SYMPOSIUM I
Interfaces in Organic and Molecular Electronics II
November 28 - December 2, 2005

Chairs

Xiaoyang Zhu
Dept. of Chemistry
University of Minnesota
Minneapolis, MN 55444
612-624-7849

Duncan Stewart
Hewlett-Packard Laboratories
1501 Page Mill Rd.
Palo Alto, CA 94304
650-857-7805

Gitti Frey
Dept. of Materials Engineering
Technion-Israel Institute of Technology
Haifa, 32000 Israel
972-4-829-4572

Kazuhiko Seki
Dept. of Chemistry
Nagoya University
Nagoya, 464-8602 Japan
81-52-789-2494

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* Invited paper
SESSION II: Theory of Electron Transport in Molecules and at Molecular-Metal Interfaces
Chair: Xiaoyang Zhu
Monday Morning, November 28, 2005
Room 302 (Hynes)

8:00 AM OPENING REMARKS


Nanostructured devices based on single-wall carbon nanotubes (SWNTs) present unique opportunities both for exploring novel device technology and for re-examining the physical principles of semiconductor microelectronics from the bottom-up atomicistic approach. Recently several groups have published works on quantum mechanical modeling of carbon nanotube nanoelectronics. However, for quantum simulation to reach its full potential of realistic performance prediction and analysis, the 3D atomicistic nature of materials/device processes and comprehensive physical models of carrier scattering in complex structured devices should be and must be considered. In this talk, we present a Green’s function based self-consistent tight-binding study of electron transport through metal-SWNT interfaces, which fully into account the 3D atomicistic nature of the electronic processes. We discuss insights obtained from such an atomistic study on the contact/diameter dependence of junction conductance and self-consistent study of current transport through metal-SWNT-metal junctions.

8:30 AM II.2 Electron-Nuclear Dynamics in Charge Transport. Donald G. Truhlar, Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota.

Proton transfer, electron transfer, and photochemistry can provide useful perspectives on electron dynamics at molecule-metal interfaces, especially regarding the quantized nature of conductance and the coupling of charge carriers to nuclear motion, as exhibited in decoherence and in the Landauer-Marcus continuum. This lecture will discuss some of these issues.

9:00 AM II.3 Light Induced Current and Current Induced Light in Molecular Junctions. Abraham Natan1 and Michael Galperin2; 1Chemistry, Tel Aviv University, Tel Aviv, Israel; 2Chemistry, Northwestern University, Evanston, Illinois.

We consider several fundamental optical phenomena involving molecules in biased metal-molecule-metal junctions. The molecule is represented by its highest occupied and lowest unoccupied molecular orbitals, and the analysis involves the simultaneous consideration of three coupled fluxes: the electronic current through the molecule, energy flow between the molecule and the leads, and the incident and/or emitted photon flux. We derive expressions for the absorption lineshape (not an observable but a useful reference for considering yields of other optical processes) and for the current induced molecular emission in such junctions. We also consider conditions under which resonant scattering can induce electronic current in an unbiased junction. We find that current driven molecular emission and resonant light induced electronic currents in single molecule junctions can be of observable magnitude under appropriate realizable conditions. In particular, light induced current should be observed in junctions involving molecular bridges that are characterized by strong charge transfer optical transitions. For observing current induced molecular emission we find that in addition to the familiar need to control the damping of molecular excitations into the metal substrate the phenomenon is also sensitive to the way in which the potential bias is distributed on the junction.

9:30 AM II.4 Charge and Spin Transport in Molecular Tunnel Junctions. Hong Guo1, 2, Nikolai Sergueev1, Danila Roubtsov1, Derek Waldron1 and Paul Haney1, 2; 1 Dept. of Physics, McGill University, Montreal, Quebec, Canada; 2 Physics, Un. of Texas at Austin, Austin, Texas.

We have carried out theoretical analysis of charge and spin transport in molecular tunnel junctions in the Metal-Molecule-Metal device configuration. The model is based on density functional theory within the Keldysh nonequilibrium Green’s functions. In this talk, I will present two topics. (i) What is the molecular vibrational spectrum and electron-phonon interaction in the device under forward bias and during current flow? In particular, we investigate the problem of which vibrational mode couple to which scattering states at what bias voltage. (ii) For ferromagnetic metal leads, we investigate molecular scale magnetic tunnel junction, spin injection, and tunnel magnetoresistance (TMR). In particular, we present results concerning various issues of molecular scale TMR.

10:30 AM **II.5 Molecular Transport Structures: Elastic Scattering, Noise and Beyond. Mark Ratner1, 2, Abe Nitzan2, 3, and Misha Galperin1, 2; 1 Department of Chemistry, Northwestern University, Evanston, Illinois; 2 Center for Nanotechnology, Northwestern University, Evanston, Illinois; 3 Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel.

Current experimental efforts are clarifying quite beautifully the nature of charge transport in so-called molecular junctions, in which a single molecule provides the channel for current flow between two electrodes. The theoretical modeling of such structures is challenging, because of the uncertainty of geometry, the nonequilibrium nature of the process, and the variety of available mechanisms. The talk will center on the first formulation of the problem in terms of scattering theory, and then on the generation of results needed to make that simple picture relevant to the real experimental situation. These include vibronic coupling, structural disorder and energy transfer. Some comments will be made on the measurements of noise spectra, and the information to be gained from them.

11:00 AM **II.6 Quantum kinetic simulations of electron transport in molecular junctions. Ralph Gehauer, Condensed Matter Group, The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy.

There is currently large interest in understanding the physics and chemistry of electron transport in nanoscale systems. Most computer simulations of electronic conduction in such systems are based on the famous Landauer approach where one solves an elastic scattering problem for electrons in the active region of the device. This is at variance with what is done in larger mesoscopic systems, where the semiclassical Boltzmann kinetic equation is commonly used to simulate electron transport. Boltzmann’s equation treats the electrons in terms of wave packets and deals with collision events quantum-mechanically using Fermi’s golden rule. This formalism explains why conduction electrons subject to a uniform electric field do not accelerate indefinitely, but settle in a steady state regime of constant current, as a consequence of inelastic collisions of the lattice that lead to energy dissipation. To describe transport in devices having spatial dimensions of the order of the electron wavelength (like e.g. molecular junctions), such a semiclassical approach is not valid. In this talk I present a generalization of the Boltzmann formalism to completely quantum-mechanical systems. Like in the semiclassical formalism, and at variance with approaches based on Landauer’s theory, this scheme is based on simulating the dynamics of electrons in the time domain. Under the combined influence of an electromotive force and dissipative electron-phonon collisions the system evoloves towards a steady state, whose physical properties (currents, charges, potentials, local energy dissipation ...) can be evaluated. In the presentation I will explain this formalism in detail and show applications to realistic nanoscale devices.

11:30 AM II.7 I-V characteristic of organic molecules on surfaces: large scale ab initio calculations. Wenchang Lu1, Vincent Menner2, Shuchun Wang1, Qinghong Zhao1 and Jerry Bernholc1, 2; 1 Center for high performance simulation, North Carolina State University, Raleigh, North Carolina; 2 Computer Science and Mathematics Division, Oak Ridge National Lab, Oak Ridge, Tennessee.

Large scale, non-equilibrium quantum transport calculations are carried out for organic molecules on silicon and gold surfaces using density functional theory. By investigating the position-dependent density of states under different biases, we show how the energies of the molecular orbitals shift with the changing Fermi levels of the leads. The molecules attached to semi-infinite leads, 1,4-diethylbenzene on Si(111) and cyclcopentene on Si(001) surfaces, our results provide a qualitative picture and quantitative understanding of the importance of self-consistent screening, broadening of quasi-molecular orbitals under large bias, and resonant enhancement of transmission, which occurs when the broadened LUMO aligns with the conduction band edge of the negative lead. Negative differential resistance (NDR) is found to be a general feature of organic molecules on surfaces. Studies of a monolayer of cyclcopentene on Si(001) surfaces show that the interactions between molecules attenuate the NDR, as seen in experiments. For ferrocenyl-anthrahiadiolate self-assembled monolayer on the Au(111) surface, resonant states around the Fermi level dominate the conduction. Similar to molecules on semiconducting surfaces, the HOMO broadens with the applied bias. The calculated I-V curves show a strong NDR around 1.5 eV, which are in fairly good agreement with experimental STM measurements.
11:45 AM 11.8 Modeling of Contact Formation in Carbon Nanotube Devices. Karthik Ravichandran and Wolfgang Windl; Materials Science & Engineering, The Ohio State University, Columbus, Ohio.

The continuous miniaturization of semiconductor devices has currently reached a stage where further progress does not seem to be feasible for much longer without changing the traditional device structure. Molecular devices with, e.g., carbon nanotubes as a channel material in field effect transistors are currently studied as a possible future replacement of the current CMOS technology. Among other challenges, such molecular devices require an unprecedented attention to the detailed geometry and electronic properties on the atomic scale. However, atomistic modeling of realistic contacts is a challenging task. We find that a straightforward relaxation of the contacts usually gets stuck in local-minima configurations with very small escape barriers, leading to unrealistic contact structures. Molecular dynamics simulations, on the other hand, cannot cover the necessary timescale to allow for a realistic evolution of the contacts. In this paper, we will discuss the simultaneous approach and electron-transport modeling on the atomic scale for the example of carbon nanotube Schottky devices, using accelerated ab-initio molecular dynamics methods to overcome the timescale limitations and atomistic transport modeling based on the Landauer theory. Our results show that the detailed contact structure is very crucial for predicting the electron transport for such nano-devices. A quantitative prediction of the magnitude difference in conductivity after optimizing the contact structure.

SESSION 12: Single Molecule Dynamics at Interfaces
Chair: Duncan Stewart
Monday Afternoon, November 28, 2005
Room 302 (Hyne's)

1:30 PM 12.1 Current-Driven Phenomena in Molecular Electronics. From Surface Nanochemistry to New Forms of Molecular Machines. Tamir Seideman, Ryan Jorn and Chao-Cheng Kaan; Chemistry, Northwestern University, Evanston, Illinois.

Inelastic electron tunneling via molecular-scale electronics can induce a variety of fascinating dynamical processes in the molecular moiety. These include vibrations, excitation, ionization, and chemical reaction. Potential applications of current-driven dynamics in molecular-scale devices range from new forms of molecular machines and new modes of conduction through molecular junctions, to new directions in surface nanochemistry and nanolithography. Interface interactions play a central role in determining not only the structure and the conductivity of molecular heterojunctions but also the likelihood, nature, and outcome of current-driven dynamics in nano-devices. Whereas strong molecule-electrode coupling gives rise to delocalized electronic orbitals and at most weak electronic-vibrational coupling, weak molecule-electrode interactions tend to spatially localize the molecular orbitals and enhance the inelasticity. In the talk I will discuss the qualitative physics underlying current-driven dynamics in molecular-scale electronics, mention the theory we developed to explore these dynamics, describe the results of ongoing research on surface nanochemistry and molecular machines, and sketch several of our dreams and plans in these areas.

2:00 PM 12.2 Theory of Electron Tunneling through Adsorbates and Defects on Ultrathin Insulating Films Supported by Metal Surfaces. Mats Persson, Fredrik E. Olsson and Sami Paavilainen; Dept of Applied Physics, Goteborg, Sweden.

The recent progress in carrying out scanning tunneling microscopy (STM) and spectroscopy of adsorbates on supported by metal surfaces has opened up a new fascinating field in atomic scale science. Examples of new physical insights and phenomena discovered by such studies include charge control of adatoms[1], single-atom spin-flip spectroscopy [Heinrich et al., Science 306, 466 (2004)], and vibronic states and bipolarity in single-molecule transport (Qu et al., Phys. Rev. Lett. 92, 206102 (2004)). All these phenomena depend critically on the electronic decoupling of adsorbate-induced states from the metal substrate states. In this talk I will present our work done in collaboration with the IBM Zurich group on the control of the charge state of a single gold adatom and on the vibronic broadening of electron states in defects and adsorbates on ultrathin, NaCl films on a copper surface [2]. We argue that this control involves an inelastic electron tunnelling (IET) attachment mechanism. For the chlorine vacancies, we find that the unoccupied vacancy state is broadened by the strong electron-phonon coupling to the phonons in the film. If time permits, I will also present our theoretical work on inelastic electron tunneling mechanisms behind single molecule vibrational spectroscopy and microscopy [3,4]. Our theoretical framework is to a large extent based on density functional calculations and the Thouless-Hamann approximation for elastic tunneling and on many body extension to inelastic electron tunneling. References: 1. J. Repp, G. Meyer, F. E. Olsson, and M. Persson, Science 305, 493 (2004). 2. J. Repp, G. Meyer, S. Paavilainen, F. E. Olsson, and M. Persson, (Phys. Rev. Lett., submitted) 3. N. Lorenzana and M. P. Tosi, Phys. Rev. B, 85, 2907 (2000). 4. N. Lorentz, M. Persson, L. J. Lauhon, and W. Ho, Phys. Rev. Lett. 86, 2954 (2001).

3:30 PM 12.3 Spatial Distribution of Contact States Studied by STM. Satoshi Katano1, Masaabumi Horii2, Yousou Kim1 and Maki Kawai1, 2, 3, RIKEN, Wako-shi, Japan; 1 Department of Advanced Materials, The University of Tokyo, Kashiwa-shi, Japan.

Contact state formed between molecules and metal electrodes plays a crucial role in transport through molecules. Hybridization between molecules and metals has been extensively studied from both experimental and theoretical points of view, to understand the nature of the molecules adsorbed on metal surfaces. Molecules having discrete levels often show pseudo-continuous levels near the Fermi level when hybridized with metal electronic states with a certain band-width. Hybridization with metal d electrons could strongly modify the charge distribution in space by mixing the molecular orbitals. In the case of CO adsorbed at hollow sites on Ni(111), 4r- and 5r-derived states of CO are strongly modified in space that considerable charge transfer occurs from the C site to the O site in the 5r-derived state and in the opposite way in the 4r-derived state [1]. In the talk, we will present our recent work on adsorption of benzene (C6H6, CO) and aminobenzene (NH2C6H5COO) on Cu(110). investigated by scanning tunneling microscope (STM) and scanning tunneling spectroscopy (STS), the effects of the substituent on both the adsorption structure and the electronic properties, i.e. the conduction states, are discussed, based on the spatial distribution. Position of the substituent is also found to modify the state. [1] S. Masuda, R. Suzuki, M. Aoki, Y. Morikawa, R. Kishi and Maki Kawai, J. Chem. Phys. 114 (2001) 8564.

4:00 PM 12.4 Single Molecular Conductivity by STM under UHV. Masamichi Fujihi, Masaki Suzuki, Kenichi Ishizuka, Shintaro Fuji, Utchi Akiba, Yumiki Takayama and Fumie Sato; Department of Biomedical Engineering, Tokyo Institute of Technology, Yokohama, Japan.

We first report switching of single alkyl chains via their conformational changes. Namely, molecularly mixed self-assembled monolayers (SAMs) of n-alkanethiols (n=5,6,7) and bicyclo[2.2.2]octylmethylthiolate (BCO) were formed on Au(111). It was found by UHV-STM that the linear alkyl chains are more conductive than the cyclic alkyl chain. In addition, we observed switching depending strongly on STM imaging condition [1]. This switching suggests that an all-trans alkyl chain transforms into its rotational isomer by tip-sample repulsive interaction and this conformational change makes the alkyl chain less conductive [2]. The dependence of electrical conduction on the absence and the presence of gauche conformation offers a simple mechanism to design molecular switches. Second, the difference in electronic conduction between single-alkyl chains and linear chains with a pi - conjugated system will be presented. The new pi - conjugated compound was used. We investigated the difference using UHV-STM and self-assembly techniques. Finally, measurements of currents through various single molecules bound to two gold electrodes under UHV will be presented. One gold electrode was an Au(111) substrate and the other gold electrode is an STM tip. The Au(111) substrate surface was covered with a SAM of one of various diithiophosphate compounds by dipping in their ethanol solution. After introducing the sample into a UHV-STM system, approaching, touching, and withdrawing the bare gold STM tip to the sample surface were repeated. Then, single molecular conductances were formed and the currents through the bonds were measured by UHV-STM. The results are compared with similar experiments in liquid [3]. The effect of solvent molecules on the single molecular conductivity will be discussed by comparing the conformational insights and physisorbed water. References [1] M. Suzuki S. Fuji, S. Wakamatsu, U. Akiba and M. Fujihi, Nanotechnology 15, S150 (2004). [2] K. Tagami, M. Tsukada, e-J. Surf. Sci. Nanotech. 2, 186 (2003). [3] B.Q. Xu, N.J. Tao, Science 301, 1221 (2003).

4:30 PM 12.5 Electronic Structures and Transport Properties of Single Molecules and Nanoparticles. J.G. Hou, Hefei National Lab. for Physical Sciences at Microscale, Univ. of Science and Technology of China, Hefei, China.

The progress of electronics means more devices in a chip but fewer electrons per device. Single electron tunneling device or single molecular device may be very important for the future nanodevice.
Single molecules and small nanoparticles have rich electronic spectrum. By introducing singles molecules or nanoparticles into the tunnel junction, the STM tip and supporting such targets are two electrodes, we can determine their electronic structures from the results of scanning tunneling spectroscopy combined with the theoretical modeling. When single molecules or nanoparticles placed as the central part in a double tunnel junction, we can studied the size dependent single-electron tunneling effect, the interplay between the charge and quantum size effect of small metal clusters, and the resonant tunneling between two molecules.

**SESSION 13: Poster Session**
**Chair: C. D. Frisbie**
**Monday, November 28, 2005**
**8:00 PM**
**Exhibition Hall D (Hynes)**

**13.1 Abstract Withdrawn**

**13.2 Dynamics of Adsorbed Organic Molecules Studied by Fast-Scanning STM: Diffusion and Conformational Dynamics.**
Roberto Otero, Peter Thostrup, Fernando Sato, Douglas Galvão, Erik Lægsgaard, Ivan Stensgaard and Flemming Besenbacher.

**13.3 Variable Temperature Electric Force Microscopy of a Molecularly Doped Polymer.**
The Nga Ng, William Silveira and John Marohn.

**13.4 Electrical Characterization of Molecular Junctions by Conducting Atomic Force Microscopy: Effect of Volt Angle and Molecular Structure under Triboelectric Charge.**
Changjo Lee, Yongku Kang and Takhee Lee.

**13.5 Current-Voltage Characteristics of Au-porphyrin Derivative-Au Junctions.**
Yutaka Noguchi, Takashi Nagase, Toto Kubota, Toshiya Kamikado and Shinro Mashiko.

**13.6 Measurements of Single Molecule Conductivity by Scanning Tunneling Microscopy under an Ultrahigh Vacuum Condition.**
Kenichi Ishimaru, Shinjo Fujii, Yuuki Takayanagi, Fumie Sato and Masahiko Fujihira.

synthesizing the linear \( \pi \)-conjugated compound, \((E)-3,4\text{-dimethyl}1,6\text{-dithioacetyls}-3,5\text{-hexyl}1,5\text{-dione (DDHDT)}, and measuring their electronic and photophysical properties of individual 1,6\text{-hexanediithiol (HDT)}, 1,4\text{-benzenediethanethiol (BDMT)} and DDHDT molecules isolated in BCO matrices. After cleavage of thioacetal groups of DDHDT, the resulting dithiol derivative (DDHDT) was used for the thiol nanogel. When the physical and STM topographic heights were compared, it was found that the conductivity of DDHDT was higher than those of HDT with a saturated alkane chain and BDMT with a phenylene \( \pi \)-system sandwiched by two methylene spacers. These experiments could not give the absolute value of single molecular conductivity \((G_m)\) through each molecule bonded to two Au electrodes at both ends, although all isolated molecules were dithiol derivatives. This is because there was a tunneling gap in each sheet between the Au tips and molecules. When two end molecules of the molecule. In this work, we will report single molecular conductivities for HDT, BDMT and DDHDT, which are bonded to an Au substrate and an Au STM tip at both ends using STM under ultra high vacuum (UHV). Under these conditions, molecules with two Au ends repeated the Au STM tip into and out of contact with the Au substrate covered with three types of self-assembled monolayers (HDT, BDMT and DDHDT) at a rate of ca. 4 nm/ s and obtained the current-distance (I−d) curves at some bias voltages [3-5]. Because each compound is terminated with two thiol groups, it can bridge the Au tip and the substrate electrode and form a molecular junction. After many I−d, curve measurements \((>1000)\) for HDT, BDMT and DDHDT, we obtained their conductance histograms and determined their values \((G_m)\). References \cite{1} I. Ishizuka, M. Suzuki, S. Fujii, U. Akiba, Y. Takayama, F. Sato, M. Fujihira, Jpn. J. Appl. Phys., in press. \cite{2} T. Tanaka, H. Hasebe, K. M. Umemura, R. Sato, J. Am. Chem. Soc. 125, 14163 (2003). \cite{3} B. Q. Xu, N. J. Tao, Science 301, 1221 (2003). \cite{4} J. He, F. Chen, J. Li, O. F. Sankey, Y. Terazono, C. Herrera, D. Gust, T. A. Moore, A. L. Moore, S. M. Lindsay, J. Am. Chem. Soc. 128, 10454 (2006). \cite{5} W. Huang, H. Zeng, S. Higgins, D. Bethell, H. Holmelen, D. J. Schiffere, R. J. Nichols, J. Am. Chem. Soc. 125, 15294 (2003).

9.7 Interaction of 2,2',6,6'-tetramethyl-3,5-heptanediene with Si(100)-2x1 Surface. Dimitri Sklar, Analia Cuadra and Brian Willis; Chemical Engineering, University of Delaware, Newark, Delaware.

Characterization of adsorption reactions on semiconductor surfaces is a topic of considerable interest due to the potential use of organic molecules in novel device applications, including molecular electronics, sensors, and nanotechnology. The construction of organic-semiconductor surface structures with custom designed properties will most likely necessitate the use of multifunctional compounds that have the ability to attach to the surface in a controlled and selective manner. Amongst various organic functional groups C=O and C=C have received the most attention due to well defined attachment to Si(100) dimers via Diels-Alder type cycloaddition reactions. In this work we report on the thermal desorption and thermal decomposition of sub-monolayer surface coverages of 2,2',6,6'-tetramethyl-3,5-heptanediene (C11H20O2) on Si(100)-2х1 surface studied using scanning tunneling microscopy (STM) and thermal programmed desorption (TPD). Considering the multifunctional nature of the compound special attention is given to identification of the adsorbate-surface binding mechanism. Thermal decomposition pathways are identified in the 260-1000K range as well as their effect on 2х1 dimer structure.

9.8 Solvent Effects on the Assembly of \( \pi \)-Conjugated Dithiol Molecules on Au and GaAs. Dmitry A. Krapelcho\-viv, Hong Meng, Alex K. Y. Jen, Daniel A. Fisher and Yueh-Lin Loo; 1 Chemical Engineering Department and Center for Nano- and Molecular Science and Technology, University of Texas at Austin, Austin, Texas; 2 Materials Science and Engineering Department, University of Washington, Seattle, Washington; 3 Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

The assembly of simple \( \pi \)-conjugated molecules has attracted substantial research interest because these molecules are model systems for more complex candidates for molecular electronics. Yet, the assembly of such conjugated molecules is only partially understood. Here, we report how the solvent from which these molecules are assembled can dramatically affect the way they organize on Au and GaAs. The molecules of interest are \( \pi \)-n-phenylenedithiols \((n=3,4,5)\). A solvent mixture of ethanol/tetrahydrofuran mixtures, in addition to the pure solvents, in the presence of n-phenylenedithiol (330 μM) NOHDT, monitored the surface coverage and the ensemble-average orientation of n-phenylenedithiol assemblies on Au and GaAs, we carried out synchrotron-based near-edge x-ray absorption fine structure spectroscopy (NEXAFS) and in situ total reflectance Fourier transform infrared (FT-IR) spectroscopy (FTIR) measurements. Both carbon-edge NEXAFS spectra and FTIR indicate that the n-phenylenedithiol surface coverage on Au is independent of the assembly solvent. Angle-resolved NEXAFS suggest that terphenylenedithiol \((n=3)\) and pentaphenylenedithiol \((n=5)\) are preferentially oriented. The NOHDT molecules are tilted on average 30°±3° away from the substrate normal independent of the assembly solvent. Our recent FTIR experiments concur with this preferentially upright orientation. In contrast to assemblies on Au, the surface coverage of n-phenylenedithiols on GaAs is extremely solvent-sensitive. Specifically, the surface coverage decreases monotonically with decreasing ethanol volume fraction in the assembly solvent. At high ethanol volume fractions, the angle of orientation of terphenyl- and quintaphenylendithiols \((n=3,4)\) similar to that on Au, but at low ethanol fractions, all the assemblies are disordered.

9.9 First-Principles Theoretical Study of n-alkane and Metal Interfaces. Yoshitada Morikawa\textsuperscript{1,2}, Hisao Ishii\textsuperscript{1} and Kazuhiko Seki\textsuperscript{1}; 1 ISIR, Osaka University, Ibaraki, Osaka, Japan; 2CREST-JST, Kogwaguchi, Saitama, Japan; 3AIST, Tsukuba, Ibaraki, Japan; 4Nagoya Univ., Nagoya, Japan; 5RIEC, Tohoku Univ., Sendai, Japan.

The formation of an interfacial dipole layer during organic molecular adsorption on metal surfaces has been attracting enormous attention, since it is directly related to the carrier injection barrier between organic molecules and metal electrodes in organic devices. Two major trends were observed, i) in most cases, organic molecules reduce the metal work function, and ii) the magnitude of the work function trend increases as the substrate metal work function increases. It is destined to elucidate the origin of these trends, with the clarification of important factors determining the substrate dependence. Because the adsorption energies of n-alkane molecules on metal surfaces are rather small (of the order of 10 kJ/mol/CH2 chain) the molecule-surface interaction has been considered to be quite weak and categorized to be a typical physisorption state. However, formation of a large interfacial dipole and significant softening of the CH stretching mode were reported for n-alkane and cyclic alkane adsorbed on metal surfaces. We studied the substrate dependence of work function change and CH stretching mode softening for n-alkane adsorbed on various metal surfaces by using density functional theoretical (DFT) calculations within a generalized gradient approximation (GGA). We demonstrated that although the GGA cannot reproduce the physisorption energy well, our calculations can reproduce the experimentally observed work function change and softening of the CH stretching mode very well. We also show that the most significant factor determining their dependence on metal substrates is the distance between the molecule and the substrate. Furthermore, we obtained clear evidence for the importance of hybridization between molecular unoccupied state and metal substrate state for CH vibrational mode softening.


Organic molecules are being investigated as active components in molecular scale devices, and in biomedical applications. For the practical application, fundamental studies regarding molecular structure on metal surfaces and material interfaces are needed. Self-assembled monolayers (SAMs) on Au(111) have been extensively investigated. However, Au may not be a suitable substrate for electronic device applications due to high density of surface defects of the SAMs resulting from its high atomic mobility at room temperature and surface reconstruction of Au(111) surface. Pt may be a more commercially viable choice. Therefore, we prepared clean and atomically flat Pt(111) surface as a bottom electrode and accessibly deposited two simple organosulfur molecules, octanethiol and benzene-thiol. Using ultrahigh vacuum scanning tunneling microscopy (SSTM), we investigated their packing order in the presence of similar ordered monolayers can be obtained on the Pt(111) surface as found previously on the Au(111) surface which has been explored extensively. We will show high resolution STM images of SAMs on Pt(111) for the first time to the best of our knowledge. The Pt(111) surface appear to be packed in the same pattern as SAMs on Au(111) at high coverage regime, that is characteristic of SAMs on Au(111) surface. However, they showed different packing behavior at lower coverage regime. In this work, we showed that the density of SAMs on Pt(111) was 6%. Electron transport measurement through Pt(111)/molecular junctions was done using STS. I-V response in the benzene-thiol/Pt(111) junction was higher than that of octanethiol/Pt(111) junction near zero bias.
thin-film-SWNT-FETs (SWNT-TFTs) [3,4] have been investigated vigorously. The SWNT-FETs have shown very high mobility (> 100 cm²/Vs), while the SWNT-TFTs have yielded easy fabrication of devices and comparatively better performance than that of the other organic TFTs. Here I report on the recent progress in the SWNT-TFTs and its carrier injection mechanisms from the Schottky barrier interfaces by controlling a band structure of SWNTs. The laser-synthesized high quality SWNTs [5] were used to fabricate the TFTs, because one can expect ballistic-like electron conduction in the laser-synthesized SWNTs and thus comparably larger mobility in the device operation. The TFTs were fabricated by a novel solution process to avoid heating processes, which enable us to use plastic (flexible) substrates that have low heat tolerance. The mobility and the on/off ratio of the TFTs were typically 3.6 cm²/Vs and 10000, respectively, and this device performance was comparable to the best performance in organic TFTs [6]. The Schottky barrier height in the TFTs was evaluated and the band line-up was determined by changing applied gate voltages. Stable and versatile carrier doping in the SWNT-TFTs was also carried out by encapsulating N2O or TTF molecules inside of the SWNTs [7,8], and the device polarity was completely changed by modifying the band alignment of the SWNTs and metal electrodes. In the TCNQ-doped SWNT-TFTs, only holes can be injected from electrodes because too large a Schottky barrier for electrons was formed by the doping. [1] A. Javey et al., Nature 424, 653 (2003). [2] T. Duerkop et al., Nano Lett. 4, 35 (2004). [3] E. S. Snow et al., Appl. Phys. Lett. 82, 2145 (2003). [4] M. Shiraiishi et al., Chem. Phys. Lett. 394, 110 (2004). [5] M. Shiraiishi et al., Chem. Phys. Lett. 358, 213 (2002). [6] M. Shiraiishi et al., in preparation. [7] M. Shiraiishi et al., submitted to Appl. Phys. Lett. [8] T. Takenobu et al., Nature Mat. 2, 633 (2003).

Towards Addressable Organic Impedance Switch Devices.
Fredrik L. E. Jakobsen; Xavier Crespin and Magnus Berggren; Department of Science and Technology, Linköping University, Norrköping, Sweden.

In recent years, several organic materials possessing bistable, electrically switchable impedance have been demonstrated. Such materials sandwiched between electrodes have been used as the active components in logic circuits as well as in non-volatile random-access memories. The two-terminal nature of these devices makes them potential candidates for memory cells in simple high-density cross-point matrices. In passively addressed matrices, leakage currents become large and deteriorate the signal-to-background ratio when reading, if the cells have a linear current density-voltage (J-V) relationship. Large leakage currents in extended matrices also result in unrealistically high current drives from circuitry. Besides this, proper addressing of the cell requires a well-defined potential drop across each cell. This, in turn, requires a negligible potential drop along the conducting lines. Thus, the device characteristics are of particular interest when using organic conductors since the potential drop is related to the line resistance. We propose a novel architecture for organic switch devices that combines memory functionality and the desired nonlinear J-V characteristics such that (i) leakage currents are diminished, and (ii) operations (read/write) on each cell becomes less sensitive to the potential drop along the conducting lines. This architecture includes a semiconducting layer of copper (II) phthalocyanine (CuPc) on top of the Ron's Bump, which is a point of view with unaddressed cells in a matrix are reduced by a factor of 17 compared to a linear device, thus improving the signal-to-background ratio, reducing device current load and reducing the potential loss along the addressing lines, in contrast to the linear behaviour. This increases the predicted maximum addressable matrix size by a factor of 32. In addition to the performance improvements, this architecture requires coating only two organic layers between the patterned metal layers, i.e. no intermediate metal layers are required. This simplified process should improve manufacturability and decrease cost, and is a step towards practical all-organic matrix memory systems.

Device Characterization of Carbon Nanotube Transistors and Its Carrier Injection Mechanisms from Schottky Barriers.
Masashi Nakamura; Toshichiro Nakamura; Taishi Takenobe and Yoshi Iwasa; 1 Graduate School of Engineering, Osaka Univ., Toyonaka, Osaka, Japan; 2 IMR, Tohoku Univ., Sendai, Miyagi, Japan; 3 CREST-JST, Kagawa, Saitama, Japan.

Single-walled carbon nanotubes (SWNTs) have quasi-one-dimensional structures with semiconductive or metallic properties, which provide various applications as molecular electronics devices with nano-sized structures. To date, various applications have been proposed, such as transistors, diodes, and other novel devices and applications. Field-effect transistors (FETs) are regarded as one of the most promising applications of SWNTs because of the high device performance, which enables us to overcome so-called Moore’s Law in a silicon-based top down type approach from the bottom up approach, that is, molecular electronics. The operation mechanism of the FETs is governed by a Schottky FET model, of which Schottky barrier is formed in the interface between SWNTs and electrodes. So far, both individual-SWNT-FETs (SWNT-FETs) [1,2] and thin-film-SWNT-FETs (SWNT-TFTs) [3,4] have been investigated vigorously. The SWNT-FETs have shown very high mobility (> 100 cm²/Vs), while the SWNT-TFTs have yielded easy fabrication of devices and comparatively better performance than that of the other organic TFTs. Here I report on the recent progress in the SWNT-TFTs and its carrier injection mechanisms from the Schottky barrier interfaces by controlling a band structure of SWNTs. The laser-synthesized high quality SWNTs [5] were used to fabricate the TFTs, because one can expect ballistic-like electron conduction in the laser-synthesized SWNTs and thus comparably larger mobility in the device operation. The TFTs were fabricated by a novel solution process to avoid heating processes, which enable us to use plastic (flexible) substrates that have low heat tolerance. The mobility and the on/off ratio of the TFTs were typically 3.6 cm²/Vs and 10000, respectively, and this device performance was comparable to the best performance in organic TFTs [6]. The Schottky barrier height in the TFTs was evaluated and the band line-up was determined by changing applied gate voltages. Stable and versatile carrier doping in the SWNT-TFTs was also carried out by encapsulating N2O or TTF molecules inside of the SWNTs [7,8], and the device polarity was completely changed by modifying the band alignment of the SWNTs and metal electrodes. In the TCNQ-doped SWNT-TFTs, only holes can be injected from electrodes because too large a Schottky barrier for electrons was formed by the doping. [1] A. Javey et al., Nature 424, 653 (2003). [2] T. Duerkop et al., Nano Lett. 4, 35 (2004). [3] E. S. Snow et al., Appl. Phys. Lett. 82, 2145 (2003). [4] M. Shiraiishi et al., Chem. Phys. Lett. 394, 110 (2004). [5] M. Shiraiishi et al., Chem. Phys. Lett. 358, 213 (2002). [6] M. Shiraiishi et al., in preparation. [7] M. Shiraiishi et al., submitted to Appl. Phys. Lett. [8] T. Takenobu et al., Nature Mat. 2, 633 (2003).

Electrical Transport Measurements Through Single DNA Nanowires by Conductive AFM: Hezy Cohen, Claude Nogues1, Daniela Ullien1, Ron Naaman1 and Danny Porath1; 1 The Hebrew University of Jerusalem, Jerusalem, Israel; 2 The Weizmann Institute of Science, Rehovot, Israel.

Seemingly contradicting results raised a debate over the ability of DNA to transport charge. We developed an experimental approach for measuring current through DNA molecules using a conductive atomic force microscope (cAFM).1, 2 The measurements were performed on double stranded DNA (dsDNA) and single stranded DNA (ssDNA) insulating monolayer. The dsDNA is chemically connected on both ends to two gold electrodes, a gold surface and a gold nanoparticle that is contacted in a controlled way by a cAFM tip. We present a multi leveled evidence for charge transport through 20 base-pairs long dsDNA, including S-shaped I-V curves showing currents higher than 220 nA at 2 V, various controls and I-Z curves. In addition, the crucial role of an efficient charge injection for transport through DNA is demonstrated by comparing measurements through monolayers comprised of molecules thiolated on both ends (enabling chemical bonding to both electrodes) with molecules thiolated on one end.1, 2 Claude Nogues, Sidney R. Cohen, Shirley D. Smalley and Ron Naaman, PCCP, 2004, 18, 225 Hezy Cohen, Claude Nogues, Ron Naaman and Danny Porath, PNAS, in press 3 Hezy Cohen, Claude Nogues, Daniela Ullien, Shirley Daube, Ron Naaman and Danny Porath, Faraday Discussions, in press.

Role of Molecular Vibration in Charge Exchange at Organic-Inorganic Interfaces. Kuniharu Fujii, Mika Sawa, Satoshi Kera, Koji K. Okuda and Nobuo Ueno; Engineering, Chiba University, Chiba, Japan.

INTRODUCTION Charge transfer through organic-inorganic interfaces dominates the performance of organic devices. Recently, Erenchenko et al. reported that electric charge is pumped back and forth between AgI (111) and PTCDA[1]. This pumping is caused by molecular vibrations and plays a crucial role in the charge exchange at organic-inorganic interfaces. In this work, high-resolution electron energy loss spectroscopy (HREELS) studies were performed for tetracene thin films deposited on highly oriented pyrolytic graphite (HOPG) to obtain detailed information on a role of the molecular vibration in the charge exchange at the interfaces. EXPERIMENTAL A HOPG substrate, on which the molecule-substrate interaction is very small, was cleaved in air, and cleaned in situ by heating at 573 K for 20 hours in ultra high vacuum (<1 x 10^-9 Torr). Purified tetracene was evaporated onto the HOPG substrate at a rate of 0.03 nm/min. HREELS spectra of the tetracene films were measured at a specular geometry with an incident and scattering angle of 60 degree relative to the surface normal. The primary electron energy and the resolution were 5.0 eV and respectively. All measurements were performed at room temperature. RESULT AND DISCUSSION In HREELS spectra of tetracene (16.0 nm)/HOPG, four energy loss peaks (8, 58, 91 110 meV) and one gain peak (~9meV) which corresponds to the loss peak at 9 meV were observed. All of the four
loss peaks can be assigned to out-of-plane vibrational modes (perpendicular to molecular plane). Intensity of each peak shows a remarkable dependence on the electric field applied, and has a sharp maximum at the peculiar scattering geometry. Therefore, these four vibration modes are excited by the dipole scattering. On the basis of the dipole selection rule, it is concluded that tetracene molecules orient with their molecular plane parallel to the substrate surface. Decrease in intensities of these energy loss peaks were observed depending on time, which indicate desorption of tetracene molecules. At the same time, peaks at 58, 91 and 110 meV are shifted to low energy loss side. The results of MO calculation demonstrate that the vibrational energies shift to low-energy side when the molecules are charged negatively. Therefore, the observed decrease at the energy loss values may originate from an increase in electron density in each molecule. Similar results were obtained for pentacene films. At the conference, we will also present temperature dependence of HREELS spectra. [1] M. Eremenko et al., Nature 425 (103) 602

18.10 Current-voltage characteristics of molecules/silicon hybrid systems using a scanning tunneling microscope. Tomohiro Nishimura1, Masato Arai2 and Hirokazu Tada1,2; 1Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan; 2JST-CREST, Kagawuchi, Saitama, Japan.

We have prepared organic molecules/silicon hybrid systems by exposing silicons[111] 7x7 surfaces to various molecules such as ethylene and phenylacetylene in an ultrahigh vacuum (UHV) chamber. The surface structure and electrical properties of the specimens were examined using a scanning tunneling microscope with a W tip at room temperature in UHV. The current-voltage (I-V) characteristics were measured in the bias range from -5V to 5V. In the I-V plot of the molecule/silicon system, a peak appeared at the sample bias of approximately +4V. The position of the peak changed depending on the polarity of the bias voltage applied to the specimen prior to the I-V measurements, indicating that charges injected into molecules and/or molecule/silicon interfaces affected the generation of the peak. The I-V characteristics of various molecules on Si(100) surfaces have also been examined. The effect of density and orientation of molecules in the system on the I-V characteristics will be discussed.

18.17 Molecular Orientation Switch of an Endohedral Metallofullerene on Alkanethiol Self-assembled Monolayer. Yuzuke Yasutake1, Zuzzo Shii1, Toshihisa Ozaki3, Hisanori Shinohara1,4 and Yutaka Majima1,2; 1Department of Physical Electronics, Tokyo Institute of Technology, Tokyo, Japan; 2SORST, Japan Science and Technology Agency, Tokyo, Japan; 3Department of Chemistry, Nagoya University, Nagoya, Japan; 4Institute for Advanced Research, Nagoya University, Nagoya, Japan.

Endohedral metallofullerenes[1] are one of the candidate materials for creating highly sensitive orientation switching devices owing to their electric dipole moment due to the exchange of electrons between the encapsulated metal atom and a fullerene cage. If there exist a strong orbital interaction between a class of fullerene materials and a metal substrate, the molecular orbital is delocalized, and molecular motion tends to be restrained because of the strong orbital interaction. Therefore, the control of the texture and the orbital interactions of surrounding endohedral metallofullerene on the sub-nanometer-scale is the key to realizing a single molecular orientation switching device by using endohedral metallofullerene. Since the alkanethiol self-assembled monolayer is useful for tunneling barrier which conductance and physical height can be controlled by changing the number of methylene groups, the orbital interactions of surrounding endohedral metallofullerenes can be controlled by introducing the alkanethiol SAM between endohedral metallofullerenes and metal substrate. Here we present the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) studies of tetrabutylammonium cation of an endohedral metallofullerene (C82@C60) [2] on an alkanethiol SAM. The I-V characteristics of a single C82@C60 molecule on an octanethiol SAM at 13 K repeatedly exhibited hysteresis loop, negative differential conductance (NDC) [3]. This observed hysteretic and NDC is interpreted in terms of a switching of the C82@C60 molecular orientation caused by the interaction between its electric dipole moment and an external electric field. Furthermore, we found the STM images of C82@C60 on hexanethiol SAM differ from that on octanethiol SAM at 68 K. We discuss alkanethiol chain length dependence of STM image of C82@C60 on alkanethiol SAM by taking into account of the interaction modulation due to the number of methylene groups in alkanethiol SAM. [1] H. Shinohara, Rep. Prog. Phys. 63, 843 (2000). [2] Z. Shi, T. Okazaki, T. Shimada, T. Sugai, K. Suenaga and H. Shinohara, J. Phys. Chem. B 107, 2485 (2003). [3] Y. Yasutake, Z. Shi, T. Okazaki, H. Shinohara and Y. Majima, Nano Lett. 5, 1057 (2005).

18.18 Tunneling resistances of double-barrier tunneling structures incorporating an alkanethiol Au nanoparticle. Yutaka Majima1,2, Hong Zhang1, Yuhuke Yasutake1 and Toshiharu Teranishi3; 1Department of Physical Electronics, Tokyo Institute of Technology, Tokyo, Japan; 2SORST, Japan Science and Technology Agency, Tokyo, Japan; 3University of Tsukuba, Tsukuba, Japan.

Nanomechanical single electron systems have attracted significant fundamental and technological interest for applications in nanoelectronic devices. Gorelik et al. proposed the electron shuttle model based on the nanomechanical double-barrier tunneling junctions (DBTJs), in which the polarity of a number of electrons on the Coulomb island can be controlled by the two tunneling resistances between the Coulomb island and two reservoirs[1]. In the DBTJ structure, a single electron shuttle via the self-excitation process will be observed if the Coulomb island can be vibrated by the charges on the island and the tunneling resistance ratio of the two junctions inverse due to the nanomechanical vibration. The design of the tunneling resistances in the nanomechanical single electron system is one of the most basic and important objectives to realize the single electron shuttle with self-excitation. Recently, we have demonstrated the electron shuttle motion by measuring the displacement and tunneling currents in nanomechanical DBTJs using a scanning vibrating probe[2,3]. As the tunneling resistance of the alkanethiol molecule depends on the length of alkanethiol[4], there exist a possibility to control the tunneling resistance ratio of DBTJ and to design the structure of the subnanometer scale that enable us to realize the electron shuttle with self-excitation. Here we demonstrate Coulomb staircases in double-barrier tunnel junctions on a Au nanocolloid probe/vacuum gap/alkanethiol-protected Au nanoparticle/Au (111) electrode as a function of the set point current of scanning tunneling spectroscopy. The tunneling resistances of the scanning probe-Au core of a nanoparticle (R1) and the Au core-Au (111) electrode (R2) are evaluated by fitting a theoretical Coulomb staircase into the experimental tunneling current-voltage characteristics measured by scanning tunneling spectroscopy. When a vacuum gap exists between the scanning probe and alkanethiol Au nanoparticles, R1 is inversely proportional to the set point current. On the contrary, in the case of R1 < R2, the top of the tip of the scanning probe tends to penetrate the octanethiol-protecting molecule of an Au nanoparticle. R2 is found to be independent of the set point current, and R1 of octanethiol- and hexanethiol-protected Au nanoparticles are evaluated as 7.6 GΩ and 400 MΩ, respectively. [1] L. Y. Gorelik, A. Isacsson, M. V. Voinova, B. Kasemo, R. I. Shketer, and M. Jonson, Phys. Rev. Lett. 80, 4526 (1998). [2] Y. Majima, K. Nagano, and A. Okuda, Jpn. J. Appl. Phys. 41, 5381 (2002). [3] K. Nagano, A. Okuda, and Y. Majima, Appl. Phys. Lett. 81, 544 (2002). [4] L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, J. Phys. Chem. B 105, 8122 (2001).

19.19 Microscopic and spectroscopic study on self-assembled monolayer film. Jongyul Lee1, Hyo Young Lee1, Nakjin Che1, Heeyoul Baek1 and Yong-Jai Cho1; 1ETRI, Daejeon, South Korea; 2Kris, Daejeon, South Korea.

We have grown several kinds of self-assembled monolayer films on Au substrate and characterized their morphological and electrical properties using microscopic and spectroscopic methods. Depending on each functional ending group, the optimal condition for the flat monolayer varied and their coverages were checked with X-ray photoelectron spectroscopy and spectroscopic ellipsometry. And we utilized conductive atomic force microscope to study their morphological and electrical property on the nanometer scale. The typical IV characteristics locally measured at the fixed position were compared between these films and we could understand the behavior change by the layer thickness and the ending functional group. Although the surface bonding to Au surface in the form of thiol was known to be strong, it should be tested that the thermal stability of these films is suitable to molecular electronic application.

19.20 Electrical Properties of DNA molecules by Top-contacted Nanogap Electrodes and Immobilization of DNA Molecules on the Patterned Self-assembled Monolayers. Yoichi Otsuka1,2, Takuji Matsumoto1-2, Hisashi Tabata1-2 and Tomoji Kawai2-3; 1ISR-SANKEN, Osaka University, Ibaraki, Osaka, Japan; 2CREST, JST, Kagawuchi, Saitama, Japan.

In spite of many studies of the electrical property of DNA, results are controversial yet. This is because many factors are involved in sample preparation processes and/or measurement procedures that affect the electrical properties. One of the important factors is the structure. As DNA molecules are flexible, they are bent easily on the solid surface. The bend of structure leads to reduce of pi-stack nature and losing
the electrical conductivity. The other important factor would be the counter ion. As the backbone of DNA molecule is negatively charged owing to the phosphate groups, counter ion is crucial to stabilize the double stranded structure. Moreover, recent reports indicated the possibility of carrier doping into DNA molecules by counter ions. We have measured the electrical conductivity of DNA molecules immobilized on gold with top-contact geometry type nanogap electrodes reported previously [Nanotechnology 15, 1630 (2004)]. Utilizing these electrodes enables us to prevent DNA molecules from structural deformation that might occur in case of bottom-contacted geometry type DNA solvated with different counter ions is prepared and dropped on the cleaned SiO2 surface. After the incubation, the surfass solution is blown away by dried nitrogen gas. Immediately after that, the surface is rinsed twice with ultra pure water and dried up in a vacuum desiccator. Top-contacted geometry type nanogap electrodes are fabricated on the DNA-immobilized surface. The gap size is about 100nm on average. The current-voltage characteristics are measured in vacuum with an enhancement current is measured. We will discuss the effect of counter ions on the conductivity. Furthermore, we observe the morphology of DNA molecules on the patterned self-assembled monolayers by atomic force microscopy. We have prepared the substrate patterned with hydrophilic and hydrophobic surface by the irradiation of deep UV light to the hydrophobic self-assembled monolayers on the silicon oxide through the lithographic mask. After the immobilization of labeled DNA molecules, we observe the localization of the molecules that DNA molecules are randomly immobilized on the hydrophilic area. On the other hand, DNA molecules are bundled, stretched and aligned in the direction of nitrogen gas flow on the hydrophobic area. 4) Work supported by CREST, JST and JSPS Fellowships for Young Scientists.

I.2.1 MultiComponent Interface Chemistry in Self-Assembled Monolayers D. Y. Petrovskiy1,2,3, H. Kimura-Suda4, A. Opdahl5, L. J. Richter6, M. J. Tabory2, M. Yang2, A. R. Laracuente2 and Lloyd J. Whitman2. 1Physics Department, University of Maryland, College Park, Maryland; 2Naval Research Laboratory, Washington, District of Columbia; 3National Institute of Standards and Technology, Gaithersburg, Maryland.

We examined formation of self-assembled monolayers (SAMs) on platinum under different deposition and surface preparation conditions. We used x-ray photoelectron spectroscopy (XPS) for quantitative analysis of surface chemistry. An array of standard techniques: fourier-transform infrared spectroscopy, spectroscopic ellipsometry, and contact angle, were used in combination with XPS for comprensive characterization of these SAMs. Understanding the surface chemistry of thiol groups on Pt is important for the proposed use of Pt substrates in molecular electronics. Our study and previous work by others indicate that the thiol-Pt interface chemistry is significantly more complicated than in the prototypical thiol-Au case. XPS of the S 2p region clearly shows multiple S bonding configurations under all the deposition and preparation conditions reported to-date. In addition, thiol molecules do not attach to heavily oxidized surfaces, and Pt adatoms are not completely removed during SAM deposition from ethanolic solutions. We will discuss the possible insight into the observed trends in thiol-metal interactions and SAM ordering on coinage metals from a comparison of the metal-sulfide bond and metal-oxygen bond strengths for benzylthiol materials. We will also discuss recent studies of SAM formation on clean, single-crystal Pt(111) in ultra-high vacuum that further elucidate the nature of the multicomponent thiol adsorption on Pt surfaces.

I.2.2 Characterization of New Molecular Memory Materials and Their Application for Molecular Electronic Devices by Using Nano-Imprinting Technique. Hyooyong Lee, Junghyun Lee, Gyeong Sook Bang, Nak-Jin Choi, Jonghyuk Park and Hee-Yool Baek; ETRI, Daejeon, South Korea.

Recently, in order to search for high density memory device in nanotechnology field, many researchers have applied functional organic molecules to electronic device by using self-assembled monolayers (SAMs) [1,2] and LB film [3] method for immobilization of organic functional materials to metal electrodes, and nano-imprinting technique, which may give cheap fabrication cost and easy fabrication process, for molecular electronic device fabrication. In order to design and realize such complex molecular electronic devices, several requirements should be satisfied such as organic memory molecules, fabrication of nano-scaled device, immobilization of organic molecule, and implementation of molecular memory device. Here, we report the synthesis and thiol-terminated organic molecules having memory effect, the characterization for the formation of single monolayer by using self-assembly process (SAM), and device fabrication by using nano-imprinting method. The self-assembled monolayer of the new thiol-terminated molecule was used to fabricate a molecular memory device in the structure of metal-molecule-metal (MNM). Finally, we will report the detailed experiments and the fabrication process in this talk, Reference [1] A. Ulman, An introduction to ultrathin organic films from Langmuir-Blodgett to self-assembly, Academic Press, San Diego, 1991, p237. [2] H. Sugimura, K. Ushiyama, A. Hozumi, O. Takeda, Langmuir 16 (2000) 885. [3] R.M. Metzger, Acc. Chem. Res. 32 (11) (1999) 950.

I.2.3 Synchrotron PES Study of Self-Assembled Diode Molecules on Au(111). Wei Chen1, Chuun Huang2, Xingyu Guo1, Donghen Qi1, Andrew Thye Shen Wei1, Zhikuan Chen1 and Kian Ping Loh1, 1Department of Physics, National University of Singapore, Singapore, Singapore; 2Institute of Materials Research and Engineering, Singapore, Singapore; 3Department of Chemistry, National University of Singapore, Singapore, Singapore.

The interface dipole formation of the diode molecules (oligo(phenylenevinylene) composed of building blocks of oligo(phenylenevinylene), perfluorosubstituted phenylenes, and a terminal thiol group) self-assembled on Au(111) surface was investigated by synchrotron photoemission spectroscopy. It was found that the total interface dipole was strongly dependent on the intrinsic dipole of the molecules. The tuning of the effective vacuum level of the surface was achieved by assembling diode molecules with different permanent dipole on Au(111). Finally, the energy level alignment at molecule/Au(111) interfaces was also reported.

I.2.4 Transport in Genetically-Engineered, Arachidyl-Based Molecular Interconnects: Mechanical, Thermal and Contact Interactions. James Raynolds1, Xiang-Yang Liu2, Christopher Wells1, Timothy Cale2, Hanchen Huang2, John Welch1 and Alain Kaloyeros1, 1University at Albany, Albany, New York; 2Rensselaer Polytechnic, Troy, New York.

This talk gives an overview of recent progress in characterizing thermal, vibrational and molecule-contact effects in arachidyl-based molecular electronic systems. Most calculations of molecular transport properties, to date, have neglected the influence of the electron-phonon interaction. We show that by including such effects, certain candidate molecular interconnects will spontaneously deform mechanically so as to lower their total energy (Peierls distortion). Unfortunately, however, this distortion leads to the creation of an electronic band gap with the consequent degradation of the transport properties. We use fully self-consistent density-functional Green’s function based calculations to determine the molecular current/voltage characteristics. Such calculations clearly indicate a lower current-voltage characteristic, which results upon letting a certain candidate molecular system (that has good properties otherwise) deform spontaneously. We also employ similar self-consistent density-functional based calculations to determine the complete phonon band structure as well as the electron-phonon interaction. Such information will be useful for determining systems that do not exhibit the Peierls distortion. We also compare to engineer superior, thermal-resistant, molecular interconnects. We also report on similar computational studies of molecule-surface interactions, adsorption sites and attachment kinetics.

I.2.5 Electrical Junctions Formed from Thiol-Terminated Oligo-(Phenylene-Vinylene): The Influence of Monolayer Formation Method on Junction Properties. Jeremy M. Beebe1, James D. Batteas2 and Roger D. van Zee1, 1Process Measurements Division, National Institute of Standards and Technology, Gaithersburg, Maryland; 2Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

The field of molecular electronics is based on the ability to correlate the electrical properties of a metal-molecule-metal junction with the physical and electronic structure of the molecule within the junction. In an ideal molecular junction, molecules exist in well-ordered, crystalline domains that extend over the entire area of contact. In this scenario, it is likely that each molecule contributes equally to the observed junction conductance. The information that can be extracted regarding the changes in junction electrical behavior that arise from inserting different molecules. In practice, monolayers are seldom comprised of long-range crystalline domains. In this study, we form self-assembled monolayers of oligo-(phenylene-vinylene) (OPV) compound by two different methods: direct deposition from solution and replacement of an ethanethiol SAM. Previous experiments (FTIR, UPS, XPS, contact angle) clearly show that the bulk film structure is improved by changing from direct deposition to ethanethiol replacement. The focus of this presentation is on the characterization of the OPV monolayers by STM. SAMs of OPV formed by direct deposition are shown to
I.3.26 Ultrasensitive Conductance Measurements of Self-Assembled Monolayer Supported Phenylen-ethylene Oligomers. Sajini Nayakara1, Meaghan M. Blake1, Arrelane A. Dameron1, Rong Zhang2, Chris Pochas1, Moonhee Kim1, Paul S. Weiss1, Thomas P. Paoli1, Sundar Upadhyay1, David L. Allara1 and James M. Tour2; 1Departments of Chemistry and Physics, The Pennsylvania State University, State College, Pennsylvania, 2Department of Physics, North Carolina State University, Raleigh, North Carolina; 3Departments of Chemistry and Materials Science and Engineering, The Pennsylvania State University, State College, Pennsylvania; 4Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, Texas.

We have used alkanedithiolate self-assembled monolayers (SAMs) to fabricate support matrices for probing the charge transport properties of both isolated and bundled phenylene-ethylene oligomers (PEOs). By utilizing solution- and vapor-phase manipulation techniques, we can select the distribution of the PEO molecules within the SAM matrix. These fabrication techniques, in combination with the spatial and energy resolution afforded by low temperature scanning tunneling microscopy and spectroscopy, have enabled us to probe the electronic properties of these molecules. We have probed individual substituted PEO molecules in analogous environments to understand the effects of chemical substitution on charge transport. We aim to understand the conductance pathways of these molecules as a function of their chemical structure, physical environment and adsorption site.


Applications of Single-Walled Carbon Nanotubes (SWNT) depend on protocols that control their diverse structural and physical properties. Accordingly, incorporation of SWNT as part of an efficiently controlled process requires (a) the tightening of SWNT length distributions and (b) the ability to chemically program their selective adhesion and organization on solid substrates. We describe here a method for the tightening of length distribution of SWNT in a CMOS grade suspension, based on the control of SWNT flow and permeation behavior through porous membranes. We also describe a photolithographic wet chemical process for the patterning of self-assembled monolayers on silicon substrates and the selective adhesion of SWNT on the organically templated surface. The length selection, selective adhesion and alignment processes hold immense potential for the applications of SWNT.

I.3.28 FTIR spectroscopy of buried molecules in tunnel junctions. Yongeok Jun and Xiaoxiao Zhang; Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

We demonstrate that ATR-FTIR spectroscopy can be used to record high quality vibrational spectra of molecules at buried interfaces in metal-molecule-silicon and metal-molecule-metal junctions. This provides quantitative information on the structure and conformation of molecules at buried interfaces, an issue of critical importance to molecular electronics. In the model systems of Au on octadecyltrichlorosilane self-assembled monolayers on Si or mercaptohexydecanoic acid multilayers on Au covered Si, ATR-FTIR suggests that metal deposition leads to not only conformational disorder within the interface, but also the direct interaction of metal atoms/clusters with alkyl backbones. We also present results for metal-molecule-metal junctions under bias.

I.3.29 Abstract Withdrawn

I.3.30 Abstract Withdrawn

I.3.31 Prediction of Transport Properties through Molecular Devices by First Principles Calculations. Hiroshi Mizusaki1, Rodion V. Beloshudy1, Amir A. Farajian1, Olga V. Pupysheva1, Chiranjib Majumder2, Jian-Tao Wang3, Hao Chen4, Tomoki Uehara5, Nobuki Igarashi2 and Yoshiyuki Kawazoe2; 1Institute for Materials Research, Tohoku Univ., Sendai, Miyagi, Japan; 2Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Center, Mumbai, India; 3Institute of Physics, Chinese Academy of Sciences, Beijing, China; 4Physics Department, Fudan University, Shanghai, China.


The use of top-down optical patterning techniques becomes much more restricted as the size of circuit components reduces below 100 nm. Nanomaterials such as DNA are currently being explored as potential application in nanotechnology. One of possible potential applications is as an attractive template for constructing nanowire from bottom up. For the purpose of connecting between nano-functional devices and macroscopic electrodes, the conductivity of DNA-templated nanowire and its corresponding conductive behaviors were investigated in this study. Alignment of DNA on SiO2 wafer was firstly manipulated through the application of a linear lamination flux. As a result, DNA was stretched and laid perpendicular to the gap of electrodes on SiO2 wafer. The DNA template was subsequently allowing binder with cis-Pt(NH3)2Cl2 (cisplatin), followed by reduction with dimethylamine borane (DMAB). This induces nanoparticle formation on the DNA chain. Low resistance was obtained by pinning electrodes where only single Pt-DNA nanowire was setting across electrodes. Pt-DNA nanowires shows a linear ohm conductive behavior at low applied voltage while it shows a resistive characteristic at a high-applied voltage. Cutting of this nanowire resulted in an insulating sample; no current was detected, proving that the measured conductance was indeed caused by DNA-templated nanowire. These characteristics indicated that DNA is an ideal template for the production of electric nanowires, which can be utilized for the nano-scale electrical circuits.

SESSION 14: Charge Transport and Spectroscopy of Molecular Junctions
Chair: Abe Nitzan
Tuesday Morning, November 29, 2005
Room 302 (Hytes)

8:00 AM


We review experimental studies of electronic transport through molecular monolayers and single molecules. Particular emphasis is placed on experimental systems that combine detailed physical and electronic characterization, and, to whatever degree possible, provide well-defined interfaces that enable quantitative data analysis. Most
device structures compromise between physical and electronic characterization capacity. Electron and photon spectroscopies including ellipsometry, XPS, Raman, UPS, and AES help define unambiguous interfaces. Analysis of transport mechanisms requires statistically significant electronic data sets including repeatable temperature dependences and IETS. As a case study, we present both physical and electronic characterization of metal/organic monolayer/metal devices built on ultra-flat Pt metal electrodes that incorporate alkoxynaphthalene thiol, and utilize scanned probe or evaporated top metal electrodes.

8:15 AM 14.2 Metal-Molecular Junctions Probed with Surface Plasmons. Ken Shimizu1, Ragip Pala2, Mark L. Brongersma1 and Nick Molev1, 1Materials Science and Engineering, Stanford, Stanford, California; 2Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California.

Understanding the molecular re-arrangements that take place within molecular layers sandwiched between metal electrodes is a key element to designing better molecular electronic devices. Currently there are few techniques aside from current-voltage scans to provide information about the molecular structure, as conventional methods are not sensitive enough to detect monolayer films between highly absorptive metal electrodes. However, it may be possible to detect electronic re-arrangements within a metal-molecule-metal junction from the optical absorption changes using surface plasmons excited on the electrode surfaces. Here we report our measurements of the optical absorption of thin and molecular films sandwiched between metal electrodes using surface plasmons. This technique takes advantage of the highly confined evanescent surface plasmon field to achieve large optical intensities within the molecular film, leading to enhanced sensitivity. The absorption of the molecular layer is calculated from a fit of the reflectivity vs incident angle curves to a Fresnel model of the dielectric constants of the molecular film. Performed over a series of wavelengths, the imaginary component of the molecular dielectric constant gives a typical absorption vs wavelength spectrum, which can be used to infer the change in HOMO-LUMO levels after the molecules are in contact with the metal electrodes. These measurements can be performed while taking I-V curves, this method may be particularly useful for understanding switching behavior in molecular devices.

8:30 AM *14.3 In-situ Comparison of Electron Transport through Different Self-Assembled and Nanografted Monolayers by Conductive Tip AFM. Giacinto Scales1, Chemistry, Princeton University, Princeton, New Jersey; 2Scuola Internazionale Superiore di Studi Avanzati (SISSA), Trieste, Italy; 3ELETTTRA, Sincrotrone Trieste S.C.p.A., Trieste, Italy.

We shall report a new, differential, method for measuring the conductivity of metal-monolayer-metal junctions that uses nanografting and conductive-probe atomic force microscopy. First, a monolayer patterned out of one kind of molecules is nanografted into a self-assembled monolayer made of a different kind. After this, a new and clean metal-coated tip is brought close to, and scanned at low force loads over, the region containing the patch. At the same time, a bias is applied between the tip and the substrate. An amplifier sensed the current passing through the junction and two correlated (current and topography) images are simultaneously obtained. The height contrast differentiates the patches made of different molecules by their heights while the current contrast differentiates their conductivities. Two pairs of molecules have been compared: biphenyl 4,4'-dithioi/1-decanethiol and 16,16,16-trithiolo-1-hexadecanethiol/1-decanethiol, where the first molecule in each pair was grafted into a matrix made with the second one. The results of these and similar experiments will be discussed also in light of DFT based slab calculations of the density of states carried out in collaboration with A. selloni and Q. Sun. The experimental work reported was carried out as part of the PhD thesis of Jian Liang. The work was funded by the NSF under the Princeton MRSEC grant.

9:00 AM 14.4 Molecular Length Dependence and Contact Effects on Electron Conduction through Molecules: Aromatic Thiols vs. Aromatic Bis(triazolyl)amines. DongXiao Kim1, Jeremy Matthew Beebe1, Vine Engelkes1, Yongseok Jun2, Xiaoyang Zhu3 and C. Daniel Frisbie1; 1Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; 2Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

The understanding of electron transport through molecular wires is of great importance for the advancement of molecular electronics. In particular, fundamental issues such as the molecular structure-transport relationships and the effect of molecule-electrode binding must be addressed. We have studied the electronic properties of self-assembled monolayers (SAMs) of aromatic (benzene, naphthalene, anthracene, biphenyl, terphenyl) thiols and isocyanides by conducting probe atomic force microscopy (CP-AFM). Nanoscopic tunnel junctions were formed by contacting Au-coated AFM tips to approximately 100 molecules in the SAMs on Au substrates at a constant applied load of 2 nN. The current-voltage (I-V) characteristics of both series of SAMs were linear over ±0.3 V. Resistance (R) increased exponentially with molecular length (s) in both cases according to the expected relationship, R = Ro exp (Bs). The thickness dependent attenuation factor (B) is 0.1 ± 0.1 for both aromatic systems, while contact resistance (Ro) of aromatic thiols on gold is much less than that of aromatic isocyanides. Specific contact resistances are 1200 Ω and 12000 Ω for junctions of aromatic thiols and isocyanides, respectively. Ultraviolet photoelectron spectroscopy (UPS) measurements on the same systems were used to determine electronic structure of these interfaces. In general, we find good correlation between measured E(HOMO)-E( Fermi) offset and the measured contact resistance, R. Characterization of SAMs was accomplished by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

9:15 AM 14.5 Infrared Spectroscopy of Metal–molecule–Metal Interfaces. Christine Amara1, Solomone Aupulei2, Richard L. McCrey1 and David F. Bocian1; 1Chemistry, University of California, Riverside, California; 2Chemistry, The Ohio State University, Columbus, Ohio.

The promise of incorporating molecules into microelectronic devices has stimulated a variety of approaches to making metal/molecule/metal junctions for various applications ranging from molecular diodes to memory devices. However, the behavior of the molecules upon metal deposition is yet to be understood. As a result, flat graphitic surfaces were modified with monolayers of nitroazobenzene, nitrophenyl, biphenyl and fluorene monolayers and multilayers of nitroazobenzene and nitrophenyl by electrospraying of their respective diazonium ion solutions. In addition, graphic carbon and silicon surfaces were modified with monolayers and films of various porphyrin structures tethered to both surfaces through a high temperature (400 °C under inert atmosphere) treatment via carbon-carbon and carbolane linkages. Afterwards, thin films (10 to 100 Å thick) of copper, gold and other semiconductor materials were deposited onto the molecules by electron–beam evaporation at low pressures. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was employed to corroborate the presence of the tethered structure and determine the preferred molecular orientation of the molecules upon surface attachment. FTIR was also used to probe the molecules in the buried interface. Of particular interest is whether infrared spectra can be obtained through a thin metal layer and to assess the survivability of the molecules upon metal deposition.

9:30 AM 14.6 Energy Level Alignment in Conjugated Self-Assembled Monolayers. Roger van Zee, NIST, Gaithersburg, Maryland.

Photoemission has been used to determine the valence electronic structure of self-assembled monolayers, chemisorbed on metal surfaces. Conjugated phenylenethiol oligomers and acenethiol have been studied. The nature of the valence states has been established using these spectra and valence effective Hamiltonian calculations. The charge-transfer states have been identified. With this identification, the hole and electron injection barriers, and thus the transport gap, can be calculated. The effects of oligomer length and chemical substitution have also been studied. Charge transfer and the intrinsic molecular dipole are found to be key components of the energy-level alignment of these systems.


The ability to measure and control current through a single molecule is a basic requirement towards the ultimate goal of building an electronic device using single molecules. It also allows one to read the chemical and biological information of the molecule electronically, which opens the door to chemical and biological sensor applications based on electrical measurements of individually wired molecules. Two reliable methods exist to measure the current, one must: 1) provide a reproducible contact between the molecule and two probing electrodes; 2) find a signature to identify that the measured conductance is due to not only the sample molecules but also a single sample molecule; 3) provide a third gate electrode to control the current; We have measured single
molecule conductance using STM- and conducting AFM-based break junction methods. The methods work in aqueous solutions which are suitable for biologically relevant molecules such as DNA, and also allow us to control electron transport through redox molecules with electrochemical gate. By oxidizing/reducing the redox molecules, the conductance can be changed over several orders of magnitude. The methods rely on statistical analysis of a large number of measurements and are reproducible. However, due to the difficulty of forming molecular junctions with identical microscopic details, the conductance can take different values corresponding to different molecule-electrode contact geometries.

11:00 AM *14.8
New Tools for Molecular Electronics: Janes Kushmerick, Surface and Microanalysis Science Division, NIST, Gaithersburg, Maryland. In this talk I will describe our magnetic direct-assembly procedure for fabricating molecular junctions on the wafer level. Results obtained for junctions containing prototypical molecular wires highlights the utility of this technique. I will also discuss recent results on molecular conductance switching and how we are using inelastic electron tunneling spectroscopy to understand the fundamental physics of molecular switches.

11:30 AM 14.9
Tuning the Interaction between Self Assembled Monolayers and Metallic Systems: a Theoretical Study, Egbert Zoeller1,2, Geoff Heimel3, Lorenz Romanek1,2, Peter Facher1,2, Mathis Gruber1,2, Stephen Barlow3, Luca Beverina3 and Jean-Luc Bredas3. 1Institute of Solid State Physics, Graz University of Technology, Graz, Austria; 2School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; 3Department of Materials Science, State University of Milano-Bicocca, Milano, Italy. Highly ordered self-assembled monolayers (SAMs) of molecules on (noble) metal surfaces are currently the focus of intense, multidisciplinary research. Applications of such SAMs include the improvement of organic electronic devices, molecular electronics, chemical sensors and the tuning of macroscopic surface properties. In order to tune the interface properties and to endow the self-assembled systems with functionality suitable for use in either macroscopic or nanoscale devices, the use of conjugated systems is highly promising. The goal of the present study is to provide an in-depth understanding of the electronic structure of the interface between metallic substrates and covalently bound organic semiconductors in order to devise strategies to tune the interaction and thus the properties of the investigated systems. To that aim we use DFT based bandstructure-type methods to describe the details of the interface morphology, charge transfer between the metal and the SAM, interface dipoles and workfunction modifications as well as the alignment between metallic and molecular levels. The investigated organic systems vary in their ionization potentials and electron affinities, intrinsic dipole moments, nature and polarizability of the conjugated backbone, and docking groups. As substrates, we study noble metals with different work functions like Au, Ag, and Pt. The extent to which the interaction is modified by mechanical stress in molecular junctions and quantum confinement effects as found, e.g., in nanoparticles are also considered.

11:45 AM 14.10
Understanding the transport mechanisms of oligo (phenylene ethynylene) molecules, Nadaban Majumdar1, Zen Martin1, Nadine Gergel1, N. Swami1, J. C. Bean1, L. Harriott1, Y. Yao1, J. M. Tour2, D. Long3 and R. Shishidhara1, 1Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia; 2Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, Texas; 3Geo-Center R&D Center, Arlington, Virginia. Various research groups, including ours, have observed switching with memory behavior in room temperature oligo(phenylene ethynylene) molecule with a nitro sidegroup.1,2 This switching behavior has potential to be used in molecular electronic devices. However, the transport mechanism of this "nitro" molecule and the underlying cause of the switching behavior are not well understood. Studying the transport mechanism of a simple OPE molecule with no nitro side groups may be the first step in understanding the behavior of the "nitro" molecule. Very little low temperature transport analysis of plain OPE molecules has been done. Thus, we tested the current-voltage characteristics of an OPE monomolecular (without the nitro group) in our nanowell test device at temperatures between 5K and 300 K. Thermally activated hopping conduction was observed to be the dominant electron transport mechanism above 100 K for the electron injection from the chemisorbed (Au-S) contact. The measured value of the activation barrier for hopping corresponds well with the theoretical rotational barrier for transformation from a twisted to a planar, conductive conformation of this molecule.3 The conduction mechanism in this molecule was observed to be direct tunneling at temperatures below 50 K, indicating insufficient thermal energy for any thermally activated motion. We will present a comprehensive low-temperature study of the I-V characteristics of OPE molecules with and without a nitro group. By comparing the transport mechanisms and the transport barriers of these molecules, we may be able to clarify the source of the switching behavior observed from nitro molecules. 1. M. A. Reed, et al., Appl. Phys. Lett. 78, 3735 (2001); 2. N. Gergel et al., J. Vac. Sci. Technol. A, to be published in July-Aug issue. 3. M. Majumdar et al., J. Vac. Sci. Technol. A, to be published in July-Aug issue. 4. J. M. Seminario et al., J. Am. Chem. Soc., 120, 3970 (1998).

SESSION 15: Electron Transport and Scanning Probe Microscopy
Chair: Maki Kawai
Tuesday Afternoon, November 29, 2005
Room 302 (Hynes)

1:30 PM 15.1
Interfaces in Carbon Nanotubes, Paul McFerran, Cornell University, Ithaca, New York. The electronic properties of single molecule devices made from carbon nanotubes are often dominated by their interfaces. These include the interface between the nanotube and metal contacts as well as the interface between p and n regions within a tube. In this talk, we will discuss transport and scanned probe measurements that directly probe these interfaces. In addition, we will discuss the interface of the nanotube with the external world, i.e., the use of nanotubes as probes of other molecules.

2:00 PM 15.2
Measuring and Controlling Molecular-Scale Properties for Molecular Devices, Paul S. Weiss, Chemistry and Physics, The Pennsylvania State University, University Park, Pennsylvania. We use molecular design, tailored syntheses, intermolecular interactions and selective chemistry to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements of single or bundled molecules. Interactions within and between molecules can be measured, understood and exploited at unprecedented scales. We look at how these interactions influence the chemistry, dynamics, structure, electronic function and other properties. Such interactions can be used to advantage to form precise molecular assemblies, nanostructures, and patterns. These nanostructures can be taken all the way down to atomic-scale precision or can be used at larger scales. We select and tailor molecules to choose the intermolecular interaction strengths and the structures formed within the film. We selectively test hypothesized mechanisms for electronic switching by varying molecular design, chemical environment, and measurement conditions to enable or to disable functions and control of these molecules with predictive and testable means. Critical to understanding these variations has been developing the means to make tens to hundreds of thousands of independent single-molecule measurements in order to develop sufficiently significant statistical distributions, comparable to those found in ensemble-averaging measurements, while retaining the heterogeneity of the measurements. We quantitatively compare the conductances of molecule-substrate junctions. We demonstrate the importance of these junctions in conductance switching of single molecules.

3:30 PM 15.3
Single-Molecule Junctions: Diodes and Noise, Heiko B. Weber, Lehrstuhl fuer Angewandte Physik, Universitaet Erlangen-Nuernberg, Erlangen, Germany. We have performed conductance measurements with a self-assembled metal-molecule-metal junction. The gap between the electrodes could be adapted in situ to the molecule's length employing the mechanically controlled break junction technique. The organic sample molecules were designed to form a stable chemical bridge between the electrodes. In particular, I will discuss recent results obtained with a donor-acceptor-like molecule, which yielded diode-like characteristics. The mechanisms leading to this behavior could be identified by comparison with a theoretical analysis. Astonishingly, the data suggest a mechanism similar to a semiconductor diode. I will further present noise measurements we obtained with single-molecule measurements. The observations underscore the notion that there is a disordered environment close to the contact molecule.

4:00 PM 15.4
Field Regulation of Single Molecule Conductivity by a
Charged Atom. Robert Wolkow 1, Department of Physics, University of Alberta, Edmonton, Alberta, Canada; 2 National Institute for Nanotechnology, National Research Council of Canada, Edmonton, Alberta, Canada.

A new concept for a single molecule transistor is demonstrated (1). A single charged silicon atom is a transducer to a single molecule; it shifts molecular energy levels into alignment with electrode levels, thereby gating current through the molecule. Seemingly paradoxically, the silicon substrate to which the molecule is covalently attached provides 2, not 1, effective contacts. This is achieved because the single charged silicon atom is at a substantially different potential than the remainder of the substrate. Charge localization at one dangling bond is ensured by covalently capping all other surface atoms. Dopant level control and local Fermi level control can change the charge state of that atom. The same configuration is shown to be an effective transducer to an electrical signal of a single molecule detection event. Because the charged atom induced shifting results in conductivity changes of substantial magnitude, these effects are easily observed at room temperature. One electron is sufficient to achieve gating because high gate efficiency is achieved. Because one electron achieves gating, compared to ~105 in a modern transistor, enormous speed, and minimal power consumption are implied. Though enormous challenges must be overcome before this concept enables a new technology, it appears to be worth facing those challenges. 1) Paul G. Pap, Gino A. DiLabio, Jason L. Pitters, Januk Zikovski, M'o Rezex, Stanislav Dogel, Werner A. Hofer and Robert A. Wolkow. Field regulation of single-molecule conductivity by a charged surface atom, Nature 435, 658-661 (2005). 

4:30 PM 16.5


In recent years, substantial progress has occurred in the field of molecular electronics [1]. In this paper, charge transport through molecular-semiconductor junctions is probed with ultra-high vacuum (UHV) scanning tunneling microscopy (STM). The presence of the semiconductor band gap enables new manifestations of resonant tunneling through individual molecules, such as unipolar negative differential resistance (NDR). Furthermore, by doping the substrate, the majority charge carrier can be tailored, thus allowing asymmetry to be designed into the I-V curve. By demonstrating these effects on silicon, molecular electronic devices have the potential of being interfaced with conventional integrated circuit technology. Three organic molecules are considered on the Si(100) surface: styrene, cyclopentene, and TEMPO. In all cases, room temperature I-V curves on individual molecules mounted on degenerately n-type Si(100) show NDR at negative sample bias. On the other hand, at positive sample bias, the I-V curves do not show NDR, although a discontinuity in the differential conductance is observed. With degenerately p-type Si(100) substrates, NDR is observed at positive sample bias while the discontinuity in the differential conductance occurs at negative sample bias. The energy band diagram can be qualitatively explained with the energy band diagram for a semiconductor-molecule-metal junction [2]. More sophisticated treatments also confirm the experimental data [3]. In addition, cryogenic variable temperature UHV STM has been used to probe isolated cyclopentene molecules adsorbed to degenerately p-type Si(100) [4]. I-V curves taken at 80 K show NDR at positive sample bias in agreement with room temperature conductance data. Due to the enhanced stability of the STM at cryogenic temperatures, repeated measurements can be routinely taken over the same molecule. In this manner, I-V curves are demonstrated to be reproducible and possess negligible hysteresis for a given tip-molecule distance. On the other hand, measurements with variable tip position show that the NDR voltage increases with increasing tip-sample distance. Using a one-dimensional capacitive equivalent circuit, this behavior can be quantitatively explained, thus providing insight into the electronic potential distribution across the semiconductor-molecule-metal junction. This model also provides a quantitative estimate for the alignment of the molecular orbitals with respect to the substrate Fermi level. Overall, these results serve as the basis for several future studies that can be applied to silicon-based molecular electronic devices. [1] M. C. Hersam and R. Reifenberger, MRS Bull., 29, 385 (2004). [2] N. P. Guisinger, M. E. Greene, R. Basu, A. S. Balch, and M. C. Hersam, Nano Lett., 4, 55 (2004). [3] T. Takahata, G. Guentert, S. Datta, and A. W. Gold, Nano Lett., 4, 1803 (2004). [4] N. P. Guisinger, N. L. Yoder, and M. C. Hersam, Proc. Nat. Acad. Sci., 102, 8838 (2005).

SESSION 16: Photoemission Spectroscopies and Energy Level Alignment at Molecule/Metal and Molecule/Semiconductor Interfaces
Chair: Tianquan Lian
Wednesday Morning, November 30, 2005
Room 302 (Hyne)

8:00 AM 16.1

Effects of Various Types of Electrical Doping on the Electronic Structure and Electric Behavior of Organic Interfaces. Kazuhiko Saki 1, 2, Naoki Hayashi 1, Toshihiko Nishii 1, Senku Tanaka 1, Asumi Jinde 1, Masato Hondo 1, and Kaname Kanai 1, 2.

1Research Center for Materials Science, Nagoya University, Nagoya, Japan; 2Chemistry, Nagoya University, Nagoya; 1Institute For Advanced Research, Nagoya University, Nagoya, Japan.


8:15 AM 16.2

Hole Injection Barrier Tuning at Organic/Metal Interfaces with Pre-adsorbed (Sub-)Monolayers of Strong Electron Acceptors. Norbert Koch 1, Steffen Duhm 1, Juergen P. Rabe 1, Antje Vollmer 2 and Robert L. Johnson 1; 1Humboldt-University Berlin, Berlin, Germany; 2BESSY GmbH, Berlin, Germany; 3University Hamburg, Hamburg, Germany.

The ability to adjust the energy level alignment at interfaces between electroactive conjugated organic materials (COMs) and metal electrodes is of paramount importance for improving the performance of novel organic-based opto-electronic devices (e.g. light emitting diodes, field effect transistors, photovoltaic cells). In particular, tuning the height of hole injection barriers (HIBs) at organic/metal interfaces is highly desirable. Here we show that this can easily be accomplished by pre-adsorbing a controlled amount of strong electron accepting molecules (tetrafluorotetracyanoquinodimethane; F4-TCNQ) on a metal surface. Using ultraviolet photoelectron spectroscopy, the energy level alignment at interfaces between three COMs - α-spiroethene (6T), p-phenylenediamine (6P) and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α-NPD) - and Au was investigated as a function of metal-substrate pre-treatment with F4-TCNQ. Significant reduction of HIBs by 6.5 eV for 6T and 1.2 eV for α-NPD was found for all three cases, independent of the ability for charge transfer complex formation between the conjugated organic materials and F4-TCNQ.

Furthemore, HIBs could be tuned over wide ranges by appropriate adjustment of F4-TCNQ pre-coverager in the sub-monolayer range. This is explained by the acceptor coverage-dependence of the areal-covered surface potential of F4-TCNQ/Au substrates, for which
A charge transfer interaction of F4-TCNQ with Au was evidenced by photoemission experiments.

8:30 AM 10.6 Evaluation of molecular level alignment at organic-metal, organic-polymer and organic-organic heterojunctions. 

The determination in the past two years of the interface energetics of a variety of interfaces involving small organic molecule and polymer semiconductor films allows a reassessment of the mechanisms that control interface molecular level alignment for this class of materials. Broadly speaking, metal-organic interfaces can be classified in two categories. The first category corresponds to organic materials in intimate contact with a clean metal surface, e.g. metal-organic interfaces formed under high vacuum on clean substrates. These interfaces often exhibit significant deviation from the Schottky-Mott limit, with large dipole shifts. The second category corresponds to interfaces formed on contaminated metal surfaces (prepared in low-vacuum or loaded from ambient), from the liquid phase (polymer spin-casting), or on conducting polymer surface (e.g. PEDOT:PSS). Interfaces of the first category are characterized by a large density of interface states induced by the metal. A recent theoretical approach based on the alignment of the metal Fermi level with the interface charge neutrality level (CNL) of the organic semiconductor allows a semi-quantitative prediction of the interface energetics [1]. The interface electronic structures of the second category are generally closer to vacuum level alignment and exhibit smaller dipole shifts. This is consistent with most observations in polymer interfaces with the fact that PEDOT:PSS, a material with work function equivalent to that of Au, gives a far smaller hole-barrier for HTL, and is a far better hole-injector, than its metallic counterpart. This general behavior is explained by a non-monotonic decrease of the density of states induced in the gap of the organic semiconductor when the metal electrode is contaminated or when it does not exhibit the continuum of states of a metal (e.g. PEDOT:PSS). Recently investigated organic-organic heterojunctions are also analyzed using an extension of the concept of charge neutrality level (CNL) to OO interfaces [2].

The energy-level alignment is driven by the alignment of the CNLs of the two organic semiconductors. The initial offset between the CNLs gives rise to a charge transfer across the interface, which induces an interface dipole and tends to align the CNLs. The initial CNL difference is reduced according to a screening factor S, a quantity related to the dielectric constants of the two organic materials. Good quantitative agreement with experiment is found, which, for the first time, a semi-quantitative prediction of the electronic structure of OO heterojunctions. 1. H. Vazquez et al., EuroPhysics Lett. 65, 802 (2004); 2. H. Vazquez et al. Phys. Rev B Rapid Comm. 71, 041306 (2005).

9:00 AM 10.6 n-Type Doping by Magnesium to Zinc Phthalocyanine (ZnPc). Jianghui Ye, Ming Zhu, Jin An and Jianhao Xin, Department of Electronic Engineering and Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China.

Doping has been proved to be an effective method to improve charge transport properties of organic semiconductors [1]. Though p-type doping of organic semiconductors with strong electron-acceptor organic molecules has been achieved [2,3], less efficient n-type doping of organic semiconductors still remains challenging. Theoretically, n-type doping of organic semiconductors can be implemented by exploiting strong electron-donor organic molecules or alkali metals, e.g., Li and Cs. In this presentation, we report one n-type doping by alkaline-earth metals, particularly, magnesium (Mg), where Mg doping of Mg into pristine p-type ZnPc organic semiconductor has been realized. Mg-doped ZnPc films with an atomic ratio of Mg to Zn of about 1:2 were co-evaporated on ITO substrate with a capping layer of Ca/Al. Samples were characterized by current-voltage (I-V) measurement, ultraviolet photoemission spectroscopy (UPS), scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS). I-V measurement reveals that the conductivity of Mg-doped ZnPc films can be increased by 1~2 orders, in comparison to that of undoped ZnPc. UPS, XPS, and STM were used to access the electronic structure and interface of Mg-doped ZnPc. It is found that the Fermi level of ZnPc is shifted close to the vacuum level with Mg doping. XPS spectra show that Mg species are presented as Mg cations in Mg-doped ZnPc and might combine with ZnPc to form Mg-ZnPc complex. This work is in part supported by Research Grants Council of Hong Kong, particularly, via Grant No. CUHK 4372/02E. Reference [1] M. Pfeiffer, K. Leo, X. Zhou, et al., Org. Electr., 4, 89 (2002). [2] W. Y. Gao and A. Kahn, Appl. Phys. Lett., 70, 4040 (2001). [3] W. Y. Gao and A. Kahn, J. Appl. Phys., 94, 559 (2003).
pentacene, which is one of the important organic semiconductors owing to its high hole mobility. Furthermore, electron/vibration coupling is a key factor in determining charge carrier mobility. Theoretical studies have been performed for gas-phase molecules using ultraviolet photoelectron spectroscopy (UPS). However, charge/vibration coupling in solid state has remained elusive to date. For deeper understanding and extraction of the reorganization energy of holes from n-GaSe into pentacene. Additional studies varied the pre-deposition treatment of the GaSe substrate with an initial in-situ treatment at 850 °C in 1 x 10⁻¹¹ Torr of flowing ammonium. This surface treatment has been previously shown to produce a clean and stoichiometric surface of GaSe and the results obtained using the ammonium treatment are compared with those obtained using GaSe without in-situ surface treatment.

11:45 AM 16.10
Electrochemical Potentials and Redox Reactions of H-, Cl-, CH₃-and C₂H₅-Terminated, Si(111) Surfaces. Patrick Timothy Hurley, Stanford University; Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California.

Wet chemical, covalent functionalization of Si with organic moieties has attracted recent significant attention. To produce surfaces with minimal or negligible interfacial oxide, these reactions generally use the well-defined H-terminated Si(111) as a starting surface. The reactivity of the H-terminated atom sites on Si(111)-H surfaces has generally been presumed to closely resemble the reaction chemistry of small molecule organosilanes, with (H3C)₃Si-H or (H3C)₃Si-H often cited as model compounds. The Si-H bond strength of H-terminated Si(111) surfaces has for example been estimated to be similar to the Si-H bond strength in (H3C)₃Si-H. Parallels between sterically non-demanding radical reactions on the H-terminated Si(111) surface and reactions of organosilanes such as (H3C)₃SiH can thus be reasonably well-anticipated and understood. For non-radical processes, however, it is not clear that the reactivity of Si(111)-H surfaces will be similar to those of organosilanes. The low-lying HOMOs and LUMOs which result from the band structure of the Si crystal can induce formation of either the one-electron oxidation or reduction processes of Si surface functionality. Such electronic stabilization would open up reactivity pathways on Si surfaces which are not accessible to organosilanes. For example, H-Si groups on porous Si surfaces have been reported to undergo exothermically induced two-step electron-transfer reactions that are not observed in organosilanes or on crystalline Si-H surfaces. Similarly, in ferrocenium (Fc⁺)-solutions of CH3OH, surfacess (H3C)₃SiH and under oxidative activation to form Si-O-CH3 bonds, whereas such reactivity is not observed for (H3C)₃SiH in CH3OH by any oxident available within the solvent stability limit of CH3OH. To evaluate the electron-transfer based reaction routes on Si surfaces, we report herein electrodechemical and chemical measurements of the redox processes of such surfaces. The comparison between the electrodechemical potentials of such functionalized surfaces and those of small molecule models reveals large differences in electrochemical activity between these two systems. We additionally show that conversion of Si-H groups on atom sites of Si(111) surfaces to Si-Si bonds shifts the potential for one-electron oxidation of the surface by over +2 V, converting surfaces that are thermodynamically oxidizable by air and other mild oxidants and into surfaces that are thermodynamically stable towards oxidation in most media. Finally, the electrodechemical information has been correlated with the electronic structure of such surfaces obtained from He photoemission spectroscopy, to produce a consistent framework for understanding the surface electronic and electronic properties of functionalized Si surfaces.

11:30 AM 16.9
Energy Level Alignment and Interfacial Chemistry of Pentacene Thin Films on GaN. John Joseph Uhrich and Thomas F. Kuech; Chemical Engineering, University of Wisconsin, Madison, Wisconsin.

Pentacene has recently shown to promise as a material for fabrication of organic thin-film transistors (TFTs), exhibiting high field-effect mobilities in both the single crystal and thin film morphologies. However, the performance of organic semiconductor devices such as TFTs can often be limited by the interfacial interaction of the organic material with its contact materials. We have proposed that GaN could make a favorable hole-injection contact to organic materials of high ionization potential due to its deep valence band with respect to the vacuum level. To evaluate this hypothesis, we studied the energy band off the pentacene/n-GaN interface using both ultraviolet and x-ray photoelectron spectroscopies (UPS and XPS). Studies were carried out using n-GaN which was grown on a sapphire substrate by metal organic vapor phase epitaxy (MOVPE). The GaN sample was degassed with organic solvents and then treated in concentrated HCl for 15 minutes ex-situ. No additional in-situ surface treatment was performed. The photoelectrons were carried out in an ultrahigh vacuum system with pressures of 1 x 10⁻¹¹ Torr. Pentacene was evaporated from a resistively heated boron nitride crucible in increments as small as 0.1 nm measured using a quartz microbalance in the adjoining sample preparation chamber. UPS and XPS were used to record deposition and to observe the evolution of the pentacene valence band structure and interfacial band bending. Our results show negligible dipole formation at the interface indicating that the pentacene/GaN interface may be accurately described using the electron affinity rule. Correspondingly, the resulting energy band offsets are in close agreement with those predicted from the individual bulk properties of pentacene and GaN, indicating that there is strong interfacial coupling.

SESSION 17: Spectroscopy and Dynamics at Interfaces
Chair: Antoine Kahn
Wednesday Afternoon, November 30, 2005
Room 302 (Hynes)

1:30 PM 17.1

Chemically resolved electrical measurements (CREM) provide unique solution to fundamental difficulties of nanoscale electrical analyses. The method, based on electron spectroscopy, uses energy-filtered ejected electrons as flexible internal electrodes. I-V curves, free of contact contributions, can be selectively derived for top and inner regions within nanoscale heterojunctions. Applied to self-assembled monolayers, rich electrical information is revealed, down to the atomic scale. The CREM approach is simple and general. It integrates several types of electrical measurements with well-established in-situ analysis capabilities. Applications to future miniaturized devices will be discussed.
Manish Dubey1, Irina Gouzman2, Steven L. Bernasek3 and Jeffrey Schwartz1, 1Department of Chemistry, Princeton University, Princeton, New Jersey; 2Space Environmental Section, Soreq NRC, Yavne, Israel.

Self assembled monolayers (SAMs) are widely used for modifying conductor and semiconductor surfaces for applications in the fields of electrical and biological devices. T-BAG (Tethering by Aggregation and Growth) has been shown to be a simple and reliable method to grow SAMs of alkylphosphonic acids on oxide surfaces [1]. Understanding the growth and structure of these SAMs is a key step for their successful implementation. The uniformity of SAMs in general is of great importance for their applications in microfabrication of devices and the presence of multilayer islands is undesirable; however, distinguishing SAMs from ultra-thin multilayers can be a challenge, especially for the surface characterization techniques. Here we present an original method that allows us to distinguish between monolayer and multilayer films of an alkylphosphonic acid on silicon oxide surfaces. This method is based on differential surface charge effects in X-ray photoelectron spectroscopy (XPS). Differential charging can be a problem for organic film characterization by XPS due to their poor conductivity; electron flood gun is commonly used to compensate for this charging effect [2]. A novel technique is suggested here to make use of differential charging to distinguish between self-assembled monolayers and ultra-thin multilayer organic films by the application of an external bias to the sample during XPS measurements. Application of either positive or negative dc electrical bias has been found to affect the carbon core-level (Cls) line shape and intensity for multilayer phosphonate films, whereas the line-shapes and intensities of all XPS lines measured for monolayer films were unaffected by such application in the 5 to 20 kV range. Differential charging therefore has been used to increase XPS resolution. The advantages of using differential charging to extract additional information from XPS spectra and dependence of this technique on the conductivity of the sample will be discussed. [1] E. L. Hanson, J. Schwartz, B. Nickel, N. Koch and M. F. Danisimov, J. Am. Chem. Soc., 2003, 125, 18074-18080 [2] K. Shahtali, L. Rubinstein, S. R. Cohen and H. Cohen, J. Am. Chem. Soc. 2000, 122, 4050-4062

Ultra-thin Metal Films in Molecular Electronic Devices. 
Jason J. Blackstock1, Duncan Stewart2, Douglas Osherberg1, Regina Ragan3, Zhiyoung Li3, Sehun Kim3 and R. Stanley Williams3, 1Quantum Science Research, Hewlett-Packard Labs, Palo Alto, California; 2Henry Samueli School of Engineering, UC Irvine, Irvine, California; 3Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

In ultra-thin film molecular electronic devices, the structure of any incorporated organic layer is strongly influenced by both the physical topography of the substrate (and, to a lesser extent, the organic layer), and the process used to form the second electrode. Our goal is to couple rigorous physical characterization with detailed electrical examination of such devices; at present, we are particularly focused on novel self-assembled monolayer/metal device structures. In our presentation, we first describe the physical characterization of ultra-thin Au and Pt metal electrodes, including UHV-STM imaging of the surface atomic configuration. Next, IR spectroscopy of organic monolayers deposited on these electrodes confirms that monolayer order and packing density are significantly enhanced by the ultra-thin surface. Finally, the second electrode is deposited by metal evaporation at controlled temperature, and the top organic/metal interface is subsequently examined using Ramanscopes. Based on this well-characterized vertical device structure, we present several techniques for fabricating electrically testable device geometries, with lateral dimensions ranging from the nanoscale to the micrometer, and present preliminary electrical temperature dependence and IETS data from these devices.

Electron Transfer Dynamics at Interfaces between Organic Thin Films and Metals Studied by fs Time-resolved Two-photon Photoelectron Spectroscopy.
Yoshiyasi Matsuoka1, Daisuke Ino2, Kazuya Watanabe1 and Noriki Takagi1, 1Institute for Molecule Science, Okazaki, Japan; 2RIKEN, Wako, Japan; 3U Tokyo, Chiba, Japan.

Electron transfer at interfaces between organic thin films and metals or semiconductors is an important process in various applications. When an organic thin film is in contact with a metal electrode, the localized electron system of an organic molecule interacts with inherently delocalized metal bands at the interface. The coupling strength between the two systems governs the energy alignment of the electronic states of the organic molecule with respect to the Fermi level of the metal and thereby electron transfer dynamics at the interface. The energy alignment and the nature of the interface are important factors for an understanding of the mechanism of electron transport in organic semiconductor devices. Tris(8-hydroxyquinoline) aluminum (Alq3) is an archetype molecule in applications to electronic devices such as organic light emitting diode. In this paper, we present the electronic structure and electron dynamics at interfaces between Alq3 thin films and noble metals. The electronic structures of Alq3 on Cu(111) and Au(111) surfaces are studied by using ultraviolet photoelectron spectroscopy and two-photon photoelectron spectroscopy (2PPE) spectroscopy. Purified Alq3 molecules were deposited on the metal surface in the UHV chamber. For time-resolved 2PPE measurements, second harmonic output power of a Ti:sapphire oscillator (pulse width: 20 fs at 800 nm) or a homemade non-collinear optical parametric amplification system (12 fs at 600 nm) was used. The work function decreases with increase of the coverage due to surface dipole of 5.1 eV along the surface normal. The ionization potential potential of the highest occupied state, 6.38 eV, does not depend on the metal substrates used in this study. The anion states of Alq3 adsorbed is created by photo-induced electron transfer from the metal substrates and are located at 2.85 and 3.71 eV above the Fermi level on Cu(111) and Au(111) surfaces, respectively. The full width at half maximum of the anion states is 0.2 eV on both the surfaces. Time-resolved 2PPE measurements show that the anion states, created by electron transfer from the metal decays with the lifetime of 31 ps on Cu(111) and about three times shorter on Au(111). The angle-resolved 2PPE and the coverage dependence of the lifetime of the anion state indicate that the electron transferred from the metal surface is localized at a molecule in the first layer. Thus, the ultrafast electron back transfer from the anion state of Alq3 in the first layer dominates over the electron hopping to the second layer. Accordingly, the electron transfer out of the interface layer is a low barrier for electron transfer in the current system. At the interface with the noble metals, the poor efficiency of electron transfer from the first to the second layer stems from the small coupling of the anion state with molecules in the second layer.

Dynamics of Electron Transfer at the Molecule-Metal Interface. Martin Wolf, Department of Physics, Freie Universitaet Berlin, Berlin, Germany.

The last few years have witnessed tremendous progress in the understanding of elementary scattering processes of excited electrons at surfaces and interfaces. In particular the advances in femtosecond time-resolved two photon photoemission (2PPE) spectroscopy provide direct insight into the dynamics of inter- and intraband scattering and coherent electron dynamics in surfaces at metals as well as electron transfer, localization and solvation processes at the adsorbate/solid interface. In this talk some recent developments and challenges in the field of ultrafast electron dynamics at surfaces based on time-resolved photoemission experiments will be discussed based on two examples: (i) Electron injection, solvation and trapping in thin layer metals at a surface step, with dynamics spanning from femtoseconds to minutes; (ii) ultrafast charge transfer dynamics of Cs2P/Cu(111) studied with time-resolved 2PPE and Resonant-Auger (GEM-TOF) spectroscopy; we will then also consider the collaboration with Boveniespen, C. Gaal, P. Kirchmann, P. Loukalou, J. Stähler, (Freie Universität Berlin) and V. Vijayalakshmi, A. Fölsch, W. Wurth (Universität Hamburg) is gratefully acknowledged. Surf. Sci. Rep. 52, 219 - 318 (2004); Appl. Phys. A 78, 125-247 (2004)

Unoccupied electronic states at the alkane/thiol SAM/Au(111) interface. Chad Lindstrom, Matthias Muntwiler and Xiaoyang Zhu; Chemistry, University of Minnesota, Minneapolis, Minnesota.

We investigate the electronic structure and electron dynamics at the alkane(thiol)/Au(111) interface using femtosecond two-photon photoemission (2PPE) spectroscopy. Alkanethiol molecules can adsorb on Au(111) in multiple phases: a physisorbed lying down phase with the S-H bond intact, a chemisorbed lying down phase, and a chemisorbed standing-up phase (i.e. self-assembled monolayer) at high coverage. The formation of the chemisorption S-Au bond is evidenced by the appearance of a non-dispersive σ* antibonding state in 2PPE. In addition to the localized σ* antibonding state, we also observe a delocalized, image-like resonance confined to the SAM/Au interface. This resonance lies near the vacuum level and results from electron confinement by the image like potential on the metal side and a tunnelling barrier on the film side due to the bandgap of the alkyl chain. The interpretation of such an interfacial resonance is supported by the observation that the ultrafast lifetime of this resonance is nearly independent of molecular length of the SAM. The possible role of such interfacial states and resonances on electron transport across SAM/Au interfaces is discussed.
Conjugated polymers are promising materials for the next generation of optoelectronic devices. In general, many conductive polymers are either good electron or hole transporting materials. To create materials having both good electron and hole transporting capability, different polymers are often blended together, resulting in materials having improved performance in both light-emitting diode (LED) and photovoltaic (PV) applications. However blends of different polymers often undergo phase-separation. Such phase-separation can have consequences for the optical and electronic properties of the blend. To gain further insight into such blends, and in particular to study the electronic properties of the interfaces between the different phase-separated domains within a blend, we have developed a scanning near field optical microscope (SNOM) coupled to a time correlated single photon counting (TCSPC) system. This provides direct information on the nano-scale electronic process that occur over length-scales of 50 to 100 nm with a time-resolution of 50 ps to 2 ns. As we show, our system permits us to gain detailed information about the local composition and morphology of complex phase-separated device-applicable polymers. We have concentrated our efforts by using TCSPC SNOM to study a prototypical system comprising of two polyfluorene polymers; namely poly(9,9-dioctyfluorene) [F8] and poly(9,9-diocetylfluorene-alt-benzothiadiazole] [FSBT]. In this particular system, excitation is made into the F8 component of the blend, which transfers to FSBT, via dipole-dipole coupling. The spectral emission characteristics of F8 and FSBT are very different, and thus by imaging the fluorescence emission from both F8 and FSBT, we can study the relative efficiency of energy and charge transfer of polymer mixing. We determine strong spatial variation in decay lifetime for both F8 and FSBT across the surface. Furthermore we provide evidence for an interface region between the blend components in which energy and charge transfer is relaxed. Results highlighted the strongly non-equilibrium structure of such phase-separated systems. We have also used our TCSPC SNOM system to investigate the consequences of mixing the polymer F8 into the optically inert polymer poly styrene (PS). Such films are also characterised by a strongly phase-separated morphology, comprised of PS and F8 rich phases. We have mapped such films, measuring the sample topography, laser transmission and fluorescence lifetime. We find that the PS rich phase appears to act as an encapsulation medium for F8 molecules trapped within it, making them less sensitive to photo-oxidation. The effective dilution of F8 molecules within the PS phase is also likely to hinder excitation migration to non-radiative defects. As a result of this, we find that the F8 emission from the PS rich phase is characterised by a significantly longer fluorescence decay lifetime.

SESSION I8: Metal-Molecule and Semiconductor-Molecule Interfaces
Chair: Kazuhiko Seki
Thursday Morning, December 1, 2005
Room 302 (Hynes)

8:00 AM AM I8.1 Fundamental Interface Issues in Electronic Devices Based on Molecular Assemblies. David L. Allara, Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Molecular Monolayer chemistry has developed to the point that a variety of molecular surface structures can be assembled on metal, semiconductor and dielectric substrates. In the attempts to utilize these structures for device applications, severe demands have been placed on the chemical and physical characteristics of the interfaces that provide new challenges and issues. Both the chemical integrity of the substrate/molecule interface and the associated molecular packing can profoundly affect electron transport characteristics while the interface chemistry and metal morphology of vapor-deposited metal top contacts can play critical roles in controlling the overall device performance. This talk will describe selected examples from recent work in our lab and with collaborators in which we have characterized substrate/molecule and molecule/deposited metal interfaces using multiple surface science probes, ranging from in-situ XPS, IR, AFM and ToF-SIMS to grazing incidence x-ray diffraction and near edge x-ray absorption spectroscopy. Examples include illustrations of problems with side reaction chemistry in isocyandate (nitrilotri)urea/Pd and Pd interfaces, severe reconstructions in GaAs/molecule interfaces and complexities in film morphologies and interface chemistry in vapor deposited top metal contact overlayers.

8:30 AM AM I8.2 Dijt vu? Importance of Interfaces and Contacts for Molecule-Based Electronic Devices. David Cohen, Materials and Interfaces, Weizmann Institute of Science, Rehovoth, Israel.


9:00 AM AM I8.3 Spectroscopic and Electrical Characterization of Buried Metal Interfaces: Metal-Molecule-Silicon Structures. Laura Richter*, Curt A. Richter* and Christina A. Hacker*, Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland; * Semiconductor Electronics Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

We present the results of experiments investigating the role that top-metal/monolayer interactions play in determining the electrical properties of molecular device structures. Direct-current and ac capacitance-voltage measurements were used to characterize capacitor structures. These devices were formed by attaching C18 alkane monolayers directly on (a) Si-substrates (via octadecaneol reactions), (b) native SiOx, or (c) thin thermally grown SiO2 (from octadecyltrichlorosilane: OTS). The IR transparent substrates allow the electrical results to be directly correlated with the results of a novel backside FTIR technique that allows the vibrational spectra to be obtained from non-chemicalized structures. Three top metals, Au, Al, and Ti, were studied. FTIR indicates minimal interaction between Au and Al and the monolayers formed on Au while Ti strongly interacts with these films. The electrical measurements support models with minimal penetration of the Au and Al on the OTS/oxide films, while Ti appears to reduce the dielectric thickness of the alkane. Surprisingly, the alkoxyl films directly attached to H-terminated Si via an ether linkage are displaced by all three metals.

9:15 AM AM I8.4 Control of the Electrical and Adhesion Properties of Metal Electrode / Organic Interfaces with Self-assembled Monolayers. Kibum Cho and Jeong Ho Cho; Chemical Engineering, Pohang University of Science and Technology, Pohang, South Korea.

With the aim of improving the electrical and adhesion properties of a metal electrode / organic interface, we tested self-assembled...
monolayers (SAMs), which react with the metal electrode, and compared the results to those obtained using an inactive SAM. Silver and indium (in oxide [ITO], already used in light emitting devices, were deposited onto the SAMs, which have different chemical reactivities with metal atoms. Silver atoms deposited on the SH-modified surface were found to bind strongly to the terminal sulfur atom as a result of the reaction between sulfur and silver. In the case of the ITO films on SAMs, indium atoms on Cl- and CF3-modified surfaces form reactive metal contacts because the terminal chloro and fluorine bonds to the indium atoms. In contrast, silver and ITO deposits on SH-modified surfaces did not react with the SAM. The contact resistance of the reactive metal contact was found to be much lower than that of the unreactive metal contact, which is due to the reaction-induced dipole layer formed at the interface between the metal contact and the SAM surface. In the reactive metal contact, the dipole moment of the organo-metallic complex is an important parameter in determining the electrical properties of the metal-organic contact. Acknowledgement. The authors would like to thank the National Research Laboratory Program (Ministry of Science and Technology of Korea), the Advanced Engineering Biotechnology Research Center at POSTECH, and the Ministry of Education of Korea for its support through its BK21 Program.


Soft contact lamination has recently shown its potential as an interesting processing method for organic electronic devices. The process of soft contact lamination involves two components. A bottom component typically consists of an active material(s) on an appropriate substrate or the layer stack and has metal contacts deposited onto it. Upon contacting the two components, van der Waals bonding holds the two parts together. In this way, top contacts can be deposited on a variety of materials in a non-invasive manner. Using this technique, one can fabricate organic thin film transistors, light emitting devices and photovoltaics. In addition, one can imagine using this technique to produce device geometries not possible using conventional materials and processing methods: the top contacting layer(s) can serve as a substrate for additional layers beyond metal contacts. For instance, mutually soluble materials can be made into bilayer devices by spin coating one material onto the bottom substrate and the other onto the top substrate. The resulting lamination produces the desired bilayer device. Furthermore, using this technique water soluble polymers (such as PEDOT:PSS) can be laminated onto water sensitive materials. We will discuss a variety of device structures produced utilizing this interesting feature of soft contact lamination.

9:45 AM 18.6 Reduction of Electrical Damage due to Au/Pentacne Contact Formation by Introducing Ar Gas during Au Evaporation. Koshi Okamura1, Tomoaki Sawabe2, Akihisa Hashimoto2, Masakazu Nakamura3 and Kazuhiro Kudo4; 1Graduate School of Science and Technology, Chiba University, Chiba, Japan; 2Department of Materials and Mechanical Engineering, Faculty of Engineering, Chiba University, Chiba, Japan.

Obtaining an ideal metal/organic contacts has been an important subject not only for the study of macroscopic electrodics but also for that of organic macroscopic devices. Characteristics of metal/organic contacts change depending on the deposition conditions of metals, since the metal atoms migrate deep into the organic layer and form composites or defects. A Au top contact is widely adopted for drain and source electrodes in pentacene-based organic field effect transistors (OFETs), and it had been believed that a conventional Au vacuum deposition technique formed nearly ohmic contact with relatively low resistance after further treatments. However, atomic-force-microscope potentiometry (AFMP) measurement has shown the existence of significant potential drops near electrodes where Au was deposited on pentacene films, which suggests that the conventional Au deposition could deteriorate electrical properties of pentacene films. In this study, we have demonstrated the reduction of the electrical damage in a simple Au/pentacne/Al diode structure by filling the Au evaporation chamber with argon gas. The results are consistent with a model of four orders of magnitude in low voltage ohmic regions. Quasi-static capacitance-voltage measurements showed no difference among the samples of which Au layers are deposited at different Ar pressures ranging from 0.5 to 8.7×10⁻³ Pa, which means that the carrier concentration is constant and independent of the condition of the Au deposition. These results indicate that reduction of the kinetic energy of Au during its deposition decreases the destruction of the pentacene and improves the carrier mobility. Dependence of hole injection barrier on the kinetic energy of Au will be also discussed. This work was supported by Grant-in-Aid for Scientific Research (No. 16300141) and by ‘21st Century Center of Excellence Program: Frontiers of Super-Functionality Organic Devices’ from the Ministry of Education, Culture, Sports, Science and Technology of Japan. [1] M. Nakamura, N. Goto, N. Ohashi, M. Sakai, and K. Kudo, Appl. Phys. Lett. 86, 122112 (2005); [2] B. Heil, M. Fiebig, G. Grabhorn, T. Ligonozoc and D. Cahen, Phys. Chem. Chem. Phys. 6, 4538 (2004); [3] M. Curry, D. Arrington, S.C. Streeta, F.T. Xu and J.A. Barnard, J. Vac. Sci. Technol. A 21, 234 (2003).

10:30 AM 18.7 Electronic Properties of Molecular Nanostructures. Dominique Vaillancourt, IEMN-CNRS, Villeneuve d’Ascq, France.


11:00 AM 18.8 Molecular Rectifying Diodes based on Aluminum /4-hydroxy-4-biphenyl carboxylic acid / p-silicon Junction. Debashish Knij1, Sridive Bala1, Rajendra Atthai1, Kody Varaharamyan1, David James2 and Pedro Doreas2; 1HM/Chemistry, Louisiana Tech University, Ruston, Louisiana; 2ECE, Purdue University West Lafayette, Indiana.

The scaling of silicon based microelectronic devices to nanoscale (MoSFTs with gate length <40 nm) is prevented by the laws of quantum mechanics and limitations of fabrication techniques. Molecular electronics is one of the approaches to develop such nanoelectronic devices, where fabrication of metal-metal/molecule and metal/molecule-semiconductor junctions and their characterizations have been performed. However, most of these molecular electronic devices demonstrated to-date are based on metal/molecule/metal junctions that have used self-assembled monolayers of alkan and aromatic thiol on gold substrates. In contrast, a very few molecular electronic devices with metal/molecule/ semiconductor junctions have been experimentally demonstrated in which the molecule is bound to silicon or GaAs (semiconductor) substrates. We report a p-n diode based on an aluminium/4-hydroxy-4-biphenyl carboxylic acid/ p-silicon junction. The device was fabricated using self assembly and the top contact was formed using thermal and e-beam evaporation of aluminium. The surface of the substrate was characterized by contact angle measurements and RAIRS for the presence of the molecule. Conductance measurements of the junction were carried out using a probe station and the barrier height is calculated based on the current-voltage measurements. Computational studies using Density Functional Theory are underway to predict energy levels available for conduction as well as energy barriers for electron transfer between electrodes through the molecule.

11:15 AM 18.9 How do electronic carriers cross Si-bound alkyl monolayers? Adi Salomon1, Olga Girshvitz1, David Cahen1, Till Bocking2, Calvin Chen2, Louise Amy3 and Amir Kahn1; 1Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; 2Department of
A key issue in (bio)molecule-based electronics is that of the mechanism(s) of electron transport across molecules. Measuring electronic transport across molecules requires contacting them electrically. We can form electrode/molecule/electrode configurations for such measurements by chemically binding molecules to an electrode surface and making a second contact to the other side of the molecule(s) in a soft, non-destructive manner. To be able to use such configurations for unraveling how electrons cross molecules we need to know the effects of the contacts on the electronic transport. This, in turn, requires knowledge of the alignment of the surface-bonded orbitals relative to the Fermi levels of the electrodes. Success in this endeavor therefore requires a combination of experimental efforts, coupled to a well-controlled experimental system. Here, we report results of such experiments on a suitable model system that allowed us to draw clear conclusions concerning the title question. Insights of this type will not only help to design devices with defined electronic properties, but they may also help to understand charge transport phenomena in biologically relevant systems. We choose to work on Si-C bound alkyl chains//Hg junctions, because of our ability to prepare high-quality samples. The use of a semiconductor as electrode gives, moreover, some control over the position of the electrode Fermi level relative to the molecular energy levels and enables us to distinguish between electron and hole transport through these alkyl chains, as we showed earlier.

Remarkably, transport measurements for st-C bound alkyl chains show a bimodal dependence on forward bias voltage, fitting to two different mechanisms; each dominating in a different voltage range. At low voltages the current depends strongly on temperature but not on molecular length. This behavior fits with transport over a barrier inside the semiconductor, as the current-voltage factor. At higher voltages the current decreases exponentially with molecular length, suggesting that the current is limited by tunneling through the organic layer. The finding that this system allows such clean and clear distinction between those two transport mechanisms was predicted but not found experimentally (e.g., with SiOx as the insulator). Its occurrence here indicates that the alkyl monolayers on Si-C alkyl//Hg devices act as ideal insulators. By combining electronic transport and photoemission experiments we can estimate the tunneling barrier for electron (hole) transport through the alkyl 
chains to be 1.5 (1.9) eV, with effective masses of 0.29 (0.28) m_e, the implications of which we will discuss.

11:30 AM *18.10 Ballistic Emission Electron Microscopy Studies of Molecular Diodes. Julia W. P. Hsu1, Wenjie Li2, Yong Jun3, Karen L. Kavanagh4, Carolyn M. Matake1, Xiaoyang Zhu4, A. Alec Talin3, W. Miles Cliff4, Sergey Faleev4 and Francois Leonard4. 1Sandia National Laboratories, Albuquerque, New Mexico; 2Simon Fraser University, Burnaby, British Columbia, Canada; 3University of Minnesota, Minneapolis, Minnesota; 4Sandia National Labs, Livermore, California.

Interfaces govern the transport behavior across dissimilar materials. However, many of these interfaces are buried and difficult to study experimentally. In this talk, I will describe the use of ballistic emission electron microscopy (BEEM), an application of scanning tunneling microscopy (STM), to examine the electronic properties at the interface between a molecular layer and the electrodes. The molecular diodes consist of an alkanethiol or alkanedithiol monolayer formed on (001) GaAs chips with Au as the top electrode. The monolayers have been characterized using X-ray photoemission spectroscopy and ellipsometry. In these devices, the molecules are sandwiched between the two electrodes and are not easily accessible. BEEM is one of the very few experimental techniques that are capable of measuring the local transport through such buried interfaces. Electrons that are transmitted ballistically across the thin Au layer, through the molecular layer, and into the GaAs conduction band are detected. The BEEM current is measured as a function of the tip bias and thus, the local interfacial barrier height is determined without applying a bias across the metal-semiconductor interface. We found that the presence of the molecule dramatically increases the BEEM threshold voltage and displays an unusual transport signature in octanethiol diodes as compared to reference Au/GaAs diodes. Calculations were performed to address the role of the molecular layer at the interface. We will examine the difference between alkanethiol and alkanedithiol molecules, the chain length dependence, and the method for depositing top Au contacts (e-beam evaporation vs. nanotransfer printing). In addition, current-voltage and BEEM measurements, scanning Auger microscopy and spectroscopy have been used to characterize the diodes. Research at SFU supported by the Natural Science and Engineering Research Council of Canada. Work done at Sandia is part of a multi-partnership program from DOE’s Center for Integrated Nanotechnology (CINT). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

SESSION 19: Organic Semiconductors: Growth and Transport
Chair: Yoshiyasu Matsumoto
Thursday Afternoon, December 1, 2005
Room 302 (Hynes)

1:30 PM 19.1
Growth, Geometric and Electronic Structure of Organic Nanostructures: What’s the Interface got to do with it? Michael G. Ramsey, Institute of Physics, Karl-Franzens-University, Graz, Austria.

Organic devices consist of a multiplicity of layers making the understanding of the organic interfaces and organic film growth a technologically important issue. On the one hand details of the interfaces are important for charge injection while the molecular/crystal/crystallite orientation and film morphology determine charge transport, and light emission/absorption - for optimum performance these key factors need to be tailored for the specific device applications. Here the chain-like conjugated molecules -sexiphenyl (6P), one of the first blue light emitting diodes, and sexithiophene (6T), the first OFET material with exploitable characteristics, will be considered. Their growth from (sub)monolayer to device relevant film thicknesses on a wide range of in- and ex-situ laboratory and synchrotron based techniques, on substrates ranging from clean and modified single crystal metals, semiconductors and oxides will be presented. The examples will stress that the atomic details of the substrate surface can have a profound influence on all important aspects of the molecular films. These include the electronic properties through the interface dipole set-up in the first monolayer and the electronic structure of the molecules themselves due to conformational changes induced by packing forces. Secondly, the interactions of the molecules with the substrate determines the molecular geometry with respect to the contacts, important for both charge transport and light emission/absorption. Thirdly, this profoundly influences the organic film morphology for instance determining whether a melts form or layer-by-layer growth is promoted. These well defined organic films will then be used as substrates to explore the growth of organics on organics and inorganics on organics. The former will illustrate that ordered organic films act as good templates for the growth of oriented organic heterostructures. The electronic level alignment between the organic layers is seen to be unaffected by the relative orientation of the molecules suggesting that no dipole is formed at the organic/organic interface. For inorganic growth on organics the measurements of band alignment is shown to be problematic as, amongst other things, the inorganic disturbs the conformation and thus the ionisation potential of the molecules at this interface. Finally it thus allows results of molecular films grown on laterally nano-patterned substrates will be presented. These are relevant for growth on ill-defined substrates and for the future of scaling down organic structures. Supported by the Austrian Science Foundation (FWF).

2:00 PM 19.2
Molecular origin of shallow trap states in pentacene thin films. Joo H. Kang1, Demetrio da Silva Filho2, Jean-Luc Bredas1 and Xiaoyang Zhu1. 1Department of Chemistry, University of Minnesota, Minneapolis, Minnesota; 2School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Pentacene is one of the most promising organic semiconductors for thin-film transistors. Transport measurements in the past have established the presence of shallow traps but their origins have remained a mystery. Here we show that shallow traps in vacuum-deposited crystalline pentacene thin films result due to local defects resulting from the sliding of pentacene molecules along their long molecular axis, while two-dimensional crystalline packing is maintained. Electronic structural calculation confirms that these shallow defects are shallow charge traps with energies less than 100 meV above (below) the valence band maximum (conduction band minimum).

2:15 PM 19.3
Structure of Ultra-thin Pentacene Films on a Silicon Dioxide Dielectric. Sandra E. Fritz1, Michael F. Toney2, Demetrio da Silva Filho3, C. Daniel Frisbie1, Michael D. Ward1 and Jean-Luc Bredas1. 1Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; 2Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; 3Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator.
We report Grazing Incidence X-ray Diffraction (GIXD) of ultra-thin pentacene films thermally evaporated on an amorphous silicon dioxide dielectric. In particular, we report the crystal structure of the first few layers of pentacene adjacent to the dielectric layer, where charge carrier transport is believed to occur in an organic thin film transistor (OTFT). From GIXD, two separate polymorphs are observed: a "monolayer" phase in pentacene films with sub-monolayer thicknesses and a "thin-film" phase in pentacene films with thicknesses near 200 Å. The "monolayer" phase has a 2-dimensional rectangular cell wherein the long axis of the pentacene molecules is perpendicular to the a-b crystal plane, or the dielectric surface. In the "thin film" phase, the long axis of the pentacene molecules is slightly tilted with respect to the dielectric surface normal. Furthermore, for the "thin-film" phase, the angle gamma, (γ), between a and b in the crystal structure has taken on a non-90° value forcing the structure into a triclinic lattice. This polymorphism is observed in the first 12-15 layers of pentacene adjacent to the dielectric and is gradual. From GIXD of various thicknesses between sub-monolayer and 200 Å, we can calculate a gradual shift in gamma from 90° to 90°, along with a gradual tilting of the pentacene molecules as film thickness is increased. The structural changes are manifested in differences in electronic structure for the pentacene films, as determined by semi-empirical calculations. This in turn has important implications for interfacial transport in OTFTs.

3:30 PM 19.6
Semiconductor/Insulator Interfaces in Organic Thin Film Transistors. C. Daniel Fisk,1 Chen Eng & Matt Sc, University of Minnesota, Minneapolis, Minnesota.

It is generally appreciated that the structural features of organic semiconductor/insulator interfaces are crucial to the performance of OTFTs, but detailed structural investigations of these interfaces are just emerging. This talk will have two parts. First, we will discuss our recent investigations of pentacene/insulator interfaces by grazing incidence X-ray scattering with monochromatic X-rays. We have determined the crystal structure of the pentacene layers next to the dielectric and have we found evidence of structural defects of various kinds, which will be discussed. These structural defects will significantly impact the transport performance of the pentacene films in OTFTs. In the second part of the talk, we will discuss the use of polymer electrolyte gate insulators to induce extremely high charge densities in organic semiconductor films. The polymer electrolyte-gated OTFTs have turn on voltages less than 1 V. We will discuss how these devices can be used to examine electrical transport at very high carrier densities.

4:00 PM 19.7
Electrical and Structural Properties of the Accumulation Layer in Pentacene Thin Film Transistors. Byoungnam Park1, Soonjoo Seo1, Fan Zheng2, Franz Himpel1 and Paul G. Evans3.

1University of Wisconsin-Madison, Madison, Wisconsin; 2Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; 3Materials Science Program, University of Wisconsin-Madison, Madison, Wisconsin;

Understanding the structure and electrical properties of the accumulation layer in organic field effect transistors is both a fundamental problem and also the key to improving transistor performance. Mobile charge carriers are confined to this layer near the gate insulator, which is typically only a few molecules thick. Transistors formed from a single layer of semiconducting molecules are sensitive probes of the charge transport in the accumulation layer. In-situ electrical measurements of pentacene FETs during pentacene deposition onto a bottom-contact transistor structure with a silicon dioxide gate dielectric have allowed us to study the formation of a transistor channel direction. The geometrically confined structure and passivation of pentacene islands plays a crucial role in the charge transport of mobile carriers. Current starts to flow at the percolation threshold where the electrical channel forms and the pentacene islands come into contact in 2D. The field effect mobility of a monolayer scale pentacene transistor (10−5 cm2/V·s to 10−4 cm2/V·s) is much lower than that of a typical thick film transistor. The mobility can be independently measured using van der Pauw sheet resistance measurements, which do not depend on contact resistance or device geometry. The mobility in a film 1.4 μm, 0.085 cm2/V·s, is much higher than that of two-contact FET. This indicates that contact resistance between metal electrodes and the pentacene layer dominates the electrical properties of monolayer transistors. Near-edge x-ray absorption fine structure measurements are used to examine the molecular orientation in a submonolayer pentacene film. The tilting angle of long axis of pentacene molecule relative to the surface normal in a submonolayer pentacene film is different from that of bulk.

4:15 PM 19.8
Organic Field-effect Transistor Channel Perturbation at Two Surfaces through Analyte Binding and Dielectric Charging. Howard Edan Katz1, Cheng Huang1, Jia Huang1, Kevin See1, Joseph Miraglia1 and Alan Becknell2.

1Materials Science/Engineering and Chemistry, Johns Hopkins University, Baltimore, Maryland; 2Applied Physics Laboratory, Johns Hopkins University, Laurel, Maryland.

Field-effect transistors, including those based on organic semiconductors, are typically gated via an electrical potential applied from a gate contact across a dielectric to the buried interface between the dielectric and the semiconductor. We are presently investigating and utilizing additional gate potentials arising from dipolar interactions at both the buried and free semiconductor interfaces. Chemisorption of polar analytes leads to changes in channel current that can be rationalized by an electrostatic model, including dipole fields and binding constants, that agrees with results reported from electron spectroscopy. Analyte binding constants >1000 M(-1) can be prepared for suitably functionalized semiconductors. The loading of the gate dielectric can occur by multiple mechanisms. Experiments that separate bulk and interface effects include the formation of self-assembled monolayers at the interface and measurements of surface potential and capacitance both at the dielectric bilayer and the dielectric itself. Charging can occur at both buried and free interfaces, and can be in electret and ferroelectric polymers. Order-of-magnitude current changes are observable from both chemisorption and dielectric charging. Utilization of these effects for
sensing of analytes relevant to national security and for new approaches to plastic electronic logic elements will be discussed.

4:30 PM I0.9

Assessing the fundamental limits of the charge carrier mobilities in organic semiconductors is important for the development of organic electronics. A crucial component of this effort is the ability to both grow and characterize ultra-pure, fully ordered molecular crystals for measurements of intrinsic charge transport. Rubrene (5,6,11,12-tetra-phenyl-tetracene) has shown to be an interesting organic molecular crystal. In particular, the charge mobility in rubrene single-crystal OFETs can be quite large, with reported values in the range from 5 to 30 cm2/Vs. Despite the high charge carrier mobilities measured in rubrene, the charge transport in this material, as in many other organic molecular crystals, is still limited by extrinsic effects. Factors that can hinder charge transport include impurities and structural defects such as dislocations, vacancies, and small angle grain boundaries. Improved characterization of the crystalline quality of rubrene is expected to lead to a better understanding of the role of defects on charge transport. Using synchrotron X-ray diffraction and high-resolution electron microscopy, we have characterized the crystalline imperfections present in current, state-of-the-art single-crystals of rubrene. We show that dislocations and grain boundaries, which may limit charge transfer, are present in the crystals. The microscopy technique may provide a means of imaging defects induced by the application of electrodes, which is essential for understanding factors that may limit the measured charge carrier mobilities.

4:45 PM I0.10
Modification of Self-Assembled Monolayers on Electrodes of Organic Thin-Film Transistors. Nobuya Hiroshita1,2, RyoTarou Kunishiro1,2, Katsumi Tanigaki1,2, Hiroshi Ishii1, Shinya Takahashi1 and Masanori Yamashita1; 1Department of Physics, Graduate School of Science, Tohoku Univ., Sendai, Japan; 2CREST, Japan Science and Technology Agency(JST), Kawaguchi, Japan; 3Research Institute of Electrical Communication, Tohoku Univ., Sendai, Japan; 4Department of Chemistry, Graduate School of Science, Tohoku Univ., Sendai, Japan.

Organic field effect transistors (FETs) are important considering future applications to electronic devices, and have intensely been investigated. In order to improve the properties of organic FETs, the methodologies, have not still been established. Especially, one of the most important key issues is the interface problem between organic thin films and metal electrodes, and this is now drawing intense attentions of many researchers. It is acquainted that the metal/organic interfaces are one of most important factors of controlling organic FET properties with a similar accuracy to that of the conventional semiconductor/insulator/metal interfaces. Using self-assembled-monolayers (SAMs) is a well known method for such a surface modification for providing microscopically good interface regulations. SAMs are the ordered monolayer assemblies that can be formed spontaneously using the adsorption of a surfactant with its headgroup to a substrate. Such efficient surface modifications have been reported to be achieved on SiO2 gate-insulators using silane molecules and on gold electrodes using thiol ones. In the case of gold electrodes, the introduction of oxygen, as a functional groups, is very effective for improving the device characteristics. Using self-assembled monolayers, interesting and predictable electrical properties have been observed. The hole carrier mobility in pentacene-FETs can be increased by the SAMs modifications when the optimized preparation conditions are employed. Organic FETs can be successfully processed depending on the end functional-substituents of benzene thiols. The changes in Vth observed in the present experiments are considered to be explained in terms of the charge transfer occurring from SAMs to pentacene or vice versa in the interfaces, which are also very important in addition to the work functions(φ) to be modified with the SAMs treatments. This technique may provide a simple but very convenient method for controlling the Vth values with improvements of carrier injection efficiency and consequently will become a good device fabrication technique of organic FETs in a low price with good quality in the near future.

SESSION I10: Poster Session
Chair: Xiaoyang Zhu
Thursday Evening, December 1, 2005
8:00 PM
Exhibition Hall D (Hynes)

I10.1
Alkalai Metal Doping and Energy Level Shift in Organic Semiconductors. Huanjun Ding and Yongli Gao; Physics and Astronomy, University of Rochester, Rochester, New York.

We have investigated Cs and Na doping in copper phthalocyanine (CuPc) and tris-(8-hydroxyquinoline) aluminum (Alq) using photoemission and inverse photoemission spectroscopy. We observed valence and core level spectra changes at different doping levels, and found that the doping induces the energy level shift that can be seen as in two different stages. The first stage is predominantly due to the Fermi level moving in the energy gap as a result of the doping of electrons from the alkalai metal to the organic, and the second stage is characterized by the significant modification of organic energy levels such as the introduction of a new gap state, new core level components, and change of the binding energies. Furthermore, we observed the energy level shift in the first stage depends in a semi-logarithmic fashion on the doping concentration, whose slope cannot be explained by the conventional model used in inorganic semiconductors. These results indicate that the molecular nature and strong correlation must be considered for doping in semiconductor. We have investigated the photoemission spectra of the interface formed by depositing Au on Cs-doped and Na-doped Alq film using ultraviolet and X-ray photoemission spectroscopy (UPS and XPS). The initial Au deposition quenches the Alq gap state caused by the alkali metal doping. Further Au deposition gradually modifies the energy levels opposite to that induced by alkali metal doping, especially the highest occupied molecular orbital (HOMO) that shows approximately full recovery to the pristine Alq position. However, the recovery is only partial for other levels, most noticeably C1 5s core level. The results indicate that the gap state and energy level positions can be decoupled in the organic semiconductors, and that it is possible to fine tune the electronic structure by selective doping in the interface region.

I10.2

Organic thin film transistors OTFTs are being developed for applications where large area coverage and low cost are required. The current delivered by the OTFT is inversely proportional to the channel length L, which motivated studies of OTFTs with submicron channel lengths. In addition, there has been increasing interest in molecular electronics, which requires samples where two metal electrodes are placed very close to each other. Recently organic transistors with channel lengths down to 30 nm have been realized [1]. To further explore the scaling limit of organic transistors, we fabricated transistors with channels of sub 10 nm using a state-of-the-art e-beam lithography. In order to avoid current leakage, a side guard structure was employed [2]. We used pentacene as the active layer and tested various deposition conditions to optimize the device characteristics. From the measurements of sub 10 nm channel length pentacene transistor exhibited good gating, with both the linear and the saturation regime observed. In addition, the devices featured a threshold behavior, which has not been observed on microwa scale organic transistors. We discuss the possible origins of this behavior. [1] Y. Zhang, J. T. Petta, S. Ambily, Y. Shen, D. Ralph and G. G. Malliaras; Adv. Mater. 2003, 15, 1632. [2] L. Wang, D. Fine, T. Jung, D. Basu, H. von Seggern, and A. Dodabalapur, Appl. Phys. Lett. 2004, 85, 1772.

I10.3
Design and Synthesis of Perfluorinated Carboroles and Phosphine Derivatives for n-Channel Organic/Molecular Semiconductors. Haiyung Liu, Jinhao Gao, Chris K. Chang and Bing Xu; Department of Chemistry, The Hong Kong University of Science & Technology, Hong Kong, NA, Hong Kong.

This paper will present the design, synthesis, and fabrication of thin films of perfluorinated phorphine, corroles, porphyrins, and their correspondent polymers as potential n-channel organic semiconductors-the crucial materials for building complementary logic elements in organic/molecular electronics. Introducing the strong electron-withdrawing fluorine moieties into corroles, phorphine, and porphyrins will modulate several properties—e.g., stability, solubility, volatility, and energy levels of molecular orbitals of the corroles, phorphine, and porphyrins. Investigation of thin films of these new systems will improve fundamental understanding of electrogative substitution effects on conjugated systems, providing guidance to design
new electro-optical materials, and ultimately contribute to the creation of new materials for electro-optical applications (e.g., photodetectors and field-effect transistors) and molecular electronic devices.

110.4 Mechanical Properties and Interfacial Structures of Dendrimer-Mediated Thin Films. Fengxi Xu, Long Li, Judith C. Yang and John A. Barnard; Department of Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Dendrimers are three-dimensional, globular, highly-branched macromolecules made up of a central core surrounded by repetitive units all enclosed by a terminal group shell. They can be synthesized with highly controllable sizes (they are determined by the core type, extent of branching, and nature of the end groups, in the range from a few to several tens of nm in diameter. Dendrimers also assemble into monolayers on technologically interesting substrates using simple de-wetting, and rinsing procedures. In this condensed monolayer phase dendrimers can act as surfactants mediating the growth of ultra-flat films, and create novel nanomechanical, adhesive, frictional, and tribological behavior [1,2].

We have recently reported on the dramatically enhanced quality (superior flatness and adhesion) of metal films deposited on dendrimer monolayers [3]. Different tribological responses are also observed in dendrimer-mediated metal thin films. The physical intermixing between dendrimer and metal was proposed to explain the distinct physical, mechanical, and chemical properties of the resulting dendrimer-based nanocomposites [4]. To better understand substrate/dendrimer monolayer/substrate interactions, we designed an experiment to better understand the intermixing between metals (in this case Au) and dendrimer monolayers as a function of deposited metal film thicknesses by AFM, TEM and XPS. The intermixing between Au and the dendrimer monolayer was directly observed to be 1.7 nm by AFM. In addition, the effect of the metal layer thicknesses were also used to conclude that Au is absorbed by the dendrimer layer up to an equivalent thickness of Au of 2 nm and beyond this a Au film grows on top of the Au saturated dendrimer-Au nanocomposite. [1].


110.5 The Hole Injection of Organic Thin Film Transistor (OTFT) by Inverting Thin Lithium Fluoride (LiF) Layer Between Pentacene Layers. Dae Sik Park, Won Chul Jang, In Sung Jung, Seong Hong Kim, Kwang Ho Jeong and Chang Nam Whang; Institute of Physics and Applied Physics, Yonsei University, Seoul, South Korea.

The pentacene-based organic thin-film transistor (OTFT) with inverted lithium fluoride (LiF) layer (1nm) between pentacene layers and metal cathode was successfully fabricated in situ with all in-situ processes, and improved electrical properties was obtained. The fabricated device structure is gold (30 nm)/pentacene/LiF (1 nm)/pentacene/SiO$_2$ (100 nm)/poly-Si (substrate). The ratio of upper pentacene layer thickness and lower pentacene layer thickness was varied, and the effect of the LiF layer thicknesses with 100 nm. As varying the ratio of two pentacene layer thicknesses, the field effect mobility and threshold voltage was affected. The field effect mobility increased when LiF layer was near drain and source, and decreased when LiF layer was near SiO$_2$ layer. In addition, the threshold voltage decreased as LiF layer approached near drain and source. These phenomena could be caused by tunneling current through the thin LiF layer and analyzed by X-ray Photoelectron Spectroscopy (XPS), and Ultra-violet Photoelectron Spectroscopy (UPS) comparison with the simulation data of molecular orbital and electronic structure. By inserting thin LiF layer, the field effect mobility and threshold voltage increased from 0.32 cm$^2$/Vs to 0.45 cm$^2$/Vs and from -21.8 V to -4.16 V, respectively.

110.6 Theoretical Investigation on the Electronic Structure of the Alq3/AI Interface. Susumu Yanagisawa$^{1,2}$ and Yoshitada Morikawa$^{1,2,3}$; 1ISIR, Osaka University, Ikari, Japan; 2CREST-JST, Kagawa University; 3AIST, Tsukuba, Japan.

Alq$_3$ [tris(8-hydroxyquinolinato) aluminum] is one of the most widely used electron transport and emissive materials in organic electroluminescent devices, due to its excellent chemical stability and high luminescence efficiencies. The electronic structure of the Alq$_3$/metal interface is of interest in elucidating the dipole layer at the interface, which significantly alters the barrier for electron injection from the metal cathode. From the experimental observation of an extra gap state at the Alq$_3$/AI interface, a strong chemical interaction between the Alq$_3$ molecule and the Al surface was suggested. Contrary to the experimental studies, previous DFT calculations concluded that the interaction was physisorptive. In that theoretical study, however the electronic roughness of the electronegative film was not taken into account. Furthermore, there was no discussion on the interfacial dipole layer. In this study, by the first-principles electronic structure calculations, we investigated the dipole layer at the Alq$_3$/AI interface by taking into account the effect of the surface roughness. We examined adsorption structures of Alq$_3$ for three Al substrates; the flat Al(111) surface, the Al(332) stepped surface, and the AI adatom adsorbed Al(111) surface. We employed a generalized gradient approximation (GGA) and local density approximation (LDA) as the exchange-correlation energy functional. The electron-ion interaction was described by ab initio pseudo potentials and the wave functions were expanded by plane-wave basis sets. In the geometry optimization of the Alq$_3$/Al interface, to avoid the local minima and to find the global minimum of potential energy surfaces of the interface, we considered as many initial geometric structures as possible and they were annealed by finite-temperature molecular dynamics method before geometry optimizations.

We have found that lowest energy configurations, in which molecular permanent dipole moments are directed to the vacuum side, reduce the work function by 1.0-1.6 eV, in reasonable agreement with experimental results. In contrast to that, downward configurations, in which the permanent dipole moments are directed to the Al side, increase the work function. The density of states (DOS) projected onto the Alq$_3$ indicates that the lowest unoccupied molecular orbitals (LUMO’s) were fractionally occupied while the characteristic of the MO’s of Alq$_3$ were kept upon adsorption. 0.5-0.9 electrons were transferred from the Al substrates to Alq$_3$. We found no hybridization of the wave function in those projected DOS. This result is strongly inconsistent with the gap state derived from the interfacial chemical interaction observed in the UPS and MAES experiments. But it is suggested that the gap state may correspond to the highest occupied molecular orbital (HOMO) levels of the Alq$_3$ in down configurations, in which the energy levels of the Alq$_3$ are located outside of those in upward configurations. Further details will be presented.


Transparent conducting oxide (TCO) films, such as indium-tin oxide (ITO) are extremely reactive in their freshly deposited state. Commercially available TCO films are unavoidably contaminated with carbonaceous materials and hydroxides, which severely limit rates of charge injection in condensed phase devices. The cleanest ITO films, commercial or freshly deposited, still must inject charge through thin passivating layers when used in contact with small molecule or polymeric device layers. A recent development to create nearly atomically clean ITO thin films by sputter deposition, followed by in-situ transfer to photodetector surface analysis will be presented and the role of these thin layers in determining effective field oxide growth and micrometre fabrication properties for systematic modifications and analysis of clean ITO surfaces by exposure to environments which permit reaction with gas-phase small molecules. Surface modification will show the passivation of the oxide reactive layer while tailoring of work function and charge carrier properties. This presentation will focus on the chemical composition and effective work functions of freshly deposited and chemically modified ITO surfaces, their electronic properties immediately following deposition and after brief periods of atmosphere exposure. The nature of the surface reactions, which lead to contamination of the ITO surface, and the characterization of organic solar cell devices deposited on both freshly deposited and "passivated" or "tailored" ITO surfaces will also be presented.

110.8 Influence of electrode contamination on organic/ electrode interfacial barriers. Alan T. Shu, Chuntao Wang, Fabrice Amy and Antoine Kahn; Electrical Engineering, Princeton University, Princeton, New Jersey.

Processing for OLEDs and other organic devices often involves exposure of surfaces and interfaces to nominally controlled atmosphere (e.g. N$_2$) or even ambient conditions. In this work, we investigate the effect of ambient exposure of Au, Al, indium tin oxide (ITO) and conductive polymers (3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS)) electrode surfaces on the hole-injection barrier on hole transport materials N,N,N',N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) and copper-phthalocyanine (CuPc) using transmission photoemission spectroscopy (UPS) and current voltage (I-V) measurements. We compare layers grown in UHV on substrates: (i) as-loaded, exposed to ambient, with decreasing only; (ii) cleaned by Ar$^+$ sputtering (except for PEDOT:PSS); (iii) clean metal deposited in UHV (for Au and Al only); (iv) exposed to UV ozone prior to
loading (except for PEDOT:PSS). Normal metal-semiconductor interface behavior is that the hole-injection barrier \( \phi \) decreases with increasing electronic function \( \Phi \). This trend is indeed observed when comparing different substrates prepared in the same manner. For example, 7-NPD on clean Au (\( \Phi = 4.5 \text{ eV} \)) gives \( \phi = 1.7 \text{ eV} \) with a positive interface dipole \( \Delta = 0.8 \text{ eV} \) (downward vacuum level shift from the electrode to the organic), whereas on clean Al (\( \Phi = 3.5-3.4 \text{ eV} \)), the barrier is \( \phi = 1.4 \text{ eV} \) and \( \Delta = 1.3 \text{ eV} \). However, some ambient-exposed electrodes actually yield smaller interface barriers with organics than clean electrodes. 7-NPD on air-exposed Au (\( \Phi = 4.7-4.9 \text{ eV} \)) leads to 0.5-0.6 eV lower than on clean Au. The same trend is also observed with CuPc. I-V measurements on Au/organic/Au devices made on clean vs. contaminated Au show several orders of magnitude increase in current injected from the contaminated Au, consistent with the UPS data. Interestingly, ITO and PEDOT:PSS, that have work functions similar to those of clean Al and Au, respectively, give hole-injection barriers and interface dipoles comparable with (or even smaller than) those observed with metal electrodes. The large differences in dipole and injection barriers at these organic/electrode interfaces are attributed to the layer of contamination (consisting primarily of hydrocarbons), which not only lowers the work function of the electrode, but also decouples the interface molecules from the electrode atoms. The effect of this physical and chemical decoupling on the interface electronic structure can be understood within the framework of the induced density of interface state model.\(^{2,3,4}\) A. Wani, J. Haring, F. Amy and A. Kahn, Organic Electronics 6, 47 (2005) 2. H. Vazquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Perez, F. Flores and A. Kahn, Europhysics Letters 65, 802 (2004) 3. H. Vazquez, F. Flores, R. Oszwaldowski, J. Ortega, R. Perez and A. Kahn, Appl. Surf. Sci. 234, 107 (2004)

10.9 Electrical Characterization of Metal/Pentacene Contacts. Lei Diao\(^1\), Dominique Vaudin\(^2\), and Paul Kudenov\(^2\).\(^{1}\)Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; \(^2\)Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

The performance of organic devices is strongly affected by the electrode materials, because the injection barrier for charge transport is determined by the property of metal/organic interface. In this research, systematic studies of the gold, silver, and platinum Schottky barrier contacts to pentacene have been carried out. The geometry of devices consists of a metal contact on top of a pentacene film thermally deposited on a conductive indium tin oxide (ITO) substrate. The diode characteristics of the Schottky barrier structures were investigated using a combination of J-V and activation energy measurements over a temperature range of 120-340 K. For Schottky contacts fabricated with different metals, the metal work function dependence of barrier height has been observed. The activation energy results under different biases exhibit a small lowering for increasing internal electric field due to the image-force potential. The injection current through contact is modeled in terms of a balance of a thermally activated carrier injection across the metal/pentacene interface and its time reverse process, the interface recombination current.

10.10 Interfacial Structure for Multilayer Cathodes with Different Metal Layers: Effect of Lif for Al and Mg Cathodes. Ayse Turak, Daniel Groza, Changjun Huang and Zhenghong Lu; Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

Unlike traditional heterojunctions in inorganic contacts, formation of multilayer cathode structures in organic devices is highly complex, with conflicting mechanisms related to interfacial molecular reactions, diffusive organic-inorganic mixing, and inorganic dipole formation. Using x-ray photoelectron spectroscopy and a novel in-situ characterization technique, the organic/inorganic interfacial structure for Al/LiF and Mg/LiF cathodes were examined, and compared with device behaviour. For tris-(8-hydroxyquinoline) aluminum (Alq), the molecular breakdown at the interface plays a significant role in the contact formation. Reactive Mg cathodes show enhanced molecular breakdown with a LiF interlayer, accompanied by marked degradation of device properties. This is the opposite effect to that observed with Al/LiF cathodes. Though Al/Alq interfaces showed no evidence of molecular breakdown, the LiF interlayer does appear to prevent interfacial oxidation by acting as a passivation barrier at the Al surface. In addition there is also evidence of a charge transfer between the LiF and the Alq molecule with Al, which is not occurring with Mg. The optimum interlayer thickness that accommodates properties with these different capping layers can be related to the by-products of interfacial oxidation observed at the metallic cathode. Device performance appears linked to the packing structure at the interface, and the lattice constant mismatch at the interface may be used as a guide to predicting future device performance.

10.11 Formation of Al Thin Films on Organic Surfaces. Tolu Ogunmimi, Ayse Turak, Changjun Huang and Zhenghong Lu; Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

For OLEDs, the metallization process is critical to ultimate device performance. Though typical device fabrication occurs under high vacuum conditions, <10^-6 Torr, the presence of oxygen and water vapor inside the deposit the hostile environment of effective processing conditions. Using x-ray photoelectron spectroscopy, scanning electron microscopy and optical reflectivity, the effect of deposition rate and thickness on cathode physical properties, including electron injection and injection, morphologically, grain size is seen to increase with both deposition rate and thickness. This change in the grain distribution suppresses metal oxidation and greatly improves the reflectivity of the metal surfaces. Device performance can also be correlated to this grain size distribution, with diminished injection properties below a critical deposition rate. As LiF is critical to device performance, the impact of an interlayer has also been examined, and its effect becomes more pronounced with increasing deposition rate. Fast deposition rates, therefore, are essential to optimizing device fabrication conditions.

10.12 Pentacene thin film transistor performance effects on modified dielectric interfaces and molecular beam parameters. Alejandro Papadimitratos\(^4\), Aravind S. Killlampalli\(^5\), Jared L. Mack\(^6\), James R. Engstrom\(^6\) and George G. Malliaras\(^7\). 1Department of Materials Science and Engineering, Cornell University, Ithaca, New York; 2School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York.

We investigated the insulator/semiconductor interface in organic thin film transistors (OTFTs). Surface treatments, especially for inorganic insulators, significantly influence molecular ordering and device performance. Moreover, the deposition technique and the growth parameters of the semiconductor layer have a further impact on the OTFTs performance. In this work, we used supersonic molecular beams for film deposition, in particular, for the deposition of pentacene thin films. We fabricated top contact pentacene thin film transistors on bare thermal SiO\(_2\) and HDMDS (hexamethyldisilazane) (OTS) coated SiO\(_2\) substrates to understand the relationship between performance characteristics of OTFTs and film-dielectric interface properties. In addition, the devices with HDMDS and OTS primed SiO\(_2\) showed improved performance characteristics compared to bare thermal SiO\(_2\). This appears to be due to better charge transport and lower trapping at the semiconductor/dielectric interface. In addition, we looked into the dependence of device characteristics to the deposition incident energy. We find that incident energy of pentacene molecules influences grain size and hence the field effect mobility obtained for the corresponding OTFTs.

10.13 Nucleation of Pentacene Films on Si Surfaces. Leonidas Tseitseris\(^8\) and Sokrates T. Pantolides\(^9,10\); 1Department of Physics, Vanderbilt University, Nashville, Tennessee, and Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Growth of films of organic molecules on various substrates has been a very active field of research recently. Strikingly different morphologies have been observed experimentally for growth of pentacene films on inert and reactive surfaces. In the former case, a very low density of initial nucleation sites suffices for growth through diffusion-limited aggregation. Here we report investigations on the initial stages of growth of pentacene on H-passivated and clean Si surfaces using first-principles density-functional calculations. In the case of H-passivated surfaces, we identify the nucleation sites as isolated Si dangling bonds and show that aggregation around these sites is consistent with the observed geometry of molecules standing perpendicular to the surface. The passivation of dangling bonds by pentacene is an exothermic reaction, and it is favored over the weak physisorption of a non-bonded molecule lying flat on the surface. After the pinning of the first molecule, subsequent dimerization can take place with a second molecule oriented either parallel or perpendicular to the anchored moiety. We also show that strong chemisorption of pentacene on clean Si surfaces is accompanied by large molecular and surface distortions. The results suggest that the selective passivation of the surface can control the growth of ordered pentacene films on Si. We also discuss the relevance of aligned atomic-scale mechanisms for growth on other inert substrates, notably silicon dioxide, and for similar organic molecules. This work was supported in part by DOE Grant DEFG0203ER46096.

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110.14 Impedance Spectroscopy and Scanning Kelvin Probe Microscopy Studies of Charge Injection and Transport in Phthalocyanine Thin Films. Richard D. Yang1,2, Xiaotian Zhou1,4, Amos Sharoni3, Corneliu Colesnicu2, Jengwon Park3, Edward T. Yu1,4, Ivan C. Schuller1 and Andrew C. Kummel2;
1Materials Science and Engineering Program, University of California, San Diego, La Jolla, California; 2Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California; 3Department of Physics, University of California, San Diego, La Jolla, California; 4Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California.

Charge injection and transport in Metallophthalocyanine (MPC) thin films has been studied by impedance spectroscopy (IS) in frequency domain and a scattering Kelvin probe microscope (SKPM) in real space. CoPc films, 50 nm thick, were grown on 5 micron spaced, interdigitated gold electrodes by organic molecular beam epitaxy (OMBE). Current density-voltage (I-V) and conductance-voltage (G-V) measurements were performed at low voltage and space-charge limited conduction (SCLC) at high voltage, where there are no more injected carriers than thermal carriers. Impedance spectroscopy studies show the co-existence of low and high frequency traps in the thin film devices. Two semicircles are found in complex impedance plane when the devices are operated at low voltage. The low frequency (below 10 Hz) semicircle diminishes at high DC bias when the conductivity becomes space-charge limited. SKPM was used to image the surface potential profile in the MPC thin film and at Au/MPC interface. At low voltages, the surface potential drops linearly from injecting to extracting electrodes consistent with Ohmic behavior. At high voltages, the potential profile revealed a nonuniform profile consistent with a build up of space charge in the film. Furthermore, the variation in potential drop at the Au/MPC interface from device to device (0.2 to 2V) is directly correlated with transition voltage between Ohmic and SCLC conductivity. The combined IS and SKPM low frequency trap states are located at MPC/Au interfaces; these states control the charge injection at low voltages. Once the low frequency trap states are filled at higher voltage, they do not limit charge injection.

110.15 Characterization of Alq3/LiF/A and Alq3/A interfaces with photoelectron spectroscopy. Stina K. M. Johansson1, William R. Salansek2, and Maximilian Braun1;
1School of Physics and Technology, Linköping University, Linköping, Sweden; 2Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden.

Optimizing charge injection properties in organic electronic devices such as light emitting diodes and solar cells is a key objective for improving device efficiency and also lifetime. We present here some new results on mechanisms for optimizing electron-injecting contacts in OLEDs. In particular we describe the different chemical and electronic properties of Alq3/LiF/A and Alq3/A interfaces that exhibit better device performance than Alq3/LiF/A. These new interfaces have been grown on Al and LiF/Al substrates by physical vapor deposition. In the case of Al there is a covalent interaction between the metal substrate and the organic monolayer (evidenced by an interfacial state observed in UPS), which is supported by a small level shifting and dipole formation at the interface, in analogy with previous results by other groups. In contrast, for the Alq3/LiF/A system, there are new interfacial states appearing for LiF layers up to about 20 A. UPS and UPS results show that these interfacial states originate from charge transfer between the Al substrate and the Alq3 monolayer onto the inert LiF sandwich layer. The molecules at the interface are then doped. Furthermore, we present evidence that fac-Alq3 is obtained when deposited on LiF/Al substrates, not the commonly found mer-Alq3 isomer. This is important to device design since the two isomers have distinctly different electronic and optical properties.

110.16 Charge injection barriers at interfaces of conjugated polymers, Wojciech Osikowicz1, Michel P. de Jong2, Slawomir Braun1, Carl Tengstedt1, Mats Fahlman2 and William R. Salansek1;
1Dept. of Physics, Linkoping, Sweden; 2Dept. of Physics and Technology, Linköping University, Linköping, Sweden.

Photoelectron spectroscopy has recently been employed to examine the energy level alignment (ELA) at various all-organic and hybrid interfaces. Those experiments defined the conditions for spontaneous charge transfer across the interface. The results from that study here are applied to ELA at two types of device-relevant interfaces: (i) Hybrid polymer/Au and vapor-deposited Au/polymer interfaces, which directly correspond to the top- and bottom contacts in organic (opto)electronic devices and (ii) different all-organic donor-acceptor interfaces, which are common in organic photovoltaics. Both, polymer/Au and Au/polymer show almost identical ELA. The vacuum deposited gold electrode behavior as if it had a work function of about 4.4 to 4.5 eV, which corresponds to an approximately 0.7 eV downward shift in the work function as compared to clean polycrystalline gold. The shift is associated with the reduction of the electron density tail that extends outside of the metal surface. ELA at these interfaces depends than on whether the Au work function, at 4.4 to 4.5 eV, exceeds the positive polaron/bipolaron formation energy per particle for the actual polymer in question. All-organic donor-acceptor interfaces show large interfacial dipoles on the order of the few tenths of eV are observed at these interfaces. However, ELA does not follow strictly the proposed model of spontaneous charge transfer, which has been consistent for the cases of metals for all-organic and hybrid interfaces, e.g. Au/polymer and polymer/Au.

110.17 Alkox-substituted conjugated polymers and oligomers for chemical and bio-sensing Langmuir-Schafer thin film transistors. Gianluca Maria Farinola1, Maria Cristina Tanese1, Luisa Ilie2,3, Patricia Ilie3, Carl-Eric Hassel2,3, Donato Colangeli3, Bruno Pignatario4, Ludovico Valli2, Serena Casilli5, Sabrina Conoci5, Philippe Lang7, Francesco Babudri1,3, Francesco Nasso1,3, Luigia Sabbatini1 and Pier Giorgio Zambonini1;
1Department of Chemistry, University of Bari, Bari, BA (Italy), Italy; 2Centro di Eccellenza TIFRES, University of Bari, Bari, BA (Italy), Italy; 3Departement of Chemistry, CNR ICOM Sezione di Bari, Department of Chemistry, University of Bari., Bari, BA (Italy), Italy; 4Department of Physical Chemistry "F. Fizzoni", University of Palermo, Palermo, PA (Italy); 5Department of Innovation and Technology, University of Lecce, LEC, LE (Italy), Italy; 6Si optic & post silicon Technologies Corporate R&D, STMicroelectronics, Catania, Italy, Catania, CT (Italy), Italy; 7ITODYS, CNRS, University of Paris 7, Paris, France, Paris, France.

Conjugated polymers and oligomers are conveniently used as active layers in resistive chemical sensors. Sensing devices based on organic thin-film transistors are particularly promising as they can be operated as multi-parameter responsive systems. One of the main advantages offered by organic semiconductors in electrical sensing devices is the possibility to adjust selectivity towards different chemical species by proper functionalization of the conjugated backbone. In this respect, alkoxy functionalization appears as a convenient synthetic methodology to covalently attach a number of substituents, including bio-molecules, on the main chain of semiconducting oligomers and polymers. In the perspective of using these functionalized conjugated systems as sensing active layers with selective recognition capabilities, it would be important to investigate such systems and to find strategies for improving their electrical performance level. With this aim, organometallic synthetic methodologies have been appointed to obtain tailored conjugated polymers and oligomers bearing ad hoc chosen side groups, such as simple alkoxy chains and/or small biological molecules, through the alkoxy linkage. As a first step, an alternating copolymer, poly(2,5-dioctyloxy-1,4-phenylene-alt-2,5-thiophene), is investigated as organic thin-film transistor active layer. It is demonstrated that the polymeric, deposited as cast or spin-coated on glass, though exhibiting similar optical properties, shows very different morphological, structural and semiconducting field-effect properties depending on the deposition technique employed. The investigation has been extended to alkoxy-substituted phenylene oligomers functionalized with alkoxy chains or with small biological molecules bonded through alkoxy linkages to the conjugated main chain. These compounds have been tested in Langmuir-Schafer multilayer architecture OTFT devices, with the aim to obtain sensing transistors for selective chemical assay and chiral discrimination.

110.18 Potassium doping effects on electronic structure and morphology of n-type molecular thin films. Kanasame Kanai1, Tadanobu Ikame1 and Kazuhiro Seki2,3,1; 1Chemistry, Nagoya University, Nagoya, Japan; 2Research Center for Materials Science, Nagoya University, Nagoya, Japan; 3Institute for Advanced Research, Nagoya University, Nagoya, Japan.

We have investigated the effects induced by potassium doping on n-type molecular, hexacenehexacenehexacenehexacene (F111,11,11,11,12,12-tetracyanobenzaphtho-2,5-quinodimethane (TNAP) thin films by means of ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS) and infrared reflection absorption spectroscopy (IRRAS). (1) UPS and IRRAS spectra of potassium doped F16ZnPc film can be basically explained by DFT simulation for F16ZnPc monolayer. The state which emerges in HOMO-LUMO gap by potassium doping is interpreted as partially filled LUMO of potassium F16ZnPc molecule. However, it was also found that XPS results show that doped potassium partially reacts with the fluorine.
group of the F16ZnPc molecule and generates KF compound. (2) Electronic structure of potassium doped TNAP film strongly depends on substrate materials, the case of copper substrate, highly evaporated states of TNAP molecule by potassium doping are observed by IRRAS, although higher ionized states than singly and doubly ionized states are not observed on potassium doped TNAP films on silver and gold substrates. Morphology of TNAP film is strongly affected by potassium doping. IRRAS results show that TNAP molecule is perfectly standing in pristine film on gold substrate. By doping a small amount of potassium, the preferred molecular orientation of TNAP is lost. By increasing the potassium doping efficiency, the electronic structure and morphology by comparison between the experimental results and simulated results.

11.0.19 Influence of the film morphology on the diffusion of Ag in the organic semiconductor diindenylene. Michael Scharnberg1, Klaus Raukmez1, Rainer Adelung1, Stefan Meyer2, Jens Flamm1 and Franz Reinbeek3. Multicolour photonics, Institute of Photonics, Kiel, Kiel, Germany; 23. Physikalisches Institut, University of Stuttgart, Stuttgart, Germany.

The application of organic field effect transistors (OFETs) for large scale low-cost electronic devices has lead to intense research. Diindenylene (DIP) thin films on SiO2 are a prominent system due to their high structural out-of-plane order. While bottom contact OFET structures can be realized easily, preparation of top contacts might cause destruction of metal atoms (Au) deep into the organic film changing the injection properties at the interface. Recently, we could establish a very sensitive radiotracer technique to measure even very low concentrations of Au atoms in generating DIP films [1]. The results show cluster formation on the surface and a low concentration of noble metal atoms dispersed throughout the film indicating that most of the metal atoms are immobilized near the surface due to Au-O interactions. Lateral and vertical variations of the cluster formation will be presented here and the influence of the structure of the organic film on the diffusion of noble metal atoms will be discussed. The strucrual influence on the diffusion in molecular organic films is a fundamental question also for other organic electronic devices like organic solar cells or OLEDs. [1] Scharnberg et al., App.Phy.Lett. 86, 204104 (2005)

11.0.20 Observations of Excitons and Phonons in High Quality Pentacene Monolayers. Ru Li1, Nancy G. Tassi1, Graciela B. Blanchet2 and Aron Finczuk3,4 1Columbia University, New York, New York; 2DuPont, Central Research and Development, Wilmington, Delaware; 3Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

Pentacene monolayers grown on poly-alpha-methyl-styrene (PAMS) are probed by photoluminescence and resonant Raman spectroscopies below 10K. These films exhibit complete coverage with high quality micron size clusters. They have exceptional uniformity and the first layer is largely complete prior to growth of the second layer. Sharp excitonic luminescence from single monolayer and submonolayer films. In the single monolayers photoluminescence of the free excitonic transition occurs at about 1.886 eV, blue-shifted by about 0.1 eV from that in high quality pentacene single crystals [1]. In submonolayers the free excitonic transition occurs at 1.826 eV, blue-shifted by about 0.6 eV from that in high quality pentacene single crystals [1].

Photoluminescence excitation spectroscopy results from the monolayer reveals that the two lowest excited states are at 1.88 and 1.99 eV. The energy separation of these two levels is very close to that observed in optical absorption of thick polycrystalline films and single crystals of pentacene. The two bands are assigned to the Davydov doublet of the lowest singlet exciton. The appearance of Davydov doublets suggests that high uniformity pentacene monolayers develop a two dimensional structure with two molecules in a unit cell. Large resonance enhancements of resonant Raman scattering intensities are found when the incoming and outgoing photon energies overlap the free excitonic transition in the monolayers. The enhancements enable the measurement of low-lying (40-200cm-1) optical lattice vibrations. To the best of our knowledge, these are the first Raman scattering observations of low-frequency phonons of pentacene in the strict two-dimensional limit. The lattice modes are assigned to hindered rotational oscillations (librations) of pentacene molecules on the PAMS substrate. The modes from the monolayers (width of 5-10cm-1) are significantly wider than those from the high quality single crystals (width of about 1cm-1) [1]. These experiments demonstrate that luminescence and resonant Raman scattering from single pentacene molecules are very promising 2D probes, studies of interface effects, and thin film characterization. Supported by the Nanoscope Science and Engineering Initiative of the National Science Foundation under NSF Award Number CHE-0117752 and by the New York State Office of Science and Technology, and Academic Research (NYSTAR), and by a research grant of the W. M. Keck Foundation. [1] Rui He, X. Chi, A. Finczuk, D. V. Lang and A. P. Ramirez, to be submitted for publication.

11.0.21 Exciton relaxation and charge transfer at molecule/metal interfaces: C60/Au(111). Greg Dutton, Daniel Quinan, Chad Lindstrom and Xiaoang Zhu, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

We used time-resolved two-photon photoemission spectroscopy (2PPE) to study the electronic structure and dynamics in a model system: epitaxial films of C60 on Au(111). This approach allowed us to map out two types of excited states: excitons in C60 and charge-transfer resonances at the C60/Au interface. Lifetime measurements revealed that the excitons in C60 were strongly coupled to the metal substrate over long distance. This could be described by a direct coupling of the C60 electronic exciton band with the substrate metal band. We measured the LUMO (0) charge transfer resonance evolved into a molecular quantum well with distinct molecular characteristics.


The electronic structure of C60 on Al was analyzed by using ultraviolet photoelectron spectroscopy (UPS). The level energy alignment was studied by using the coupled quantum chemistry (CQCI) method [2]. The occupied HOMO (HOMO) level and the shift of the vacuum level of the C60 layer, which was deposited on a clean Al surface in a stepwise manner. Several organic materials are used to fabricate n-type organic thin-film transistors (OTFTs). Among these n-type materials, C60 is one of the most attractive materials, which is reported the highest field effect mobility (>0.5cm2/Vs). If the advantages of C60 are considered, the electronic structure of C60 is important because the electronic structure directly affects charge transport in semiconductor devices. If the charge-transport mechanism in organic semiconductor devices is to be understood, the onset position of the HOMO level from the Fermi level and the vacuum level shift should be studied by analyzing the valence-band spectra in detail. In this report, we will present the valence-band spectra of the C60/Al interface obtained from UPS.

11.0.23 Chemical Interactions between LiF, MEH-PPV, and Al as determined by Photoelectron Spectroscopy. Korhan Demiralp, Anoop Mathew, Conan Weiland, Yashpal Bhandari and Robert L. Opila; Department of Materials Science and Engineering, University of Delaware, Newark, Delaware.

A small amount of LiF at the organic semiconductor/Al interface can dramatically improve the device characteristics by enhancing the voltage in organic light emitting diodes [1]. Some research groups have attributed this improvement to different models including: i) a chemical reaction between LiF and Al, forming a Li/Al alloy, that intervenes in the anode work function [2]; ii) a reaction between the organic where F acts as an n-type donor and modifies the energy levels of the organic [3]. In our study, we followed the interface reactions between LiF, Al, and MEH-PPV by X-ray Photoelectron Spectroscopy (XPS) and synchrotron source Ultraviolet Photoelectron Spectroscopy (UPS). Evaporation of LiF onto MEH-PPV surface caused change in the valence band of MEH-PPV indicating a chemical reaction between the two, suggesting a break in the conjugation of the polymer. Reaction of the polymer with F was confirmed in the C 1s spectra of the MEH-PPV film. The broadening of Li 1s and F 2p spectra of Au/MEH-PPV/LiF compared to Au/LiF suggests the interaction of both Li and F with the polymer, consistent with the doping mechanism. When Al was evaporated on the Au/MEH-PPV/LiF surface, Al-Li alloy formation was observed, as suggested by the electrode work function mechanism. Reaction between Al and MEH-PPV was still observed even after deposition of approximately 30Å LiF layer. While our photoemission results suggest that the reactions between the LiF and the polymer may break the conjugation of the polymer, limiting its conductivity, overall our results support the advantageous mechanisms proposed previously. [1] S. D. Wang, M. K. Fung, S. L. Lai, S. W. Tong, C. S. Lee, S. T. Lee, H. J. Zhang, S. A. B. J. Appl. Phys. 94, 1203 (2003) [2] Y. Yuan, D. Grozha, S. Han and Z. H. Lu, Appl. Phys. Lett. 85, 4059 (2004)

11.0.24 Interface Disorder and Charge Injection into Copper Phthalocyanine. Benjie Limketkai, Kaveh Milani, Madhusudan Singh and Macer Baldo; Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.
We examine the effect of morphological disorder at the injection to the growth boundary on the property of CuPc. For CuPc grown on single-crystal flat gold Au(110) and CuPc grown on a rough polycrystalline surface. As a consequence of the interfacial morphological differences, the current-voltage characteristics for CuPc grown on polycrystalline gold show much higher operating voltages and a steeper power-law slope at room temperature. This is attributed to the addition of deep interface traps created by structural disorder at the interface between CuPc and rough polycrystalline gold. Indeed, this also results in the broadening of the interfacial CuPc HOMO levels on polycrystalline gold. Thus, although almost all organic devices have disordered contact interfaces, this work suggests that contact resistance may be reduced or eliminated by using metal interfaces. [1] H. Peisert, M. Kuepper, T. Schiewer, J.M. Auerhammer, M.S. Golden, and J. Finik, Journal of Appl. Phys., 91, 4872

110.25 Enhanced Light Emission Using Thin Metal-Halide Cathode Interlayers for Improved Electron Injection into MEH-PPV Polymer Light-Emitting Diodes. Woon-Jin Young1, Scott B. Orlowsky1 and Paul R. Berger1,2. Department of Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio;
2Department of Physics, The Ohio State University, Columbus, Ohio.

The interface between the active light emitting conjugated polymer layer and the metal cathode is an important factor limiting polymer light emitting diodes (PLEDs) performance. Numerous groups have shown that the insertion of a thin compound interlayer, such as alkaline earth metal halides between Al cathode and the electroluminescent polymer improves PLED device performance by enhancing electron injection. The physical mechanism behind this improved performance remains a topic of some speculation, but it has been proposed that this effect is due to the screening of the metal ions diffuse into the electroluminescent polymer layer, donating electrons to the r-system, thus, enhancing electron injection and therefore leading to higher electroluminescent external quantum efficiencies. Previous work has primarily focused on the halides as studied in this paper and this study extends that work by examining other halide based chemistries (LiF, LiCl, LiBr and LiI). PLEDs with varying metal-halide interlayers between the electroluminescent layer and Al cathode were fabricated and tested. PLED fabrication was performed on indium tin oxide (ITO) coated glass substrates. PEDOT:PSS layers were then added atop the ITO anodes by spin-coating and curing. The electroluminescent layers of poly (2-methoxy, 5-(2-ethyl-hexyloxy)-1, 4-phenylene vinylene) (MEH-PPV) were then spin-coated atop the PEDOT:PSS layer from a 0.5% MEH-PPV solution in 80% toluene and 20% tetrahydrofuran in a nitrogen-rich environment. Li-halides were varied down the group VII column of the periodic table. Metal-halide interlayer was deposited by thermal evaporation at a 6–10 Torr to a nominal thickness of 30 Å. The ITO/PEDOT:PSS/MEH-PPV/metal-halide/Al PLEDs were finally completed by the shadowmask evaporation of an Al cathode.

Light-current-voltage (L-J-V) measurements were performed in the nitrogen glovebox with a semiconductor characterization system (Keithley CS-236) with a calibrated light detector at room temperature under darkness. We then examined the effects of metal-halide on the electron injection in the electroluminescent layers of PLEDs from the L-J-V measurement. A lowering of the turn-on voltage is observed down the group VII column of the periodic table, resulting in an order of magnitude increase in the current density. The turn-on voltage and current density measured at 4 volts was: LiF (3.10 volts and 0.15 A/cm²); LiCl (2.35 volts and 0.30 A/cm²); LiBr (2.10 volts and 0.51 A/cm²); and Li (2.30 volts and 0.19 A/cm²). However, when considering the normalized light output LiCl was 2.5× greater than LiF, whereas LiBr and Li were 3.8× and 4.2× greater, respectively. This resulting enhanced current density and significant light output, as the Li-halide compound decreases, could be due to a high surface charge density with increased Li doping density at the cathode interface in the electroluminescent layers of PLEDs.

110.26 The Early Stages of Growth of Pentacene on Si(111) and the Structure of the Pentacene-Substrate Interface. Peter Kuek1,2, Kelly R. Roon1, Kevin Kimberlin2, Dagmar Thiern1, Michael Horn-von Hoegen1,3 and Stephen C. Hawker. Institute for Laser and Plasma Physics, University of Duisburg-Essen, Essen, Germany;
1Department of Physics, Bradley University, Peoria (IL), Illinois.

We investigate the initial stages of growth of pentacene (C22H14), which is among the organic semiconductors with the highest carrier mobilities, on the Si(111) surface by means of photoelectron emission, atomic force and scanning tunneling microscopy and especially by in-situ measurement of the surface stress. While the large influence of surface stress on growth processes of inorganic adsorbates on semiconductor substrates is well known and sometimes also well understood, the information about stress effects on the growth of inorganic thin film growth. We show that the observation of the surface stress yields valuable information especially about the structural integrity of the initial reconstruction. In the case of pentacene growth on the Si(111) surface, we obtain mainly results which support the idea of a general relevance for organic thin film growth on covalent semiconductor surfaces: The chemical saturation of the molecules in contrast to atomic adsorbates makes it possible that the initial surface reconstruction remains undisturbed [1], observed in this study to cause a large density of electronic states at the interface. Secondly, a saturation of reactive surface sites may occur within the wetting layer, thus passivating the surface, which explains why the density of structural defects of pentacene islands on Si surfaces is much lower than the density of defects (like steps, grain boundaries, point defects etc.) of the initial clean Si surface.

110.27 Effect of Chemically Modified Dielectric Interfaces on Semiconducting Polymer Chain Orientation. Brandon M. Vogel1, Dean M. DeLonchamp1, Youngsuk Jung1, Daniel A. Fischer1, Sharadha Sambasivan1, Lee J. Richter1, Marc C. Finan1 and Eric K. Lin1, 1Polymers Division, NIST, Gaithersburg, Maryland; 2Ceramics Division, NIST, Gaithersburg, Maryland; 3Surface and Microanalysis Science Division, NIST, Gaithersburg, Maryland.

Conjugated organic semiconductors such as poly(3-hexylthiophene) (P3HT) have shown promise for use in applications such as flexible display technology and radio frequency identification tags. Unlike inorganic materials, organic polymers typically have intrinsic limitations on the structure and properties of the interfaces between materials. Previous research has shown that P3HT films spin-coated onto modified dielectric interfaces can show an increase in the charge carrier mobility presumably due to changes in microstructure caused by improved p-p interactions in the plane of charge transport. A clear understanding of the effect of interfacial properties on the structure and electrical characteristics of the polymer, however, remains incomplete. Here, we systematically investigate the influence of interfacial chemistries on the microstructure of conjugated semiconducting polymers. Specifically, we use two strategies to vary the interfacial chemistry to clarify the influence of either surface energy or chemical functionality on the charge transport properties of P3HT. First, linear surface energy gradients were prepared by systematically oxidizing several aliphatic silane chemically modified surfaces with a UV ozone lamp. P3HT was spin coated on top of these substrates and the polymer axis tilt was determined using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. We find a weak dependence of chain orientation on substrate surface energy and some dependence on the aliphatic surface functionality. Second, the chemical functionality at the polymer monolayer-interface was modified using a versatile monolayer chemistry based on isocyanate-amine chemistry. This strategy allows the production of monolayers with aromatic functionality such as phenylene, fluorene, and thiophene units. We quantitatively and qualitatively investigated the relationship of the reactive units using NEXAFS and characterize the monolayer before coating with polymer. P3HT exhibited varying levels of orientation depending upon the monolayer chemistry and the solvent from which the P3HT was spin coated, dependent on the contact angle. These results suggest that specific interfacial chemical interactions as well as the film formation variables (casting solvent) can strongly influence the polymer conjugated plane tilt.  

110.28 Rubrene Thin Film Transistors. Soonjooh Seo1, Byoung-Nam Park1 and Paul Evans2, 1Materials Science, University of Wisconsin-Madison, Madison, Wisconsin; 2Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Soonjooh Seo1, Byoung-Nam Park1, and Paul G. Evans2 1Materials Science Program; 2Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI.  

There has been increasing interest in field-effect transistors based on organic single crystals because their field effect mobilities are relatively high, in some cases comparable to those of conventional transistors. Thin films, however, are technologically more desirable since they allow the fabrication of a variety of applications. Rubrene (C24H18) has higher surface carrier mobility in single crystals than other organic materials and exhibits p-type conductivity. Rubrene thin film transistors have not previously been reported. We have fabricated thin film transistors that show ambipolar characteristics. The mobilities of holes and electrons were 8.0×10−6 cm²/Vs and 2.2×10−12 cm²/Vs, respectively. Atomic force microscopy images show 3 dimensional growth of circular rubrene islands on the orientation of the substrate. In-situ electrical measurements made during the vacuum evaporation of rubrene onto the silicon/silicon dioxide substrates probed the formation of the current path between source and drain, and its
relationship to geometrical effects. Current began to flow between the source and the drain electrodes at a sharp threshold at which the conducting channel of a rubrene transistor is formed due to the geometrical percolation of islands.

I10.29 UPS Studies of VUV-Induced and Air-Exposed Doping into Copper Phthalocyanine Thin Film, Tomoki Sueyoshi, Masaki Ono, YingKang Zhang, Satoshi Kera, Koji K. Okudaira and Nobuo Ueno; Engineering, Chiba University, Chiba, Japan.

1. Introduction Doping technique becomes a focus for significantly improving efficiency of organic devices. It has recently been reported that n-type titanyl phthalocyanine (TiOPc) film is changed to p-type by exposing to air [1]. However, there are a few reports on the effects of the oxygen doping from the aspect of electronic structure of thin film[2]. In addition to gas doping we are endeavoring to utilize photodissociation processes generated by VUV or soft X-ray irradiation as dopant. Advantages of these methods of development are its capability in realizing "uniform doping" and "doping control only by irradiation dose". We present UPS study of the electronic structure of copper phthalocyanine (CuPc) thin film doped by the two methods; one is air exposure, and the other is the newly developing method "VUV-induced doping". All measurements were performed at 296 K.

2. VUV-induced doping: n-type doping? We observed previously the shift of UPS spectra derived from Fermi level shift in polytetrafluoroethylene (PTFE) thin film[3]. In this symposium we report the highest occupied molecular orbital (HOMO) band shift of CuPc thin film (thickness:5.3 nm) by VUV irradiation. Upon VUV irradiation the HOMO band position was shifted toward high binding energy (BE) by 0.29 eV to 1.52 eV. This shift is not attributed to charge-up of the film, which was confirmed by other experiments. The HOMO band position shifted linearly with logarithm of the irradiation dose. This indicates that photodissociation processes act as donors and set Fermi level shifts toward lowest unoccupied molecular orbital (LUMO) band. Gap state generated in CuPc band gap will be also presented. 3. Air exposure and annealing effect: p-type doping We alternately performed the following two treatments on CuPc thin film (6.5 nm thickness) deposited onto a gold substrate in ultrahigh vacuum (UHV, 7 x 10^-8 Pa): (a) Air exposure, and (b) Anneal (330 ~ 340 K) in UHV. UPS measurements were performed before and after every treatment.

Shape of the peaks in the valence band region did not change by the treatments. The BE position of the HOMO band of the film relative to the Fermi level of the substrate was 1.38 eV after deposition. The HOMO band position then decreased to 1.10 eV after air exposure for 10 hours and increased to 1.42 eV after anneal for 15 hours. The treatments were repeated once more (1.17 eV after air exposure for 7 hours and 1.40 eV after anneal for 16 hours). This indicates that molecules(probably oxygen) by air exposure are removed from the film by annealing and CuPc film recovers the undoped film. [1] H.Tada et al., Appl.Phys.Lett., 76, 873-875 (2000) [2] T.Nishi et al., Chem.Phys.Lett. accepted. [3] M.Ono et al., IPAP Conference Proceedings Series, in press.


Knowing the distribution of Fermi level, electrostatic potential in other words, is crucial to understand the behavior of charge carriers in working semiconductor devices since it indicates the direction and the velocity of a carrier flow. For this purpose, we have been developing atomic-force-microscope (AFM) potentiometry where local potential is measured by conductive AFM tip in an electrical way [1]. By optimizing the measurement circuit and cantilever holder, AFM potentiometry is expected to be able to sense the potential of organic semiconducting materials simultaneously with the topographic imaging using intermittent contact [2]. AFM potentiometry can visualize a potential distribution more directly and precisely with higher spatial resolution typically around 100 nm, than well-known Kelvin probe force microscopy (KFM) does. Using this technique, we have investigated the potential distribution of working organic thin-film transistors (TFTs) [2, 3]. In the metal-organic contact area, a contact resistance widely distributed over relatively wide range near the electrode edge was observed for top-contact TFTs and that concentrated at the interface as an carrier injection barrier is observed for bottom-contact TFTs. Potential drops at grain boundaries, which are other important issues as 'interfaces' in organic TFTs, are found to be classified into several groups depending on the crystallographic and morphological differences. This work was supported in part by NEDO’s “Nano-Technology Materials Program Revestable Paper Project” based program, provided by MEXT, M. Nall, A. M. Fukuyo, E. Wakata, M. Izuka, K. Kudo, K. Tanaka, Synthetic Metals, 137, 887-888 (2003). [2] M. Nakamura, N. Goto, N. Ohashi, M. Sakai, and K. Kudo, Appl. Phys. Lett. 86, 122112 (2005). [3] M. Nakamura, H. Yamauchi, H. Yanagisawa and K. Kudo, Int. Symp. Super-Functionality Organic Devices, IPAC Conference Series 6 (2005) in press.


Poly(9,9-dicynfluorene) (PFO) is considered to be one of the most promising hole transporting and blue light-emitting conjugated polymers used in polymeric light-emitting diodes (PLED) due to its good hole mobility and solution processable ability. Since arylene compounds possess a superior hole drift mobility (up to 10^-3 cm^2/V·s) and a high-lying highest occupied molecular orbital (HOMO) with respect to PFO, the copolymer of poly(9,9-diocetyfluorene) and arylene is of great importance in blue-emitting PLED fabrication. It is therefore desirable to investigate the charge injection and transport in these model copolymers. Our work attempts to provide a comprehensive understanding on the injection of fluorine-arylene model copolymer, in combination with the charge transport measurement. Time-of-flight (TOF) technique is employed to estimate the charge drift mobility under a certain temperature range at the thick film regime. By applying the electronic hopping model to the temperature dependent mobilities, the microscopic understanding in the transport manifold can be thus established. Alternatively, the charge injection between the interface of indium-tin-oxide (ITO)/copolymer is then studied by the space-charge-limited dark injection (SCL DI) transient current method, together with the current-voltage measurement. Importantly, DI technique can further extent the drift mobility measurement down to device application thickness (~100μm). Hence, the relationship between injection and the drift mobility in the model polymer with various thicknesses (0.1-10 microns) can be disclosed. Results will shed light on the enhancement of device efficiency in the future polymeric electronic devices by engineering the charge injection and transport characteristics.


The process of charge injection significantly dominates the device performance in organic electronic devices such as luminescent efficiency and operating lifetime. As many organic devices are injection-limited, a proper electrical characterization for the injection barrier is required. Internal Photoemission Spectroscopy (IPS) technique is essential for directly probing the charge injection barrier between the electrical contact and the doped organic/polymeric thin films. As yet, the injection barrier between the interfaces of ITO/ molecules-doped polymer (MDP) model layer has not been understood. A robust MDP, triphenylamine-doped polycarbonate (TPD:PC), is chosen for our injection studies since their corresponding hole drift mobilities under various concentrations of TPD:PC could be well characterized [2]. By the aid of current-voltage characterization, all indium-tin-oxide (ITO) /TPD:PC contacts behave injection limited, independent of the concentration of TPD. The charge injection barriers between ITO/MDP can be directly measured by the IPS. Voltage-bias dependence is also concerned so as to observe the behavior of injection barrier lowering. Model injection layers are also inserted between ITO and MDP for improving the injection efficiency; for instance, poly(ethylene-oxide) : poly (styrene-sulfonate) (PEDOT:PS) and metal- phthalocyanine (Metal-Pc). IPS is further used to characterize the change of injection barrier after inserting the model injection layer into the MDP devices. The research outcome will be further extended to improve the charge injection in small-molecule organic / polymeric photovoltaic cells (PVs) and field effect transistors (FETs). Reference: 1. Y. Shen, M.W. Klein, D.B. Jacobs, J.C. Scott, G.G. Malliaras, Phys. Rev. Lett. 86, 3867 (2001). 2. H. F. Fong, K. C. Lun, S.K. So, Chem. Phys. Lett. 353, 407 (2002).

SESSION II1/D14: Joint Session: Interfaces in Organic and Hybrid Devices
Chairs: Sean Shaheen and Xiaoyang Zhu
Friday Morning, December 2, 2005
Room 302 (Hyes)

8:00 AM II1.1/D14.1
Buried organic/inorganic interfaces in polymer optoelectronic devices: functional nanocomposites.
Charge injection and extraction from polymer devices is controlled by the structure and interfacial interactions at the electrode-polymer interface. Charge separation in photovoltaic devices, on the other hand, is dominated by semiconductor/semiconductor interfaces buried in the active layer, designed to govern charge recombination and transport in polymer devices. Hybrid materials based on the incorporation of organic molecular species into the galleries of inorganic scaffolds have already been applied in thin film transistor analysis, separations, and sensors. Organic-inorganic hybrids present several advantages as optical materials due to the ability to tailor the optical properties through host/guest material selection and control of organic/inorganic interaction at the molecular level. In polymer/inorganic/guest host composites the polymer is confined into well-defined voids of an inorganic scaffold. Such hybrid materials have been used as active components in polymer devices. For example 3D TiO2 scaffolds infiltrated with PAN-PPV have been utilized in photovoltaic cells and 2D layered MoS2 intercalated with polyfluorenes have shown stable blue emission in light-emitting diodes. A variety of 2D and 3D guest/host hybrids have been designed, synthesized, characterized, and integrated into devices. The device performances, in these systems, provide insight into the electronic processes across the molecular interfaces.

8:15 AM A111.2/D14.2
1Department of Science and Technology, Linköping University, Norrköping, Sweden; 2Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden; 3Chemie des Matériaux Nouveaux, Université of Mons-Hainaut, Mons, Belgium.

Although many essential elements involved in low-cost production of polymer (opto)electronics are available, reduction in cost is still inhibited by the complex fabrication of the electrode injecting the light into the polymer and the light out of the device. In a light-emitting diode or a solar cell the low work function metal (WF) metal electrode is deposited onto a polymer layer under high vacuum conditions. Unfortunately, almost all low WF metals are highly reactive, and quickly oxidized in air. Consequently, they are difficult to handle in a cleanroom environment. Therefore, alternative routes for the preparation of cathodes are highly desirable in order to fully exploit the potential of low-cost fabrication of polymer (opto)electronics, such as roll to roll or bar coating combined with lamination. Tuning the workfunction of such metal electrodes can be obtained by controlling the orientation of an electric dipole, the interface dipole Dint. The metal work function change, DW, upon monolayer adsorption is a measure of this interface dipole. Although there are various possible origins for the dipole potential Dint [1], it generally consists mainly of the following three contributions [2]: (i) the reduction of the metal surface electron density tail upon adsorption, which always decreases the metal surface dipole potential EDmeta, (ii) the intrinsic dipole moment Dmol of the adsorbed molecule, and (iii) the chemical dipole potential eDchem created by partial electron transfer between the metal and the adsorbate upon chemisorption. Therefore, DW can be written as a function of these contributions: EDmeta + Dmol + eDchem. In this work, we propose a route to produce transparent low-workfunction indium tin oxide and plastic electrodes (Poly(3,4-ethylenedioxythiophene), or PEDOT). The workfunction of the transparent electrode is decreased upon chemisorption of a monolayer of strong electron-donor molecule, namely tetraakis(dimethylamino)ethylene -TDAE( (Me2-N)-2C=CC(N-Me2)2). Upon electron transfer reaction at the interface, TDAE molecules become positively charged and a chemical dipole potential eDchem is created leading to a significant workfunction decrease (>1.3 eV). High workfunction surfaces such as ITO [3] and PEDT-PSS [4] (WF=4.9 eV) have been transformed in stable, transparent low-workfunction electrodes (WF=3.6 eV). We demonstrate that electrons can now be injected from those modified electrodes, allowing to form novel all-transparent polymer light-emitting diodes. [1] H. Ishii, K. Sugiyama, E. Ro, and K. Seki, Advanced Materials, 11, 605 (1999). [2] X. Crispin, V. M. Geskin, A. Crispin, J. Corni, R.Lazarzoni, W.R.Salaneck, J.L. Bredas, Journal of the American Chemical Society, 124, 8312-8314 (2002). [3] W. Osikowicz, X. Crispin, C. Tengstedt, L. Lindell, Th. Kugler, W.R. Salaneck, Nature, 405, 1017 (2000). [4] L. Lindell, F. Jakobsson, J. Corni, P. Andersson, W. R. Salaneck, M. Berggren, X. Crispin, submitted.

8:30 AM A111.3/D14.3
Ultrafast electron transfer at the molecule-semiconductor nanoparticle junction. Tianquan Lin, Chemistry, Emory University, Atlanta, Georgia.

Interfacial electron transfer (ET) at the molecule-nanoparticle junction plays important roles in many nanoparticle-based devices, such as hybrid molecule/semiconductor photovoltaics and molecular electronics. We are carrying out systematic studies of photoinduced electron injection dynamics from molecular adsorbates to semiconductor nanoparticles from the interface of ET. On molecular excited state to metal oxide nanoparticles was directly measured using femtosecond transient absorption spectroscopy. We will discuss the dependence of ET rates on the nature of semiconductors, molecules (adsorbing group, spacing, metal storage and impacts), and environments (solvent, pH). We will also present recent advances on probing electron transfer dynamics at the single-molecule-nanoparticle junction using single molecule spectroscopy.

9:00 AM A111.4/D14.4
Interfacial control of electron transfer dynamics in dye sensitised and organic solar cells. James Durrant, Imperial College London, London, United Kingdom.

Electron transfer dynamics across donor / acceptor interfaces are central to the function of excitonic solar cells. Optimisation of device function requires the systematic control of both charge separation and recombination dynamics at this interface. In this paper we will address the parameters controlling electron transfer dynamics in such devices, and evaluate strategies to achieve optimization of these dynamics. We will start by considering what are optimum electron transfer dynamics which yield highest device efficiency. We will then go on to consider a range of interface engineering based strategies to achieve more optimised dynamics. Examples will be taken from a range of different exciton solar cells, including dye and CdS sensitised, hybrid polymer / metal oxide and all organic devices. Our paper focuses on the correlation between interfacial electron transfer dynamics and materials design / morphology, and their impact upon device function. Particular attention will be paid to supermolecular strategies to achieve electron transfer cascades, leading to long lived charge separation at nanostructured interfaces. References J. Durrant et al. Coord. Chem. Rev. (2004) 1247-1257 2. Hauke et al. J. Am. Chem. Soc. 25 (2005) 3456-3462 3. Handa et al. Angew Chemie (2005) in press.

9:30 AM A111.5/D14.5
Triplet Triolate Self-Assembled Monolayer: A Novel SAM to interface Zeolites to Gold(111). Andrew S. Ichimura and Wanda Low; Chemistry and Biochemistry, San Francisco State University, San Francisco, California.

A number of applications for thin films or monolayers of zeolites on surfaces have been proposed. For example, they may be used as porous membranes for separations or as low-k dielectric materials. Our interest zeolite monolayers originates in the unique optical properties of alkali metal doped pure silica zeolites, such as, cesium doped MFI (ZSM-5), or, Cs@MFI. Cs@MFI exhibits broad near infrared (NIR) absorption characteristic of nearly free electrons [1]. A related material, Cs@MFI has been characterized [2,3] and was predicted to have metallic properties [4]. In order to take advantage of the electronic properties of these novel materials and to facilitate the measurement of their fundamental properties, we set out to interface silica zeolites with a conducting surface. Our strategy employs bifunctional molecules to tether the zeolite to a gold (111) surface. The molecular tether uses the thiolate-gold interaction on one end and a functional group that can react with the surface silanol (Si-OH) groups of the zeolite on the opposite end. In order to prepare mechanically robust self-assembled monolayers to act as linking molecules, we devised a strategy whereby a mercaptoethanol SAM is reacted with silicon tetrachloride to form a triad thiolate monolayer. In this SAM, three adjacent mercaptoethanol molecules form silyl ether linkages leaving a reactive silicon chloride bond in a suitable position to react with zeolite silanol functional groups. One advantage of this SAM is that the zeolite may be tethered close to the gold surface, which should minimize the tunneling barrier between the zeolite and gold surface. Upon doping with alkali metals, the zeolite monolayer may find applications as sensors or detectors. In addition, this triad SAM can be used under hydrothermal synthesis conditions to prepare continuous thin films of crystalline MFI. This report will focus on our spectroscopic and theoretical studies of the triplet thiolate SAM, and preliminary XRD and SEM measurements of the zeolite monolayers and films. 1. Ichimura, A. S.; Lew, W. unpublished results. 2. E. Ichimura, A. Sanei, Nature, 405, 1017 (2000). 3. L. Durrant, F. Jakobsson, J. Corni, P. Andersson, W. R. Salaneck, M. Berggren, X. Crispin, submitted.

9:45 AM A111.6/D14.6
Optical electronic devices (OLEDs) are beginning to play a significant role in commercially available flat panel displays, so improvement in the lifetime of these devices is an important challenge. The short lifetimes of organic light emitting diodes (OLEDs) are caused by the chemical degradation of the organic materials. In particular, the cathode deposited on the organic layers may be a source of instability [1,2]. A common compound cathode consists of a ~1 nm thick metal halide salt deposited by vacuum evaporation or metal-organic vapor phase transport or by the deposition of a thick >10 nm aluminum layer, so the effect on stability of the choice of metal halide salt, and the thickness of the salt chosen is examined. For this study, all OLEDs were fabricated by sequentially depositing onto solution cast, thin film. The anode was a cost-effective, low-cost, and high-quality device, of devices without AgCl, was 1.5% (5.2 cd/ A) and 0.04%, respectively, and the operating voltage deviated from a mean value by ±0.5 V, at any given current density. Devices were electrically stressed at 40 mA/cm² for 2000 hours of their initial luminance. The mean initial luminance was 2100 cd/m², and the amount of time needed to degrade to 90% initial luminance increased according to the salt used in the following order: AgCl < NaBr < CsCl < CsF < NaF (210 hours) < CsF < NaF (200 hours) < CsCl (217 hours) < NaF (138 hours). The luminance after 400 hours also depended on the salt and increased as follows: AgCl (0 cd/m²) < NaBr < CsCl < CsF < NaF (180 cd/m²). These results are interesting because devices have the same initial performance characteristics regardless of the salt used in the OLED, and there seems to be no correlation between the properties of the salt used, such as density and sublimation temperature, and the stability of an OLED. [1] Y. Cao, G. Yu, I. D. Parker, and A. J. Heeger, J. Appl. Phys. 88, 3618 (2000). [2] M. Y. Chah, S. L. Lai, M. K. Fung, C. S. Lee, and S. T. Lee, J. Appl. Phys. 95, 5307 (2004). [3] 10:30 AM *E11.7/D14.7
Zn-porphyrin/C₇₀ complexes for solar cell devices: Molecular orientations, electronic properties and charge transfer time. Andrea Goldoni1, Carla Castellarin-Cudia1, Paolo Vilmercati1, Luca Petacchi1, Giuseppe Cipriani2, Silvano Lizzio2, Chiara Ceppe2, Luca Floreano2, Alberto Verdini2, Alberto Morgante3, Albano Cossaro1, Rosanna Lacripere1, Luigi Sangaletti2, Stefania Pagliara2, Chiara Battocchio2 and Giovanni Polzonetti2,2,3
Synchrotron Trieste S.C.p.A., Trieste, Italy. 2 Dip. Matematica e Fisica, Università Cattolica del Sacro Cuore, Brescia, Italy. 3 CNR-Istituto dei Sistemi Complessi, Rome, Italy.
Molecular dyes composed of electron donors capable of photo-induced electron transfer to linked acceptors have been used to mimic the natural photosynthetic reaction centers in photosynthetic devices. Porphyrin is among the most employed building blocks as electron donors [1]. Intriguing is the system formed by metallo-porphyrins directly bonded and facing fullerenes, actually realized in co-crystalline glasses and formation of inter connected molecular systems, with the ability to control and tailor the orientation of both molecules (geometric structure and arrangement of the molecules are responsible for the physical properties of the system). Here, we demonstrate that the UVB deposition of porphyrins and C₇₀ molecules on clean substrates allows the formation of films having selected intermolecular interactions and electronic properties. Using polarization-dependent x-ray absorption and photoemission spectroscopy we have investigated the ground state electronic structure and optical properties of Zn-Tetraphenyl-porphyrin (ZnTPP)/C₇₀ films deposited on Ag(110), Si(111) and TiO₂(110). The quite strong ZnTPP-fullerene interaction allows the growth of a single ZnTPP layer on top of a C₇₀ monolayer (and vice versa) and it allows the formation of the two molecular species in ordered multilayer structures when co-deposited. The interactions with the substrate and with C₇₀ modify the ZnTTP electronic states, indicating formation of bands and charge redistribution. Resonant photoemission, which probes the delocalization (charge transfer) of an excited electron on the time scale of the core-hole lifetime [4], indicates that the ZnTPP/C₇₀ may extensively delocalize more efficiently the excited electronic states compared to pure ZnTTP films. The charge transfer time depends on the empty <p>^* state in which the electron is excited and on the relative molecular orientations, but in general is below 10 fs and in some cases faster than Si(111) [1]. J. Chen et al, Science 286, 1550 (1999); A. Tsuda et al, Science 293, 79 (2001). [2] Y. P. Sun et al, J. Org. Chem. 62, 3042 (1997); P.D.W. Boyd et al, J. Am. Chem. Soc. 121, 10487(1999); T. Ishii et al, Coordination Chem. Rev. 220, 113 (2002). [3] J. J. Milanesio, J. P. Herob, F. P. de Mello, R. B. Fletcher, and M. Bernius, Appl. Phys. Lett. 83, 3611 (2003). [4] P.A. Lane, J.C. deMello, R. Fletcher, and M. Bernius, Proc. SPIE 5214, 102 (2003). [5] D. Poplavskyy, J. Nelson, D.D.C. Bradley, Proc. SPIE 5214, 107 (2004).
11:00 AM E11.8/D14.8
We present measurements of internal electric fields and charge injection in poly(9,9-diocytfluorene) (PFO) and PFO/poly(9,9-diocytfluorene-co-benzothiadiazole) (F8BT) blend based diode structures. In PFO/F8BT blend diodes with poly(2,3-ethylenedioxythiophene)/poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) anode the internal electric field in the device, measured using electromodulation techniques, has been reported to be smaller than expected [1,2]. This electric field screening was attributed to electron trapping near the anode. Here, we present a detailed study of electromodulation measurements of PFO/F8BT blend diodes nominally identical to those previously reported that do not exhibit this electric field screening. We discuss the possible origins of the different results observed in these internal electric field measurements. Similarly, electrons trapped near the anode have been invoked to explain enhanced hole injection from PEDOT:PSS into PFO [3]. Electrons injected to lead to an increase in current that was attributed to a trapped electron layer near the anode. This trapped electron layer increases the effective work function of the PEDOT:PSS contact. Here, we present measurements of charge injection in devices employing platinum and PEDOT:PSS anodes with identical built-in potentials. We find that charge injection from PEDOT:PSS is significantly greater than that from Pt. We discuss the differences in charge injection in these two structures that appear to be independent of contact energy levels. [1] P. A. Lane, J. C. deMello, R. B. Fletcher, and M. Bernius, Appl. Phys. Lett. 83, 3611 (2003). [2] P.A. Lane, J.C. deMello, R. Fletcher, and M. Bernius, Proc. SPIE 5214, 102 (2003). [3] D. Poplavskyy, J. Nelson, D.D.C. Bradley, Proc. SPIE 5214, 107 (2004).
Tailored Doping and Modification of Indium Thin Films for Organic Photovoltaics with Increased Photoactivity. Michael T. Brumbach\textsuperscript{1}, Thomas Schulmeyer\textsuperscript{1,2}, Neal R. Armstrong\textsuperscript{1}, Simon Jones\textsuperscript{1,3} and Seth Marder\textsuperscript{2};\textsuperscript{1}Chemistry, University of Arizona, Tucson, Arizona;\textsuperscript{2}Chemistry, Georgia Institute of Technology, Atlanta, Georgia.

Transparent conducting oxides (TCOs) are a significant component of molecular electronic devices such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs); however, the chemistry at the inorganic/organic interface has not been optimized. Small molecule chemisorption from solution or the gas phase has been developed as a strategy for enhancing the physical and chemical compatibility between freshly deposited inorganic material with organic thin films, thereby increasing the chemical stability while tuning the effective work function and rates of charge injection. This contribution will discuss the effect of small molecule modified ITO interfaces with near-IR sensitive photovoltaic phenazines (trivially and tetravalent metal Ps) in optimized Pce/C60 OPV devices. This scheme produces, on average, photopotentials which are higher by ca. 0.1 volts (as predicted from UV-photoemission studies) and higher photocurrents from near-IR excitation, than conventional phthalocyanine OPVs (e.g. those using CuPc/C60). New device architectures will also be presented which arise because of the development of low work function, highly conductive TCO films.

Properties of Polymer/Inorganic Semiconductor Interface Barriers Used in WORM Memories. Xin Xu and Stephen R. Forrest; Electrical Engineering, Princeton University, Princeton, New Jersey.

A simple, non-volatile, write-once-read-many-times (WORM) memory device can be fashioned from an organic/inorganic heterojunction (OH-IH) diode that serves both as a fuse and a rectifier in a 2D memory array\cite{1}. A layer of polyethylene dioxythiophene: poly(styrene sulfonyl acid (PEDOT:PSS) span onto the surface of an inorganic semiconductor have been shown to form a highly asymmetric rectifying junction that can be open circuited on the application of current. For the first time, we analyze the nature of the PEDOT:PSS/SC (where SC=Si, InP, GaAs) heterointerface. A model for charge transport over this barrier is applied, and application to the analysis of the experimental data illustrate that thermionic emission over the PEDOT:PSS/inorganic contact barrier dominates at low current densities under forward bias. For the PEDOT:PSS/In-Si interface, for example, a contact barrier energy of E_Bu=0.54+/-0.01 eV is obtained. There is no dependence of the measured barrier on the top contacting metal, indicating that control of charge in the rectifying junction is largely dependent on the organic/inorganic interface. Under reverse bias, the activation energy is (0.96+/-0.02 eV), or half the value of the Si bandgap, indicating that the reverse current is due primarily to generation-recombination in the Si bulk. Complementary results are obtained for a p-Si device. Polymer/III-V semiconductor heterojunctions will be the focus of this work, which provides fundamental insights into the nature of charge transport across hybrid organic/inorganic interfaces.\cite{1} S Moller, C Perlov, W Jackson, C Taussig, S R Forrest, Nature, 426, 166 (2003)

SESSION I2: Polymer-Inorganic Interfaces and Devices
Chair: Janice Reutt-Robey
Friday Afternoon, December 2, 2005
Room 302 (Hynes)

1:30 PM I2.1 Investigation of Charge-Injection Barriers in Finished PLEDs by Means of Non-Invasive Optical Probing. Franco Cacialli\textsuperscript{1}, Thomas Meredith Brown\textsuperscript{2} and Vladimir Bodorzeck\textsuperscript{3};\textsuperscript{1}Physics and Astronomy and London Centre for Nanotechnology, University College London, London, United Kingdom;\textsuperscript{2}MINAS-Dept. of Electronic Engineering, University of Rome Tor Vergata, Rome, Italy.

The electronic nature of metal-semiconductor contacts is a fundamental issue in the understanding of semiconductor physics, because such contacts control charge injection, and therefore play a major role in determining the electron/hole population in the semiconductor. Charge carrier injection and transport in organic semiconductors is important for organic semiconductors as they are generally used in their pristine, undoped form. Here, we review our progress in understanding the energy level line-up in finished, polymer-based light-emitting diodes, which exploit a variety of anodic or cathodic buffer-layers to obtain anodes and/or cathodes with low injection barriers. We have used electroabsorption measurements, as they allow the non-invasive determination of the built-in potential when changing the cathode.

This provides precious experimental information on the alteration of the polymer/electrode interfacial energy level line-up. The latter is known to depend strongly on the electrode work function. Thus, the Schottky-Mott model for the energy level alignment is found to be a better first-order approximation than those models where strong pinning or large interface dipoles determine the alignment (e.g. Beenakker model), except for electrodes which extensively react with the polymer, and introduce deep gap states.

2:00 PM I2.2 Organic Thin Film Transistors with Surface-Initiated ATRP Polymer Dielectrics. Jason Christopher Pinto\textsuperscript{1}, Gregory Whiting\textsuperscript{2}, Wilhelm Huck\textsuperscript{2}, Richard Friend\textsuperscript{1} and Henning Sirringhaus\textsuperscript{1};\textsuperscript{1}Optoelectronics Group, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom;\textsuperscript{2}Department of Chemistry, Molecular Laboratory, University of Cambridge, Cambridge, United Kingdom.

Recent interest in organic electronics has been motivated by the many advantages of organic materials over traditional inorganic semiconductors. Ease of processing through solution deposition is one of the key advantages of polymeric semiconductors and dielectrics. If high-speed organic circuits are to be realized, though, short channel length transistors must be fabricated from these materials. Short channel organic transistors are plagued by non-ideal device characteristics when fabricated with thick gate dielectrics. Ultra thin dielectrics are needed for these devices to show saturated transistor behaviour. Typical deposition methods suffer, as spin coating has difficulty in scaling to these very thin layers. The use of surface initiated atom transfer radical polymerisation (ATRP) offers an alternate approach to achieving ultra-thin dielectrics. Ultra thin nature of the polymerisation allows the formation of pinhole free ultra-thin films. We report here the fabrication of pentacene TFTs with polymer dielectric layers as thin as 60 nm grown with ATRP. Operation of these transistors at gate voltages as low as 0 Volts has been demonstrated in contrast to the high voltages traditionally employed with thick spun cast dielectrics. These thin dielectrics displayed leakage currents as low as 3 μA/cm2 at fields of 25 V/μm well within the operating range required for organic TFTs. A critical feature of organic TFTs that strongly influences their performance is the dielectric-semiconductor interface. ATRP offers precise control of the polymer brush chemistry and we demonstrate the use of this control to study the dielectric-semiconductor interface via such techniques as atomic force microscopy (AFM), x-ray diffraction and neutron reflectivity.

2:15 PM I2.3 Self-Assembled Monolayer of π-Conjugated Molecules as the Semiconducting Component of New Organic Transistor Structures. Kangho Lee\textsuperscript{1}, Sanghyun Ju\textsuperscript{1}, Rand Jean\textsuperscript{1}, Myung-Han Yoon\textsuperscript{2}, Antonio Fachetti\textsuperscript{1}, Gang Lu\textsuperscript{2}, Tobin Marks\textsuperscript{2} and David Janes\textsuperscript{1};\textsuperscript{1}Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana;\textsuperscript{2}Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois.

In disordered systems such as organic solids, hopping transport is the dominant conduction mechanism. Hopping generally results in relatively low charge carrier mobility, which has been the major limitation of organic field-effect transistors (TFETs). However, it has been demonstrated that organic solids composed by π-conjugated molecules with efficient intermolecular σ-orbital overlap exhibit improved charge transport characteristics. Very pure organic single crystals have been used to fabricate TFETs with mobilities as high as ~3500 cm2/V-sec, illustrating the improvements that can be achieved with well-ordered systems. Another approach would be to use well-ordered self-assembled π-molecules as the active TFET channel component. A 3-terminal transistor using a self-assembled tetracene derivative monolayer on an aluminum oxide dielectric was fabricated and exhibits current modulation. However, there is room to greatly improve device performance. In this study, the possibility of using self-assembled monolayers (SAMs) of π-conjugated oligothiophenes as the semiconducting component of organic TFETs has been examined. For this purpose, two questions should be addressed: 1) How much current is expected to pass through a SAM of π-molecules? 2) How efficiently are charges injected from the metal contact into a SAM? To answer these questions, thiolated π-molecules such as thiophenol have been self-assembled on GaAs substrates with two gold contacts separated by 2 μm. Compared to the pre-deposition leakage current (< 1nA) through a GaAs substrate, more than 10X increase in conductivity is observed after depositing thiophenol. Note that thiolated molecules can be self-assembled on both GaAs and Au. In contrast, depositing octadecanethiol decreases the current by 30% with respect to the leakage value, which is attributed to the passivation of GaAs surface by octadecanethiol. Based on these results, a single self-assembled SAM was performed with a dihexylquaterthiophene (DHDTH) derivative having a SiC3 group at one molecular end, allowing self-assembly on OH-terminated surfaces such as SiO2 and ITO. Similar devices with identical gold or ITO contacts separated by 2 μm, 5 μm or 10 μm
were fabricated on a heavily doped n-type Si substrates with 5000 A thermally grown SiO2. No significant increase in conductivity was observed in the devices with Au contacts. However, the devices with ITO contacts separated by 500 nm showed conductivity enhancement by 5 orders of magnitude after depositing SDHAT, which leads us to propose that self-assembled p-n junctions on metal contacts facilitate the carrier injection across the metal/polymer interface. To further investigate the mechanism of the observed conductivity increase, electrical, optical, and photoresponse measurements were performed. The device structures were characterized using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and transmission electron microscopy (TEM).

The experimental results show that the devices fabricated with ITO contacts exhibit a significant increase in conductivity compared to those with Au contacts. This enhancement is attributed to the improved injection of carriers from the metal contacts into the polymer film. Furthermore, the devices with ITO contacts show a lower threshold voltage for the onset of current, indicating a more efficient carrier injection process.

2:30 PM **112.4**
**Electronic structure of hybrid interfaces for polymer-based electronics.** William R. Salaneck, Wojciech Osikowics and Sławomir Braun; Dept. Physics, Linköping University, Linköping, Sweden.

Conjugated polymers are currently used in organic molecular and polymer based electronics. The interface between the organic material (molecular or polymeric) and inorganic electrode materials controls a great deal of the interfacial charge transfer characteristics. This talk will cover recent work on hybrid interfaces, especially where molecular adsorption may be used to control interfacial electronic parameters. The characterization of the interface between spin-coated polymer films and metallic substrates (the device fabrication mode), carried out using photoelectron spectroscopies, will be reviewed, highlighting work done in Linköping.

3:30 PM **112.5**
**STM-Excited Electroluminescence and Spectroscopy on Organic Materials.** Santos F. Alvarado1, Martijn Kemerink2, Peter Mueller1, Laura Ross1 and Laurent Libiioule; 1Science and Technology Department, IBM GmbH Zurich Research Laboratory, 8093 Zurich, Switzerland; 2Molecular Materials and Nanosystems Department, Dept. of Applied Physics and Chemical Engineering, Eindhoven University Of Technology, Eindhoven, Netherlands.

Three-dimensional numerical model calculations for charge-carrier injection and transport in organic materials are compared with experimental results to elucidate the conditions under which the 2-D/3-D transport model is applicable. The following conditions are necessary: (a) a sufficiently sharp STM-tip apex, leading to field enhancement of the injected current; (b) a sample that can stably sustain the high electric field; (c) a sample that is a good conductor, allowing for efficient charge injection. The model predicts an enhancement of the radiative recombination rate by the field-enhanced injection. The comparison of the model predictions with experimental results shows the ability of the model to accurately predict the effects of the experimental conditions on the efficiency of charge injection and transport in organic materials.

4:15 PM **112.7**
**Effect of chain conformation and external fields on the electronic structure of conjugated polymers.** Florian Schindler1, John Mark Lupton1, Klaus Becker1, Jochen Feldmann1 and Ullrich Scherf2; 1Department of Physics, Ludwig-Maximilians-Universitaet, Munich, Germany; 2Department of Chemistry, University of Wuppertal, Wuppertal, Germany.

Conjugated polymers, which are intrinsically multichromophoric assemblies, constitute an important class of materials for molecular electronics applications. Intramolecular interfaces between adjacent chromophores on one chain are of particular importance in these systems. Low temperature single molecule fluorescence spectroscopy provides insight into molecular subunits by overcoming disorder broadening [1] and can highlight the relative roles of chain conformation, intramolecular energy transfer, intramolecular aggregation and local fields. We apply this technique to the ordered ladder-type poly(para-phenylene) and disordered poly(phenylene-vinylene), as well as to single molecules of polythiophene, which exist both in a disordered (glassy) and in the planar ordered (beta) phase [2]. In spite of the rather different chemical structures, we observe identical spectral features on the single chromophore level, such as fluorescence linewidths and spectral diffusion dynamics due to temporal variations in local fields [2]. In particular, the photoluminescence linewidths for PPV are around one hundred times narrower when compared to the ensemble. Despite these similarities, interchromophoric coupling mechanisms differ strongly. In PPV, intramolecular aggregation results in spectral broadening. This behaviour is absent in ladder-type polymers, where the linewidth of the emissive species is identical for all molecules. The fundamental quantity governing intramolecular couplings is the conjugation length, which can be determined on the single molecule level and is found to substantially exceed the size of isoenergetic model oligomers [4]. Our results provide important insight into material design by demonstrating that structure-property relationships in conjugated polymers differ significantly from those found in inorganic materials. Highly local perturbations of the pi-electrons, which are not immediately apparent in ensemble measurements, can therefore strongly modify electronic interactions at the interface to adjacent molecules or electrodes [5].

4:00 PM **112.6**
**Investigation of Novel Photo FET using Photo-Sensitive Gate Dielectric.** Manabu Yoshida, Hiroki Kawai, Takeshi Kawai, Sei Umemura, Satoshi Hoshino, Takehito Kodzasa and Toshihide Kamata; 1Organic Semiconductor Device Group, AIST, Tsukuba, Ibaraki, Japan; 2Tokyo University of Science, Tokyo, Tokyo, Japan.

Organic Field Effect Transistors (OFETs) have been noticed as a possible candidate for next-generation electronic devices for recent years. With the appearance of many kinds of organic materials, they give various special functions to OFETs. Especially, we have paid attention to and investigated polymeric gate insulators employed in the part of the OFETs. Some sorts of polymeric materials, utilized as plasticizing agents or dopants, can improve the photoconductive properties. Therefore, they work as insulators in dark condition and as conductors in photo-illumination condition, reversibly. By using their photoconductive properties, we have intended to make photo-switching and photo-memory functions. For example, poly-N-vinylcarbazole (PVK) has been known as a good photconductor. Further, the PVK has high processability and high durability to applied voltage, therefore, it is expected to work as a good polymeric insulator for OFETs in dark condition. For the purpose of giving photofunctions to OFETs, we have fabricated a pentacene FET having a PVK insulator, and we have been especially interested in transistor behavior of the OFET on illuminating the PVK insulator by light with different wavelengths. An ITO electrode was employed as a transparent gate electrode in the OFETs. As a result, under appropriate conditions, the photo-illuminations of the PVK insulator drastically increase the field effect mobility values (ON current) by about two orders of magnitude. We have considered that the increase of the field effect mobility results from occurrence of efficient hole accumulations at the pentacene / PVK interface by the capacitance change of the PVK layer originated from the photo-illumination.

4:30 PM **112.8**
**Fermi Level Pinning at Conjugated Polymer Interfaces.** Carl Tengstedt1, Wojciech Osikowicza, William R. Salanecka and Mats Fahlin1; 1Science and Technology, Linköping University, Norrkoping, Sweden; 2Physics and Materials Technology, Linköping University, Linköping, Sweden.

Photoelectron spectroscopy has been used to map energy level alignment of conjugated polymers at various organic-organic and...
hybrid interfaces. Specifically, we have investigated the hole-injection interface between metallic substrates (organic and inorganic) and light-emitting conjugated polymers. Two different alignment regimes are observed: (i) vacuum level alignment, which corresponds to the lack of vacuum level offsets (Schottky-Mott limit) and (ii) Fermi level pinning, where the substrate Fermi level and the positive polaronic level of the polymer align. The observation is rationalized in terms of spontaneous charge transfer whenever the substrate Fermi level exceeds the positive polaron/bipolaron formation energy per particle. The charge transfer leads to the formation of an interfacial dipole, and the Fermi level is pinned to the positive polaronic level. In analogy with our results, we expect that the same mechanisms should hold true at electron-injecting polymer on metal interfaces, i.e., pinning of the Fermi level to the negative polaron/bipolaron level of the CLP when the metal work function is smaller than the negative polaron/bipolaron formation energy.

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Fabrication of Organic Thin Film Transistors Using Layer-by-Layer Assembly. Jeffery Byron Strickler1,2 and Michael F. Durstock2; 1Department of Chemistry, University of Cincinnati, Cincinnati, Ohio; 2Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio.

Layer-by-layer assembly is presented as a deposition technique to incorporate ultra-thin dielectric layers into thin film transistors for low-voltage applications. This study focuses on thin film transistors currently being investigated with highly doped conducting polymers as the active layer, in particular poly(3,4-ethylendioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS). The transistor \(I_{on}/I_{off}\) ratio and switching speed have been shown to be controlled by the number of bilayers deposited for, and the ultimate thickness of, the gate dielectric. The devices operate in the depletion mode as a result of de-doping of the active layer with the application of the gate bias. The depletion and recovery are shown to be highly dependent on the level of hydration in the film and the environment under which the device is operated. These observations are consistent with an electrochemical de-doping of the conducting polymer during operation.