## Tuesday Afternoon, October 3, 2000

#### Semiconductors

#### Room 306 - Session SC+EL+OF-TuA

#### **Organic Chemistry on Semiconductor Surfaces**

Moderator: J.E. Crowell, University of California, San Diego

#### 2:00pm SC+EL+OF-TuA1 Novel Reactions of Organic Molecules for Controlled Modification of Semiconductor Surfaces, D.J. Doren, University of Delaware INVITED

Recent theoretical work on reactions of organic molecules with semiconductor surfaces will be described. The focus will be on several mechanisms that allow molecules to react with low activation barriers on (100) surfaces of Si, Ge and diamond. Cycloaddition reactions are the most thoroughly understood reactions of organic molecules on these surfaces, having been studied extensively by both theory and experiment. This work has established several families of molecules that readily chemisorb. However, in several cases, there are competing side reactions. The origins of this competition, and some approaches to controlling selectivity tbrough the choice of precursor molecule, will be discussed. Finally, a reaction that attaches an organic molecule to the surface by dissociation (as opposed to cycloaddition) will be described.

#### 2:40pm SC+EL+OF-TuA3 Peter Mark Memorial Award Address, S.F. Bent<sup>1</sup>, Stanford University INVITED

Tailoring the surface properties of semiconductor materials through organic modification is one means of providing new functionality to the semiconductor surface, incorporating properties such as passivation, lubrication, optical response, molecular recognition, or biocompatibility. Chemical modification also has tremendous utility for the controlled synthesis of organic/semiconductor interfaces for numerous electronic and optical applications, including the coupling of organic-based devices to silicon-based microchip technology. In this presentation, I will discuss different organic attachment strategies used to functionalize semiconductor surfaces in a dry processing environment. Unsaturated molecules, such as alkenes or dienes, can be attached by cycloaddition reaction across the Si-Si dimer at the Si(100)-2x1 surface; the reaction occurs at the surfaces of Ge and diamond, as well. Amine groups provide another reactive functionality for surface attachment. The relative reactivities of cycloaddition, N-H bond dissociation, and nitrogen lone pair interactions at the Si(100)-2x1 surface will be described using a series of pyrrole compounds. The use of protecting groups to manipulate the surface reaction pathway will be demonstrated. The potential for these different classes of attachment reactions to impact future applications will also be discussed.

#### 3:20pm SC+EL+OF-TuA5 Structure of Cyclopentene Adsorbed on InP (001)-(2x1) Surface, Q. Fu, C.H. Li, D.C. Law, M.J. Begarney, R.F. Hicks, University of California, Los Angeles

It has been a growing interest in engineering ordered, defect free organic thin films on semiconductor substrates for the next generation miniature electronic devices. Using metalorganic vapor phase epitaxy, we have successfully grown indium phosphide (2x1) surface terminated with a complete layer of phosphorous dimers. On InP (2x1) surface, a dangling bond on each phosphorous dimer is filled with a single electron, which makes it an ideal substrate for growing organic films through reactions with @pi@-bond of unsaturated molecules. Here, we have characterized the molecular structure of cyclopentene adsorbed on the InP (2x1) surface by scanning tunneling microscopy, internal-reflectance infrared spectroscopy, reflectance difference spectroscopy, and molecular cluster calculations. It is found that the exposed phosphorous dimers are the adsorption sites for the unsaturated organic molecule. Two adsorption configurations were identified: one with the C@sub 5@H@sub 8@ molecule sitting on top of a P dimer, and another one with the C@sub 5@H@sub 8@ molecule bridging across two neighboring P dimers. At the meeting, we will present a comparison of cyclopentene adsorption characteristics on InP (001)-(2x1) versus Si (100)-(2x1).

3:40pm SC+EL+OF-TuA6 Formation and Reaction of Organic Layers on Germanium: Reaction of 1,5-cyclooctadiene with the Ge(100) Surface, P. Prayongpan, D.S. Stripe, C.M. Greenlief, University of Missouri, Columbia Organic alkenes can bond to Ge(100) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered.

The bonding of these molecules to the Ge(100)-(2x1) reconstructed surface is analogous to a class of ring-forming reactions known in organic chemistry as [2+2] cycloaddition reactions. While the bulk reactions involve the reaction of two alkene groups to form a four-member ring, the analogous surface reaction involves two electrons from the organic alkene and two electrons from the surface Ge=Ge dimers. Here, the formation of ordered organic layers on Ge(100) substrates is examined by the reaction of 1,5cycloocatadiene with Ge(100). This molecule reacts with the Ge dimers leading to a [2+2] cycloaddition reaction product. A combination of ab initio calculations and surface sensitive experimental techniques are used to probe the interactions. Surface modification of the organic layers is also explored. The reaction of the organic layers with atomic hydrogen and a series of alcohols will be discussed.

#### 4:00pm SC+EL+OF-TuA7 A Comparative Study of the Bonding of N-Containing Heterocyclic Molecules to the Si(001) Surface, X. Cao, S.K. Coulter, H. Liu, J. Liu, R.J. Hamers, University of Wisconsin, Madison

Recent studies of a variety of unsaturated hydrocarbons has lead to increased interest in understanding the factors controlling bonding of more complex organic molecules to silicon surfaces. By understanding the propensity for heterocyclic molecules to bond into various possible configurations, we are able to gain insight into the factors controlling selectivity in molecule-surface bonding. We have studied the adsorption of pyrrole and its partially-unsaturated analog, 3-pyrroline, onto the Si(001)-(2x1) surface using Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning tunneling microscopy (STM). At 300 K, XPS spectra of pyrrole show a single, sharp N(1s) level, while FTIR spectra show that the molecule retains the high-frequency peaks that are characteristic of aromatic molecules; isotropic labeling studies show that attachment occurs through the N atom via cleavage of the N-H bond. These results show that pyrrole retains its aromatic character after bonding to the surface. In contrast, XPS and FTIR data for 3-pyrolline shows that it can bond through the N atoms or through its C=C bond via the surface equivalent of a [2+2] cycloaddition reaction. This study shows that molecules with aromatic rings show a strong preference for retention of this aromaticity, while molecules without aromaticity have more diverse chemical bonding configurations. Implications for understanding the attachment of other N-containing molecules to surfaces will be discussed.

## 4:20pm SC+EL+OF-TuA8 Reaction of Pyrrole and Pyrrole Derivatives on Si(100)-2x1, G.T. Wang, C. Mui, C.B. Musgrave, S.F. Bent, Stanford University

The ability to covalently bond to semiconductor surfaces organic layers with custom-tailored functionality could have applications in a number of areas, including lithography, molecular electronics, sensors, and low k dielectric materials. Previous studies have shown that the Si(100)-2x1 surface dimer can react with unsaturated hydrocarbons, forming covalently bound [4+2] Diels-Alder and [2+2] cycloaddition products at the surface. Amines have shown promise as alternative candidates for layer-by-layer growth and the model amine ammonia is known to react with silicon via N-H dissociation across the surface dimer. The use of more complex amines for surface modification requires an understanding of how various functional groups in the amine affect its reactivity and bonding configuration with the surface. In this study, the interaction of pyrrole and pyrrole derivatives, including saturated and unsaturated secondary and tertiary amines, with the Si(100)-2x1 surface under ultra-high vacuum is investigated via multiple internal reflection infrared spectroscopy, Auger electron spectroscopy, temperature programmed desorption studies, and ab initio quantum chemistry calculations. The results show that the nitrogen lone pair plays an important role in the reaction of amines with the Si(100) surface. In particular, the stable room temperature molecular adsorption of methylpyrrolidine through its lone pair is permitted due to the presence of a protecting methyl group, while its unprotected analogue, pyrrolidine, proceeds to covalently bond to the surface through N-H dissociation. Additionally, results examining the reaction of the Si(100) surface with a model amide (N-methylacetamide), which contains both carbonyl and amine functionalities through a peptide unit and hence could serve as a bifunctional unit for layer-by-layer growth, are presented.

#### 4:40pm SC+EL+OF-TuA9 Attaching Aromatic Molecules to the Si(001) Surface via Oxygen and Sulfur Tethers, S.K. Coulter, M.P. Schwartz, J. Liu, R.J. Hamers, University of Wisconsin, Madison

Phenol, benzenethiol and phenyl disulfide have been used as model systems to compare the bonding of chemically-similar aromatic molecules to the Si(001)-2x1 surface through different Group VI tethers. The behavior of these substituted aromatic hydrocarbons on the Si(001) surface has

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been investigated using Fourier transform Infrared Spectroscopy (FTIR), Xray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). Both FTIR and XPS indicate that phenyl disulfide bonds exclusively through the sulfur substituent groups. Phenol and benzenethiol molecules bond predominately through their oxygen/sulfur substituent groups, although a small minority may chemisorb on the surface via ring attachment. Thermal studies indicate that the molecules attached to the surface via sulfur or oxygen tethers are stable to temperatures above 550 K. STM studies show that these molecules attach directly to the silicon dimer and, in the case of phenyl disulfide, form ordered rows of aromatic rings.

#### 5:00pm SC+EL+OF-TuA10 Chemical Reactions on the Diamond(100) Surface: First-principles Theory and Comparisons to Experiment, *D.R. Fitzgerald*, *D.J. Doren*, University of Delaware

Density functional theory calculations have been used to investigate the structures, energetics, and reaction pathways of the [4+2] and [2+2] cycloaddition reactions of butadiene with the C(100)-2x1 surface. Onedimer and three-dimer cluster models were used to represent the surface. Vibrational spectra of the product species were also calculated. Activation free energies suggest that the [4+2], or Diels-Alder mechanism, will be kinetically favored. The presence of adjacent unreacted surface dimers affects the orientation of the cycloaddition product. The adsorption of hydrogen on the surface has also been studied. Cluster size is seen to have a large effect on the vibrational spectrum of the adsorbed hydrogen. Theoretical results are compared to recent experiments.

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#### Organic Films and Devices Room 313 - Session OF+EL+SS-WeM

#### Transport and Device Issues in Organic Thin Films Moderator: A. Kahn, Princeton University

8:20am OF+EL+SS-WeM1 The Transport and Injection of Positive Carriers in Conjugated Electroluminescent Polymers and their Devices, A.J. Campbell, University of Sheffield, UK, U.K.; D.D.C. Bradley, University of Sheffield, UK; H. Antoniadis, Infineon Technologies Corp. INVITED Organic light emitting diodes (OLEDs) based on electroluminescent conjugated polymers are an important emerging technology with a wide range of display and lighting applications. Polyfluorene and its copolymers are considered to be amongst the most promising materials for use in commercial OLEDs. Indium tin oxide (ITO) is also the hole injecting electrode of choice in any practical device. Here we report the results of time-of-flight measurements on the transport of positive carriers in polyfluorene and its copolymers. The field and temperature dependence of the charge carrier mobility is compared to theoretical models for charge transport in disordered organic materials. We also report the results of dark injection and current density-voltage measurements on the injection of holes from differently prepared ITO contacts. The absolute injection efficiency of the contacts is calculated by comparison to trap-free, spacecharge-limited current (TFSCLC). The injection efficiency is shown to vary with not only polymer ionisation potential but also with the nature of the ITO preparation (i.e. washed in solvents, exposed to an oxygen plasma, coated with a film of poly(ethylenedioxythiophene) / polystyrenesulphonic acid). The variation of the injection efficiency with temperature is also reported.

#### 9:00am OF+EL+SS-WeM3 Grain Boundary Effects on Electrical Transport in Polycrystalline Organic Semiconductor Thin Films, *R.J. Chesterfield*, *A.B. Chwang*, *K. Puntambekar*, *C.D. Frisbie*, University of Minnesota

The role of microstructure in electrical transport in polycrystalline thin films of organic semiconducting oligomers (e.g., pentacene, sexithiophene) has not been extensively explored. This talk describes experiments in which transport through single grain boundaries (GBs) is probed using field effect transistor (FET) structures and Kelvin probe force microscopy (KPFM). In the FET studies, closely spaced gold source and drain electrodes are connected to pairs of pentacene or sexithiophene microcrystals grown on insulating substrates, such as SiO@sub 2@. The microcrystals, or grains, share a common boundary that dominates the transport through the FET. Conduction through the GB is measured as a function of gate field and temperature, and the results are compared with a recent model by Schon and Batlogg.@footnote 1@) In the KPFM studies, a metal-coated AFM tip is used to record potential distributions across an operating microcrystal FET. The resulting images reveal where the voltage is dropped across the device and thus point to the chief bottlenecks in the current transport. In general, both the microcrystal FET and Kelvin probe experiments show that microstructure, and in particular GBs, can potentially dominate transport in polycrystalline organic semiconductor films. @FootnoteText@ @footnote 1@J. H. Schon, B. Batlogg, Appl. Phys. Letters, 74(2), 1999, 260-262.

## 9:20am OF+EL+SS-WeM4 Quantum Confinement and Electron Transfer at Organic-Metal Interfaces, G. Dutton, H. Wang, X.-Y. Zhu, University of Minnesota

Electron transfer at organic-metal interfaces is important in moleculebased electronic and optoelectronic devices, such as light-emitting devices (LEDs), field-effect transistors (FETs), and molecular quantum wires (QW). We probe interfacial electronic structure and electron transfer dynamics using two-photon photoemission in model systems: thin films of hexafluorobenzene and naphthalene adsorbed on Cu(111). Electron transfer to the lowest unoccupied molecular orbitals, as well as to those mixed with image-type states, are observed. In both systems, these resonances display quantum well behavior: the electronic wavefunction is delocalized parallel to the surface but confined in the direction normal to the surface. The detailed structure and dynamics are established by dispersion measurements and by femto-second time-resolved two-photon photoemission. We believe the formation of these molecular quantum wells is a result of the strong interaction of molecular states with the metal substrate. A simple theoretical framework is developed to describe the formation of these molecular quantum wells.

9:40am OF+EL+SS-WeM5 Chemistry and Electronic Properties at Metals (Al, Mg and Au)-Organic Molecular Semiconductor (F@sub 16@CuPc) Interfaces, C. Shen, J. Schwartz, A. Kahn, Princeton University

The fabrication of efficient and stable metal-organic contacts is exceedingly important for the optimization of organic devices such as organic light emitting diodes (OLED) and thin film transistors. Al and Mg have low work functions and are typically used as electron injecting cathode materials. Au is a mostly inert metal in contact with organic materials. F@sub 16@CuPc is a candidate for n-channel thin film transistor material because of it relatively high electron mobility. Chemistry and physical processes (e.g. interdiffusion) that take place at metal/organic interfaces have a direct impact on the electronic properties of the contacts. It is generally believed that metals deposited on organics lead to more extensive interface chemistry and broader interfaces than organics deposited on metals. In some cases, these interfaces have actually been reported to lead to drastically different electrical behavior. The interfaces fabricated in ultrahigh vacuum, however, shows identical electrical behavior.@footnote 1@ We have investigated the interface chemistry, electronic structure and electrical transport in nominally symmetric metal/F@sub 16@CuPc/metal structures fabricated and tested in ultra-high vacuum. For these structures, we performed detailed ultra-violet and X-ray photoemission spectroscopy (UPS, XPS) photoemission spectroscopy measurements that suggest that the chemistry at metal-on-organic interfaces is very similar to, if not identical with, that at organic-on-metal interfaces. Using current-voltage measurements performed in vacuum, we demonstrate that carrier injection is identical from top and bottom cathodes. @FootnoteText@ @footnote 1@Role of electrode contamination in electron injection at Mg:Ag/Alq@sub 3@ interfaces, C. Shen, I.G. Hill and A. Kahn, Adv. Mat. 11, 1523 (1999).

## 10:00am OF+EL+SS-WeM6 Microcontacts to Self-Assembled Monolayers with a Conducting AFM Tip, D.J. Wold, C.D. Frisbie, University of Minnesota

Molecular level electrical transport studies require innovative approaches for making electrical contacts to oriented molecules. While scanning tunneling microscopy (STM) and electrochemical methods have been used for years to study transport in surface-confined molecules, conducting probe atomic force microscopy (CP-AFM) provides an alternative approach to electrically contacting monolayer films and the formation of metalmolecule-metal junctions. In CP-AFM, a metal-coated AFM tip is placed in direct contact, under controlled load, with the material to be probed. The technique differs from STM in that the probe is positioned using normal force feedback, which decouples probe positioning from electrical measurements. Using this technique, we show that CP-AFM may be used to make mechanically stable electrical contact to SAMs of alkane thiols on Au. We have probed the current-voltage (I-V) characteristics of the resulting junctions as a function of the number of methylenes in the alkane chains and the load applied to the tip-sample contact. The ease of this technique and the fine control of the probe during measurements make CP-AFM a promising approach for studying transport through molecular junctions. Further studies of dependence on conjugation, functional group distributions, orientations, and molecular dimensions will also be discussed.

#### 10:20am OF+EL+SS-WeM7 White-Light-Emitting Organic EL Devices Based on Vacuum Deposited Thin Films, J. Kido, Yamagata University, Japan INVITED

In this paper, we describe the design and fabrication of bright and high efficiency white-light-emitting EL devices based on vacuum deposited organic thin films. In order to archive high quantum efficiency, multilayer structures are employed. White light can be generated by using two emitter layers composed of blue and yellow emitters. For the blue emitter layer, distyrylbiphenyl derivative is doped with a few percent of distyrylarylene derivative with carbazolyl groups. For the yellow emitter layer, rubrene was doped into hole-transporting arylamine derivative (NPD). Reduction of drive voltage was realized by using metal-doped electron injection layer,@footnote 1@ which is composed of electrontransporting bathophenantroline (Bphen) doped with Cs metal. Cs-doping to Bohen reduces resistivity of the Bohen film, and the contact between cathode and the Bphen layer becomes ohmic, which results in the low drive voltage. The typical device structure is ITO/NPD/yellow-emitting layer/blue-emitting/Bphen doped with Cs/Al. By optimizing the thickness of each layer and dopant concentration, the white EL devices exhibited extremely high luminous efficiency of 15 lm/W and external quantum efficiency of 4% which are the highest values reported for white organic EL

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devices. @FootnoteText@@footnote 1@J.Kido and T.Matsumoto, Apply. Phys. Lett, 73, 2868(1998).

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#### Organic Films and Devices Room Exhibit Hall C & D - Session OF-WeP

#### **Poster Session**

#### OF-WeP1 Electrical Properties of Polyvinylidene Fluoride Films Prepared by Physical Vapor Deposition Method, *G.B. Park*, Yuhan College, Korea; *M.Y. Chung, S.W. Lee, S.H. Park, D.C. Lee*, Inha University, Korea

Poly Vinylidene Fluoride thin films were prepared by using a physical vapor deposition and high electric field applying method. Thin films were studied with DSC, FT-IR, X-ray diffraction and electrical conduction measuring system. The melting point of PVDF thin film increases with increasing substrate temperature. It is identified by FT-IR that the crystalline phase of @alpha@ type PVDF is transformed to @beta@ type with increasing electric field applied during preparation. It is found that the crystallinity of PVDF thin films increases from 49.8% to 67% with increasing substrate temperature from 30 to 80. The absorption current of @alpha@ and @beta@ type PVDF increases with increasing the electric field applied under measurement and the current increment of @beta@ type is higher than that of @alpha@ type. The ion hopping distance, derived from a relation between current density and measuring temperature. From above results, the conduction mechanism of PVDF thin film is estimated as ionic.

#### OF-WeP2 Transport Gap and Polarization Energy at Metals (Ag, Au) -Organic Molecular Semiconductor PTCDA Interfaces, *W. Gao, A. Kahn,* Princeton University

The complexity of localization and polarization in molecular solids demands experimental determination of more reliable energy diagrams for charge carrier injection and transport phenomena than just from optical measurements. We use inverse photoelectron spectroscopy (IPES) and ultraviolet photoelectron spectroscopy (UPS) to investigate unoccupied and occupied electronic states of PTCDA (3,4,9,10 - perylenetetracarboxylic dianhydride) deposited on Ag. The interface shows metal-to-organic charge transfer and formation of polaron states. The relative shifts of the vacuum level and molecular levels were analyzed in the context of interface dipole model, extended to account for the evolution of polarization energy. The comparison between the splitting of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) measured via UPS and IPES, and the optical gap measured via absorption measurements leads to an estimate of exciton binding energy E@sub e-h@ to be large (0.6eV), in accordance with the highly correlated nature of this molecular solid. We also use scanning tunneling microscopy (STM) and spectroscopy (STS) for PTCDA deposited on Au(111), and find results consistent with the UPS/IPES results. Work is supported by the National Science Foundation (DMR-98-09483).

# OF-WeP3 Controlled Doping of Polycrystalline and Amorphous Molecular Organic Layers: Physics and Device Prospects, X. Zhou, B. Maennig, M. Pfeiffer, J. Blochwitz, T. Fritz, K. Leo, TU Dresden, Institut fuer Angewandte Photophysik, Germany

Organic dyes with a conjugated electron system are currently investigated intensively for optoelectronic applications. In contrast to classical silicon technology, the materials used for both research and devices such as organic light-emitting diodes (OLED) are usually prepared in a nominally undoped form, leading to scattering of device parameters and higher operating voltages as compared to e.g. polymeric devices. Shifting the Fermi level towards the transport states by doping can reduce ohmic losses, ease carrier injection from contacts and increase the built-in potential of Schottky- or pn-junctions. We present here the results of a comprehensive study of controlled p-type doping of various polycrystalline and amorphous organic materials by the strong organic acceptor F4-TCNQ (tetrafluoro-tetracyano-quinodimethane). It turns out that doping is more efficient for the polycrystalline materials like the phthalocyanines where doping enhances the conductivity by up to eight orders of magnitude (10@super -2@ S/cm). Nevertheless, we could show for the first time that also amorphous phthalocyanine layers (deposited onto cooled substrates) and amorphous wide-gap materials can be doped, i.e. their conductivity increases and their Seebeck coefficient decreases indicating a shift of the Fermi level towards the hole transport state. Amorphous wide gap materials like TDATA or TPD are commonly used as hole transport materials in OLEDs because they form smooth and stable layers. We show here that controlled intentional doping of these layers strongly reduces the operating voltages of OLEDs.

OF-WeP4 Cascade-Like Hybrid Organic-CdS Quantum Particle Architectures Studied by the Attenuated Low Energy Photoelectron Spectroscopy, A. Samokhvalov, M. Berfeld, M. Lahav, R. Naaman, Weizmann Institute of Science, Israel; E. Rabani, Tel Aviv University, Israel Hybrid organic/inorganic matrices containing CdS quantum particles (QP) arranged in periodic layers separated by bilayers of arachidic acid/thioarachidic acid were prepared by Langmuir-Blodgett deposition on gold substrate. Within each layer, the QP are of the same average size of about 2.5 or 5nm, and the layers are arranged in cascade-like pattern. Electronic properties of the structures above were studied by the Attenuated Low Energy Photoelectron Spectroscopy in which a "pump" laser excites QP and a "probe" laser ejects photoelectrons either from gold or from the QP. This spectroscopy provides detailed information on electronic states of the QP and shows that they depend on the specific organization of the QP within the matrix, as well as on the interaction of the QP with the underlaying gold substrate.

## **OF-WeP5 Photoemission Investigation of Metal/CuPc Interfaces**, *L. Yan*, *Y. Gao*, University of Rochester; *M.G. Mason*, *C.W. Tang*, Eastman Kodak Company

Metal/organic interface play an important role in organic light emitting diodes (OLED), which has been a very active field in the past few years because of their scientific and commercial significance. Copper phthalocyanine (CuPc) has been found to improve the electron injection when it is inserted as a buffer layer between the metal cathode and Tris(8hydroxyguinoline) aluminum (Alg@sub 3@), the mostly used light emitting material in OLED. It is intriguing that CuPc, traditionally used as a hole transport material in OLED, can enhance electron injection at the cathode. To address this question, we investigated the formation and the energy level alignment at the interface between metals and CuPc, using X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) simultaneously. We found that unlike many other organic materials, CuPc has two components in C1s, whose relative intensity varies as the interface formation progresses. This property provides a unique avenue to determine the charge transfer, dipole formation and energy level alignment at the interface.

#### OF-WeP6 Photoemission Investigation of Energy Level Alignment and Chemistry in Al/CsF/Alq@sub 3@ Interfaces, L. Yan, Y. Gao, University of Rochester; *M.G. Mason*, *C.W. Tang*, Eastman Kodak Company

Organic light emitting diode (OLED) have attract great attention in recent years since the discovery of Tris(8-hydroxyquinoline) aluminum (Alq@sub 3@) based devices. One surprising discovery is that certain kind of metal/salt complex such as Al/LiF forms excellent cathode for electron injection, which is comparable in device performance to those made from low work function metal such as Li and Ca. However, Li has very small X-ray photoelectron spectroscopy (XPS) cross section, making it hard to investigate any possible interface chemistry. We have investigated the interface formation and energy alignment between Al/CsF and Alq@sub 3@, using ultraviolet photoelectron spectroscopy (UPS) and XPS simultaneously. The experiment result indicates that charge transfer to Alq@sub 3@ had occurred at the Al/CsF/Alq@sub 3@ interface, similar to Al/LiF/Alq@sub 3@ interface. While there is no reaction is detectable by photoemission between Al and LiF, there are significant changes in core level spectra between Al and CsF. On the other hand, the energy level alignment for the two systems is strikingly similar, which is consistent to the device performance studies. Based on these observation and simplified thermodynamic calculation, possible decomposition is proposed at the Al/LiF(CsF)/Alg@sub 3@ interfaces.

#### OF-WeP7 Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy of Metal(Au,Ag) Deposited Alkanethiol and Alkanedithiol Layers, *T. Ohgi*, *W.-L. Deng*, *D. Fujita*, *H. Nejoh*, National Research Institute for Metals, Japan

The self-assembled monolayers (SAMs) of thiol molecules on Au(111) substrates have been extensively studied because of their easy preparation and potential for many applications. For example, in nano-electronics studies, application of the SAMs as a tunneling barrier@footnote 1@ is one of the attractive candidates since it is very easy to obtain widely spread, densely packed, well ordered and atomicaly flat surface and moreover, the thickness of the SAMs can be easily and exactly controlled by changing the length of the molecules. Electrical property of SAMs has so far been investigated by using a metal/SAMs/metal heterostructure, and their structural analysis has been mainly carried out by XPS, UPS, and ISS.@footnote 2@ In the previous study,@footnote 3@ we reported that in the case of SAMs of thiol molecules (HS(CH@sub 2@)@sub n-

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1@CH@sub 3@: C@sub n@S), evaporated gold atoms penetrate through the SAMs. They cannot support metal overlayers, but monoatomic-height Au islands grow at the interface of the Au(111) substrate and SAMs. On the other hand, in the case of dithiol (HS(CH@sub 2@)@sub n@SH: C@sub n@S@sub 2@)layers, small Au particles are formed on them. In this paper, we show the result of Ag deposited octanethiol SAMs and alkanedithiol layers and discuss the difference from Au deposited ones. Ag atoms penetrate through both layers and do not form particles on them. The temporal change of Au particles/alkanedithiol/Au(111) structure were also studied. Sequential observation shows that particles penetrate through layers in weeks and form monatomic height islands under layers. @FootnoteText@ @footnote 1@ R. P. Andres, et. al., J. Vac. Sci. Technol. A14,(1996) 1178 @footnote 2@ D. R. Jung, et.al., J. Vac. Sci. Technol. A14,(1996) 1779 @footnote 3@ T. Ohgi, H. -Y. Sheng, H. Nejoh, Applied Surface Science 130-132, (1998) 919, T. Ohgi, H. -Y. Sheng, Z. -C. Dong, H. Nejoh, Surface Science 442, (1999) 277.

#### OF-WeP8 Wavelength- and Time-Dependent Two-Photon Photoemission Spectroscopy of the Dye Coated Silicon Surface, A. Samokhvalov, R. Naaman, Weizmann Institute of Science, Israel

Two dye molecules of similar structure, Rhodamine B and Sulforhodamine, were adsorbed on n- and p-doped silicon. The effect of photoexcitation of the adsorbed species on electronic properties of the surface of silicon was investigated applying the Wavelength- and Time-Dependent Two-Photon Photoemission Spectroscopy (WD-TPPE). It was found that the adsorption of Sulforhodamine, but not of Rhodamine B, causes a decrease in workfunction. For both dyes, the photoemission from the dye-covered silicon is reduced upon photoexcitation. The time-dependent recovery of the photoemission gets shorter for Sulforhodamine and longer for Rhodamine B, compared to the non-covered silicon. These observations are explained based on the electron donating properties of the molecules. In the case of Rhodamine B, photoexcitation of less than 10@super-4@ of the molecules on the surface was enough to affect the photoemission yield.

**OF-WeP9 Structure and Molecular Recognition Ability of Thiolatedcyclodextrin Monolayer on Au(111) Surface**, *S. Yasuda*, University of Tsukuba, Japan; *I. Suzuki*, Tohoku University, Japan; *K. Yase*, National Institute of Materials and Chemical Research, Japan; *J. Sumaoka*, *M. Komiyama*, University of Tokyo, Japan; *H. Shigekawa*, University of Tsukuba, Japan

Chemisorbed monolayers of thiols and disulfides on gold, so-called selfassembled monolayers (SAMs), have been studied to develop the novel interfacial systems. Since they easily form stable and highly packed monolayers, they are considered to have high potential to fabricate the micro-morphology of materials. From the point of view to develop a molecular recognition sensor using this technique, we analyzed structure and molecular recognition ability of the LP-@beta@-CyD (@beta@cyclodextrin modified with lipoamide residue) monolayers formed on Au(111) surfaces, by using scanning tunneling microscopy (STM) and cyclic voltammetry (CV) measurement. The detailed adsorption process was completely different from that predicted from the macroscopic analyses. According to the macroscopic analysis, the growth process was explained by the Elovich model, which is based on the repulsive interaction between adsorbed molecules. However, many island structures were formed with the immersion time, indicating that the interaction between LP-@beta@-CyD molecules is attractive. Although the structure of the LP-@beta@-CyD molecules in the adsorbed layer was disorder, formation of the monolayer structure was clearly shown by STM. In order to examine the molecular recognition ability of the LP-@beta@-CyD/Au(111), we performed CV measurement using two electroactive makers; ferrocenecarboxylic acid (FCA) and hexacyanoferrate (HCF). FCA molecules can be included into @beta@-CyD cavity, but HCF molecules can not be. Therefore, if the monolayer structure is densely formed with the CyD cavity being perpendicular to the surface, the oxidation-reduction current is expected to be observed only for the case of the FCA molecules, which in fact was clearly shown by our experiment. These results indicate that the LP-@beta@-CyD/Au(111) structure has high potential as a novel molecular recognition sensor with its selective permeability. http://dora.ims.tsukuba.ac.jp Appl. Phys. Lett., 76 (2000).)

OF-WeP10 Growth Modes of Vacuum Evaporated Pentacene on SiO2, MoS2 and Au Substrates, S. Zorba, Q.T. Toan, N.J. Watkins, Y. Gao, University of Rochester

Pentacene is one of the most widely used active material in organic thinfilm transistors because of its remarkably high mobility. We studied the growth modes of vacuum evaporated pentacene on SiO2, MoS2 and Au substrates using Atomic Force Microscopy. Pentacene films were grown side by side on SiO2 and MoS2 substrates and separately on Au substrate by vacuum evaporation at room temperature with a deposition rate of 0.6 @Ao@/s. Pentacene films grow on SiO2 substrate in a layer by layer manner with full coverage at average thickness of 20 @Ao@ and have the highest degree of molecular ordering with large dendritic grains among the three materials. Films grown on MoS2 substrate reveal two different growth modes, ice-flake like growth and granular growth, both of which seem to compete with each other. On the other hand, films deposited on Au substrate show granular structure.

**OF-WeP11** Analysis of the Surface Morphology of the Initial Growth Layers of p-quaterphenyl on NaCl (001), *E.J. Kintzel, Jr.*<sup>12</sup>, *E.A. Akhadov, T.W. Trelenberg, J.G. Skofronick, S.A. Safron, D.H. Van Winkle,* Florida State University; *F. Flaherty,* Valdosta State University; *D.-M. Smilgies,* European Synchrotron Radiation Facility

We have investigated the structural properties of the initial growth layers of p-quaterphenyl (p-4P) vapor deposited on NaCl (001) using Atomic Force Microscopy (AFM), Helium Atom Scattering (HAS), and X-Ray Grazing Incidence Diffraction (GID). The series of AFM studies provides evidence of needle-like accumulations of p-4P nucleating around surface defects, a striped-phase region with a lateral spacing of approximately 25 nm, and a region which displays a transition from lying to standing orientation of the molecules. HAS investigations at ~50K for films grown at 200K reveal many diffraction peaks which do not appear at the higher temperature. The helium diffraction pattern suggests the formation of randomly oriented micro-crystallites. Our GID studies indicate self-assembly of oriented crystallites in thin films. In thicker samples the diffraction becomes isotropic, like a powder pattern, indicating a random distribution of crystallite orientations.

## OF-WeP12 Preparation of Stable Organic Layers Attached to Metals via a Double Bond, *H. Oudghiri-Hassani*, *M. Siaj*, *E.M. Zahidi*, *P.H. McBreen*, Laval University, Canada

New methods for preparing inorganic-organic interfaces lead to new types of functionalized surfaces. We describe a method to attach organic layers to a conducting solid via the formation of a carbon-metal double bond. The substrate is bulk molybdenum carbide, a material displaying metallic- like conductivity and ceramic-like hardness, as well as excellent catalytic activity. Early transition metal carbides are also of interest because they may form natural electrical contacts to carbon nanotubes in molecular electronics applications. The organic layers were formed by dissociatively chemisorbing carbonyl compounds on the carbide surface. By suitable preparation of the surface, and careful coverage control, layers stable to 1000 K could be prepared. The stability, structure and reactivity of these unprecedently stable layers were evaluated using several surface spectroscopies.

<sup>1</sup> Morton S. Traum Award Finalist <sup>2</sup> NSTD Student Award Finalist

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#### Organic Films and Devices Room 313 - Session OF-WeA

## Self-Assembled Monolayers: Electron Transfer and Film Properties

Moderator: J.N. Russell, Jr., Naval Research Laboratory

2:00pm **OF-WeA1 Rates of Interfacial Electron Transfer Across Well-Defined Model Interfaces,** *C.E.D. Chidsey***, Stanford University <b>INVITED** The injection of electrons and holes into molecular or polymeric organic materials is a key process in many organic devices such as light-emitting diodes, transistors and sensors. Injection is normally accomplished by the thermal transfer of electrons across interfaces between metallic or semiconducting electrodes and the organic material. I will discuss methods to measure the rate of this process across well-defined model interfaces and our developing understanding of the role of molecular structure in determining these rates.

#### 2:40pm OF-WeA3 Charge Transfer in Alkanethiol Self-Assembled Monolayers on Au Surfaces, K. Son, H.I. Kim, J.E. Houston, Sandia National Laboratories

Charge transfer in self-assembled monolayers (SAM) has been studied extensively for molecular electronics applications, and Scanning Probe Microscopy studies have led to a general agreement on the role of force induced structural deformation on the conductivity of alkyl based SAMs. However, controversies about the level of tip/sample contact remain unresolved, and the evidence for structural deformation is vague. Here we investigate charge transfer in alkanethiol SAMs on Au(111) using Interfacial Force Microscopy (IFM). This technique enables the first simultaneous measurements of conductivity, normal-force, and friction over the entire range of tip/sample interaction. For alkanethiols (C@sub n@H@sub 2n+1@SH, n>10), we observe no current until the IFM tip makes physical contact with the SAM surface (down to the fA level). The current then increases exponentially with applied stress. Current and force profiles track each other from the initial conduction point, and both show a strong correlation with the rise in friction. I-V data taken at various force levels show both linear and resonance regions while the slope and the transition point are strongly dependent on the force level as well as molecular chain length. Based on these results, we conclude that the current flow through SAM films occurs by a tunneling process with necessary tip/film contact. We attribute the conductivity increase to the force-induced changes in film structure resulting in a redistribution of the film's electronic states, as evidenced by both the friction and the I-V characteristics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Dept. of Energy under Contract DE-AC04-94AI 85000

#### 3:00pm OF-WeA4 Low Energy Electron Microscopy Studies of the Growth of Thin Pentacene Films, *R.M. Tromp*, *F. Meyer zu Heringdorf, C. Dimitrakopoulos, J. Shaw*, IBM T.J. Watson Research Center

We have used Low Energy Electron Microscopy (LEEM) to study the growth and structural evolution of thin pentacene films on a variety of surfaces and substrates. LEEM allows the growth process to be followed in real time with high spatial resolution (5 nm), and at videorate. Thin film nucleation and subsequent growth can be studied in much detail. For instance, diffusion of pentacene on the starting substrate (for instance clean Si, or SiO2) is isotropic, giving rise to fractal two-dimensional islands. These islands are nonetheless crystalline. The second layer grows on this crystalline template, with highly anisotropic diffusion. Substrate and substrate preparation give a certain degree of control over the polycrystalline grain size. In addition to the growth morphology, LEEM allows the observation of what appear to be molecular size defects in the film, giving rise to charge trapping. Such traps charge and discharge on timescales of 0.1 to several seconds. The density of such traps depends critically on the growth conditions. It appears that traps can be eliminated by careful control of the evaporation parameters. These studies, the first to observe the growth of organic semiconductors in real space, and in real time, enable a detailed understanding of the basic processes underlying the growth process. Direct parallels can be drawn between organic thin film growth, and the epitaxial growth of very different materials such as Si and Pt. These basic insight allow a careful optimization of the growth conditions, optimizing defect densities, grain size, and growth morphology.

3:20pm OF-WeA5 Self-assembled Monolayers on Silicon Surfaces via Si-O Linkages, V. Boiadjiev, R.C. Major, X.-Y. Zhu, University of Minnesota

Monolayer assemblies on silicon surfaces are of interest for a number of technological reasons. Here, we present a novel, two-step strategy for assembly formation directly on silicon surfaces. In the first step, a Hterminated Si(100) or Si(111) surface reacts with Cl2 to give a Cl-capped surface. In the second step, the CI-Si surface is immersed in an alcohol/isooctane solution for monolayer formation via Si-O linkages, with the removal of surface CI likely in the form of HCI. This reaction mechanism is confirmed by X-ray photoelectron spectroscopy. X-ray reflectivity measurement shows that the thickness of the monolayer film is close to molecular dimension and the density is about 85% of that in crystalline paraffine. Fourier transform infrared spectroscopy and water contact angle measurements suggest that the alkyl chains within the monolayer possess, to a limited degree, conformational order. Atomic force microscopy image with molecular lattice resolution shows intermolecular distance corresponding to close packing of alkyl chains. The monolayer coatings show both chemical and mechanical stability. The possible mechanism for monolayer assembly formation on covalent Si surfaces is discussed.

#### 3:40pm OF-WeA6 Friction Force Microscopy Study on Photodegradation of Organosilane Self-assembled Monolayers Irradiated with a Vacuum Ultraviolet Light at 172 nm, *H. Sugimura*, *K. Hayashi, O. Takai*, Nagoya University, Japan

Photodegradation of organosilane self-assembled monolayers (SAMs), under the presence of atmospheric oxygen molecules, has been studied using an excimer lamp radiating vacuum ultra-violet (VUV) light of 172 nm in wavelength. A SAM was prepared on each of Si substrates covered with native oxide from a precursor of octadecyltrimethoxysilane by a chemical vapor deposition method.@footnote 1@ The SAM-covered samples were photoirradiated under a controlled pressure from 10 to 10@super 5@ Pa. As confirmed by water contact angle measurements, infrared reflectionabsorption spectroscopy and X-ray photoelectron spectroscopy, the SAM was decomposed and removed due to the VUV-irradiation. This photodegradation mechanism is ascribed to dissociative excitation of C-C and C-H bondings in the organosilane molecules and to subsequently proceeded oxidation with atomic oxygen radicals generated simultaneously by the VUV-irradiation of O@sub 2@ molecules. Furthermore, micropatterning of the SAM was demonstrated by a simple photomaskcontacting method.@footnote 2@ Due to a distinct difference in frictional force in contact-mode atomic force microscopy between the VUVirradiated and unirradiated regions, the photoprinted pattern was clearly imaged. The VUV-irradiated region showed stronger frictional force than the unirradiated SAM surface. Patterning conditions were optimized based on these results obtained by frictional force microscopy. A micropattern of 2 µm in width was successfully photoprinted on the SAM. @FootnoteText@ @footnote 1@A. Hozumi et al. Langmuir,15 (1999) 7600. @footnote 2@H. Sugimura et al. Langmuir,16 (2000) 885.

#### 4:00pm OF-WeA7 Generation of Reactive Intermediates on Platinum by Photolysis of Pyridyl-@alpha@-Diazocarbonyl Self Assembled Monolayers, J.L. Pitters, D.K. Adkinson, P.R. Norton, M.S. Workentin, University of Western Ontario, Canada

There is considerable current interest in understanding the chemistry of organic molecules as Self Assembled Monolayers (SAMs) on metal surfaces. Much of the effort in this regard has focused on long chain alkyl thiols on gold with the ultimate goal of being able to control the interfacial properties for use in wide ranging material and device applications. However, there has been a growing interest in small molecule SAMs and their relevance to surface modification. We have prepared a series of photoreactive pyridine based molecules for study as SAMs on single crystal Pt. Monolayers (saturated layers) of pyridyl-diazoketones, pyridyldiazoesters and pyridyl-diazoaldehydes have been characterized using Ultra High Vacuum (UHV) Reflection Absorption Infrared Spectroscopy (RAIRS) and other surface sensitive techniques. Diagnostic out-of-phase C=N=N and C=O absorptions indicate that the diazo and carbonyl groups are stable on the Pt surface and that binding most likely takes place through the pyridyl nitrogen as is the case in most substituted pyridines. Upon exposure to 300-400 nm light, the diazo group releases nitrogen quantitatively to yield either carbene or ketene intermediates depending on the original substrate. Most notably is the formation of a ketene functionality (C=C=O) at the interface through the Photo-Wolff rearrangement. The ketene is identified by the diagnostic out-of-phase infrared absorption at approximately 2110 wavenumbers. This study represents the first direct spectroscopic evidence of a photoreactive diazo-

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carbonyl monolayer and the subsequent photochemical formation of a stable ketene monolayer on a metal surface. Ketene and carbene reactivity is versatile and we believe that knowledge of the interfacial reactivity in the present systems can be extended to provide a novel surface for template synthesis and surface modification.

4:20pm **OF-WeA8 X-Ray Induced Changes in Thiol-SAMs on Gold**, *B. Zeysing*, *T. Eickhoff*, University of Hamburg, Germany; *W. Drube*, Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchrotron DESY, Germany; *A. Terfort*, University of Hamburg, Germany

Self-assembled monolayers (SAMs), in particular SAMs of alkanethiols on coinage metals, such as gold, receive a growing interest as convenient possibility to modify surfaces in an experimentally simple but very well adjustable manner. Since these layers are very thin (about 0.5 to 10 nm), they are typically characterized by surface sensitive techniques, often involving x-rays. On the other hand, it is known for some time that these monolayers are subject to massive changes upon irradiation, mainly caused by primary or secondary electrons generated in the supporting high-z material, which penetrate the monolayer.@footnote 1-4@ These electrons remove binding electrons from the molecules by impact ionization, leaving positive charges (holes) within the surface molecules. In alkane chains these holes remain localized and trigger chemical reactions. This results in altered monolayers with different properties and mixed' results which are usually difficult to interpret. In our talk, we present results obtained by using synchrotron radiation based methods to demonstrate how fast monolayers transform under illumination with x-rays, and what the detailed mechanism of this transformation is. Using total external reflection x-ray photoelectron spectroscopy (TER-XPS),@footnote 5@ we could determine the fate of the sulfur atoms. By understanding the mechanisms of destruction, we were able to design SAMs with significantly increased stability towards x-rays. @FootnoteText@ @footnote 1@Wirde, M.; Gelius, U.; Dunbar, T.; Allara, D. L. Nuclear Instr. Methods Phys. Res. B 1997, 131, 245. @footnote 2@Zubragel, Ch.; Deuper, C.; Schneider, F.; M. Neumann, N.; Grunze, M.; Schertel, A.; W@um o@ll, Ch. Chem. Phys. Lett. 1995, 238, 308. @footnote 3@Olsen, C.; Rowntree, P. A. J. Chem. Phys. 1998, 108, 3750. @footnote 4@Zerulla, D.; Chass@aa e@, T. Langmuir 1999, 15, 5285. @footnote 5@M.J. Bedzyk, G.M. Bommarito, J.S. Schildkraut, Phys. Rev. Lett. 1989, 62, 1376.

4:40pm OF-WeA9 Surface Stress of Self-Assembled Alkanethiols on Gold-Coated Cantilevers, *M. Godin*, McGill University, Canada; *P.J. Williams*, Acadia University, Canada; *V. Tabard-Cossa*, *P. Grütter*, McGill University, Canada

The commercial availability of atomic force microscope (AFM) microcantilevers has made possible the development of new ultrasensitive techniques aimed at measuring nanoscale quantities such as mass, heat and surface stress. We have adapted standard gold-coated silicon nitride AFM cantilevers as a chemical sensor. During chemical sensing, the cantilever bends due to the surface stress associated with the adsorption of specific target molecules onto a single side of the cantilever, which has been coated with a receptive layer. We have used our cantilever sensor to measure the surface stress associated with the self-assembly of alkanethiols on gold-coated cantilevers. This surface stress is strongly associated with the structural organization of the self-assembled thiol monolayer, as well as molecular chain-length. We will discuss the importance of the quality of the gold receptive surface with respect to thiol monolayer formation, as well as the kinetics of vapor-phase self-assembly of alkanethiols onto gold.

#### 5:00pm OF-WeA10 Self-assembled Monolayers of 6-Phenyl-n-Hexanethiol and 6-(p-Vinylphenyl)-n-Hexanethiol on Au: An Investigation of Structure, Stability and Reactivity, *L. Duan, S. Garrett,* Michigan State University

The structure, stability and reactivity of 6-Phenyl-n-Hexanethiol (PHT) and 6-(p-Vinylphenyl)-n-Hexanethiol (VHT) monolayers on Au (111) is presented. RAIR spectroscopy, ellipsometry and STM have been used to characterize the self-assembled monolayers (SAMs). The RAIR spectral data indicated that both molecules chemisorbed on gold as thiolates, however, the alkyl chains were disordered for both SAMs. We investigated the structural changes of PHT monolayers with decreasing molecular surface density by annealing in ultrahigh vacuum. Three different "stripe" phases have been observed by STM. All three condensed phases are characterized by alignment of the molecular axes with the surface plane, but with decreasing degrees of out-of-plane interdigitation. On the contrary, VHT molecules are oriented almost parallel to the surface normal at room temperature. Polymerization of VHT SAMs can be achieved by either UV-

light irradiation or annealing. The polymerization process was followed by RAIR spectroscopy by observing the decrease in peak intensities associated with vinyl functionalities. UV-light irradiation produced long chain polymers with ~70% conversion rate after 25 min, while annealing produced short-chain polymers with CH@sub 3@ as the end group. The UV-light polymerized film is more robust to heating than thermally polymerized film.

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#### Organic Films and Devices Room 313 - Session OF+EL+SS-ThM

#### **Organic Thin Films**

8:20am OF+EL+SS-ThM1 Highly Ordered Layers of Large Conjugated @pi@-systems on Cu(111): A Novel Preparation Method, G. Beernink, K. Weiss, A. Birkner, Ruhr-Universität Bochum, Germany; F. Dötz, K. Müllen, Max-Planck-Institut für Polymerforschung, Germany; C. Wöll, Ruhr-Universität Bochum, Germany

With regard to applications in molecular electronics and the fabrication of nanoelectronic devices, polycyclic aromatic hydrocarbons (PAH), e.g. the graphite segment hexa-peri-hexabenzocoronene (HBC), have recently received considerable attention. For such large PAHs, however, the low solubility in organic or polar solvents and the rather large sublimation temperatures make the application of the commonly used deposition methods, namely adsorption from solution or evaporation in a vacuum system (CVD, OMBE) difficult or even impossible. In this work, we present a direct way to synthesize one particular polycyclic aromatic hydrocarbon, namely hexa-peri-hexabenzocoronene (HBC) by using a surface as a template. A modified precursor molecule, 1,2,3,4,5,6-Hexakis(4dodecyloxyphen-1-yl)benzene (HPB), which is not planar, is evaporated on a Cu(111) surface. Heating of the substrate leads via thermally induced cyclodehydrogenation to the product HBC, which is characterized by XPS, X-ray absorption spectroscopy (NEXAFS) and STM. The NEXAFS-data directly demonstrate the formation of flat, graphite-like segments which interact only weakly with the substrate, whereas the STM data reveal a high of lateral order.

#### 8:40am OF+EL+SS-ThM2 The Effect of Conjugation Length on the Frontier Orbital Position of Oligothiophene Derivatives at Metal-organic Interface, *A.J. Makinen, I.G. Hill,* Naval Research Laboratory; *T. Noda, Y. Shirota,* Osaka University, Japan; *Z.H. Kafafi,* Naval Research Laboratory

We report an ultraviolet photoelectron spectroscopy (UPS) study of a novel family of end-substituted oligothiophene derivatives with a varying conjugation length, BMA-nT (n=1-4), where n indicates the number of thiophene rings. These new oligothiophene derivatives are thermally and morphologically stable, and unlike unsubstituted oligothiophenes, which undergo luminescence quenching due to the polycrystalline nature of their solid films, the thiophene derivatives form amorphous films. The BMA-nT compounds show luminescence from the blue (n=1) to the orange (n=4), and additionally they posses hole-transport properties making them attractive materials for organic light-emitting diodes (OLEDs). The UPS results show that the position of the highest occupied molecular orbital (HOMO) of the end-substituted oligothiophenes at the metal-organic interface is dependent on the number of thiophene rings present, i.e. the effective conjugation length of the molecule. We will discuss this property and its implications in the context of carrier injection in an OLED.

#### 9:00am OF+EL+SS-ThM3 Electronic Properties of @pi@-Conjugated Organic Molecular Semiconductor Interfaces, A. Kahn, Princeton University INVITED

Metal/organic interfaces are central to a number of organic-based devices. Their electronic structure and chemistry control charge injection. Modeling these interfaces requires an accurate knowledge of the injection barriers, i.e. the position of the transport levels with respect to the metal Fermi level, and of the role of interface chemical reactions. This talk reviews our latest results obtained via direct and inverse photoemission and scanning tunneling spectroscopy on metal interfaces with five organic materials (PTCDA, CuPc, Alg@sub 3@, @alpha@-NPD, @alpha@-6T) of interest for light emitting device and TFT applications. We present the first accurate picture of the transport levels in these materials, levels which are generally unknown because of the strongly correlated nature of molecular solids. The transport gap is found to be significantly larger, i.e. by the exciton binding energy, than the optical gap usually used to describe interface and bulk molecular level diagrams. The exciton binding energy ranges from 0.4eV to 1.4 eV in the materials investigated. Furthermore, we present a detailed and systematic investigation of molecular level alignment at interfaces of organic thin films deposited on a series of metals with different work function. These demonstrate that one of three mechanisms is involved in the formation of the dipole barriers generally observed at such interfaces: (1) lowering of the metal work function by the molecules; (2) electron transfer from the metal to the organics; (3) chemical bonding. Knowledge of the transport gap, interface level alignment mechanisms and interface chemistry leads to a more accurate description of these organic interfaces. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483).

#### 9:40am OF+EL+SS-ThM5 Effect of Alkyl Substituents on the Adsorption of Thienylenevinylene Oligomers on the Si(100) Surface, B. Grandidier, J.P. Nys, D. Stievenard, C. Krzeminski, C. Delerue, IEMN/ISEN, France; P. Blanchard, J. Roncali, IMMO Universite d'Angers, France

Conjugated thiophene-based oligomers are subject to intense research activity due among others to their potential use as molecular wires in future molecular electronic devices. As microelectronics technology is based on the use of silicon substrates, there is an increasing need to connect these organic molecules to the existing silicon technology. Due to the low intrinsic solubility of the rigid conjugated chains, the synthesis of the longuest chains required the substitution of alkyl chains to the thiophene ring in order to increase the solubility. Whereas such a substitution has limited effect on the electronic structure of the oligomers, it exerts a strong effect on the interactions of the molecules with their physical and chemical environment. The adsorption of unsubstituted and substituted thienylenevinylene oligomers on the Si(100) surface has been investigated using scanning tunneling microscopy. The mode of substitution of the thiophene ring exerts a strong influence on the adsorption configurations and the images of the oligomer based on 3,4dihexyl thiophene are highly voltage dependent. We discuss the influence of the alkyl chains on the adsorption process and on the appearance of the molecules in the STM images.

10:00am OF+EL+SS-ThM6 Growth of Films of Thiophene Oligomers by Seeded Supersonic Beams to Improve Control on their Quality and Properties, *S. Iannotta*, *T. Toccoli*, *A. Boschetti*, CeFSA - Research Center CNR-ITC for the Physics of Aggregates, Italy; *P. Milani*, INFM - Universit@aa a@ di Milano, Italy; *S. Ronchin*, INFM - Universit@aa a@ di Trento, Italy; *A. Podest@aa a@*, INFM - Universit@aa a@ Bicocca, Italy

The growing interest in pi-conjugated organic molecular materials and polymers, driven by wide potential technological impact in electronics and photonics, still faces severe limitations. Applications would be much more favored by improving control on morphology and structure in the solid state. Standard growth methods are based on the self-assembling of the molecules resulting more or less affected by the interaction with the substrate. Very often the resulting films show an inadequate ordering. These problems become severe as the thickness increases over a few monolayers. Fully considering the major role played by the initial state of the molecules at early stages of growth, we approached the problem combining a supersonic free jets that permit to control kinetic energy, momentum and flux with a UHV deposition apparatus. We perform the deposition and simultaneously control the initial state of the seeded organic molecules by varying the parameters of the supersonic expansion (dilution, temperature of the source, form and diameter of nozzle, etc) [P. Milani and S. Iannotta, Synthesis of Nanophase Materials by Cluster Beam Deposition, Springer, Berlin (1999)]. We have prepared a series of films of alpha guaterthiophene that are then characterized by optical measurement, TM-AFM and X-ray diffraction. We report an overall strong evidence of an unprecedented control on morphology, structure and optical response that correlate well to the beam's parameters. PL spectra at low temperature show the vibronic molecular structure very well resolved depending on the initial state of the oligomer in the beam. Films, several hundreds nm thick, show a high degree of ordering with surface morphologies characterized by layered structures of molecular height. Xray diffraction confirms the high degree of ordering induced by the growth from highly supersonic beams. Correlation between morphology, degree of ordering and the optical response of these films will be discussed.

#### 10:20am OF+EL+SS-ThM7 Scanning Tunneling Microscopy/Spectroscopy Investigation of the Organic Molecules PTCDA and HBC on Au(100), *T. Fritz*, *M. Toerker*, *H. Proehl*, *F. Sellam*, *K. Leo*, TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on gold single crystals have been investigated by Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) at room temperature. The organic dye molecule perylene-tetracarboxylic-dianhydride (PTCDA) has been deposited as submonolayer coverage on Au(100). I-V-spectroscopy at fixed tip-sample-separations has been performed alternately on the PTCDA islands and on uncovered areas of the Au(100) surface. The corresponding normalized derivatives of these I-V-curves have then been compared to inverse photoelectron spectroscopy data known from literature, indicating resonant tunneling via the lowest unoccupied molecular orbital. As a

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second molecule peri-hexabenzocorone (HBC), also deposited on Au(100), has been investigated. The Au(100) surface has been fully covered by a few monolayers thick, highly ordered HBC film. The normalized derivatives of I-V-curves measured on these films show a pronounced local maximum at a negative voltage of about -1.4 V. By comparison with ultraviolet photoelectron spectroscopy (UPS) measurements of HBC on Au(111) we can show that this peak in the tunneling spectroscopy plot is due to resonant tunneling via the highest occupied molecular orbital of HBC.

## 10:40am OF+EL+SS-ThM8 STM, AFM, & Electrochemical Investigations of Squaraine Thin Films, *M.E. Stawasz*, *N. Takeda, B.A. Parkinson*, Colorado State University

Squaraines are a class of organic photoconductors which have found industrial use in photoreceptors of laser printers and xerographic devices. as well as in ablative optical recording material. They have also been investigated for their nonlinear optical characteristics as well as their ability to sensitize large-bandgap semiconductors in photoelectrochemical solar cells. Central to its various uses and characteristics is the squaraine molecules' ability to form organized aggregates, both in solution and in the solid state. Few studies have been done, however, to relate the molecular structure of squaraines to the structure of the aggregates that spontaneously form in thin films. We report STM and AFM data which unambiguously determines thin film/monolayer aggregate structure for a series of hydroxylated and non-hydroxylated dialkylamino-phenyl squaraines with varying alkyl tail lengths deposited on HOPG. Results show that alkyl tail length significantly affects squaraine aggregate structure while the presence or absence of hydroxyl groups does not. Electrochemical investigations of the redox behavior of squaraine thin films using HOPG as the working electrode were also performed. Remarkable redox behavior was observed suggesting a structural change in the squaraine aggregate state upon oxidation. In addition, the effect of electrolyte anion and film thickness on the redox behavior of squaraines was observed, thus providing additional insight into the charge transfer abilities of the squaraine film in the direction normal to the substrate surface.

11:00am OF+EL+SS-ThM9 Work Function Modification and Surface Chemistry of Indium Tin Oxide with Organosilane Self Assembled Monolayers, J.A. Chaney, Naval Research Laboratory; F. Farzad, Geo-Centers, Inc. and Naval Research Laboratory; C.S. Dulcey, R. Shashidar, P.E. Pehrsson, Naval Research Laboratory

Attachment of organosilane SAM's with monomers having different dipole magnitude and direction may permit control of the work function (@PHI@) of indium tin oxide (ITO) substrates used in OLED's. However, reliable measurement of @DELTA@@PHI@ requires reproducible control of the environmental conditions. In this work, ITO substrates were treated with SAM's having different head and attachment groups and then inserted into an ultra high vacuum (UHV) chamber. The SAM/ITO work function was measured using an in-vacuo Kelvin probe calibrated with a graphite standard. Surface chemistry was probed by high resolution electron energy loss spectroscopy (HREELS), and electronic structure was investigated by energy loss spectroscopy (ELS). The SAM-modified surfaces usually had lower work functions (@PHI@ = ~4.8-5.3 eV), than bare, oxygen-plasma treated ITO (@PHI@ = ~5.3 eV). The SAM monomers had either one or three Si-OCH@sub 2@CH@sub 3@ units for attachment to the ITO surface. Trifunctional SAM's gave higher @PHI@ values than monofunctional SAM's. The HREELS of monofunctional SAM/ITO showed structure which may be attributable to bending modes. These modes were more intense than on the trifunctional counterpart, possibly due to tighter binding of the latter with ITO. Most SAM modified surfaces showed significant deviation in @PHI@ with time and temperature (up to 200°C), suggesting that adsorption of ambient gasses, even in UHV, affects the SAM/ITO system. However, the work function of some SAM's with hydrophobic head groups was apparently unaffected by adsorption. Differences in the band edge transitions of clean ITO vs. SAM/ITO indicate electronic interactions between the SAM and substrate.

11:20am OF+EL+SS-ThM10 Effect of Fluoride Layer Insertion on the Electronic Structures of Al/Organic Interfaces@footnote 1@, Y. Park, Korea Research Institute of Standards and Science, Korea; D. Kim, Hallym University, Korea; S. Cho, O. Kwon, G. Lee, Korea Research Institute of Standards and Science, Korea; F. Cho, Chonnam National University, Korea We have investigated the electronic structures of interfaces between Al and tris-(8-hydroxyquinoline)aluminum (Alq@sub 3@), which is a prototypical organic electroluminescent (EL) material. It has been well known that the insertion of alkali metal fluoride, such as LiF, greatly

enhances the EL performance and the origin of such behaviors have been controversial. We used photoelectron spectroscopy techniques including Xray and UV photoelectron spectroscopy (XPS and UPS) as well as resonant photoemission (RPES) to probe the electronic structure change caused by the insertion of thin layer of various alkaline and alkaline earth metal fluorides between Al and Alq@sub 3@. As previously known, the presence of LiF layer enhanced gap-state formation, but even without the LiF layer, Al deposition significantly alters the electronic structures of Alq@sub 3@. While the insertion of CsF layer showed clear enhancement of the gap states, it was much less obvious for CaF@sub 2@ layer. For both materials, the RPES showed very weak resonant enhancement when excited with photons with the energy near Cs and Ca core level absorption edge. We report similar measurements for various other fluoride materials and discuss their implications. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through National Research Laboratory Program and Atomic-scale Surface Science Research Center.

11:40am OF+EL+SS-ThM11 Interface of Aluminum and Poly(vinylidene fluoride with Trifluoroethylene) Copolymer, B. Xu, C.N. Borca, S. Ducharme, A.V. Sorokin, P.A. Dowben, University of Nebraska, Lincoln; V.M. Fridkin, S.P. Palto, N. Petukhova, S.G. Yudin, Institute of Crystallography, Russia

The interface between aluminum and crystalline copolymer thin films of vinylidene fluoride (70%) with trifluoroethylene (30%) [PVDF-TrFE] has been studied. The ratio of carbon 1s and aluminum 2p core level photoemission peak intensities changes little with increasing emission angle, even after deposition of 5 Å aluminum on the surface of PVDF-TrFE. This indicates that the distribution of aluminum atoms in the copolymer film is quite uniform in the near surface region and that the interface is not abrupt. The contributions to the C 1s core level shift ~1eV to lower binding energy, while the relative ratio of the intensity of C 1s peaks changes, provides further evidence for changes in screening with aluminum doping within the polymer film. The XRD data also shows the crystalline structure of the copolymer film can be deformed with aluminum doping, if the polymer film is annealed.

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