with both low molecular and polymer (of home synthesized BDA-PV poly) emissive layers.

13.35 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 box 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.


The adhesion and sticking of a Mg:Ag cathode to the tris(8-hydroxyquinoline) aluminum (AlQ3) in organic light-emitting devices (OLEDs) can be greatly enhanced by a remote plasma treatment of the AlO3 layer using either air or N2 prior to metal deposition. The increase in the adhesion results from the creation 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 capillary treatment, as judged by 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 AlO3 layer. For OLEDs subjected to short treatment times, 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 devices to become non-emissive. N2 treated devices on the other hand, developed black spots on a comparable rate to the non-treated devices. Thus, a short N2 plasma treatment of the AlO3 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.

13.37 Surface Morphology Investigations of Conjugated Polyrotaxane Based Blends for LECs: A Supermolecular Approach to Organic Electronics, Laura Sardone1,2, Franco Cacialli1,4, Joanne S Wilson5, Anna Maria Petrozza3,5, David G Bucknall5, Charlotte Williams5, Harry L Anderson6 and Giovanni Marletta7; CNR, Bologna, Italy; 1Chemistry, University of Cambridge, Cambridge, United Kingdom; 2Physics, University of Cambridge, Cambridge, United Kingdom; 3Materins, University of Oxford, Oxford, United Kingdom; 4Chemistry, University of Oxford, Oxford, United Kingdom.


13.38 AC conductivity model for polymer light-emitting diodes, Rodrigo Fernandez Biondi, Lucas F Santos and Roberto M Ferri; Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil.

Alternating conductivity, σ(ω) = Re[σ(ω)] + Im[σ(ω)], measurements of [Au or (ITO)fo{x}0.3methoxy-thiophene]0.7polystyrene)0.3polystyrene]0.3poly(styrene)(Au or ITO) 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 loglog graph, while σ(ω) increases linearly with the frequency and obey the relation σ(ω) = σ0 + ω^n [n
~ 1) in the domain of higher frequencies. It is the typical behavior of disordered material, where the electrode influence is negligible. However, screening of the influence of the current-voltage characteristic which occurs 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 barriers already present in the bulk free energy landscape contact and the influence of polymer/Al interface is of the order of 50 nm.

13.30 Abstract Withdrawn


Poly[(9,9-bisfluorenyl-2,7-diy)-N,N-dicyanomethylene]-N,N-dibutylphényl-1,4-disulfonic 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). A polymer film is spun in a nitrogen box from a 0.2wt% xylene solution on ITO substrates and dried at 80 °C. Measurements are performed in ultra high vacuum. Films investigated here were exposed to environmental atmosphere for a very short time (less than 3 minutes). Measurements on films 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. A combination of 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 centers 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 pole wavevector. 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 can 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 2.85 eV, 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 0.95 eV. This value is in agreement 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-dianhydride (PTCDI) [1].

13.41 A study of charge transport of a conducting polymer hybrid/metal parallel interface to indium phosphate. Frank Eugene Jones,1 and Mark C. Loudenaga,b,c.1 Physics, 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 a mesoscopic titanium oxide/metal interface. Nanotube structures have 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 nanotubular interfaces will also give insight into viewing molecular and nanoscale materials into microelectronic devices. The specific system in this study is a parallel contact to indium phosphate (IP) with both a low-barrier metal and a high-barrier poly[pyrrole] phosphomolybdate hybrid polymer (PMI). 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 microscopic contact down to nanometer-scale lines PMI was found to be an efficient vehicle of hole transport to two reasons. First, the PMI -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 PMI -InP interface can be controlled by manipulating the electrode potential of the PMI, thus changing the forward current by orders of magnitude. Therefore, the PMI barrier can be tuned in order to control the relative difference in current between the two contacts. The electrical measurements from these parallel contacts are compared to the theoretical predictions, including the very good dependence of large interactions. Finally, the consequences of these results for charge transport descriptors for devices ranging from macroscopic to the nanoscale are considered.

13.42 Interface Modification of ITO Thin Films: Organic Photovoltaic Cells. Adam Simmons,1 Cett Carter,2 Carie Donley1, Michael Brunbuhl1, Seunghyo Yoo2, Benoit Demequez1, Bernard Kippelen2, and Neil 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) amorphous vacuum deposited copper phthalocyanine (C60) system with an electron transport layer of P3HT and a barrier transport layer, respectively. The surface of as-received ITO films, and those cleaned by various solution and plasma treatments, are unavoidable hydroxylated to In(OH)3, like, and O1s surface species. One research into the modification of the ITO surface through the chemisorption of small carboxylic acid substituted organic molecules, such as ferrocene dicarboxylic acid and triphenylamine moieties 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 poly ITO and the subsequent non-polar organic layers.

13.43 Electrochemical Treatment of Tin-Doped Indium Oxide for Improvement of Hole Injection Efficiency. Zhaozong Huang, Xiaoting Zeng, E T King, and Y H Fuh.1 Surface 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 metal active polymer layer is reported. The ITO film was electrochemically treated in an electrode under a low current. The surface energy and LV characteristics of ITO/polymer junctional 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. Moreover, 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 desorption and possibly the higher work function of ITO surface. The high polarity and stability are possibly resulted from the formation of hydrogen bonding and the isolation of unpaired electrons. 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 further enhancement of performance of polymeric light-emitting devices, especially in presence of the water soluble PEDOT layer as the hole injection layer.
Chirality and electron tunneling in solution and at surfaces.

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 adsortates on clusters. Tunneling currents mediated by conformationally disordered molecules and open shell adsortates will also be discussed.

Characterization of Nanotransfer-Printed Electrical Contacts in Au/Alkanedithiol/GaAs Diodes. Yue-Lin Loo1,3, John A. Rogers2,3, Julia W. P. Hau1 and David V. Lang1.1Chemical 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 transfer thin 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 photomission 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 (0.82-0.91 V) in the current-voltage measurements. Further, the exponential energy dependence in the photoresponse yield indicates transport through disordered materials. These measurements contrast dramatically 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 photomission 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 conductance through diodes whose electrical contacts consist of evaporated Au pads is dominated by direct Au-GaAs contact.

Characterization of Molecular Monolayers on Template-striped Pt and Au for use in Molecular Electronic Devices. Jason J Blackstock1,2, Zhiyong Li3, Duncan R. Stewart4, R. Stanley Williams5 and Mark R. Freeman6. 1Physics, University of Alberta, Edmonton, Alberta, Canada; 2 Hewlett-Packard Labs, Palo Alto, California.

Ultrasil thin-electrode surfaces may be a critical component in the fabrication of reproducible molecular electronic devices. We report physical characterization of ultrathin template-striped platinum and gold surfaces, including physical characterization of various length alkanethiol monolayers (C6 to C22) prepared on these surfaces. For the bare template-striped 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 gold and platinum surfaces. The high flatness of the template striped surfaces was found to influence the packing behavior of alkanethiol, delivering better observable ordering for several intermediate chain lengths. Finally, electrical measurements of the alkanethiols on Pt and Au were obtained using a conductive probe AFM, and correlations with the physical studies of the molecular films and underlying metal surfaces are examined.
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 tunnelling effect is better conductor than a saturated alkane chain, the band structure is significantly more conductive than other molecules of similar length. 2,5-diphenylethyl-4-(trimethyl)silane, another candidate "molecular wire".

11:45 AM 14.8
Electrochemical Gate Controlled Electron Transport in Molecular Junctions. Bingbing Xu, Xinyin 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 chains or heterocyclic rings on two ends that can attach to Au electrodes via S-gold or N-Au bonds. For a given molecule, a considerable amount of variation in the conductance is observed from one junction to another, which likely reflects the difference in the molecular-Au contact geometry. Conductance histograms obtained from over thousands of measurements show 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 part of the window is chosen to model the description of the molecules from the Au electrodes, and the upper limit is determined by the oxidation of the Au electrodes at positive potentials.

SESSION 55
Chair: Masamichi Fujihira
Tuesday Afternoon, December 2, 2003
Back Bay D (Sheraton)

1:30 PM 15.1
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 metal 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 15.2
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 the electrochemical methods 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 15.3
Redox Sites Confined in a Nanometer Gap Junction. Maria Rampa* and George M Whitesides*; 1 Dipartimento di Chimica, University of Ferrara, Ferrara, Italy; 2 Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.


4:30 PM 15.4
Electron Transport through Non-Covalent Contacts in Tunneling Junctions. Slawomir Sek, Roger York; Krysztof Slowinski* and Marcin Majda*, 1 Department of Chemistry, University of California at Berkeley, Berkeley, California; 2 Department of Chemistry, University of California, Los Angeles, Los Angeles, University, Long Beach, California. 3 Current address: Global Research Center, General Electric Co, Niskayuna, New York.

We describe electron transfer (ET) through monolayers and bilayers of alkylthiols self-assembled in the Me-S-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) Tunnelling currents for a bilayer of 1-monohexadecanethiol or 1-monononaneethiol is ca. 50% larger than a corresponding tunneling current recorded for monolayers of 1-hexadecanethiol or 1-hexadecanethiol, respectively. This result is explained in terms of weak electronic coupling across the noncovalent molecular-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 all-trans forms 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].


4:00 PM 15.5
Ab initio Study of Quantum Capacitance of Nanotube/Metal and Nanotube/Nanotube Junctions. Pawel Penczak*, Leszek Pustewka*, Christopher Martin Roland, Hong Guo and Jin Wang; 1 Physics, NC State University, Raleigh, North Carolina; 2 Physics, McGill University, Montreal, Quebec, Canada; 3 Physics, 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 shows 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 change 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 common gap; and (iv) a nanotube interacting with a large 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 screening of surfaces will also be discussed.

4:15 PM 15.6
Electron Transport in Molecular-Molecule-Metal Junctions: A TranSIESTA Study of the Adsorption Site Dependence of Molecular-Molecule Contacts. Antti Grijpma, 1 Groes Wessels, Zeljko Grjozevski and Kurt Stickel; 1 MOCU, Chalmers University of
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' orientations and also after diaxide 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 recognition of the molecular orientation. Reference: Y. Selzer, A. Salomon, J. Ghidhoun, and D. Cohen, Angew. Chem. B 105, 1201 (2001)

SESSION 16
Chair: Neal Armstrong
Wednesday Morning, December 3, 2003
Back Bay D (Sheraton)

8:30 AM 16.1
Schottky Barriers and Metal-Molecule Interfaces
Raymond T. Tang, Physics, Brooklyn College, Brooklyn, New York

Due to the apparent similarities between the organic molecules-metal interfaces and the semiconductor-metal interfaces, many concepts and theories presently used to describe and model the electronic transport properties of metal-organic interfaces have been borrowed straight from the Schottky barrier literature. Perhaps unknowingly 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 mechanism, and the various problems associated with the traditional view of interface dipole, through an analysis of the Schottky barrier height. 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 present view of Schottky barrier formation can be applied to the metal-metal interfaces. Some specific differences between the two types of interfaces are also pointed out.

9:00 AM 16.2
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 study the behavior of organic and organometallic molecules 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 16.3
Nanoscale Charge Injection Tuning at Indium-Tin-Oxide Anode-Organic Interface in Organic Light-Emitting Diodes
Qinglan Huang, \(^1\) and Tobin J Marks \(^2,)\)

Chemistry, Northwestern University, Evanston, Illinois, \(^1\)Materials 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. A self-assembled anode is needed to control the emission profile. This requires the development of a new technology that can control the emission profile. A series of silyliridium molecules are designed and coated on ITO anode 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 silarylimine-based olefins reveals that changes in hybridization from 
sp-HOMO dominates the metal-to-metal charge transfer process. 
HOMO and LUMO, respectively. Conjugation length of the HOMO orbital increases with increasing conjugation length of the LUMO orbital decreases with increasing bond order.

9:45 AM 36.4

Simple solution and plasma etching procedures have been developed by a number of research groups to change the surface chemistry of indium tin oxide coated transparent conducting oxide surfaces, to improve work function, decrease contaminants levels, and enhance overall device performance. Recent work from our group, however, suggests that hydrolysis of the ITO surface can contribute to a significant component of the electrical inactive sites on the ITO surface, and that at least 40% of a monolayer of electronically active ITO may result. Solution electrochemical probes of the one-electron oxidation of ferrocene in acetone 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 a change in kET versus the untreated ITO surface. We have recently seen, however, that even better performance can be obtained from the ITO node 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/Modifer/PEDOT: PSS/PD/Pd(Alkyl), 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 100s of volt, and device efficiencies nearly double that of unmodified devices. These results suggest that there is a significant amount of electron transport at the ITO: polymer interface, and that this may be limited to the ITO device efficiency, considerable gains are still to be made with modes whose surface composition has been tailored to optimize electron transfer rates. Similar enhancement of the device performance has been noted, the subject of the companion paper in this symposium.

10:50 AM 36.5

The nature of the interface between an organic semiconductor and a metal electrode is critical to the performance of organic electronic and optoelectronic devices. Modifying the conventional devices with evaporated Au 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 electroless deposition (EL) of metallic films, (2) the Au contact is deposited on the ELdized films, and on the organic layer. The device is completed by evaporation of the holes to the ELdized Au contact and the ELdized EL. The process is reversible, i.e., the Au electrode can be peeled off the organic without visible damage. We have the highest EQE of more than 100% for devices with ELdized Au contacts. In fact, the QE of the SCL devices with Au contacts is also higher than conventional ITO/MEH-PPV:Al devices with a lower work function metal (Al). Using a film of MEH-PPV blended with organic molecules having electron-acceptor properties, we have achieved ELdized EL at 3.4 V. To better understand the difference in the QEs between the two types of devices, we perform photoluminescence (PL) experiments on ~100m 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 ~150nm wide Au electrodes.

11:00 AM 36.6
Impact of electrical doping on molecular level alignment at metal-organic and organic-organic heterojunctions. Antoine Kahn and Waying 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 in MO/OO structures, consistent with weaker intermolecular interactions and absence of free charges at interfaces between wide gap materials [2]. We focus here on the impact of electrical doping on the energetics of these interfaces. Using direct and inverse photoemission spectroscopy (IPES), we demonstrate [2] that doping at MO interfaces between Au and ZnO or α-NPD p-doped with the strong electron acceptor PbS-TCNO 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 MO interfaces between electron transport layers (ETL) (CBP, BCP, Alq3) and hole transport layers (HTL) (ZnO, 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 ETL 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 the decay to MO and OO level alignment, is discussed. 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, 2003) 3. W. Gao and A. Kahn, Appl. Phys. Lett. (June 30, 2003)

11:30 AM 36.7

The organic-metal interfaces have attracted much attention in relation to organic electronic and optoelectronic devices. We have studied the electronic structure and various phenomena at interfaces by using various optical and electronic techniques such as UPS, XPS, MAES, ELD, HRRAS, NEXAFS, and Kelvin probe, and here we will report on our recent progress. The alkylmetal interface offers a unique combination of metal and a molecule with very deep HOMO [1] and very high LUMO (even above the vacuum level) [2]. Although the charge-transfer was thus expected, recent experimental and theoretical studies reported the existence of electronic transfer [3,4]. Our own theoretical studies by DFT method [5] also indicated some mixing of the molecular orbitals with the occupied levels of the metal. Our results quantitatively explained the structural and functional change of the metal deposition on organic layers can often lead to charge-transfer (CT) and chemical reaction. There was theoretical prediction that alkyl metal deposition on Alk3 layers to CT complex with the conversion of Alk3 layer to CT complex with the conversion of Alk3 layer to face the insulator, which should work as an electron trap [6]. Since UPS cannot distinguish these, we

SESSION 37
Chair: Ian Frazier
Wednesday Afternoon, December 3, 2003
Back Bay D (Sheraton)

1:30 PM 37.1
Charge Carrier Tunneling and Effects of Anode Properties on Device Performance in Multilayer Organic Photodetectors. Jiageng Xie1,2 and Stephen R. Forrest1,2,1 Center 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 index of refraction, as well as the chemist's 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 70% in the visible spectrum and bandwidths approaching 450 MHz have been demonstrated using an ultrathin alternating multilayer stack in the optically active region [P. Peumans, V. Bukow; 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 ≤ 50 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 active organic region dominates the dark current at T ≥ 200 K, which can also be described using a semiclassical 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 reduced 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 37.2
Charge transport through organic single crystals using elastomeric transistor stamps. Vikram Sundar1, Jian Zou2,3, Robert Willett1, Vitaly Podzorov1, Michael Gershenson4 and John A. Rogers1,1 Laboratory for Matrix Materials, Bell Labs, Holmdel, New Jersey; 2physics and astronomy, rutgers university, new brunswick, New Jersey; 3material science and engineering, University of Illinois, urbana-champaign, 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 organic. 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 37.3
Diodelectric Dependent Contact Resistance in Organic Thin Film Transistors. Michael Lefeldt1,2, Graciela Blanchet1, Curtis Finch1 and John A. Rogers1,1 Central Research & Development, DuPont, Wilmington, Delaware; Materials 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 polymers. Results include pentacene, dimethylsilane sulfonic acid doped polyaniline (DNNSA-PANI), containing several weight percent of single walled carbon nanotubes (SWNT) to improve its conductivity. Pentacene served as the p-type organic semiconductor material. We have studied a family of styrene polymer dielectrics ranging from mildly basic to basic in nature. The morphological structures of the pentacene grains were nearly indistinguishable with the different dielectric surfaces. While the mobilities across the thin semiconducting film decreased 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 diodelectric, 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 and their interface, and their effect on the contact resistance will be needed to achieve deeper understanding of device performance.

2:15 PM 37.4

The electrical properties of the gate-channel interface play a crucial role in determining the transfer 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 multilayer pentacene island and the underlying pentacene monolayer. This indicates that the multilayers screens the static interface field and suggests that the interface dipole is an intrinsic property of the oxide-pentacene monolayer interface.

2:30 PM 37.5
Surface potential variation in a molecularly doped polymer system observed by ultrasonic electric force microscopy. William Richard Silveira, Erik Muller, Neil Jenkins, Brian To and John Marcini; 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. Examining charge injection in the presence of metal objects, 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 unwieldily disordered, one might worry that but characterization techniques will not be good enough for microscopic theories. We have used variable temperature electric force microscopy to study and image the static potential of films of the hopping conductor triphenylamine-doped polycarbonate (TPD,PC), a molecularly doped polymer specifically used in organic electronics. 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 suggests 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 TFP-PC and gold. This means that, even in this system, charge insertion is not necessarily the reverse of the initial process that has been assumed. We have incorporated ultrasonication of silicon microwells into our microscope to dramatically increase sensitivity. We find that the resonance frequency and quality factor of the cantilever are very sensitive to the laser scan distance, and the underlying sample. Such nanomechanical dissipation measurements promise for quantifying and imaging in-plane conductivity in thin organic films.

2:45 PM 17.6
Characterization of Pentacene Thin Films by Field Effect Transistor Measurements with Micro Four-Point Probe.
Masakazu Nakamura, Hirokazu Ogoshi, Tatsuo Tanaka, Hiroto Yamagami, Masaki Ikuda and Kazunari Kudo, Department of Electronics and Mechanical Engineering, Chiba University, Chiba, Japan.

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 mobility 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 work, we have therefore adopted micro four-point probe (MFP) [CAPRES A/S, http://www.capres.com/] source, drain and sensing electrodes for FET measurements. The intrinsic electrical properties at the semiconductor/insulator interface could be extracted using this method. MFP-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 LV characteristics due to the metal/semiconductor contact were removed. Moreover, the estimated mobilities by MFP-P-FET were invariably higher than those by conventional top-contact FET measurements performed with the same films, which is probably due to the deterioration of organic films by the top metal deposition having been removed. 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 17.7
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 electro-optic methods as reflection electron diffraction oscillation, 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 destructive nature, 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, i.e., ellipsometry and reflectance anisotropy spectroscopy (RAS), solve these problems, contemporary 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 on the 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 as function of the incident angle gives unique information on 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 organo-thiophene (OT) 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 OT is observed to increase with the film thickness and to vary slightly in spectral position and line shape for thicknesses above 2 monolayers. As a consequence of the change in their electronic properties and spin multiplicity for the first layers, a dramatic modification of the molecular anisotropy is observed. These results suggest that RAS can be used in the characterization of new organic thin film materials and their interfaces.

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Deposition of pentacene on silicon surfaces: A computational study. Devashish Choudhury, Paulette Clancy, Ritesh Shetty and Fernando Escobedo, School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York.

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 presence of organic compounds in the substrate surface, and growth conditions. Here we report multi-wavelength simulations to understand the effect of the first adsorbed layer on the growth mechanism of subsequent layers of pentacene. Our studies predict interesting insights 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 (110)-(2×1) 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 previously observed in experimental STM images. Using Gaussian, we also studied the weak intermolecular 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 weaker than the pentacene-pentacene interactions, confirming that the passivation of the substrate surface dulls the strong attractive effect of the surface. These binding energies are subsequently used in a microscopic scale study of the layer-by-layer deposition of organic thin films in a Letter-based Kinetic Monte Carlo simulation, providing direction for future device simulation.

Nanoscale Polymer Field-Effect Chemical Sensors. Wang, J., Faye, D., Jung, I., Khandaker, S., Qiao, Z., von Seggern, H. and Dodabalapur, A.; 1-microelectronics research center, University of Texas at Austin, TX; 2-Department of Physics, University of Texas at Austin, TX; 3-Institut für Materialwissenschaft, Technical University of Darmstadt, Darmstadt, Germany.

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 FETs 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 guard electrodes at the two sides of the channel. The dependence of chemical sensing responses on channel lengths has been investigated. The chemical sensing responses of both 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.


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 optimize 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 polymer 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/pho-to-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-diocytfluorene) and poly(methylmethacrylate). Higgins, A. M. et al., Appl. Phys. Lett. [2002] 81 4945-4951. [2] Interfacial structure in semiconducting polymer devices. Higgins, A. M. et al., J. Mater. Chem. [2002] 12 1.