

SYMPOSIUM I

Interfaces in Organic and Molecular Electronics II

November 28 - December 2, 2005

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* Invited paper

8:00 AM OPENING REMARKS

8:15 AM II.1

Quantum atomistic theory and modeling of carbon nanotube nanoelectronics. Yongqiang Xue, College of Nanoscale Science and Engineering, University at Albany-SUNY, Albany, New York.

Nanostructured devices based on single-wall carbon nanotubes (SWNTs) present unique opportunities both for exploring novel device technology functioning at the nano/molecular-scale and for re-examining the physical principles of semiconductor microelectronics from the bottom-up atomistic 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 atomistic 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 takes fully into account the 3D atomistic nature of the electronic processes. We discuss insights obtained from such 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 Nitzan¹ 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 electron-hole excitations in 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 resonance radiation 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, Nikolai Sergueev¹, Danila Roubtsov¹, Derek Waldron¹ and Paul Haney^{2,1}; ¹Dept. of Physics, McGill University, Montreal, Quebec, Canada; ²Physics, Univ. 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. Our theoretical formalism 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 external bias and during current flow? In particular, we investigate the problem of which vibrational modes 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 magneto resistance (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 Ratner^{1,2}, Abe Nitzan^{1,2,3} and Misha Galperin^{1,2};

¹Department of Chemistry, Northwestern University, Evanston, Illinois; ²Center for Nanotechnology, Northwestern University, Evanston, Illinois; ³Department 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 generalizations 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 Gebauer, 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 with 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 evolves towards a steady state, whose physical properties (currents, charges, potentials, local energy dissipation ...) can be evaluated. In the presentation I will explain the 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 Meunier², Shuchun Wang¹, Qingzhong Zhao¹ and Jerry Bernholc^{1,2};

¹Center for high performance simulation, North Carolina State University, Raleigh, North Carolina; ²Computer 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 the Fermi levels of the leads. For molecules attached to semiconducting leads, 1,4 diethynylbenzene on Si(111) and cyclopentene 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 Si surfaces. Studies of a monolayer of cyclopentene on Si(001) surfaces show that the interactions between molecules attenuate the NDR, as seen in experiments. For ferrocenyl-alkanethiolate self-assembled monolayer on the Au(111) surface, resonant states around the Fermi level dominate the conductance. Similarly 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 **I1.8**

Modeling of Contact Formation in Carbon Nanotube Devices.

Karthik Ravichandran and Wolfgang Windl; Materials Science & Engineering, The Ohio State University, Columbus, Ohio.

The continuing 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 process 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 systems, with changes on the order of two orders of magnitude difference in conductivity after optimizing the contact structure.

SESSION I2: Single Molecule Dynamics at Interfaces

Chair: Duncan Stewart

Monday Afternoon, November 28, 2005

Room 302 (Hynes)

1:30 PM ***I2.1**

Current-Driven Phenomena in Molecular Electronics. From Surface Nanochemistry to New Forms of Molecular Machines. Tamar Seideman, Ryan Jorn and Chao-Cheng Kaun; 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 vibration, rotation, inter-mode energy flow and 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 molecule-derived orbitals and thus 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 ***I2.2**

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 [Qiu 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 tunnelling 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 Tersoff-Hamann approximation for elastic tunnelling and its many body extension to inelastic electron tunnelling. 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. Lorente and M. Persson, Phys. Rev. Lett. 85, 2997 (2000). 4. N. Lorente, M. Persson, L. J. Lauhon, and W. Ho, Phys. Rev. Lett. 86, 2954 (2001).

3:30 PM ***I2.3**

Spatial Distribution of Contact States Studied by STM.

Satoshi Katano¹, Masafumi Hori^{1,2}, Yousoo Kim¹ and Maki Kawai^{1,2}; ¹RIKEN, Wako-shi, Japan; ²Department 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 the catalysis point 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), 4 σ - and 5 σ - derived states of CO are strongly modified in space that considerable charge transfer occurs from the C site to the O site in the 5 σ -derived state and in the opposite way in the 4 σ -derived state [1]. In the talk, we will present our recent work on the adsorption of benzoate (C₆H₅COO) and aminobenzoate (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 contact 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 ***I2.4**

Single Molecular Conductivity by STM under UHV.

Masamichi Fujihira, Masaaki Suzuki, Kenichi Ishizuka, Shintaro Fujii, Uichi Akiba, Yuuki Takayama and Fumie Sato; Department of Biomolecular 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-alkanethiolates (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 rotamers 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. Secondly, the difference in electronic conduction between saturated 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 dithiol 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 bridges were formed and the currents through these bridges 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 conductivity in liquid with that in vacuo. References [1] M. Suzuki S. Fujii, S. Wakamatsu, U. Akiba and M. Fujihira, Nanotechnology 15, S150 (2004). [2] K. Tagami, M. Tsukada, e-J. Surf. Sci. Nanotech. 2, 186 (2004). [3] B.Q. Xu, N.J. Tao, Science 301, 1221 (2003).

4:30 PM ***I2.5**

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 single molecules or nanoparticles into the tunnel junctions in which the STM tip and supporting surface 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 center electrode in a double barrier tunnel junction, we can study 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 I3: Poster Session
Chair: C. D. Frisbie
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)

I3.1 **Abstract Withdrawn**

I3.2
Dynamics of Adsorbed Organic Molecules Studied by Fast-Scanning STM: Diffusion and Conformational Dynamics. Roberto Otero^{1,2}, Peter Thosttrup², Fernando Sato³, Douglas Galvao³, Erik Laegsgaard², Ivan Stensgaard² and Flemming Besenbacher²; ¹Dept. of Condensed Matter Physics, Universidad Autonoma de Madrid, Madrid, Spain; ²Dept. of Physics and Astronomy, iNANO and University of Aarhus, Aarhus, Denmark; ³Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Campinas, Brazil.

The study of large organic adsorbates on solid surfaces has gained momentum in recent years. This is motivated partly by the fundamental challenge of understanding processes such as self-assembly and molecular recognition down to the single-molecule level, and partly by the promising prospective of these systems for a broad range of applications such as optoelectronic and molecular electronic devices, nanomechanical biosensors and new improved materials for implants. While much is known about the adsorption properties (physisorption, chemisorption, diffusion, desorption, dissociation) of simple adsorbates like NO, CO, O₂ etc. on a great number of host surfaces, comparatively much less is understood about the properties of larger molecules when adsorbed on a substrate. Unlike simpler adsorbates, to describe the state of an organic molecule deposited on a solid substrate not only the position must be given, but also its adsorption orientation and its conformation. Moreover, the energy landscape for organic adsorbates turns out to be rather complex, in such a way that the various degrees of freedom are intricately coupled, a fact of the utmost importance to understand the dynamics of adsorbed molecules on solid surfaces. Understanding the intricacies associated to the dynamics of adsorbed large organic molecules is essential for the rational design of organic nanostructures. In this talk we will show two examples in which variable-temperature fast-scanning STM is used to follow the dynamics of an organic species known as Violet Lander (VL, C₁₀₈H₁₀₄) adsorbed on Cu (110). On the one hand we will demonstrate that the diffusion coefficient of the VL molecule strongly depends on the molecular orientation, changing by at least 2 orders of magnitude by a 70° rotation. This effect, basic for the understanding of kinetic effects on 2D self-assembly, can be traced back to the shape complementarity between substrate and adsorbate, and underlines this complementarity as a major factor to take into account when designing molecular devices for given substrates. Secondly, we will show that the conformations of adsorbed VL molecules are not static, as described so far, but can also change with time. We have studied the fraction of time spent in one conformation or the other as a function of temperature in a broad temperature range. Our results clearly demonstrate that entropic effects govern the conformational dynamics of adsorbed VL molecules over energetic effects. The possible effect of interaction with diffusing particles such as Cu adatoms will be discussed.

I3.3
Variable Temperature Electric Force Microscopy of a Molecularly Doped Polymer. Tse Nga Ng, William Silveira and John Marohn; Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

We have investigated the charge transport and injection process in a model system of molecularly-doped polymer [a triarylamine (TPD) dispersed in polystyrene (PS)] by variable temperature electric force microscopy (EFM) under high vacuum. In contrast to bulk current-voltage measurements, this microscopic study unambiguously reveals space-charge-limited conduction within TPD-PS. The temperature dependence of charge transport indicates that free charge carrier density increases with lower temperature, which can be explained by energetic disorder in the polymer. Contact degradation

at elevated temperature and after crystallization is directly observed and quantified through potential profiles obtained by EFM.

I3.4
Electrical Characterization of Molecular Junctions by Conducting Atomic Force Microscopy: Effect of Tilt Angle and Molecular Structure under Tip Loads. Hyunwook Song¹, Changjin Lee², Yongku Kang² and Takhee Lee¹; ¹Material Science and Engineering, Gwangju Institute Science and Technology, Gwangju, South Korea; ²Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, South Korea.

We conduct electronic transport measurement of metal-molecule-metal junction currently being considered as key elements in molecule-based electronic devices, using conducting atomic force microscopy (CAFM). The CAFM technique is an attractive and easy accessible approach as a tool to study molecular scale charge transport across self-assembled monolayer (SAM) [1, 2]. There is, however, important consideration to measure current-voltage I(V) characteristics across monolayers by CAFM technique, that is, tip-loading force effect which has recently been unfolded to significantly affect junction properties [2-4]. Generally, the current through the junction increases with increasing loading force [2-4]. By evaluating current density for a given loading force, this increasing current with increasing loading force is not simply due to increasing contact junction area caused [4]. Such the result implies that deformation of SAM may influence molecular transport property. Especially, molecular tilt angle is expected to increase under CAFM tip contact with certain loads in addition to a possibility of other structural deformations [3, 5]. Slowinski, et. al. and Waldeck, et. al. suggested highly tilt angle of the monolayer can provide an additional tunneling pathway involving through-space mechanism [6, 7]. In our research work, we estimate a degree of molecular tilt of alkanethiols using a mechanical contact theory, and then study the effect of tilt angle on I(V) characteristics, e.g., chain-to-chain coupling under the influence of tip contact to SAM. Furthermore, the different sensitivity to tip-loading effect for different molecular structures comprised of flexible versus rigid rod-like backbone is studied. [1] X. D. Cui, et al. Science 2001, 294, 571-574. [2] D. J. Wold, et al. J. Am. Chem. Soc. 2001, 123, 5549-5556. [3] X. D. Cui, et al. Nanotechnology 2002, 13, 5-14. [4] T. Lee, et al. J. Phys. Chem. B. 2004, 108, 8742-8750. [5] J. I. Siepmann, et al Phys. Rev. Lett. 1993, 70, 453-456. [6] K. Slowinski, et al. J. Am. Chem. Soc. 1997, 119, 11910-11919. [7] H. Yamamoto, et al. J. Phys. Chem. B. 2002, 106, 7469-7473

I3.5
Current-Voltage Characteristics of Au-porphyrin Derivative-Au Junctions. Yutaka Noguchi, Takashi Nagase, Tohru Kubota, Toshiya Kamikado and Shinro Mashiko; Nano Technology Group, Kansai Advanced Research Center, National Institute of Information and Communications Technology, Kobe, Japan.

Current-voltage (I-V) characteristics of Au-molecule-Au junctions with a back gate electrode structure using an electromigration method were examined[1]. By the scanning electron microscope observation, the successful formation of the nanogap electrodes with narrow gap width ~5 nm was confirmed. The molecule used for the measurements was 5,15-bis(3,5-di-*t*-butylphenyl)-10,20-bis(4-methylthiophenyl)porphyrin. The molecular orbital calculation results showed the π orbitals originated from the porphyrin core are spatially isolated and they are expected acting as a Coulomb island. The molecules were adsorbed on Au electrodes by self-assembly and the I-V characteristics of more than 200 junctions were measured at a temperature below 10 K. Three types of I-V characteristics were observed, i.e., very small current less than 1 pA with the applied voltages ± 1.0 V, the exponential curves as a tunneling current (more than 10 pA at 0.5 V), and the Coulomb staircase like characteristics. Most of junctions showing Coulomb staircase were unstable and the characteristics were easily disappeared. We will discuss the properties of these three types of I-V characteristics. [1] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen and D. C. Ralph, Nature 417 (2002) 722.

I3.6
Measurements of single molecule conductivity by scanning tunneling microscopy under an ultrahigh vacuum condition. Kenichi Ishizuka, Shintaro Fujii, Yuuki Takayama, Fumie Sato and Masamichi Fujihira; Department of Biomolecular Engineering, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

Recently designing organic molecules and understanding how electrons flow through themselves have become important more and more in molecular electronics. Innovations in synthetic chemistry have made it possible to tailor the electronic properties of molecules. In a previous work [1], a linear π -conjugated compound was synthesized using a recently developed method [2]. Namely, we succeeded in

synthesizing the linear π -conjugated compound, (E)-3,4-dimethyl-1,6-dithioacetyl-3-hexen-1,5-diyne (DDHD), and measuring scanning tunneling microscopy (STM) topographic heights of individual 1,6-hexanedithiol (HDT), 1,4-benzenedimethanethiol (BDMT) and DDHD molecules isolated in BCO matrices. After cleavage of thioacetate groups of DDHD, the resulting dithiol derivative (DDHD') was used for the measurements. When the physical and STM topographic heights were compared, it was found that the conductivity of DDHD' was higher than those of HDT with a saturated alkane chain and BDMT with a phenylene π -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 vacuum gap between a W tip and one unbound end of the molecule. In this work, we will report single molecular conductivities for HDT, BDMT and DDHD', which are bonded to an Au substrate and an Au STM tip at both ends using STM under ultra high vacuum (UHV). Under UHV, we created molecular junctions by moving repeatedly the Au STM tip into and out of contact with the Au substrates covered with three types of self-assembled monolayers (HDT, BDMT and DDHD') 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 DDHD', we obtained their conductance histograms and determined their values of (G_m). References [1] K. Ishizuka, M. Suzuki, S. Fujii, U. Akiba, Y. Takayama, F. Sato, M. Fujihira, *Jpn. J. Appl. Phys.*, in press. [2] Y. Takayama, C. Delas, K. Muraoka, M. Uemura, F. Sato, *J. Am. Chem. Soc.* 125, 14163 (2003). [3] B. Q. Xu, N. J. Tao, *Science* 301, 1221 (2003). [4] J. He, F. Chen, J. Li, O. F. Sankey, Y. Terazono, C. Herrero, D. Gust, T. A. Moore, A. L. Moore, S. M. Lindsay, *J. Am. Chem. Soc.* 127, 1384 (2005). [5] W. Haiss, H. Zalinge, S. J. Higgins, D. Bethell, H. Hobenreich, D. J. Schiffrin, R. J. Nichols, *J. Am. Chem. Soc.* 125, 15294 (2003).

13.7

Interaction of 2,2,6,6-tetramethyl-3,5-heptanedione with Si(100)-2x1 Surface. Dimitri Skliar, Amalia 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 room temperature adsorption and thermal decomposition of sub-monolayer surface coverages of 2,2,6,6-tetramethyl-3,5-heptanedione (C₁₁H₂₀O₂) on Si(100)-2x1 surface is 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 298-1000K range as well as their effect on 2x1 dimer structure.

13.8

Solvent Effects on the Assembly of π -Conjugated Dithiol Molecules on Au and GaAs. Dmitry A. Krapchetov¹, Hong Ma², Alex K. Y. Jen², Daniel A. Fischer³ and Yueh-Lin Loo¹; ¹Chemical Engineering Department and Center for Nano- and Molecular Science and Technology, University of Texas at Austin, Austin, Texas; ²Materials Science and Engineering Department, University of Washington, Seattle, Washington; ³Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

The assembly of simple π -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 π -conjugated molecules is not completely 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 n-phenyldithiols (n=3,4). As synthesized, these molecules are protected by acetyl end groups. To convert the acetyl end groups into thiols, NH₄OH is added. We investigated the assembly of these molecules from ethanol/tetrahydrofuran mixtures, in addition to the pure solvents, in the presence of dilute (<35 mM) NH₄OH. To examine the surface coverage and the ensemble-average orientation of n-phenyldithiol

assemblies on Au and GaAs, we carried out synchrotron-based near-edge x-ray absorption fine structure spectroscopy (NEXAFS) and in-house Fourier transform infrared spectroscopy (FTIR) experiments. Both carbon-edge NEXAFS spectra and FTIR indicate that the n-phenyldithiol surface coverage on Au is independent of the assembly solvent. Angle-resolved NEXAFS suggest that terphenyldithiol (n=3) and quaterphenyldithiol (n=4) are preferentially oriented on Au and the molecules are tilted on average $30^\circ \pm 3^\circ$ 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-phenyldithiols 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 average orientation of terphenyl- and quaterphenyldithiols (n=3,4) is similar to that on Au, but at low ethanol fractions, all the assemblies are disordered.

13.9

First-Principles Theoretical Study of n-alkane and Metal Interfaces. Yoshitada Morikawa^{1,2,3}, Hisao Ishii⁵ and Kazuhiko Seki⁴; ¹ISIR, Osaka University, Ibaraki, Osaka, Japan; ²CREST-JST, Kawaguchi, 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 interfacial dipole tends to increase as the substrate metal work function increases. It is desired 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 demonstrate 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.

13.10

Measurement of Molecular Packing Order and Electron Transport in Self-Assembled Monolayer on Pt(111) substrate using Scanning Tunneling Microscopy. Sangyeob Lee and Regina Ragan; Chem. Eng. & Mat. Sci., Univ. of California, Irvine, Irvine, California.

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 successfully deposited two simple organosulfur molecules, octanethiol and benzenethiol. Using ultrahigh vacuum scanning tunneling microscopy (STM), we investigated their packing order in order to determine if 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. SAMs on 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. SAMs on Au showed high surface defects density about 15%. However, Surface defect density of octanethiol monolayer on Pt(111) was 6%. Electron transport measurement through Pt(111)/molecular junctions was done using STS. I-V response in the benzenethiol/Pt(111) junction was higher than that of octanethiol/Pt(111) junction near zero bias.

13.11

Synthesis and Charge Transport Properties of OPV Molecular Wires. Dwight S. Seferos¹, James G. Kushmerick² and Guillermo C. Bazan¹, ¹Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, California; ²Surface and Microanalysis Science Division, NIST, Gaithersburg, Maryland.

To better understand how molecular structure can influence charge transport we have synthesized a series of related molecular wire molecules based on thiol-terminated oligomers of phenylenevinylene (OPV). Our synthetic library includes molecules with through-bond and through-space delocalized structures, and molecular rods terminated with zero, one, and two methylene spacer units between the OPV structure and the thiol points of attachment. The charge transport properties of these structures have been examined by two methods: 1) by inserting the conductive molecules into a monolayer film that was imaged using scanning tunneling microscopy, and 2) by forming metal-molecule-metal junctions with Au colloid top contacts which were contacted by a scanning probe tip. We compare the conductivity data of the various structures obtained by these two techniques as well as compare these measurements with our previous cross-wire junction experiments and find good agreement between the different methods. A thorough discussion of molecular structure and charge transport will be presented.

13.12

Towards Addressable Organic Impedance Switch Devices. Fredrik L. E. Jakobsson, Xavier Crispin 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 proposed 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 input currents from drive 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 Rose Bengal (RB) sodium salt switch layer. Leakage currents from 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 driver current load and reducing the potential loss along the addressing lines. Adding the CuPc layer to the linear RB switch device 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.

13.13

Device Characterization of Carbon Nanotube Transistors and Its Carrier Injection Mechanisms from Schottky Barriers. Masashi Shiraishi^{1,3}, Shuichi Nakamura¹, Tomohiro Fukao¹, Taishi Takenobu^{2,3} and Yoshi Iwasa^{2,3}, ¹Graduate School of Engineering Science, Osaka Univ., Toyonaka, Osaka, Japan; ²IMR, Tohoku Univ., Sendai, Miyagi, Japan; ³CREST-JST, Kawaguchi, Saitama, Japan.

Single-walled carbon nanotubes (SWNTs) have quasi-one-dimensional structures with semiconductive or metallic properties, which promise various applications as molecular electronics devices with nano-sized structures. To date, various applications have been proposed, such as transistors, diodes, spin valves and so on. 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 stand point of a bottom up type 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 ($> 1000000 \text{ cm}^2/\text{Vs}$), while the SWNT-TFTs have advantages of an easy fabrication of devices and comparably 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. 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 $3.6 \text{ cm}^2/\text{Vs}$ and 10000, respectively, and this device performance was comparably 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 encapsulation of TCNQ 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 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. Shiraishi et al., Chem. Phys. Lett. 394, 110 (2004). [5] M. Shiraishi et al., Chem. Phys. Lett. 358, 213 (2002). [6] M. Shiraishi et al., in preparation. [7] M. Shiraishi et al., submitted to Appl. Phys. Lett. [8] T. Takenobu et al., Nature Mat. 2, 633 (2003).

13.14

Electrical Transport Measurements Through Single DNA Molecules by Conductive AFM. Hezy Cohen¹, Claude Noguez^{2,1}, Daniela Ullien¹, Ron Naaman¹ and Danny Porath¹; ¹The Hebrew University of Jerusalem, Jerusalem, Israel; ²The 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) embedded in a single stranded (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 26 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.² 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.³ 1. Claude Noguez, Sidney R. Cohen, Shirley S. Daube and Ron Naaman, PCCP, 2004, 18, 2 2. Hezy Cohen, Claude Noguez, Ron Naaman and Danny Porath, PNAS, in press 3. Hezy Cohen, Claude Noguez, Daniela Ullien, Shirley Daube, Ron Naaman and Danny Porath, Faraday Discussions, in press

13.15

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

INTRODUCTION Charge transfer through organic-inorganic interfaces dominates the performance of organic devices. Recently, Eremchenko et al. reported that electric charge is pumped back and forth between Ag(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 ($< 1 \times 10^{-9}$ Torr). Purified tetracene was evaporated onto the HOPG substrate at deposition rate of $\sim 0.4 \text{ nm}/\text{min}$. 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 3.8 meV, respectively. All measurements were performed at room temperature. RESULT AND DISCUSSION In HREELS spectra of tetracene (16.0 nm)/HOPG, four energy loss peaks (9, 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 electron scattering angle, and has a sharp maximum at the specular 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 by 1 meV. 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. Eremitchenko et al., *Nature* 425 (03) 602

13.16

Current-voltage characteristics of molecules/silicon hybrid systems using a scanning tunneling microscope.

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We have prepared organic molecules/silicon hybrid systems by exposing silicon(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 investigated 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 +4 V. The polarity of the peak position 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 onto the I-V characteristics will be discussed.

13.17

Molecular Orientation Switch of an Endohedral Metallofullerene on Alkanethiol Self-assembled Monolayer.

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Endohedral metallofullerenes [1] are one of the candidate materials for creating single molecular 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 are modulated, 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 the 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 terbium endohedral metallofullerene (Tb@C82) [2] on an alkanethiol SAM. The I-V characteristics of a single Tb@C82 molecule on an octanethiol SAM at 13 K repeatedly exhibited hysteresis and negative differential conductance (NDC) [3]. This observed hysteresis and NDC is interpreted in terms of a switching of the Tb@C82 molecular orientation caused by the interaction between its electric dipole moment and an external electric field. Furthermore, we found the STM images of Tb@C82 on hexanethiol SAM differ from that of on octanethiol SAM at 68 K. We discuss alkanethiol chain length dependence of STM image of Tb@C82 on alkanethiol SAM by taking into account of the interaction modulation due to the number of methylene groups of 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).

13.18

Tunneling resistances of double-barrier tunneling structures including an alkanethiol-protected Au nanoparticle.

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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, single electron shuttle phenomena based on 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 inverses 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 in a subnanometer scale that enable us to realize the electron shuttle with self-excitation. Here we demonstrate Coulomb staircases in double-barrier tunneling junctions consisting of a scanning 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 R₂ of octanethiol- and hexanethiol-protected Au nanoparticles are evaluated as 7.6 GΩ and 460 MΩ, respectively. [1] L. Y. Gorelik, A. Isacsson, M. V. Voinova, B. Kasemo, R. I. Shekhter, 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* 103, 8122 (1999).

13.19

Microscopic and spectroscopic study on self-assembled monolayer film.

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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 transport behavior changing 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 be suitable to molecular electronic application.

13.20

Electrical Properties of DNA molecules by Top-contacted Nanogap Electrodes and Immobilization of DNA Molecules on the Patterned Self-assembled Monolayers.

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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 the surface with top-contacted geometry type nanogap electrodes reported previously [*Nanotechnology* **15**, 1639 (2004)]. Utilizing these electrodes enables us to prevent DNA molecules from structural deformation that might occur in case of bottom-contacted geometry type electrodes. DNA solutions with different counter ions is prepared and dropped on the cleaned SiO₂ surface. After the incubation, the surplus 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 and the enhancement of 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 lambda DNA on the patterned substrate, we have found 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. *Work supported by CREST, JST and JSPS Fellowships for Young Scientists

13.21

Multicomponent Interface Chemistry in Self-Assembled Monolayers on Platinum. D. Y. Petrovykh^{1,2}, H. Kimura-Suda³, A. Opdahl³, L. J. Richter³, M. J. Tarlov³, M. Yang², A. R. Laracuent² 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 comprehensive 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 attach to heavily-oxidized Pt surfaces, and Pt oxides 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-sulfur and metal-oxygen bond strengths for these 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.

13.22

Characterization of New Molecular Memory Materials and Their Application for Molecular Electronic Devices by Using Nano-Imprinting Technique. Hyoyoung Lee, Junghyun Lee, Gyeong Sook Bang, Nak-Jin Choi, Jonghyuk Park and Hee-Yeol Baik; 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 nano-scaled molecular memory 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 characterization of novel 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 (MMM). 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. Takai, Langmuir **16** (2000) 885. [3] R.M. Metzger, Acc. Chem. Res. **32** (11) (1999) 950.

13.23

Synchrotron PES Study of Self-Assembled Diode Molecules on Au(111). Wei Chen¹, Chun Huang², Xingyu Gao¹, Dongchen Qi¹, Andrew Thye Shen Wee¹, Zhikuan Chen² and Kian Ping Loh³; 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 (oligophenylenes composed of building blocks of dimethoxy-substituted phenylenes, perfluoro-substituted 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.

13.24

Transport in Genetically-Engineered, Arene-based Molecular Interconnects: Mechanical, Thermal and Contact Interactions. James Reynolds¹, 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 arene-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 often leads to the opening 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. In this way we hope to engineer superior, thermal-resistant, molecular interconnects. We also report on similar computational studies of molecule-surface interactions, adsorption sites and attachment kinetics.

13.25

Electrical Junctions Formed from Thiol-Terminated Oligo-(Phenylene-Vinylenes): 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. Therefore, meaningful information 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 (SAMs) of the 3-ring 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) have shown 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

have local areas (~10 nm in diameter) of crystallinity, but poor long-range order. SAMs formed via ethanethiol replacement have good long-range order, but appear to be totally amorphous. We examine the effects this change in molecular structure has on the observed properties of molecular electronic junctions formed by STM.

13.26

Ultrastable Conductance Measurements of Self-Assembled Monolayer Supported Phenylene-ethylene Oligomers. Sanjini Nanayakkara¹, Meaghan M. Blake¹, Arrelaine A. Dameron¹, Rong Zhang¹, Chris Pochas¹, Moonhee Kim¹, Paul S. Weiss¹, Thomas P. Pearl², Sundar Uppili², David L. Allara³ and James M. Tour⁴; 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 alkanethiolate self-assembled monolayers (SAMs) to fabricate support matrices for probing the charge transport properties of both isolated and bundled phenylene-ethylene oligomers (OPEs). By utilizing solution- and vapor-phase manipulation techniques, we can select the distribution of the OPE 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 OPE 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.

13.27

Protocols for Length Selection, Selective Adhesion and Alignment of Single Walled Carbon Nanotubes. Ramesh Sivarajan, Jonathan Belcher, Rahul Sen, Tzong-ru Han, Thomas R. Bengston, Stephen J. Buffat and Thomas Rueckes; Nantero Inc, Woburn, Massachusetts.

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 organic monolayers on a silicon surface 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.

13.28

FTIR spectroscopy of buried molecules in tunnel junctions. Yongseok Jun and Xiaoyang Zhu; 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 monolayer on Si or mercaptohexadecanoic acid multilayers on Au covered Si, ATR-FTIR suggests that metal deposition leads to not only conformational disorder within the film, but also the direct interaction of metal atoms/clusters with alkyl backbones. We also present results for metal-molecule-metal junctions under bias.

13.29

Abstract Withdrawn

13.30

Abstract Withdrawn

13.31

Prediction of Transport Properties through Molecular Devices by First Principles Calculations. Hiroshi Mizuseki¹, Rodion V. Belosludov¹, Amir A. Farajian¹, Olga V. Pupyshcheva¹, Chiranjib Majumder², Jian-Tao Wang³, Hao Chen⁴, Tomoki Uehara¹, Nobuaki Igarashi¹ and Yoshiyuki Kawazoe¹; 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.

For many years, progress in microelectronics has been associated with a reduction in the minimum feature size of integrated circuits. However, this trend, as described by Moore's Law, seems to be ending due to process and physical limitations, and therefore a new paradigm shift has been expected. Molecular devices are potential candidates for this next step, and they would make it possible to realize the most advantageous devices. However, a major predicament and source of expenditure is necessary that such a large number of organic molecules can be obtained by synthetic chemistry, so any means of exploring their properties and behavior in order to predict the relevant properties of a molecule in advance of its synthesis would be extremely useful. One established approach is to use the computational methods developed for the prediction of a stable molecular structure and conductance properties. Our group has covered a wide range of molecular systems which have potential application in molecular electronics using first-principles calculations [1]; supramolecular enamel wires (covered wires) [2], connection between organic molecules and metal electrodes [3], self-assembled nanowires on silicon surface [4]. Moreover we examine electronic transport properties through small molecules for a building block, such as benzene [5], bent carbon nanotube [6], DNA, porphyrin and ferrocene molecules and so on. In this presentation, we will present recent investigations related to nanoscale devices, using molecular orbital analysis. [1] <http://www-lab.imr.edu/~mizuseki/nanowire.html> [2] R. V. Belosludov, A. A. Farajian, H. Baba, H. Mizuseki, and Y. Kawazoe, Jpn. J. Appl. Phys., 44, 2823 (2005). [3] C. Majumder, H. Mizuseki, and Y. Kawazoe, J. Chem. Phys., 118, 9809 (2003). [4] J.-T. Wang, E. G. Wang, D. S. Wang, H. Mizuseki, Y. Kawazoe, M. Naitoh, and S. Nishigaki, Phys. Rev. Lett., 94, 226103 (2005). [5] H. Chen, J. Q. Lu, J. Wu, R. Note, H. Mizuseki, and Y. Kawazoe, Phys. Rev. B, 67, 113408 (2003). [6] A. A. Farajian, B. I. Yakobson, H. Mizuseki, and Y. Kawazoe, Phys. Rev. B, 67, 205423 (2003).

13.32

Conductivity Measurement of Platinum DNA-Templated Nanowire. Chia-Hsin Lin, Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan.

The use of top-down optical patterning techniques becomes much more restricted as the size of circuit components reduces below 100 nm. Biomaterials 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 -ADNA on SiO₂ wafer was firstly manipulated through the application of a rectilinear laminar flow. As a result, -ADNA was stretched and laid perpendicular to the gap of electrodes on SiO₂ wafer. The DNA template was subsequently allowed binding with cis-Pt(NH₃)₂Cl₂ (cisplatin), followed by reduction with dimethylamine borane (DMAB) that 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 varistor-like 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 I4: Charge Transport and Spectroscopy of
Molecular Junctions
Chair: Abe Nitzan
Tuesday Morning, November 29, 2005
Room 302 (Hynes)

8:00 AM I4.1

Electronic Transport through Organic Monolayer Devices. Duncan Stewart, Jason J. Blackstock, Zhiyong Li, Douglas Ohlberg, Alex Bratkovski and R. Stanley Williams; Hewlett-Packard Labs, Palo Alto, California.

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, RAIR, Raman, UPS, XPS, and 2PPE 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 alkoxy-naphthalene thiols, and utilize scanned probe or evaporated top metal electrodes.

8:15 AM I4.2

Metal-Molecular Junctions Probed with Surface Plasmons. Ken Shimizu¹, Ragip Pala², Mark L. Brongersma¹ and Nick Melosh¹; 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 new 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 to find 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. As 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 *I4.3

In-situ Comparison of Electron Transport through Different Self-Assembled and Nanografted Monolayers by Conductive Tip AFM. Giacinto Scoles, ¹Chemistry, Princeton University, Princeton, New Jersey; ²Scuola Internazionale Superiore di Studi Avanzati (SISSA), Trieste, Italy; ³ELETTRA, 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 patch composed 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'-dithiol/1-decanethiol and 16,16,16-trifluoro-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 other experiments shall 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 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 I4.4

Molecular Length Dependence and Contact Effects on Electron Conduction through Molecules: Aromatic Thiols vs. Aromatic Isocyanides. BongSoo Kim¹, Jeremy Matthew Beebe¹, Vince Engelkes¹, Yongseok Jun², Xiaoyang Zhu² and C. Daniel Frisbie³; 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, $R = R_0 \exp(\beta s)$. The length dependent attenuation factor (β) is $0.4 (\pm 0.1) / \text{\AA}$ for both aromatic systems, while contact resistance (R_0) of aromatic thiols on gold is much less than that of aromatic isocyanides. Specific contact resistances are 1200Ω and 12000Ω 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 resistances. Characterization of SAMs was accomplished by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

9:15 AM I4.5

Infrared Spectroscopy of Metal-molecule-Metal Interfaces. Franklin E. Anariba¹, Solomon Ssenyange², Uma Viswanathan², Richard L. McCreery² 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, nitrobiphenyl, biphenyl and fluorene monolayers and multilayers of nitroazobenzene and nitrobiphenyl by electroreduction of their respective diazonium ion solutions. In addition, graphitic 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 carbosilane 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 *I4.6

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 molecular monolayers, chemisorbed on metal surfaces. Conjugated phenylenethiol oligomers and acenethiols have been studied. The nature of the valence states has been established using these spectra and valence effective Hamiltonian calculations. The charge-transport 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.

10:30 AM *I4.7

Measurement of Single Molecule Conductance using STM and AFM-Based Break Junctions. Xiulan Li, Joshua Hihath, Bingqian Xu, Xiaoyin Xiao and N. J. Tao; Electrical Engineering, Arizona State, Tempe, Arizona.

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 measurement of individually wired molecules. To reliably 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 peptides, 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 *I4.8

New Tools for Molecular Electronics. James Kushmerick, Surface and Microanalysis Science Division, NIST, Gaithersburg, Maryland.

In this talk I will describe our magnetic directed-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 I4.9

Tuning the Interaction between Self Assembled Monolayers and Metallic Systems: a Theoretical Study. Egbert Zojer^{1,2},

Georg Heimel², Lorenz Romaner^{1,2}, Peter Pacher^{1,2}, Mathis Gruber^{1,2}, Stephen Barlow², Luca Beverina³ and Jean-Luc Bredas²; 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 π -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 molecules, 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 varying work functions like Au, Ag, and Pt. The extents 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 I4.10

Understanding the transport mechanisms of oligo (phenylene ethynylene) molecules. Nabanita Majumdar¹, Zena Martin¹,

Nadine Gergel¹, N. Swami¹, J. C. Bean¹, L. Harriott¹, Y. Yao², J. M. Tour², D. Long³ and R. Shashidhar³; 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 at room temperature from an 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 mechanisms 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 monothiol molecule (without the nitro group) in our nanowell test device³ 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 corresponded well with the theoretical rotational barrier for transformation from a twisted to a planar, conductive

conformation of this molecule⁴. 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. N. Majumdar et al., J. Vac. Sci. Technol. B, to be published in July-Aug issue. 4. J. M. Seminario et al., J. Am. Chem. Soc., 120, 3970 (1998).

SESSION I5: Electron Transport and Scanning Probe
Microscopy
Chair: Maki Kawai
Tuesday Afternoon, November 29, 2005
Room 302 (Hynes)

1:30 PM *I5.1

Interfaces in Carbon Nanotubes. Paul McEuen, 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 interfaces 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 *I5.2

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 *I5.3

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 *I5.4

Field Regulation of Single Molecule Conductivity by a

Charged Atom. Robert Wolkow, ¹Department of Physics, University of Alberta, Edmonton, Alberta, Canada; ²National Institute for Nanotechnology, National Research Council of Canada, Edmonton, Alberta, Canada.

A new concept for a single molecule transistor is demonstrated (1). A single chargeable atom adjacent to a molecule 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 to the molecule. 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 $\sim 10^5$ 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. Piva, Gino A. DiLabio, Jason L. Pitters, Janik Zikovsky, Moh'd Rezeg, 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 *15.5

Probing silicon-molecule junctions with scanning tunneling microscopy. Mark C. Hersam, Materials Science and Engineering, Northwestern University, Evanston, Illinois.

In recent years, substantial progress has occurred in the field of molecular electronics [1]. In this paper, charge transport through molecule-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. These empirical observations can be qualitatively explained with the energy band diagram for a semiconductor-molecule-metal junction [2]. More sophisticated theoretical 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 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-molecule distance. Using a one-dimensional capacitive equivalent circuit, this behavior can be quantitatively explained, thus providing insight into the electrostatic potential distribution across a 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 a series of design rules 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. Baluch, and M. C. Hersam, *Nano Lett.*, 4, 55 (2004). [3] T. Rakshit, G.-C. Liang, A. W. Ghosh, and S. Datta, *Nano Lett.*, 4, 1803 (2004). [4] N. P. Guisinger, N. L. Yoder, and M. C. Hersam, *Proc. Nat. Acad. Sci.*, 102, 8838 (2005).

SESSION I6: Photoemission Spectroscopies and Energy Level Alignment at Molecule/Metal and Molecule/Semiconductor Interfaces
Chair: Tianquan Lian
Wednesday Morning, November 30, 2005
Room 302 (Hynes)

8:00 AM I6.1

Effects of Various Types of Electrical Doping on the Electronic Structure and Electric Behavior of Organic Interfaces. Kazuhiko Seki^{1,3}, Naoki Hayashi¹, Toshio Nishi², Senku Tanaka¹, Asumi Jindo², Masato Honda² and Kaname Kanai²; ¹Research Center for Materials Science, Nagoya University, Nagoya, Japan; ²Chemistry, Nagoya University, Nagoya; ³Institute For Advanced Research, Nagoya University, Nagoya, Japan.

In the rapid recent developments of organic electronics, new techniques to control the electronic structure and electric properties of organic interfaces are required. Various types of electrical doping has been exploited by various groups [1-3], and shows promising possibility. In this talk, we will examine the present status of the understanding about various types of doping in molecular materials in a wide sense, including the unintentional doping by residual impurities and atmospheric doping, with attention to the possible Fermi level alignment. (1) For materials which can be well purified (e.g. TPD [4] and p-sexiphenyl[5]), no significant band bending was found in ultrahigh vacuum (UHV) for the interfaces with metals, without the alignment of metal Fermi level with the Fermi level of the organic material pinned at fixed energy between the HOMO and the LUMO. (2) For some materials which cannot be thoroughly purified (e.g. C60 [6] and phthalocyanines [7]), residual impurities can act as unintentional dopants even for nominally "undoped" materials, leading to slow band bending and possible Fermi level alignment. (3) Atmospheric doping (e.g. by oxygen) can significantly affect the type of band bending and can lead to Fermi level alignment [8]. The change of ionization energy by gas exposure is also being measured [9]. (4) Intentional doping, both by donors and acceptors, can be used for manipulating the interfacial electronic structure. The search for efficient, stable, and non-diffusive donors and acceptors are desired. Also more detailed characterization of the doped states, such as the state of aggregation and the possible interaction with metal substrates, should be performed. [1] M. Pfeiffer, K. Leo, X. Zhou, J. S. Huang, M. Hofmann, A. Werner, and J. Blochwitz-Nimoth, *Org. Electronics*, 4, 89 (2003) and references therein. [2] A. Kahn and W. Gao, *J. Phys.*, C15, S2757 (2003) and references therein. [3] S. F. Chen, Y. K. Fang, S. C. Hou, C. Y. Lin, C. S. Lin, W. R. Chang, and T. H. Chou, *Org. electronics*, 6, 92 (2005). [4] N. Hayashi, *Synth. Metals*, 121, 1717 (2001). [5] H. Oji, E. Ito, M. Furuta, K. Kajikawa, H. Ishii, Y. Ouchi, and K. Seki, *J. Electron Spectrosc. Rel. Phenom.*, 101-103, 517-518 (1999) and unpublished results. [6] N. Hayashi, H. Ishii, Y. Ouchi, and K. Seki, *J. Appl. Phys.*, 92, 3784 (2002). [7] S. Tanaka, K. Kanai, E. Kawabe, T. Iwahashi, T. Nishi, Y. Ouchi, and K. Seki, *Jpn. J. Appl. Phys.*, in press. [8] T. Nishi, K. Kanai, Y. Ouchi, M. R. Willis, and K. Seki, *Chem. Phys. Lett.*, submitted. [9] M. Honda et al., unpublished results in collaboration with Prof. H. Ishii of Tohoku University.

8:15 AM I6.2

Hole Injection Barrier Tuning at Organic/Metal Interfaces with Pre-adsorbed (Sub-)Monolayers of Strong Electron Acceptors. Norbert Koch¹, Steffen Duhm¹, Juergen P. Rabe¹, Antje Vollmer² and Robert L. Johnson³; 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 desired. Here we show that this can easily be accomplished by pre-adsorbing a controlled amount of strong electron accepting molecules (tetrafluoro-tetracyanoquinodimethane; F4-TCNQ) on a metal surface. Using ultraviolet photoelectron spectroscopy, the energy level alignment at interfaces between three COMs - α -sexithiophene (6T), p-sexiphenyl (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-coverage with F4-TCNQ. Significant reduction of HIBs (0.65 eV for 6T and α -NPD, 1.2 eV for 6P) was found for all three cases, independent of the ability for charge transfer complex formation between the conjugated organic materials and F4-TCNQ. Furthermore, HIBs could be tuned over wide ranges by appropriate adjustment of F4-TCNQ pre-coverage in the sub-monolayer range. This is explained by the acceptor coverage-dependence of the area-averaged surface potential of F4-TCNQ/Au substrates, for which

a charge transfer type interaction of F4-TCNQ with Au was evidenced by photoemission experiments.

8:30 AM *I6.3

Evaluation of molecular level alignment at organic-metal, organic-polymer and organic-organic heterojunctions.

Antoine Kahn, Jaehyung Hwang, Alan Wan and Wei Zhao; Electrical Engineering, Princeton University, Princeton, New Jersey.

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 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 departure from the Schottky-Mott limit, with large interface dipoles. 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 dipoles. This is consistent with most observations involving polymer interfaces and 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 the exponential decrease of the density of interface 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 allows, 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 I6.4

n-Type Doping by Magnesium to Zinc Phthalocyanine (ZnPc). Jianbin Xu, Ming Zhu, Jin An and Jianbin Xu; 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 (e.g. F4-TCNQ) have been achieved [2,3], 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 n-type 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 at 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 spectroscopy (STS), 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 STS were used to examine the electronic band structures 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 (2003). [2] W. Y. Gao and A. Kahn, Appl. Phys. Lett., 79, 4040 (2001). [3] W. Y. Gao and A. Kahn, J. Appl. Phys., 94, 359 (2003).

9:15 AM I6.5

Spin Injection through Co/CuPc Interface. Yongli Gao¹, Oleksiy Andreyev², Michael Bauer² and Martin Aeschlimann²;

¹Physics and Astronomy, University of Rochester, Rochester, New York; ²Physics, University of Kaiserslautern, Kaiserslautern, Germany.

We present experimental evidence of loss-free spin injection of hot electrons from ferromagnetic Co(111) surface into organic semiconductor copper phthalocyanine (CuPc). We used spin-resolved two-photon photoemission (SR-2PPE) spectroscopy, which allows us to study the dynamics of both electron and spin relaxation in solids and interfaces with femtosecond time resolution. With SR-2PPE, we investigated the energy distribution and spin polarization of hot electrons excited originally in Co and injected in CuPc, and observed almost unchanged spin polarization in comparison to that of the initial Co surface. This demonstrates a negligible role of interface spin scattering processes. The loss-free spin injection into CuPc suggests that it can be a promising material for spin-based electronic devices. We further compared Co/CuPc junctions formed by depositing CuPc on freshly grown or Ar sputtered Co surfaces. We found little effect of the junction quality on the efficiency of the spin injection. In fact, we observed a surprising recovery of defect-induced reduction of Co surface magnetization by submonolayer CuPc coverages. A simple model for this unexpected organic-induced spin enhancement will be discussed.

9:30 AM *I6.6

Interface Bonding and the Position of Transport Levels in Organic Thin Films. Eberhard Umbach, M. B. Casu, A. Schoell, S. Krause and Y. Zou; Experimental Physics II, University of Wuerzburg, Wuerzburg, Germany.

The properties of organic thin films and devices depend not only on the properties of the isolated molecule but also on the intermolecular interaction, the geometric structure, and the interfaces between molecules and contacts. The influence of the interfaces is often underestimated because these can only be well controlled in UHV and under very clean substrate and deposition conditions. However, they determine the interaction between molecules and contacts, the molecular orientation (hence the optical properties), the growth mechanism (hence the layer homogeneity), the order within the organic layer (hence the formation of bands and defects), and the electronic properties. The interface interaction gives rise to interface dipoles, band offsets, and special interface states which pin the Fermi level or facilitate charge injection. This presentation will address three interrelated issues. First, we will discuss chemisorptive *interfacebonding* between various molecules and metal surfaces. It will be shown that a detailed experimental picture can be derived by using very well-defined model interfaces and various methods such as HR-XPS, (AR)UPS, HR-NEXAFS, and HREELS. These give insight into the formation of new hybrid (interface) bonds, interface dipoles, and band offsets; two-dimensional band structures yield information about the admixtures to the hybrid orbitals at the interface. It will become clear that subtle changes of substrate, functional groups, and preparation conditions may lead to completely different properties. Secondly, we address the electronic properties of *organicsurfaces*. They are not only important for the interface formation but also for the determination of bulk properties since electron spectroscopies as source of important electronic information predominantly probe surfaces. In particular, we provide information on the so called surface core level shifts which can be rather large in the case of metals, conventional semiconductors, or rare gases. In the case of organic layers they may arise because of reduced polarization screening at the surface. The results show no significant surface effect, in contrast to expectation. These results are corroborated by optical data, which also indicate the absence of a different polarization at the organic surface as compared to the bulk. Finally, we comment on the determination of the energy position of the *transportbands* and the size of the *transportgap* in organic materials which are often derived from photoemission and inverse photoemission experiments. We suggest an assignment similar to that in inorganic semiconductors which leads to smaller exciton binding energies than presently discussed.

10:30 AM *I6.7

Advanced UPS studies of organic thin films:HOMO hole/vibration coupling in pentacene ultrathin films.

Nobuo Ueno, ¹Department of Electronics and Mechanical Engineering, Faculty of Engineering, Chiba university, Chiba, Japan; ²Graduate School of Science & Technology, Chiba University, Chiba, Japan.

The recent success in realizing organic optoelectronic devices has accelerated comprehensive research on electronic processes in organic solids. The charge-vibration interaction plays a crucial role in the hopping charge transport mechanism (i.e., charge mobility) in organic solids. Therefore, the hole/vibration coupling of the highest occupied molecular orbital (HOMO) band has been studied theoretically to understand the hole transport mechanism in organic solids including

pentacene, which is one of the important organic semiconductors owing to its high hole mobility. Furthermore, electron/vibration coupling is also a key parameter in superconductivity. The 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 of the charge transport properties of organic solids, a more pertinent experimental approach to resolving this issue is required. We succeeded to measure the hole/vibration coupling of the HOMO band of a pentacene monolayer film prepared on graphite by high-resolution ultraviolet photoelectron spectroscopy.

Pentacene-graphite interaction can be considered as a first-step model of HOMO-HOMO interaction in a pentacene crystal. We found that vibration satellites in the film are more intense than those in the gas phase, and that the vibration energy in the film is slightly lower than that in the gas phase. This demonstrates that the reorganization energy of a pentacene thin film is slightly larger than that estimated from the photoelectron spectrum of gas-phase pentacene. Furthermore, a tailing of the HOMO band was observed in the low binding energy side at low temperature. The tailing may originate from the lifetime of the hole that is eliminated by electron transfer from the substrate. It is thus pointed out that the electron hopping may occur on the femtosecond scale before the electronic polarization of the surrounding molecules or substrate is completed.

11:00 AM *I6.8

Tuning the Composition and Electrical Properties of Metal and Metal Oxide Electrodes: Characterization by UV and X-ray Photoemission, Conducting-Tip AFM and By Characterization of Organic Electronic Devices.

Neal R. Armstrong^{1,2}, Amy Graham¹, Dana Alloway¹, Michael Brumbach¹, Thomas Schultmeyer¹, Beatrice Muriithi¹, Alex Veneman¹, Simmonds Adam¹ and Wei Wei¹; ¹Chemistry, University of Arizona, Tucson, Arizona, Arizona; ²Optical Sciences, University of Arizona, Tucson, Arizona, Arizona.

The effective work functions of both metal and metal oxide electrodes, intended for use as contacts to organic thin films in organic electronic devices, are critically affected by the surface composition of the contact. In the case of metal electrodes, such as Au, we show that the effective work function can be smoothly changed by over 1.5 eV using combinations of alkanethiols, functionalized at their terminus with methyl, phenyl, chlorine, bromine and fluorine substituents, and by formation of 99:1 ? 1:99 mixtures of methyl-terminated and semi-fluorinated alkanethiols on the Au surface. In the case of metal oxides, such as ITO, the situation heretofore has been more complicated, owing to the fact that the modifiers attach primarily to ultra-thin, electrically passive layers over the conducting bulk oxide (as revealed by our recent C-AFM studies of acid-etched and freshly deposited ITO). Our recent attempts at chemical modification of freshly deposited ITO films, their in vacuo modification, and the effects of these modifications will also be reviewed in this talk. Many of these modified electrodes are now being incorporated into organic electronic devices, and their preliminary characterization will also be discussed.

11:30 AM I6.9

Energy Level Alignment and Interfacial Chemistry of Pentacene Thin Films on GaN. John Joseph Uhrlich 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. In order to evaluate this hypothesis, we studied the energy band offset of 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 degaused with organic solvents and then treated in concentrated HCl for 15 minutes ex-situ. No additional in-situ surface treatment was performed. The photoelectron experiments were carried out in an ultra-high vacuum system with a base pressure of $\sim 5 \times 10^{-11}$ Torr. Pentacene was evaporated from a resistively heated boron nitride crucible in increments as small as 0.1 nm as measured using a quartz microbalance in the adjoining sample preparation chamber. UPS and XPS spectra were obtained after each deposition step 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 a small or negligible barrier for injection of holes from n-GaN into pentacene. Additional studies varied the pre-deposition treatment of the GaN surface through an initial in-situ treatment at 865 C in 1×10^{-4} Torr of flowing ammonia. This surface treatment has been previously shown to produce a clean and stoichiometric surface of GaN and the results obtained using the ammonia treatment are compared with those obtained using GaN without in-situ surface treatment.

11:45 AM I6.10

Electrochemical Potentials and Redox Reactions of H-, Cl-, CH₃- and C₂H₅-Terminated, Si(111) Surfaces.

Patrick Timothy Hurlley and Nathan S. Lewis; Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California.

Wet chemical, covalent functionalization of Si with organic moieties has attracted significant recent attention. To produce surfaces with minimal or negligible interfacial Si oxide, these reactions generally use the well-defined H-terminated Si(111) as a starting surface. The reactivity of the H-terminated atop sites on Si(111)-H surfaces has generally been presumed to closely resemble the reaction chemistry of small molecule organosilanes, with (H₃C)₃-Si-H or ((H₃C)₃Si)₃-Si-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)₃-Si-H. Parallels between sterically non-demanding radical reactions on the H-terminated Si(111) surface and reactions of organosilanes such as ((H₃C)₃Si)₃-Si-H 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 in principle stabilize the 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 excitonically 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, crystalline Si(111)-H surfaces undergo oxidative activation to form Si-O-CH₃ bonds, whereas such reactivity is not observed for ((H₃C)₃Si)₃-Si-H in CH₃OH by any oxidant available within the solvent stability limit of CH₃OH. To evaluate the electron-transfer based reaction routes on Si surfaces, we report herein electrochemical and chemical measurements of the redox processes of such surfaces. The comparison between the electrochemical 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 atop sites of Si(111) surfaces to Si-CH₃ groups 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 electrochemical 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 electrical and electronic properties of functionalized Si surfaces.

SESSION I7: Spectroscopy and Dynamics at Interfaces

Chair: Antoine Kahn

Wednesday Afternoon, November 30, 2005

Room 302 (Hyne)

1:30 PM *I7.1

Chemically Resolved Electrical Measurements - A Future Probe of Nanoscale Devices? Hagai Cohen, Chemical Research Support, Weizmann, Rehovot, Israel.

Chemically resolved electrical measurements (CREM) provide unique solutions 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 heterostructures. 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 analytical capabilities. Applications to future miniaturized devices will be discussed.

2:00 PM **I7.2**

Characterization of Self-Assembled Organic Films Using Differential Charging in X-ray Photoelectron Spectroscopy.

Manish Dubey¹, Irina Gouzman², Steven L. Bernasek¹ 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 for most of the conventional 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 charging 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 (C1s) 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 +/-30V 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. Danisman, J. Am. Chem. Soc., 2003, 125, 16074-16080 [2] K. Shabtai, I. Rubinstein, S. R. Cohen and H. Cohen, J. Am. Chem. Soc. 2000, 122, 4959-4962

2:15 PM **I7.3**

Ultra-flat Metal Surfaces in Molecular Electronic Devices.

Jason J. Blackstock¹, Duncan Stewart¹, Douglas Ohlberg¹, Regina Ragan², Zhiyong Li¹, Sehun Kim³ and R. Stanley Williams¹; 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 first electrode surface (prior to the organic deposition), 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 metal/organic-monolayer/metal device structures. In our presentation, we first describe the physical characterization of ultra-flat 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-flat surface. Finally, the second electrode is deposited by metal evaporation at controlled temperature, and the top organic/metal interface is subsequently examined using Raman and XPS spectroscopies. 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 microscale, and present preliminary electrical temperature dependence and IETS data from these devices.

3:30 PM ***I7.4**

Electron Transfer Dynamics at Interfaces between Organic Thin Films and Metals Studied by fs Time-resolved Two-photon Photoelectron Spectroscopy.

Yoshiyasu Matsumoto¹, Daisuke Ino², Kazuya Watanabe¹ and Noriaki Takagi³; ¹Institute for Molecular 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 electron dynamics at 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 (2PPE) spectroscopy. Purified Alq3 molecules were deposited on the metal surface in the UHV chamber. For time-resolved 2PPE measurements, second harmonic output pulses of a Ti:sapphire oscillator (pulse width= 20 fs at 400 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 D along the surface normal. The ionization potential from 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 state created by electron transfer from the metal decays with the lifetime of 31 ± 2 fs 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 key step for electron transfer in the current systems. At the interfaces 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.

4:00 PM ***I7.5**

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.¹ 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 surface states 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 ice layers at a metal surface, with dynamics spanning from femtoseconds to minutes; (ii) ultrafast charge transfer dynamics of C₆F₆/Cu(111) studied with time-resolved 2PPE and Resonant-Auger (core hole clock) spectroscopy. The collaboration with U. Bovensiepen, C. Gahl, P. Kirchmann, P. Loukakos, J. Stähler, (Freie Universität Berlin) and V. Vijayalakshmi, A. Fölsch, W. Wurth (Universität Hamburg) is gratefully acknowledged. ¹Surf. Sci. Rep. **52**, 219 - 318 (2004); Appl. Phys. A **78**, 125-247 (2004)

4:30 PM **I7.6**

Unoccupied electronic states at the alkanethiol 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 alkanethiol/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 tunneling barrier on the film side due to the bandgap of the alkyl layer. The interpretation of such an interfacial resonance is supported by the observation that the ultrashort lifetime of this resonance is nearly independent of molecular length of the SAM. The possible role of these interfacial states and resonances on electron transport across SAM/Au interfaces is discussed.

4:45 PM **I7.7**

Time-Resolved Scanning Near-Field Optical Microscopy of Interfaces in Phase-Separated Blends of Conjugated Polymers. Ashley James Cadby, Richard Dean, Mark Fox, Richard A. L. Jones and David G. Lidzey; Physics and Astronomy, University of Sheffield, Sheffield, South Yorkshire, United Kingdom.

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-dioctylfluorene) [F8] and poly(9,9-dioctylfluorene-alt-benzothiadiazole) [F8BT]. In this particular system, excitation is made into the F8 component of the blend, which is followed by rapid energy transfer to F8BT via dipole-dipole coupling. The spectral emission characteristics of F8 and F8BT are very different, and thus by imaging the fluorescence emission from both F8 and F8BT, we can study the relative efficiency of energy transfer and thus the efficiency of polymer mixing. We determine strong spatial variation in decay lifetime for both F8 and F8BT across the surface. Furthermore we provide evidence for an interface region between the blend components in which energy transfer is relatively hindered. Our measurements highlight 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 polystyrene (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 exciton 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 ***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 fine structure. Examples include illustrations of problems with side reaction chemistry in isocyanide (isonitrile)/Au 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 ***I8.2**

Déjà vu? Importance of Interfaces and Contacts for Molecule-Based Electronic Devices. David Cahen, Materials and Interfaces, Weizmann Institute of Science, Rehovoth, Israel.

Electron energetics at interfaces determine the electronic behaviour of semiconductor/semiconductor and /metal contacts.[1] Molecules can control semiconductor and metal surface energetics.[2] Therefore, if we would know how to place molecules at interfaces of electronic materials, even if only as poorly organized, partial, rather than ideal monolayers, this would give a significant degree of electronic control over electronic devices. We distinguish between two types of control, electrostatic and electrodynamic ones: * For electrostatic control requirements for (near-)ideally structured monolayers are relaxed because no current needs to flow through the molecules, which act here as "gatekeepers",[1] via a "Cooperative Molecular Field Effect".[3] This has enormous implications, because it makes it possible to consider many more types of molecules than with electrodynamic control, and stability issues circumvented. *For electrodynamic control one requires systems with near-ideal molecular films, Now electronic transport is through the molecules. Esp. for saturated molecules this is mostly by tunneling, which can be direct, resonatively, "through bond", or a mixture of these.[4] To study these issues it is imperative to be able to make device structures reproducibly, something that requires non-invasive contacting methods.[5] Results obtained with such methods show how intimate contact between molecules and metal can polarize the contacts.[1,5] All in all, experimental evidence is accumulating that in most devices with molecules, the nature of the molecule/electrode contact is crucial for the resulting junction.[4,6] **Acknowledgements** Work done in cooperation with many students, postdoctoral fellows and colleagues, who appear as co-authors in the references cited. **References** 1. DC, A. Kahn, Adv. Mater., 14 (2003) 271; ...DC, A. Kahn, E. Umbach, Mater. Today, July 2005 issue. 2. G. Ashkenasy, DC, R. Cohen, A. Shanzer and A. Vilan, Acc. Chem. Res. 35 (2002) 121. 3. DC, R. Naaman, Z. Vager, Adv. Funct. Mater., revised. 4. A. Salomon, DC, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, Adv. Mater., 15 (2003) 1881. 5. A. Vilan, DC, Adv. Funct. Mater. 12 (2002) 795; AV, J. Ghabboun, DC, J. Phys. Chem B, 107 (2003) 6360; ...H. Haick, M. Ambrico, J. Ghabboun, T. Ligonzo, DC, PSSC, 6 (2004) 4538; HH, M. Ambrico, T. Ligonzo, DC, Adv. Mater., 16 (2004) 2145; HH, J. Ghabboun DC, Appl. Phys. Lett., 86 (2005) 042113-5; , HH, J. Ghabboun, O. Niitsoo, H. Cohen, DC, A. Vilan, J. Hwang, A. Wan, F. Amy, A. Kahn, J. Phys. Chem. B, 109 (2005) 9622. 6. Y. Selzer, A. Salomon, J. Ghabboun, DC et al., Angew. Chem. Int. Ed., 41 (2002) 827; ...A. Salomon, R. Arad-Yellin, A. Shanzer, DC, JACS, 126 (2004) 11648

9:00 AM **I8.3**

Spectroscopic and Electrical Characterization of Buried Metal Interfaces: Metal-Molecule-Silicon Structures. Lee Richter¹, Curt A. Richter² and Christina A. Hacker²; ¹Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ²Semiconductor 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-voltage and ac capacitance-voltage measurements were used to characterize molecular capacitor structures. These devices were formed by attaching C18 alkane monolayers directly on (a) Si-substrates (via octadecanol reactions), (b) native SiO_x, 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 fully-metallized structures. Three top metals, Au, Al, and Ti, were studied. FTIR indicates minimal interaction between Au and Al and the monolayers formed on SiO₂ 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 alkoxy films directly attached to H-terminated Si via an ether linkage are displaced by all three metals.

9:15 AM **I8.4**

Control of the Electrical and Adhesion Properties of Metal Electrode / Organic Interfaces with Self-assembled Monolayers. Kilwon 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 unreactive SAM. Silver and indium tin oxide (ITO), widely used in organic 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 atoms 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 chlorine and fluorine atoms bind to the indium atoms. In contrast, silver and ITO deposited onto a CH₃-modified surface do 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 electrode 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.

9:30 AM I8.5

Lamination of High Quality Interfaces. Daniel A. Bernards¹, Samuel Flores-Torres², Hector D. Abruna² and George G. Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

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. A top component is elastomeric 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 contact portion of a laminated device may be used 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 I8.6

Reduction of Electrical Damage due to Au/Pentacene Contact Formation by Introducing Ar Gas during Au Evaporation. Koshi Okamura¹, Tomoaki Sawabe², Akimasa Hashimoto², Masakazu Nakamura² and Kazuhiro Kudo²; ¹Graduate School of Science and Technology, Chiba University, Chiba, Japan; ²Department of Electronics and Mechanical Engineering, Faculty of Engineering, Chiba University, Chiba, Japan.

Obtaining an ideal metal/organic 'top' contact has been an important subject not only for the study of molecular scale electronics 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 at the interface without 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 the physical properties of pentacene films [1]. In this study, we have demonstrated the reduction of the electrical damage in a simple Au/pentacene/Al diode structure by filling the Au evaporation chamber with Ar to an appropriate pressure. Collisions of Au atoms in Ar ambient reduce the kinetic energy of Au atoms reaching pentacene films, resulting in soft-landing deposition, which is expected to suppress the reactivity of Au with organic materials [2, 3]. This technique increased the conductivity of pentacene films by 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 8.7×10⁻¹ 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 drastically reduces the damage in 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. 15686014) 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] H. Haick, M. Ambrico, J. Ghabboun, T. Ligonzoc 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 I8.7

Electronic Properties of Molecular Nanostructures. Dominique Vuillaume, IEMN-CNRS, Villeneuve d'Ascq, France.

I will review some of our recent experimental results on charge transport in organic nanostructures such as self-assembled monolayers and monolayers of organic semiconductors. We demonstrated [1] a molecular rectifying junction made from a sequential self-assembly on silicon. Our device features a simple synthesis with only one donor group and an alkyl spacer chain. These devices exhibit a marked current-voltage rectification behavior due to resonant transport between the Si conduction band and the molecule highest occupied molecular orbital. I will discuss the role of metal Fermi level pinning in the current-voltage behaviors of these molecular junctions [2]. I will also discuss some recent insights on the role of the metal/molecule interface in the electron tunnelling behavior of Si/alkyl chain/metal junctions [3]. Electrons and holes can be locally injected in a single pentacene monolayer island from the tip of an electrical force microscope [4]. The two-dimensional distribution and concentration of the injected carriers are measured by EFM. I will discuss the relationship between the carrier distribution in the island and its molecular structure. In crystalline monolayer islands, both carriers are delocalized over the whole island. On disordered monolayer, carriers stay localized at their injection point. Some other molecular systems (SAM and monolayer island of other organic semiconductors) will be also presented and compared to the case of pentacene monolayers. [1] S. Lenfant, C. Krzeminski, C. Delerue, G. Allan & D. Vuillaume. Nano Letters 3(6), 741-746 (2003). [2] S. Lenfant, D. Guerin, C. Delerue & D. Vuillaume. Phys. Rev. Lett. (submitted). [3] D.K. Aswal, S. Lenfant, D. Guerin, J.V. Yakhmi & D. Vuillaume. Small (in press). [4] T. Heim, K. Lmimouni & D. Vuillaume. Nano Letters 4(11), 2145-2150 (2004)

11:00 AM I8.8

Molecular Rectifying Diodes based on Aluminum /4-hydroxy-4-biphenyl carboxylic acid / p+-silicon Junction. Debashish Kuila¹, Sridevi Bala¹, Rajendra Aithal¹, Kody Varahramyan¹, David Janes² and Pedro Derosa¹; ¹IfM/Chemistry, Louisiana Tech University, Ruston, Louisiana; ²ECE, Purdue University, West Lafayette, Indiana.

The scaling of silicon based microelectronic devices to nanoscale (MOSFETs with gate length < 30 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-molecule-metal and metal-molecule-semiconductor junctions and their electrical 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 alkane and aromatic thiols 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 present a molecular rectifying diode based on an aluminum/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 aluminum. The surface of the substrate was characterized using 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 I8.9

How do electronic carriers cross Si-bound alkyl monolayers? Adi Salomon¹, Olga Girshevitz¹, David Cahen¹, Till Bocking², Calvin Chan³, Fabrice Amy³ and Antoine Kahn³; 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(s)/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-bound molecular 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, which, indeed allow 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 chose 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 n-Si-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-limiting 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 these transport mechanisms was predicted but not found experimentally (e.g., with SiO_x as the insulator). Its occurrence here indicates that the alkyl monolayers in on Si-C alkyl//Hg devices act as ideal insulators. By combining electronic transport and photoemission spectroscopy measurements 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 0.25 (0.28) m_e , the implications of which we will discuss.

11:30 AM *I8.10

Ballistic Emission Electron Microscopy Studies of Molecular Diodes. Julia W. P. Hsu¹, Wenjie Li², Yong Jun³, Karen L. Kavanagh², Carolyn M. Matzke¹, Xiaoyang Zhu³, A. Alec Talin⁴, W. Miles Cliff⁴, Sergey Faleev⁴ and Francois Leonard¹; 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 probe experimentally. In this talk, I will describe the use of ballistic electron emission 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 octanedithiol 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 to 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 partially supported by a jump-start program from DOE's Center for Integrated Nanotechnology (CINT). Sandia is a

SESSION I9: Organic Semiconductors: Growth and Transport
Chair: Yoshiyasu Matsumoto
Thursday Afternoon, December 1, 2005
Room 302 (Hynes)

1:30 PM *I9.1

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/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, using a wide variety 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 surfaces 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 needles 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-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 measurement 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 if time 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 I9.2

Molecular origin of shallow trap states in pentacene thin films. Joo H. Kang¹, Demetrio da Silva Filho², Jean-Luc Bredas² 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 vapor-deposited crystalline pentacene thin films are 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 sliding defects are shallow charge traps with energies less than 100 meV above (below) the valence band maximum (conduction band minimum).

2:15 PM I9.3

Structure of Ultra-thin Pentacene Films on a Silicon Dioxide Dielectric. Sandra E. Fritz¹, Michael F. Toney³, Demetrio da Silva Filho², C. Daniel Frisbie¹, Michael D. Ward¹ and Jean-Luc Bredas²; 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

Center, Menlo Park, California.

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 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 γ from 90° to not 90°, along with a gradual tilting of the pentacene molecules as film thickness is increased. The structural differences 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.

2:30 PM I9.4

Structure, morphology and electrical properties of pentacene thin films. Alex Christopher Mayer¹, Ricardo Ruiz⁴, Alexis

Papadimitratos¹, Randall Headrick² and Alex Kazimirov³; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Physics, University of Vermont, Burlington, Vermont, Vanuatu; ³Cornell High Energy Synchrotron Source, Ithaca, New York; ⁴IBM, Yorktown Heights, New York.

The electrical properties in organic thin-film transistors are still not completely understood. For example whether or not the transport is band-like or hopping and how to decouple the effects of grain-boundaries and dislocations in the charge-carrier mobility. To study this, we have chosen the top-contact geometry transistors based on pentacene films grown under different conditions. Synchrotron x-ray data about the structure and defect density is related to atomic force microscopy of the grain-boundary density and temperature-dependent measurements of the transistor characteristics. We find that dislocation density and grain size increases with substrate temperature and that mobility seems to be independent.

2:45 PM I9.5

Aromate Interactions and Adlayer Architecture: INA, ACA, and AA Monolayer Films on Ag(111). Janice Ellen Reutt-Robey, Bo Xu, Hui Li and Diane Evans; University of Maryland, College Park, Maryland.

The molecular architecture of aromate thin films is of considerable fundamental and technological interest. This architecture represents a balance of molecule-surface and molecule-molecule interactions, which are best revealed by comparison of related aromates. Using physical vapor deposition methods, we have prepared monolayer films of isonicotinic acid (INA), acridine-9-carboxylic acid (ACA), and anthranic acid (AA) on Ag(111) substrates, determined their structures with UHV-STM measurements, and corroborated structural models with XPS and surface infrared spectroscopy. All three aromatic carboxylic acid derivatives undergo molecular adsorption to form ordered structures. The single ring INA adopts a slightly tilted (10 deg) orientation on the Ag(111) substrate in a head-to-tail H-bonding network that undergoes a secondary H bond stabilization between phenyl H and the carbonyl O. Domain orientations indicate a weak INA-Ag(111) interaction. Although the triple-ring ACA molecule also adopts a head-to-tail H-bonding motif, the ACA molecular architecture is distinct: Two ACA are arranged on the surface per unit cell with (+/-) 40 deg twist angles. The commensurate structure, [4 0 ; 2 4]-ACA/Ag(111), reflects a stronger ACA-surface interaction. Structural differences between INA and ACA adlayer architecture follow the orientational differences in their electrostatic interactions, with secondary H-bonding associations favoring a near-planar INA adlayer, while more substantial quadrupole-quadrupole interactions (~10 kcal/mol) driving the tilted ACA architecture. To assess the influence of the head-to-tail H bond, Anthranic Acid was also investigated. AA is restricted to tail-tail H-bonded dimers, which organize into several metastable adlayer structures on Ag(111). The most robust monolayer structures (ACA/Ag(111)) reflect the strongest adsorbate - substrate and adsorbate - adsorbate interactions, and yield expansive domains with sizes that are dictated by substrate morphology.

3:30 PM *I9.6

Semiconductor/Insulator Interfaces in Organic Thin Film Transistors. C. Daniel Frisbie, Chem Eng & Mat Sci, University of Minnesota, Minneapolis, Minnesota.

It is generally appreciated that the structure of organic semiconductor/insulator interfaces is 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 and Kelvin probe force microscopy. We have determined the crystal structure of the pentacene layers next to the dielectric and have found evidence of structural defects of various kinds, which will be discussed. These structural defects will significantly impact the electrical 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 I9.7

Electrical and Structural Properties of the Accumulation Layer in Pentacene Thin Film Transistors. Byoungnam Park¹,

Soonjoo Seo¹, Fan Zheng³, Franz Himpel³ and Paul G. Evans²; ¹Materials Science Program, University of Wisconsin-Madison, Madison, Wisconsin; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ³Department of Physics, 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 directly. The geometry 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^{-6} cm²/Vs to 10^{-4} cm²/Vs) 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 ML, 0.085 cm²/Vs, 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 were carried 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 I9.8

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 Miragliotta² 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 projected for suitably functionalized semiconductor films. Charging 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 on both the semiconductor-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 I9.9

Dislocations and grain boundaries in single-crystal organic semiconductors. Brandon Douglas Chapman¹, Ronald Pindak¹, Christian Kloc² and Theo Siegrist²; ¹National Synchrotron Light Source, Brookhaven National Lab, Upton, New York; ²Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

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 double-crystal x-ray topography and high resolution diffraction, 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 prominent in these crystals. The x-ray topography 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 I9.10

Modification of Self-Assembled Monolayers on Electrodes of Organic Thin-Film Transistors. Nobuya Hiroshiba¹, Ryotaro Kumashiro^{1,2}, Katsumi Tanigaki^{1,2}, Hisao Ishii³, Shinya Takaishi⁴ and Masahiro Yamashita⁴; 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 intensively 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 interfacial problems between organic thin films and gate-insulators and/or 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 silicon semiconductor devices. The surface control using self-assembled-monolayers (SAMs) is a well known method as 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. In the present study, interfacial modifications of source and drain gold-electrodes using thiol molecules have been studied in detail for pentacene-FETs, using three thiol molecules as SAMs with different functional groups, 4-methyl (4MeBzT), 4-nitro(4-NBzT) and 4-amino (4-ABzT) benzene thiols and the organic FET properties have been investigated. The hole carrier mobility in pentacene-FETs can be increased by the SAMs modifications when the optimized preparation conditions are employed. Threshold-voltage (V_{th}) has been successfully controlled depending on the end functional-substituents of benzene thiol molecules. The changes in V_{th} 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 V_{th} 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

Alkali 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 change 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 alkaline 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 organic semiconductors. We have investigated the electronic structure 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 depositions shift gradually 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 the C 1s 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

Nanoscale Organic Transistors. Yuanjia Zhang and George G. Malliaras; Materials Science and Engineering, Cornell University, Ithaca, New York.

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 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. The current-voltage characteristics of a 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 micron 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 Corroles and Porphine Derivatives for n-Channel Organic/Molecular Semiconductors. Haiyang Liu, Jinhao Gao, Chris C. 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 porphine, 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, porphine, and porphyrins will modulate several properties-e.g., stability, solubility, volatility, and energies of molecular orbitals-of the corroles, porphine, and porphyrins. Investigation of thin films of these new systems will improve fundamental understanding of electronegative substitution effects on conjugated systems, provide guiding principles to design

new electro-optical materials, and ultimately contribute to the creation of new materials for electro-optical applications (e.g., photoconductors and field-effect transistors) and molecular electronic devices.

I10.4

Mechanical Properties and Interfacial Structures of Dendrimer-Mediated Thin Films. Fengting 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 monodisperse) 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 cleaning, dipping, 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/adlayer 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. LFM, FMM, and step height measurements 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]. L. A. Baker, F. P. Zamborini, L. Sun, et al., *Anal.Chem.* **71**, 4403 (1999). [2]. F. T. Xu, P. P. Ye, M. Curry, et al., *Trib.Lett.* **12**, 189 (2002). [3]. S. C. Street, A. Rar, J. N. Zhou, et al., *Chem.Mater.* **13**, 3669 (2001). [4]. F. T. Xu, S. M. Thaler and J.A. Barnard, *J. Vac.Sci. Technol. A*, in press.

I10.5

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

The pentacene-based organic thin-film transistor (OTFT) with inserted lithium fluoride (LiF) thin layer (1nm) between pentacene layers was fabricated in ultrahigh vacuum (UHV) condition with all in-situ. processes, and improved electrical properties was achieved. The fabricated device structure is gold (30 nm) / pentacene / LiF (1 nm) / pentacene / SiO₂ (100 nm) / p⁺-Si (substrate); the ratio of upper pentacene layer thickness and lower pentacene layer thickness was varied, keeping the sums of two pentacene 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 SiO₂ layer. In addition, the threshold voltage decreased as LiF layer approached near drain and source. These phenomena were caused by tunneling current through 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 cm²/Vs to 0.45 cm²/Vs and from -21.89 V to -4.16 V, respectively.

I10.6

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

Alq3 [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 Alq3/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 Alq3/Al interface, a strong chemical interaction between the Alq3 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 roughness of the electrode surfaces 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 Alq3/Al interface by taking into account the effect of the surface roughness. We examined adsorption structures of Alq3 for three Al substrates; the flat Al(111) surface, the Al(332) stepped surface, and the Al adatom adsorbed Al(111) surface. We employed a generalized gradient approximation (GGA) and local density approximation (LDA) for the exchange-correlation energy functional. The electron-ion interaction was described by ab initio pseudopotentials and the wave functions were expanded by plane-wave basis sets. In the geometry optimization of the Alq3/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 upward 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 Alq3 indicates that the lowest unoccupied molecular orbitals (LUMO's) were fractionally occupied while the characteristic of the MO's of Alq3 were kept upon adsorption. 0.5-0.9 electrons were transferred from the Al substrates to Alq3. We found no hybridization of the wave function in those projected DOS. This result is seemingly 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) level of the Alq3 in downward configurations, in which the energy levels of the Alq3 are located quite higher than those in upward configurations. Further details will be presented.

I10.7

Systematic modification of freshly sputter deposited indium-tin-oxide films: surfaces and interfaces.

Thomas Schulmeyer, Michael Brumbach and Neal R. Armstrong; Chemistry, The University of Arizona, Tucson, Arizona.

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-vacuo transfer to photoelectron surface analysis will be presented in this contribution. This transfer technology provides the possibility 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 reactivity while tailoring of work function and charge injection 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.

I10.8

Influence of electrode contamination on organic/electrode hole-injection barriers. Alan Shu-Chung Wan, Jaehyung Hwang, 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. N₂) or even ambient conditions. In this work, we investigate the effect of ambient exposure of Au, Al, indium tin oxide (ITO), and conductive polymer poly(3,4 ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) electrode surfaces on the hole-injection barrier on hole transport materials N,N'-diphenyl-N,N'-bis (1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) and copper-phthalocyanine (CuPc) using ultraviolet photoemission spectroscopy (UPS) and current voltage (I-V) measurements. We compare layers grown in UHV on substrates: (i) as-loaded, exposed to ambient, with degreasing 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 ϕ decreases with increasing electrode work function Φ . This trend is indeed observed when comparing different substrates prepared in the same manner. For example, γ -NPD on clean Al ($\Phi = 4.5$ eV) gives $\phi = 1.7$ eV with a positive interface dipole $\Delta = 0.6$ eV (downward vacuum level shift from the electrode to the organic), whereas on clean Au ($\Phi = 5.3$ - 5.4 eV), the barrier is $\phi = 1.4$ eV and $\Delta = 1.3$ eV. However, some ambient-exposed electrodes actually yield smaller interface barriers with organics than clean electrodes. γ -NPD on air-exposed Au ($\Phi = 4.7$ - 4.9 eV) leads to ϕ 0.5-0.6 eV lower than on clean Au.¹ The same trend is 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 to those obtained with ambient-exposed metals. 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 1. A. Wan, J. Hwang, 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)

110.9

Electrical Characterization of Metal/Pentacene Contacts. Lei Diao¹, Daniel Frisbie¹, Dominic Schroepfer² and Paul Ruden²;
¹Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; ²Electrical 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 undoped pentacene films 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.

110.10

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

Unlike traditional heterojunctions in inorganic devices, contact formation of multilayer cathodic 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 method, 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 contact formation. Highly 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 opposing impact that a LiF interlayer has on device 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 bulk lattice constant match at the interface may be used as a guide to predicting future device performance.

110.11

Formation of Al Thin Films on Organic Surfaces. Tolu Ogundimu, 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 vapour inside the deposition chamber can limit the range 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, was examined. 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.

110.12

Pentacene thin film transistor performance effects on modified dielectric interfaces and molecular beam parameters. Alexios Papadimitratos¹, Aravind S. Killampalli², Jared L. Mack², James R. Engstrom² and George G. Malliaras¹;
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 organic thin film transistors on bare thermal SiO₂, hexamethyldisilazane (HMDS) and octadecyltrichlorosilane (OTS) coated SiO₂ substrates to understand the relationship between performance characteristics of OTFTs and film-dielectric interface properties. In addition, the devices with HMDS and OTS primed SiO₂ showed improved performance characteristics compared to bare thermal SiO₂. This appears to be so 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.

110.13

Nucleation of Pentacene Films on Si Surfaces. Leonidas Tsetseris¹ and Sokrates T. Pantelides^{1,2};
¹Department of Physics & Astronomy, Vanderbilt University, Nashville, Tennessee; ²Condensed 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 we 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 the studied 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.

I10.14

Impedance Spectroscopy and Scanning Kelvin Probe Microscopy Studies of Charge Injection and Transport in Phthalocyanine Thin Films. Richard D. Yang^{1,2}, Xiaotian

Zhou^{1,4}, Amos Sharoni³, Corneliu Colesniuc³, Jengwon Park¹, Edward T. Yu^{4,1}, Ivan C. Schuller³ 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 scanning Kelvin probe microscopy (SKPM) in real space. CoPc films, 50 nm thick, were grown on 5 micron spacing interdigitated gold electrodes by organic molecular beam epitaxy (OMBE). Current-voltage measurements show Ohmic conduction at low voltage and space-charge limited conduction (SCLC) at high voltage, where there are 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 electric field 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 studies suggest the 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.

I10.15

Characterization of Alq₃/LiF/Al and Alq₃/Al interfaces with photoelectron spectroscopy. Stina K. M. Joensson¹, William R. Salaneck² and Mats Fahlman³; ¹School of Engineering and Science, International University of Bremen, Bremen, Germany; ²Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden; ³Department of Science and Technology, Linköping University, Norrköping, 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/Al structures that exhibit better device performance than Alq₃/Al structures. Monolayers of Alq₃ have been grown on Al and LiF/Al substrates by physical vapor deposition. In the case of Al there is covalent interaction between the metal substrate and the organic monolayer (evidenced by an interfacial state observed in the UPS spectra), which is also supported by a vacuum level shift indicating dipole formation at the interface, in analogy with previous results by other groups. In contrast, for the Alq₃/LiF/Al system, there are new interfacial states appearing for LiF layers up to about 20 Å. XPS and UPS results show that these interfacial states originate from charge transfer between the Al-substrate and the Alq₃ monolayer across 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.

I10.16

Charge injection barriers at interfaces of conjugated polymers. Wojciech Osikowicz¹, Michel P. de Jong¹, Slawomir

Braun¹, Carl Tengstedt², Mats Fahlman² and William R. Salaneck¹; ¹Dept. of Physics, IFM, Linköping University, Linköping, Sweden; ²Dept. of Science and Technology, Linköping University, Norrköping, 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 interpret 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 vapor-deposited gold electrode behaves 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 more complex behavior. Large interfacial dipoles on the order of a 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 consistently observed for the cases of metallic/semiconducting all-organic and hybrid interfaces, e.g. Au/polymer and polymer/Au.

I10.17

Alkoxy-substituted conjugated polymers and oligomers for chemical and bio-sensing Langmuir-Schafer thin film

transistors. Gianluca Maria Farinola¹, Maria Cristina Tanese¹, Luisa Torsi^{1,2}, Patrizia Iliade¹, Omar Hassan Omar³, Donato Colangiuli¹, Bruno Pignataro⁴, Ludovico Valli⁵, Serena Casilli⁵, Sabrina Conoci⁶, Philippe Lang⁷, Francesco Babudri^{1,3}, Francesco Naso^{1,3}, Luigia Sabbatini¹ and Pier Giorgio Zamboni¹; ¹Department of Chemistry, University of Bari, Bari, BA (Italy), Italy; ²Centro di Eccellenza TIRES, University of Bari, Bari, BA (Italy), Italy; ³Department of Chemistry, CNR ICCOM Sezione di Bari, Department of Chemistry, University of Bari, Bari, BA (Italy), Italy; ⁴Department of Physical Chemistry "Filippo Accascina", University of Palermo, Palermo, PA (Italy), Italy; ⁵Department of Ingegneria dell'Innovazione, University of Lecce, Lecce, 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 bonded through the alkoxy linkage. As a first step, an alternating copolymer, poly(2,5-dioctyloxy-1,4-phenylene-alt-2,5-thienylene), is investigated as organic thin-film transistor active layer. It is demonstrated that the polymer, deposited as cast or Langmuir-Schafer thin-films, 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-thienylene 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.

I10.18

Potassium doping effects on electronic structure and morphology of n-type molecular thin films. Kaname Kanai¹,

Tadanobu Ikame¹ and Kazuhiko Seki^{2,3}; 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 molecules, hexadecafluorozincphthalocyanine (F16ZnPc) and 11,11,12,12-tetracyanonaphtho-2,6-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 monoanion. The state which emerges in HOMO-LUMO gap by potassium doping is interpreted as partially filled LUMO of pristine 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 metal. In the case of copper substrate, highly-ionized 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. We will discuss the potassium doping effects on electronic structure and morphology by comparison between the experimental results and simulated results.

I10.19

Influence of the film morphology on the diffusion of Ag in the organic semiconductor diindenoperylene. Michael Scharnberg¹, Klaus Raetzke¹, Rainer Adelung¹, Stefan Meyer², Jens Pflaum² and Franz Faupel¹; ¹Chair for Multicomponent Materials, University of 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. Diindenoperylene (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 diffusion of metal atoms (typically 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 tiny concentrations of atoms penetrating into organic 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 agglomeration. Latest experiments with DIP films of varying structure 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 structural 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, 024104 (2005)

I10.20

Observations of Excitons and Phonons in High Quality Pentacene Monolayers. Rui He¹, Nancy G. Tassi², Graciela B. Blanchet² and Aron Pinczuk^{1,3}; 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 exciton luminescence bands are observed in single monolayer and submonolayer films. In the single monolayers photoluminescence of the free exciton optical transition occurs at about 1.88eV, blue-shifted by about 0.1eV from that in high quality pentacene single crystals [1]. In films of average thickness of two monolayers the free exciton optical emission is at 1.866eV. The self-trapped exciton transition, which is the dominant optical emission band in high quality pentacene single crystals at low temperature [1], is quenched in the monolayers. Photoluminescence excitation spectroscopy results from the monolayer reveals that the lowest two excited states are at 1.88 and 1.99eV. The energy separation of these two states 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 Raman scattering intensities are found when the incoming and outgoing photon energies overlap the free exciton optical 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 substrates. Lattice 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 monolayers are venues for probing 2D properties, studies of interface effects, and thin film characterization. Supported by the Nanoscale 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. Pinczuk, D. V. Lang and A. P. Ramirez, to be submitted for publication.

I10.21

Exciton relaxation and charge transfer at molecule/metal interfaces: C60/Au(111). Gregory Dutton, Daniel Quinn, Chad Lindstrom and Xiaoyang 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 also discovered that the metal-to-molecule (LUMO 2) charge transfer resonance evolved into a molecular quantum well with distinct molecular characteristics.

I10.22

Electronic structure of C60 on Al studied by using UV photoelectron spectroscopy. J. H. Seo, S. W. Cho, C. Y. Kim, S. J. Kang and C. N. Whang; Institute of Physics & Applied Physics, Yonsei university, Seoul, South Korea.

The electronic structure of C₆₀ on Al was analyzed by using ultraviolet photoelectron spectroscopy (UPS). The energy level alignment was studied by using the onset of the highest occupied molecular orbital (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 transistor (OTFTs). Among those 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.

I10.23

Chemical Interactions between LiF, MEH-PPV, and Al as determined by Photoelectron Spectroscopy. Korhan Demirkan, 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 efficiency and the turn-on 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 lowers the anode work function [2], ii) interaction of LiF with 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 spectrum 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] L.S.Hung, C.W.Tang and M.G.Mason, Appl.Phys.Lett. 70, 152 (1997) [2] S.D.Wang, M.K.Fung, S.L.Lai, S.W.Tong, C.S.Lee, S.T.Lee, H.J.Zhang, S.N.Ba, J.Appl.Phys. 94, 169 (2003) [3] Y.Yuan, D.Grozea, S.Han and Z.H.Lu, Appl.Phys.Lett. 85, 4959 (2004)

I10.24

Interface Disorder and Charge Injection into Copper Phthalocyanine. Benjie Limketkai, Kaveh Milaninia, Madhusudan Singh and Marc Baldo; Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We examine the effect of morphological disorder at the injection interface between gold and copper phthalocyanine (CuPC). We compare CuPC grown on single-crystal flat gold Au(110) and CuPC grown on a rough polycrystalline interface. 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 UPS studies[1] observe significant 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 at atomically flat metal interfaces. [1] H. Peisert, M. Knupfer, T. Schwieger, J.M. Auerhammer, M.S. Golden, and J. Fink, *Journal of Appl. Phys.*, 91, 4872

110.25

Enhanced Light Emission using Thin Metal-Halide Cathodic Interlayers for Improved Electron Injection into MEH-PPV Polymer Light-Emitting Diodes. Woo-Jun Yoon¹, Scott B. Orlove¹ and Paul R. Berger^{1,2}; ¹Department 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 fluorides between the 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 the metal-halide compounds dissociate, and the metal ions diffuse into the electroluminescent polymer layer, donating electrons to the π -system, thus, enhancing electron injection and therefore leading to higher electroluminescent external quantum efficiencies. Previous work has principally investigated fluoride-based chemistries and this study extends that work by examining other halide based chemistries (LiF, LiCl, LiBr and LiI). PLEDs with varying metal-halides 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-halides interlayer was deposited by thermal evaporation at a 10^{-6} Torr to a nominal thickness of 50 Å. The ITO/PEDOT:PSS/MEH-PPV/metal-halides/Al PLEDs were finally completed by the shadowmask evaporation of an Al cathode. Light-current density-voltage (L-J-V) measurements were performed in the nitrogen glovebox with a semiconductor characterization system (Keithley 4200) with a calibrated Si-photodetector at room temperature under darkness. We then examined the effects of metal-halides 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 as halides were varied 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 LiI (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 LiI were 3.6× and 4.2× greater, respectively. This resulting enhanced current density and subsequent light output, as the lattice energy of 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 Kury¹, Kelly R. Roos², Kevin Kimberlin², Dagmar Thien¹, Michael Horn-von Hoegen¹ and Frank-J. Meyer zur Heringdorf¹; ¹Institute for Laser and Plasma Physics, University of Duisburg-Essen, Essen, Germany; ²Department 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, only little is known about stress effects in organic 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 two results which we believe are of 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 nearly untouched, and this is likely 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. This 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. Fischer², Sharadha Sambasivan², Lee J. Richter³, Marc C. Gurau³ 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 device performance is strongly dependent 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 the charge carrier mobility presumably due to changes in microstructure that result in 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 chain orientation 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 thiophene, fluorine, and pyridine surfaces. We quantify the relative surface coverage 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 polymer was spin coated, even for surfaces with the same water 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. Soonjoo 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.

Soonjoo 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 desirable since they facilitate a variety of applications. Rubrene (C₄₂H₂₈) 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 rubrene thin film field effect transistors that show ambipolar characteristics. The mobilities of holes and electrons were 8.0×10^{-6} cm²/Vs and 2.2×10^{-6} cm²/Vs, respectively. Atomic force microscopy images show 3 dimensional growth of circular rubrene islands even in the initial stages of growth. 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 geometric percolation of islands.

110.29

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 oxygen gas[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 products generated by VUV or soft X-ray irradiation as dopant. Advantages of the newly developing method 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) side (from 1.29 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 products act as donor and that 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 anneal 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, 7×10^{-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 just after deposition. The HOMO band position then decreased to 1.10 eV after air exposure for 16 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) doped 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 (2000) [2] T.Nishi et al., Chem.Phys.Lett. accepted. [3] M.Ono et al., IPAP Conference Proceedings Series, in press.

110.30

Visualization of Electrical Potential Distributions in Working Organic Thin-Film Transistors Using Purely Electric AFM Potentiometry. Masakazu Nakamura, Naoyuki Goto, Hiroshi Tomii, Mingsheng Xu and Kazuhiro Kudo; Electronics and Mechanical Engineering, Chiba University, Chiba, Japan.

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 became 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 10 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' distributed over relatively wider range near the electrode edge was observed for top-contact TFTs and that concentrated at the interface as a 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 'Nanotechnology Materials Program Rewritable Paper Project' based on funds provided by METI. [1] M. Nakamura, M. Fukuyo, E. Wakata, M. Iizuka, K. Kudo, K. Tanaka, Synthetic Metals,

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110.31

Charge Injection and Transport in Diocetylfluorene-arylamine Copolymers. H. H. Fong, A. Papadimitratos and G. G. Malliaras; Materials Science and Engineering, Cornell University, Ithaca, New York.

Poly(9,9-dicycylfluorene) (PFO) is considered to be one of the most promising hole transporting and blue light-emitting conjugated polymers used in polymeric light-emitting diodes (PLEDs) due to its good hole mobility and solution processable ability. Since arylamine compounds possess a superior hole drift mobility (up to 10^{-3} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) and a high-lying highest occupied molecular orbital (HOMO) with respect to PFO, the copolymers of diocetylfluorene and arylamine is of great importance in blue-emitting PLED fabrications. 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-arylamine 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 extend the drift mobility measurement down to device application thickness ($\sim 100\text{nm}$). 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 polymer electronic devices by engineering the charge injection and transport characteristics.

110.32

Investigation of Injection Barriers of Organic Model Interfaces in the Molecularly-doped Polymer Devices by Internal Photoemission Spectroscopy. H. H. Fong and G. G. Malliaras; Materials Science and Engineering, Cornell University, Ithaca, New York.

The process of charge injection significantly dominates the device performance in organic electronic devices such as luminous efficiency and operating lifetime. As many organic devices are injection-limited, a proper electrical characterization for the injection barrier is requisite. 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/ molecularly-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 can be well-characterized [1,2]. 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 (ethylenedioxythiophene) : poly (styrenesulfonate) (PEDOT:PSS) 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.H. Fong, K.C. Lun, S.K. So, Chem. Phys. Lett. 353, 407 (2002).

SESSION I11/D14: Joint Session: Interfaces in Organic and Hybrid Devices
Chairs: Sean Shaheen and Xiaoyang Zhu
Friday Morning, December 2, 2005
Room 302 (Hynes)

8:00 AM I11.1/D14.1

Buried organic/inorganic interfaces in polymer optoelectronic devices: functional nanocomposites.

Gitti L. Frey, Materials Engineering, Technion, Haifa, Israel.

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. Similarly, designed buried interfaces could be used 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 the fields of catalysis, separation, data storage and optics. 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 MEH-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 I11.2/D14.2

Towards Transparent Inorganic and Plastic Low-Workfunction Electrodes. Linda Lindell², Fredrik Jakobsson¹, Wojciech Osikowicz², Peter Andersson¹, William Salaneck², Magnus Berggren¹, Jerome Cornil³ and Crispin Xavier¹; ¹Department of Science and Technology, Linköping University, Norrköping, Sweden; ²Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden; ³Chimie des Matériaux Nouveaux, University 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 electron injecting electrode. In a p-LED or a solar cell, the low work function (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 processing steps. 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 an electrode surface can be achieved by controlling the orientation of an electric dipole, the interface dipole D_{int} . 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 eD_{int} [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 eD_{Dmet} , (ii) the intrinsic dipole moment D_{mol} of the adsorbed molecule, and (iii) the chemical dipole potential eD_{chem} created by partial electron transfer between the metal and the adsorbate upon chemisorption. Therefore, DW can be written as a function of these contributions: $DW = eD_{int} = f(eD_{Dmet}, eD_{mol}, eD_{chem})$. 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 tetrakis(dimethylamino)ethylene -TDAE- ($\{Me_2N\}_2C=C\{N-Me_2\}_2$). Upon electron transfer reaction at the interface, the TDAE molecules become positively charged and an chemical dipole potential eD_{chem} 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. Ito, and K. Seki, *Advanced Materials*, 11, 605 (1999). [2] X. Crispin, V. M. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W. R. Salaneck, J. L. Bredas, *Journal of the American Chemical Society*, 124, 8132-8141 (2002). [3] W. Osikowicz, X. Crispin, C. Tengstedt, L. Lindell, Th. Kugler, W. R. Salaneck, *Applied Physics Letters*, 85, 1616-1618 (2004). [4] L. Lindell, F. Jakobsson, J. Cornil, P. Andersson, W. R. Salaneck, M. Berggren, X. Crispin, submitted.

8:30 AM *I11.3/D14.3

Ultrafast electron transfer at the molecule-semiconductor nanoparticle junction. Tianquan Lian, 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. The rate of ET from 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 (anchoring group, spacer and chromophores), and junction 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 *I11.4/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 of 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 excitonic solar cells, including dye sensitised nanocrystalline, hybrid polymer / metal oxide and all organic devices. Our paper focus 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 1. Durrant et al. *Coord. Chem. Rev.* (2004) 1247-1257 2. Haque et al. *J. Am. Chem. Soc.*, 125 (2005) 3456-3462. 3. Handa et al. *Angew Chemie* (2005) in press.

9:30 AM I11.5/D14.5

Tripod Thiolate Self-Assembled Monolayer: A Novel SAM to interface Zeolites to Gold(111). Andrew S. Ichimura and Wanda Lew; 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) absorptions characteristic of nearly free electrons.[1] A related material, Cs@IFR, 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 tripod thiolate monolayer. In this SAM, three adjacent mercaptoethanol molecules form silyl ether linkages leaving a reactive silicon chlorine 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 tripod 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 tripod thiolate SAM, and preliminary XRD and SEM measurements of the zeolite monolayers and films. 1. Ichimura, A. S.; Lew, W. unpublished results. 2. Ichimura, A. S.; Dye, J. L.; Cambor, M. A.; Villaescusa, L. A. *J. Am. Chem. Soc.* 2002, 124, 1170-1171. 3. Wernette, D. P.; Ichimura, A. S.; Urbin, S. A.; Dye, J. L. *Chem. Mater.*, 2003, 15(7), 1441-1448. 4. Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q.; *J. Am. Chem. Soc.*, 2003, 125, 1170-1171.

9:45 AM I11.6/D14.6

Organic Light Emitting Device Stability Dependence on the Metal Halide Salt Electron Injection Layer. Brian D'Andrade,

Organic light emitting 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. There are many degradation mechanisms that decrease the operational stability of OLEDs. 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 on the electron transport layer before the deposition of a thick >10nm 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 solvent-cleaned and dried indium-tin-oxide coated glass, using vacuum (~6x10⁻⁸ Torr) thermal evaporation, 10 nm of copper phthalocyanine (CuPc), 50 nm of 4,4'-bis[N-(1-naphyl)-N-phenyl-amino]biphenyl (NPD), and 50 nm of tris-(8-hydroxy-quinoline)aluminum. The cathode consisted of various thicknesses (1-10 nm) of either CaF₂, CsCl, CsF, KF, LiCl, LiF, NaBr, NaCl, NaF, or AgCl and 100 nm of Al. The thickness of the salt layer is a crucial factor in device stability and operating voltage, so this layer thickness was optimized for maximum stability. Except for devices with AgCl, the initial current-density versus voltage (J-V) and external quantum efficiency of all optimized devices were similar, within experimental error. For example, the mean and standard deviation of the peak efficiency, of devices without AgCl, was 1.6% (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 400 hrs or until they attained 90% 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 (3 hrs) < NaCl (10 hrs) < LiCl (183 hrs) < CaF₂ (210 hrs) < LiF (290 hrs) < CsF (296 hrs) < CsCl (317 hrs) < NaF (348 hrs) < KF (395 hrs). The luminance after 400 hrs also depended on the salt and increased as follows: AgCl (0 cd/m²) < NaBr < NaCl < LiCl < KF < CaF₂ < CsF = CsCl = LiF < NaF (1870 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, ion size, or 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. Chan, S. L. Lai, M. K. Fung, C. S. Lee, and S. T. Lee, *J. Appl. Phys.* 95, 5397 (2004).

10:30 AM *I11.7/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 Petaccia¹, Guillermo Zampieri¹, Silvano Lizzit¹, Cinzia Cepek², Luca Floreano², Alberto Verdini², Alberto Morgante², Albano Cossaro², Rosanna Larciprete³, Luigi Sangaletti⁴, Stefania Pagliara⁴, Chiara Battocchio⁵ and Giovanni Polzonetti⁶, ¹Sincrotrone Trieste S.C.p.A., Trieste, Italy; ²Lab. Nazionale TASC-INFN, Trieste, Italy; ³CNR-Istituto dei Sistemi Complessi, Rome, Italy; ⁴Dip. Matematica & Fisica, Università Cattolica del Sacro Cuore, Brescia, Italy; ⁵INFN-Ogg, ESRF, GILDA CRG, Grenoble, France; ⁶Dip. Fisica, Università "Roma Tre", 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 photochemical devices. Porphyrins are 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-crystallites and solution form only [2], for which the typical fluorescence decay of the excited porphyrins is strongly quenched [3], i.e. non-radiative decay channels are favored. Next step toward an efficient solar cell is the deposition of similar metallo-porphyrin/fullerene systems on substrates, 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 UHV 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 growth, molecular orientation and electronic 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), as well as it allows the self-assembling of the two molecular species in ordered multilayer structures when co-deposited. The interactions with the substrate and with C₇₀ modify the ZnTPP electronic states, indicating formation of bonds 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 mixed systems delocalize more efficiently the excited electrons as compared to pure ZnTPP films. The charge transfer time depends on the empty <pi>* 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 5 fs. [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, 3642 (1997); P.D.W. Boyd et al, *J. Am. Chem. Soc.* 121, 10487 (1999); T. Ishii et al, *Coordination Chem. Rev.* 226, 113 (2002). [3] M.E. Milanese et al, *J. Phys. Org. Chem.* 15, 844 (2002). [4] W. Wurth & D. Menzel, *Chem. Phys.* 251, 141 (2000); J. Schnadt et al, *Nature* 418, 620 (2002).

11:00 AM I11.8/D14.8

Internal Electric Fields and Charge Injection in PFO Based Diode Structures. Ian H. Campbell, Brian K. Crone and Darryl L. Smith; Los Alamos National Lab, Los Alamos, New Mexico.

We present measurements of internal electric fields and charge injection in poly(9,9-dioctylfluorene) (PFO) and PFO/poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) blend based diode structures. In PFO/F8BT blend diodes with poly(2,3-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT:PSS) anodes 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 complementary 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]. Electron injection leads to an increase in diode built in potential 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, 162 (2004). [3] D. Poplavskyy, J. Nelson, D.D.C. Bradley, *Proc. SPIE* 5214, 197 (2004).

11:15 AM I11.9/D14.9

Tuning of Injection Barrier for Organic Electronics with Self-Assembled Monolayers. Bert de Boer, Magda Mandoc, Valy Mihailetchi, Afshin Hadipour and Paul Blom; Molecular Electronics, Materials Science Centre / University of Groningen, Groningen, Netherlands.

Metallic contacts in organic, opto-electronic devices are determinative for the ultimate device performance. Preparation methods, diffusion of metal atoms, reactivity of metals toward air and organics, can have a detrimental influence on the stability and performance of organic thin-film devices like light-emitting diodes (LEDs), photovoltaic (PV) cells, and (ambipolar) field-effect transistors (FETs). Although these influences have to be addressed before a reliable and reproducible opto-electronics device can be measured, one first has to take into account the intrinsic properties of the metal namely its work function. We demonstrate the tuning of metal work functions by modifying the metal surface through the formation of self-assembled monolayers (SAMs) derived from 1H,1H,2H,2H-perfluoro alkanethiols and hexadecanethiol. The ordering inherent in the SAMs creates an effective, molecular dipole at the metal/SAM interface, which increased the work function of Ag (4.4 eV) to 5.5 eV for 1H,1H,2H,2H-perfluoro alkanethiols. Hexadecanethiol on the other hand shifted FAg to 3.8 eV. On Au, the SAM of 1H,1H,2H,2H-perfluorodecanethiol raised the work function of Au (4.9 eV) with 0.6 eV to 5.5 eV, whereas hexadecanethiol decreased the work function of Au by 0.8 eV. These chemically modified electrodes were applied in the fabrication of polymer LEDs and the hole injection into MEH-PPV was investigated. An Ohmic contact for hole injection between a silver electrode functionalized with the perfluorinated SAMs, and MEH-PPV with a HOMO of 5.3 eV was established. Conversely, a silver electrode modified with a SAM of hexadecanethiol lowered the Ag work function to 3.8 eV blocked the hole injection into PPV, which enables studying the electron transport in composite devices. The electron-only current was measured in a polymer/polymer blend photovoltaic cell based on MDMO-PPV and PCNEPV. This method demonstrates a simple and attractive approach to modify and improve metal/organic contacts in organic electronic devices like LEDs, photovoltaic cells, and FETs.

11:30 AM I11.10/D14.10

Tailored Doping and Modification of Indium Oxide Thin Films for Organic Photovoltaics with Increased Photoactivity.

Michael T. Brumbach¹, Thomas Schultze¹, Neal R. Armstrong¹, Simon Jones^{2,1} and Seth Marder²; ¹Chemistry, University of Arizona, Tucson, Arizona; ²Chemistry, 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 of the 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 absorbing highly photoactive phthalocyanines (trivalent and tetravalent metal Pcs) in optimized Pc/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.

11:45 AM I11.11/D14.11

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 formed by an organic-inorganic heterojunction (OI-HJ) diode that serves both as a fuse and a rectifier in a 2D memory array[1]. A layer of polyethylene dioxythiophene: polystyrene sulfonic acid (PEDOT:PSS) spun 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/n-Si interface, for example, a contact barrier energy of $E_{bn}=0.50\pm 0.01$ 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 (0.56 ± 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 also be discussed in this work, which provides fundamental insights into the nature of charge transport across hybrid organic/inorganic interfaces. [1] S Moller, C Perlov, W Jackson, C Taussig, S R Forrest, Nature, 426, 166 (2003)

SESSION I12: Polymer-Inorganic Interfaces and Devices

Chair: Janice Reutt-Robey

Friday Afternoon, December 2, 2005

Room 302 (Hynes)

1:30 PM *I12.1

Investigation of Charge-Injection Barriers in Finished PLEDs by Means of Non-Invasive Optical Probing. Franco Cacialli¹,

Thomas Meredith Brown² and Vladimir Bodrozic¹; ¹Physics and Astronomy and London Centre for Nanotechnology, University College London, London, United Kingdom; ²MINAS-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 itself. This role is particularly important for organic semiconductors as they are generally used in their pristine, undoped form. Here, we review our progress in the understanding of 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 found 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. Bardeen model), except for electrodes which extensively react with the polymer, and introduce deep gap states.

2:00 PM I12.2

Organic Thin Film Transistors with Surface-Initiated ATRP Polymer Dielectrics. Jason Christopher Pinto¹, Gregory Whiting²,

Wilhelm Huck², Richard Friend¹ and Henning Sirringhaus¹; ¹Optoelectronics Group, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; ²Department of Chemistry, Melville Laboratory, University of Cambridge, Cambridge, United Kingdom.

Recent interest in organic electronics has been motivated by the many advantages organics offer 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 realised, 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 such as spin coating, however, show 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. The robust 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 90 nm grown with ATRP. Operation of these transistors at gate voltages as low as 5 V is demonstrated in contrast to the high voltages traditionally employed with thick spun cast dielectrics. These thin dielectrics displayed leakage currents as low as $3 \mu\text{A}/\text{cm}^2$ at fields of $25 \text{ V}/\mu\text{m}$ 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 polymer brush chemistry and we demonstrate the use of this control to study the dielectric-semiconductor interface via such tools as atomic force microscopy (AFM), x-ray diffraction and neutron reflectivity.

2:15 PM I12.3

Self-Assembled Monolayer of π -Conjugated Molecules as the Semiconducting Component of New Organic Transistor Structures. Kangho Lee¹, Sanghyun Ju¹, Rand Jean¹, Myung-Han Yoon², Antonio Facchetti², Gang Lu², Tobin Marks² and David Janes¹;

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In disordered systems such as organic solids, hopping transport is the dominant conduction mechanism. Hopping generally causes a relatively low charge carrier mobility, which has been the major limitation of organic field-effect transistors (TFTs). However, it has been demonstrated that organic solids composed by π -conjugated molecules with efficient intermolecular π -orbital overlap, exhibit improved charge transport characteristics. Very pure organic single crystals have been used to fabricate TFTs with mobilities as high as $\sim 25 \text{ cm}^2/\text{V}\cdot\text{sec}$, 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 TFT channel components. 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 TFTs 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 were self-assembled on GaAs substrates with two gold contacts separated by $2 \mu\text{m}$. Compared to the pre-deposition leakage current ($< 1 \text{ nA}$) 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 bulk leakage value, which is attributed to the passivation of GaAs surface states by octadecanethiol. Based on this result, a similar experiment was performed with a dihexylquaterthiophene (SDH4T) derivative having a SiCl_3 group at one molecular end, allowing self-assembly on OH-terminated surfaces such as SiO_2 and ITO. Similar devices with identical gold or ITO contacts separated by $2 \mu\text{m}$, $5 \mu\text{m}$ or $10 \mu\text{m}$

were fabricated on a heavily doped n-type Si substrates with 5000 Å thermally-grown SiO₂. No significant increase in conductivity was observed in the samples with Au electrodes. However, the devices with ITO contacts separated by μm showed conductivity enhancement by 5 orders of magnitude after depositing SDH4T, which leads us to propose that self-assembled π-molecules on metal contacts facilitate the carrier injection from the metal contact to a SAM. The experiments to investigate gate modulation effects are in progress using similar device structures with a thinner SiO₂ layer. In addition, a new device structure has been developed to integrate self-assembled π-molecules with high-quality multilayer organic insulators, recently introduced to enable low-power organic transistors.

2:30 PM *I12.4

Electronic structure of hybrid interfaces for polymer-based electronics. William R. Salaneck, Wojciech Osikowicz and Slawomir 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, high lighting work done in Linköping.

3:30 PM *I12.5

STM-Excited Electroluminescence and Spectroscopy on Organic Materials. Santos F. Alvarado¹, Martijn Kemerink², Peter Mueller¹, Laura Rossi¹ and Laurent Libioulle¹; ¹Science and Technology Department, IBM GmbH Zurich Research Laboratory, 8803 Rüschlikon, 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 $z - V$ spectroscopy technique is applicable. We show that a necessary condition is having a sufficiently sharp STM-tip apex, leading to field enhancement of the injected current. This can actually determine the polarity of the predominant charge carrier, thus allowing one to probe injection and transport of both carriers. We discuss results obtained on a series of π-conjugated polymers and small molecules deposited on metallic substrates, including ferromagnets of interest for spin-polarized charge-carrier injection. Under adequate experimental conditions the following can be extracted from the data: (a) The alignment of the empty and occupied molecular orbital levels relative to the Fermi level of the substrate; (b) the energy band gap for charge-carrier injection into the organic material, and (c) the exciton binding energy of the organic material. The alignment of the molecular energy levels indicates the presence of interface interactions leading to dipole formation. For most of the materials studied, the charge-injection threshold values obtained on different positions on the plane of the substrate surface exhibit a single-peaked statistical distribution. An exception is *tris*(8-hydroquinolato)-aluminum (AlQ₃), where a two-peaked distribution (splitting of a few 100 meV) of the electron injection threshold is found, suggesting the influence of the electronic properties of the facial and meridian isomers of (AlQ₃). The exciton binding energy, E_b , of polymers lies in the range from a few 100 meV to almost 1 eV, depending on the materials. For derivatives of poly(*p*-phenylenevinylene) (PPV) E_b depends on the kind of radicals attached to the polymer chain. For small molecules E_b is a few 100 meV. STM-excited electroluminescence measurements on a thin film of PPV on indium tin oxide (ITO) show variations of the electroluminescence (EL) intensity that correlate with the threshold energy for the onset of EL. This indicates a balance shift of negative vs. positive charge carriers in favor of the latter, resulting in an EL intensity enhancement by up to two orders of magnitude. This correlates with an increase of the hole-injection threshold at the PPV/ITO interface by approx. 600 meV.

4:00 PM I12.6

Investigation of Novel Photo FET using Photo-Sensitive Gate Dielectric. Manabu Yoshida¹, Hiroki Kawai², Takeshi Kawai², Sei Uemura¹, Satoshi Hoshino¹, Takehito Kodzasa¹ and Toshihide Kamata¹; 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. Since there are many kinds of organic materials, they can 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 photosensitizing drums in laser printers or photocopiers, have 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 intent to add photo-switching and photo-memory functions to OFETs. For example, poly-N-vinylcarbazole (PVK) has been known as a good photoconductor. Further, the PVK has high processability and high durability to applied voltage, therefore, this is expected to work as a good gate 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 lights with different wavelengths. An ITO electrode was employed as a transparent gate electrode in the OFETs. As a result, under proper 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.

4:15 PM I12.7

Effect of chain conformation and external fields on the electronic structure of single conjugated polymer molecules.

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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 polyfluorene, which exist both in the twisted disordered (glassy) and in the planar ordered (beta) phase [2]. In spite of the rather different chemical structures, we observe identical spectroscopic features on the single chromophore level, such as fluorescence linewidths and spectral diffusion dynamics due to temporal variations in local fields [3]. 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 accurately on the single molecule level and is found to substantially exceed the size of isoenergetic model oligomers [4]. Our results provide important input into material design by demonstrating that structure-property relationships in conjugated polymers derive mainly from chain morphology rather than from the chemical details of the conjugated backbone. An important exception to this rule is given by oxidative defects on the polymer backbone, which (in the case of polyfluorene) yield well defined spectroscopic signatures in the single molecule emission red shifted by over 100 nm from the backbone transition. Besides simply monitoring the single molecule emission, a direct manipulation of the excited state species through electrothermal or electrostatic perturbations shows that single chromophores are not static entities and indeed respond sensitively to the respective environment. Stark spectroscopy reveals a permanent dipole moment on the single chromophore level in these nominally non-polar 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. [1] Muller, Lupton et al., PRL 91, 267403 (2003) [2] Becker and Lupton, JACS 127, 7306 (2005) [3] Schindler et al., PNAS 101, 14695 (2004) [4] Schindler et al., Angew. Chem. 117, 1544 (2005)

4:30 PM I12.8

Fermi Level Pinning at Conjugated Polymer Interfaces. Carl Tengstedt¹, Wojciech Osikowicz², William R. Salaneck² and Mats Fahlman¹; ¹Science and Technology, Linköping University, Norrköping, Sweden; ²Physics and Measurement Technology, Linköping University, Linköping, Sweden.

Photoelectron spectroscopy has been used to map out 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 ELP when the metal work function is smaller than the negative polaron/bipolaron formation energy.

4:45 PM 112.9

Fabrication of Organic Thin Film Transistors Using Layer-by-Layer Assembly. Jeffery Tyron Stricker^{1,2} 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-ethylenedioxythiophene)/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.