

## Contacts to Organic Materials Topical Conference Room 318/319 - Session OM-MoM

### Contacts to Molecules and Molecular Films (I)

Moderator: A. Kahn, Princeton University

8:20am **OM-MoM1 Coupling Molecules to Electronic Materials Chemical Bonding and Polarization Effects at Metal-Molecular Monolayer-Semiconductor Junctions**, *D. Cahen*, Weizmann Institute of Science, Israel  
**INVITED**

All-molecular nm scale optoelectronic devices face many practical and fundamental obstacles, which, however, do not preclude use of molecules to control hybrid devices. In such systems nm- or even sub-nm molecular structures need to be incorporated in device structures. Judicious choice of such systems allows, apart from potentially practical possibilities, fundamental investigations of the effects, limitations and possibilities of molecules in optoelectronics. By placing molecules at metal-semiconductor interfaces, even if only as poorly organized, partial, rather than ideal monolayers, they can control these interfaces electronically. This is primarily because electron energetics at interfaces determine the electronic behaviour of semiconductor & metal contacts. Normal requirement for (near-)ideally structured monolayers can be relaxed because the molecules can act as "gatekeepers", i.e., electrostatically rather than dynamically. This leads to molecular devices, with no current flow through molecules. Devices are made reproducibly because soft contacting methods were developed. These also show how intimate contact between molecules and metal can polarize the contacts. In systems with near-ideal molecular films, molecules electronic transport through molecules is often by "through bond" tunneling. Experimental evidence is accumulating both from our and other groups, that in most devices with molecules, the nature of the molecule/electrode contact is crucial for the resulting junction. @FootnoteText@ @footnote 1@ A.Vilan et al. Nature404(2000)166; J.Phys.Chem B, in press; G.Ashkenasy et al. Acc.Chem.Res.35(2002)121@footnote 2@ D.Cahen, A.Kahn, Adv. Mater.,14(2003)271@footnote 3@ A.Vilan, D.Cahen, Adv.Funct.Mater.12(2002)795; H. Haick et al., to be published@footnote 4@ Y.Selzer et al., J.Phys.Chem.B 106(2002)10432; D.Cahen, G.Hodes, Adv.Mater. 14(2002)789@footnote 5@ Y.Selzer et al., Angew.Chem.Int.Ed., 41(2002)827.

9:00am **OM-MoM3 Long Range Electronic Coupling at Molecule-metal Interfaces: C60/Cu(111)**, *G. Dutton, X.-Y. Zhu*, University of Minnesota

It is well-recognized that electronic interaction at molecule-metal interface is one of the key factors governing the performance of molecular-semiconductor devices. The efficiency or rate of injection at such an interface is determined by (1) the energetic alignment of molecular orbitals to the metal Fermi level, (2) the electronic coupling strength (wavefunction mixing) between molecular orbitals and metal bands, and (3) the dynamics of charge carrier localization at the interface. While energetic alignment has been probed by photoemission spectroscopies, electronic coupling strength and charge localization dynamics remain largely unknown at the present time. We attempt to address these issues in the present study using the model system of C60/Cu(111) and the experimental technique of time-resolved two-photon photoemission (2PPE) spectroscopy. The lowest unoccupied molecular orbital (LUMO) and LUMO+1 levels in C60 are transiently populated via the creation of charge-transfer excitons, with lifetimes < 100 fs. The lifetimes decrease substantially as film thickness decreases, due to quenching by the Cu substrate; this effect is seen for films as thick as 50 Å. Such a long-range effect is attributed to charge transfer between the Cu substrate and electronic bands in C60.

9:20am **OM-MoM4 Molecule on Metal versus Metal on Molecule: The Sexiphenyl/Al Interfaces**, *B. Winter, J. Ivanco, F.P. Netzer, M.G. Ramsey*, Karl-Franzens University, Austria

Here the formation of both the organic/metal and metal/organic interfaces has been investigated with particular attention given to both their electronic and geometric structure as elucidated by angle resolved UV-photoemission and low energy electron diffraction. Despite the weak electrostatic bond found, a dense well ordered wetting monolayer results for sexiphenyl (6P) on single crystal Al(111), irrespective of growth temperature. The interface dipole of this layer determines the band alignment for the subsequent films that develop. For the converse, Al on

6P, a similarly weak bonding interaction is observed with no evidence for the commonly invoked scenarios of either a strong chemical bond formation or diffusion into the organic film. Under UHV growth conditions a wetting layer is impossible to achieve and the Al balls-up on the organic film. In spite of this weak interaction the evaporation of Al disturbs the surface of the crystalline 6P film, changing the conformation of the molecules at the surface and thereby effecting a 0.6 eV change in the HOMO binding energy and concomitantly the band alignment. If oxygen is introduced at the interface a change of up to 2 eV in the band alignment results, due to both a change in the interface dipole and in the ionisation potential of the interfacial molecules brought about by an increase in their conjugation. Not only does the oxygen improve the electron injection ability at the Al interfaces, the changes in surface energy allows the formation of a metallic wetting layer. Acknowledgments: Supported by the Austrian Science Foundation SFB Electroactive Materials

9:40am **OM-MoM5 Adsorption of Sexithiophene on Clean and Potassium-Doped Al(111)**, *J.E. Whitten, H. Ahn, S.K. Sengupta*, University of Massachusetts, Lowell

Oligo- and polythiophenes are finding important organic electronic device applications that include light-emitting diodes, photovoltaics, and field-effect transistors. Low work function vacuum-deposited metals, such as aluminum, are commonly used as electrode materials, and understanding the nature of the organic/metal interface may lead to improved device performance. In this study, we have taken the approach of adsorbing the organic layer on top of bulk metal in order to obtain complementary information to previous investigations of aluminium deposition on sexithiophene. X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) have been used to study the interfaces between sexithiophene sublimed in ultrahigh vacuum onto clean and potassium-doped Al(111) surfaces at 130 K. These investigations demonstrate that sexithiophene adsorbs very weakly on the clean surface, as suggested by minimal work function changes and a lack of shifts in the binding energies of the C1s and S2p core levels and in the frontier valence orbitals of the adsorbate. In contrast, even a small amount of deposited potassium leads to strong interaction between the surface and interfacial sexithiophene. The adsorption of this oligomer on the K-doped aluminum surface has been studied as a function of potassium dose. Even at low potassium coverage, strong interaction of sexithiophene with the surface is indicated by low binding energy components in the C1s and S2p peaks and the emergence of a potassium-induced peak near the Fermi level.

10:00am **OM-MoM6 Interaction between Metals and Organic Semiconductors Studied by Raman Spectroscopy**, *D.R.T. Zahn, G. Salvan, B. Paez*, Technische Universität Chemnitz, Germany

Silver and indium were deposited onto molecular layers of two perylene derivatives, viz. 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and N,N'-dimethylperylene 3,4,9,10-dicarboximide (DiMe-PTCDI). The interaction between the metals and the organic semiconductors was probed in situ by Raman spectroscopy. The molecular structure is found to be preserved when Ag or In are deposited onto PTCDA and DiMe-PTCDI layers. For In this is in contrast to previous suggestions of strong reactivity with PTCDA and covalent bond formation between In and O atoms in PTCDA. However, the molecules having direct contact with the metal are involved in a weak ground state dynamical charge transfer with different strength for Ag and In, resulting in a breakdown of vibrational selection rules. A significant enhancement of Raman internal vibrational modes is observed both for Ag and In deposition as a result of metal-induced surface enhanced Raman scattering (SERS). The enhancement factors observed for the internal modes reflect a rough morphology of the metal films which is influenced by the morphology of the underlying organic film, i.e., Ag on PTCDA grows predominantly (111) oriented, while Ag on DiMe-PTCDI has a much more polycrystalline nature. Moreover, conclusions regarding the interdiffusion of the two metals can be drawn from the comparison of the breakdown of the selection rules for the internal modes and the spectral evolution of the external molecular modes. @FootnoteText@ @footnote 1@ Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic, and S.R. Forrest, Phys.Rev. B 54, 13748 (1996)@footnote 2@ S. Kera, H. Setoyama, M. Onoue, K. Okudaira, Y. Harada, N. Ueno, Phys.Rev. B 63, 115204 (2001).

# Monday Morning, November 3, 2003

10:20am **OM-MoM7 Electronic Structure and Hole Injection Barriers for Pure and Substituted Phenylene Ethynylene Oligomer Self-Assembled Monolayers**, *S.W. Robey, C. Zangmeister, R.D. van Zee*, National Institute of Standards and Technology

Ultraviolet photoelectron spectroscopy was used to determine the electronic structure of self-assembled monolayers (SAMs) of phenylene ethynylene oligomers on Au. Monolayers comprised of the three ring oligomer (OPE) and molecules with -NO@sub2@ (NO@sub2@-OPE) substitutions on the central ring were investigated. This study provides the first glimpse of the electronic structure and band alignment for SAMs of these molecular systems linked to interesting transport characteristics in nanoscale junctions.@super1@ For the unsubstituted oligomer, the electronic structure is interpreted using simple molecular systems and related polymers as guidance. The states above ~ 5 eV binding energy are primarily C-C and C-H @sigma@ bonding states. Their polarization dependence is found to be consistent with a nearly upright orientation. Near the Fermi level (E@subf@), orbitals traceable to benzene e@sub1g@ @pi@ states are split by the C-C coupling along the backbone into density localized primarily on the ortho-carbon atoms of individual phenyl rings (at ~ 3.9 eV) and potentially delocalized @pi@ levels along the backbone that can provide the primary channels for transport. The hole injection barrier (energy separation between E@subf@ and the HOMO level) is about 0.8 eV. Substitution of electron withdrawing groups on the central ring induces negative differential resistance in transport measurements.@footnote 1@ The effects on electronic structure were investigated in monolayers of the NO@sub2@-OPE oligomers. Compared to the unsubstituted OPE, there is an overall shift of intensity for @pi@ states near E@subf@ to higher binding energy by about 0.5 eV. The hole injection barrier also appears to increase to approximately 1.0 eV. Connections with calculations of transport properties for related molecular systems and experimental and theoretical results for substituent effects in conjugated polymers will be discussed. @FootnoteText@@footnote 1@Chen et al.,Science 286,1550(1999).

10:40am **OM-MoM8 Direct Double-Bond Contacts to Metal Carbides: A New Surface Functionalization Reaction**, *M. Sijaj, H. Oudghiri Hassani, P.H. McBreen*, Universite Laval, Canada

Functional nanoelectronics devices require optimal electrical contact between their components as well as adequate protection from the environment. In the context of SWCNT-based field-emission transistor devices, metal carbides can be used as chemically bonded high-transmission source/drain contacts.@footnote 1@ We will present results showing that organic layers can be attached to the surface of molybdenum carbide via a metal-carbon double bond. This new surface reaction involves the insertion of a surface metal atom into the carbonyl bond of ketones or aldehydes, as in the following process;  $R_2C=O + Mo \rightarrow R_2C=Mo=O$ . Furthermore, the  $R_2C=Mo$  surface groups (termed surface alkylidenes) are found to be thermally stable to above 900 K, if the surface is rendered inert through carbon deposition.@footnote 2@ The fact that the contact between the organic layer and the carbide is a double bond points to three advantages. First, a double bond is intuitively a better electrical contact than a sulfur atom. Second, it is possible to form carbides from a wide variety of metals. Third, we have demonstrated that alkylidene functionalized molybdenum carbide is active for metathesis reactions. Thus, ring opening polymerization (ROMP) can be used to grow polymeric layers directly from the carbide surface. Extensive results obtained using RAIRS and XPS will be presented to describe these new methods for the preparation of double bond contacts on a technically relevant substrate. @FootnoteText@@footnote 1@R. Martel, V.Derycke, C. Lavoie, J. Appenzeller, K. K. Chen, J. Tersoff and Ph. Avouris, Phys. Rev. Lett. 87, 256805, 2001. @footnote 2@E. Zahidi, H. Oudghiri Hassani and P. H. McBreen, Nature, 409,1023,2001.

11:00am **OM-MoM9 Study of Transport Through Organic Molecules on Semiconductor Surfaces Using STM-SPV**, *I. Nevo, S.R. Cohen, D. Cahen, G. Haase*, Weizmann Institute of Science, Israel

Mapping the potential of semiconductor surfaces using STM provides the ability to investigate electron transport properties through single molecules. The potential mapping is performed by monitoring the tip-surface bias required to maintain a constant tunneling current under illumination termed - surface photovoltage (SPV). There is currently great interest in electron conduction through organic molecules attached to inorganic surfaces. However, many experiments probe an ensemble of nano-scale systems, thus, the effect of interface inhomogeneity is averaged out. Namely, it is not clear if and which of the molecular states participate in the electronic current passing through a system of a single molecule

confined between two electrodes. Moreover, of the effect of an organic molecule on the local potential is unknown. In this work we investigate the transport properties of poly-aromatic molecules adsorbed on GaAs(110) and GaP(110) surfaces in ultra high vacuum and room temperature conditions. The bias dependence of the SPV images that are acquired simultaneously with the topography images indicates different tunneling mechanisms: direct tunneling, and resonant tunneling involving the molecular states. In addition, the potential surface varies with bias due to the changing overlap of molecular states with the tunneling energy interval.

11:20am **OM-MoM10 Contact Effects in Molecular Junctions**, *C.D. Frisbie*, University of Minnesota **INVITED**

The importance of metal-molecule interfaces in determining the current-voltage (I-V) characteristics of molecular junctions has been made clear in theoretical work over the past 5 years. Yet systematic experimental investigations, in which the contact effects are mapped out as a function of the metal work function and the type of surface linker used to bind the molecules to the electrodes, have not been carried out. This talk describes a conducting probe atomic force microscopy (CP-AFM) approach to the experimental examination of contact effects in molecular junctions. Junctions are fabricated by contacting self-assembled monolayers (SAMs) on metal substrates with metal-coated AFM tips; it is possible to contact SAMs with any metal that can be coated onto an AFM tip. Contact resistances are estimated by measuring total junction resistance (at different bias voltages) as a function of the length of the molecules between the tip and substrate contacts, and then extrapolating resistance versus length plots to zero length. We find that contact resistances in molecular junctions are sensitive to the metal work function, the type of surface linker (e.g., -SH vs  $\text{â€“NC}$ ), and the bonding in the molecular backbone (i.e., conjugated vs saturated). Importantly, the work function dependence allows qualitative estimation of where the Fermi level of the junction lies with respect to the HOMO and LUMO of the molecules. We will summarize our findings to date on contact effects in junctions composed of molecules with alkane or oligophenylene backbones.

## Contacts to Organic Materials Topical Conference Room 318/319 - Session OM-MoA

### Contacts to Molecules and Molecular Films (II)

**Moderator:** D.R.T. Zahn, Technische Universität Chemnitz, Germany

#### 2:00pm OM-MoA1 Characterization of Organic-Metal and Organic-Organic Interfaces, *J.L. Bredas*, Georgia Institute of Technology **INVITED**

In organics-based (opto)electronic devices, organic/metal and organic/organic interfaces play a key role in determining the device performance. Here, we focus first on the interface dipole present at organic-on-metal interfaces. The origin of this dipole is rationalized from the results of a joint experimental and theoretical study based on the interaction between pi-conjugated molecules and transition metal surfaces. It is found that the interface dipole formed at the organic/metal interface can be divided into two contributions: (i) the first corresponds to the "chemical" dipole induced by a partial charge transfer between the organic layers and the metal upon chemisorption of the organic molecules on the metal surface; and (ii) the second relates to the change in metal surface dipole due to the modification of the metal electron density tail that is induced by the presence of the adsorbed organic molecules. In a second part, we investigate the electronic structure of metal-on-oligomer and organic/organic interfaces.

#### 2:40pm OM-MoA3 The Role of Charge Neutrality Level in Molecular Level Alignment at All-organic Heterojunctions, *W. Gao, A. Kahn*, Princeton University

Alignment of molecular levels at organic-organic (OO) heterojunctions controls charge injection and transport in multilayer organic devices. Because of weak intermolecular interaction and absence of free charges, vacuum level alignment is often observed at heterojunctions between intrinsic (undoped) molecular films. We present here the first experimental evidence that an alignment mechanism based on the charge neutrality level of the molecular semiconductor becomes important when one of the interface constituents is doped. Our direct and inverse photoemission (UPS, XPS, IPES) investigation focuses on interfaces between hole transport layers (HTL) and electron transport layers (ETL). We use the strong electron acceptor F@sub 4@-TCNQ to p-dope the HTLs. We show that, unlike at metal-organic (MO) interfaces, molecular levels and energy barriers across the interfaces are not strongly anchored and shift with respect to each other upon doping of the HTL. The shift is accompanied by the formation of an interface dipole, the size of which depends on the constituents of the heterojunction. The key result is that the Fermi level position in the gap of the undoped ETL remains fixed and independent of the HTL when the HTL is doped. This important observation suggests that the introduction of charges and of electronic states at the interface in the gap of the HTL and ETL via doping results in a pinning of the Fermi level at or near a specific energy level, tentatively related to the charge neutrality level of the organic material. W. Gao and A. Kahn, Appl. Phys. Lett., (in press) W. Gao and A. Kahn, Organic Electronics 3, 53 (2002).

#### 3:00pm OM-MoA4 Au/CuPc Interface: A Photoemission Investigation, *L. Lozzi, S. Santucci*, INFN and University of L'Aquila, Italy; *S. La Rosa*, Sincrotrone Trieste SCpa, Trieste, Italy

Copper phthalocyanine (CuPc) are deeply investigated for many different applications as thin films. One of the most promising application is the fabrication of photovoltaic cells, in which the CuPc film is the active part. Au is a widely used metal for metallic contact, in particular for organic photovoltaic cells, because of its high work function. In this study we will show our results on the investigation of the interface between CuPc and Au by means of photoemission. We have deposited, by means of thermal evaporation in ultra high vacuum conditions, very thin Au films on a 70 nm thick CuPc film and we have investigated both core levels and valence band features as a function of the Au thickness. We have used different photon energies (from X-ray to UV) to investigate surface and in depth properties. Moreover we have performed high spatial resolution photoemission experiments (Spectromicroscopy beamline at Elettra Synchrotron Radiation Center, spatial resolution about 0.5@micron@) to investigate the homogeneity of the Au film on the organic film. The evolution of the Au 4f spectrum, as a function of the Au film thickness shows indicates the formation of gold cluster. Comparing the valence band acquired using low photon energy with those using X-ray photons, it is evident that these clusters are dispersed inside the organic

film. No evident variations are observed in the core levels of the CuPc elements. The spatially resolved photoemission spectra do not show any difference of the valence band spectra as a function of the position and also the images, acquired looking at different energies of the valence band, showed a very high homogeneity of the deposition, although the CuPc surface is quite rough. P. Peumans and S.R. Forrest, Appl.Phys.Lett. 79, 126 (2001) S.B. Di Censo, S.D. Berry, and E.H. Hartford Jr., Phys.Rev.B38, 8465 (1988).

#### 3:20pm OM-MoA5 XPS and HRSEM Studies on the Interfaces of Au/CuPc vs. Au/FCuPc, *X. Yu, T.E. Madey*, Rutgers, The State University of New Jersey

Ultrathin films of Au have been grown on both copper phthalocyanine (CuPc) and copper hexadecafluorophthalocyanine (FCuPc) samples at room temperature (RT). These are model systems for metal contacts on organic semiconductors. X-ray photoelectron spectroscopy (XPS) measurements, corresponding to various average Au film thicknesses (from 0.3 to 3.0 Å), show that Au deposited on CuPc does not react, but for Au on FCuPc there is evidence for possible charge transfer from Au atoms to the four aromatic rings of FCuPc. Annealing the films at 125°C for one hour enhances charge transfer at the interfaces of Au/FCuPc, while it does not cause any chemical reactions at the interfaces of Au/CuPc. High-resolution field emission scanning electron microscopy (HRSEM) was employed to examine the nucleation and growth of Au (average thicknesses from 5 to 180 Å) on CuPc and FCuPc films at room temperature. Au grows in an island mode on four types of samples CuPc (RT), CuPc (125), FCuPc (RT), and FCuPc (125) in the initial stages of Au deposition (average thicknesses from 5 to 15 Å). The number in the parentheses is the temperature of substrates (in degrees Celsius) during CuPc or FCuPc deposition. Au atoms tend to form bigger clusters with a lower cluster density on CuPc surfaces than on FCuPc surfaces. This may indicate a lower diffusivity for Au on FCuPc than on CuPc, perhaps because of a stronger interaction between Au and FCuPc. These observations support our results from XPS studies. The onset of percolation occurs at a Au thickness of 90 Å for Au/CuPc (RT) and Au/CuPc (125), and 90 Å for Au/FCuPc (RT) and Au/FCuPc (125). A continuous and hole-free Au film is formed at a thickness of 180 Å.

#### 3:40pm OM-MoA6 A Combined Photoemission Spectroscopy and Scanning Probe Microscopy Study of Organic Charge Injection Layer / Metal Interfaces, *A.J. Mäkinen, J.P. Long, N.J. Watkins, Z.H. Kafafi*, Naval Research Laboratory

The electronic structure of organic/metal interfaces was investigated using photoemission spectroscopy in combination with scanning probe microscopy. Organic films of copperphthalocyanine (CuPc) and 6T were vacuum-deposited onto a single-crystal Au(111) substrate step-by-step, and ultraviolet and x-ray photoemission spectroscopies (UPS and XPS) were performed on the sample, together with scanning probe microscopy (SPM), at each step. By correlating different organic film structures revealed by SPM measurements with the corresponding electron energy spectra measured with UPS and XPS, we have been able to gain insights into how the frontier orbital character and position evolve with the organic film growth on the Au substrate. Since CuPc/Au and 6T/Au interfaces serve as model systems for similar structures responsible for charge injection and transport in many organic electronic devices, such as organic light-emitting diodes and photovoltaics, the results of this investigation will be useful for the characterization of such systems.

#### 4:00pm OM-MoA7 Electronic Structures of Al/Liq/Alq Interfaces Studied by Photoemission Spectroscopy, *Y. Park*, Korea Research Institute of Standards and Science, Korea; *J. Lee*, Samsung Advanced Institute of Technology, Korea; *J.W. Choi*, KRISS, Korea; *M. Han*, University of Seoul, Korea

Lithium quinoate (Liq) has recently been attracting a good deal of attention for a cathode interlayer material in organic light-emitting devices (OLEDs) as it showed electron injection performance as good as most commonly used LiF. Using X-ray and UV photoemission spectroscopy (XPS & UPS) techniques, we studied the evolution of the electronic structures at Al/Liq/Alq interface as it is formed in ultrahigh vacuum condition. The valence region spectra taken with UPS showed that the HOMO peaks move to higher binding energy (relative to Fermi level, E<sub>F</sub>) as Liq is deposited on Alq interface. This indicates that the deposition of Liq caused density of states inside the HOMO-LUMO gap although its intensity is too weak to be observed clearly with UPS. The total amount of the peak movement is ~ 1.8 eV comparable to the value for

# Monday Afternoon, November 3, 2003

LiF (~1.9 eV). We believe this shift of Fermi level (relative to vacuum level) toward LUMO level is principal cause of the observed improvement in device performance. The evolution of XPS peaks during the interface formation is very similar to the case of LiF and there is no appreciable direct chemical reaction when Liq was initially deposited on Alq@sub 3@. We further discuss the possible origins of the observed HOMO peak movement.

4:20pm **OM-MoA8 Direct Observation of the Evolution of the Molecular Orbital Energy Levels of a Silole Derivative as a Function of Magnesium Deposition**, *N.J. Watkins, A.J. Mäkinen*, Naval Research Laboratory; *Y. Gao*, University of Rochester; *M. Uchida*, Chisso Corporation, Japan; *Z.H. Kafafi*, Naval Research Laboratory

The electronic structure of the interface formed by Mg deposition onto 2,5-bis(6-(2,2-bipyridyl))-1,1-dimethyl-3,4-diphenyl silacyclopentadiene (PyPySPyPy) was investigated using ultraviolet photoemission, inverse photoemission, and X-ray photoemission spectroscopies. PyPySPyPy is of interest due to its high electron mobility. In addition, organic light-emitting diodes (OLEDs) using this silole derivative in the electron injection/transport layer exhibit very low operating voltages. Upon deposition of Mg onto PyPySPyPy a shift of the occupied molecular orbital energy level structure to higher binding energy, away from the Fermi level, was observed and accompanied by the appearance of two new levels within the energy gap of PyPySPyPy. These new levels have been assigned to a charge transfer complex between Mg and PyPySPyPy. At high Mg coverage, the shift in the lowest unoccupied molecular orbital can be correlated with the formation of "metallic-like" Mg clusters. The impact of these results on charge injection at the Mg metal contact in an OLED structure will be discussed.

4:40pm **OM-MoA9 Band Alignment on Patterned Surfaces**, *G. Koller, F.P. Netzer, M.G. Ramsey*, Karl-Franzens University, Austria

An important parameter for the function of organic electronic devices is the barrier to charge injection which is controlled by the interface dipole. This is determined by the details of the interaction of the first layer of molecules with the contact material. In reality the interface is not perfectly homogeneous and thus local differences in band alignment are to be expected although not necessarily observable with standard area averaging techniques. In this contribution we explore the local variation in band alignment on a nanoscopically patterned substrate surface by investigating the growth of bithiophene films, from sub-monolayer to multilayer coverages, with angle resolved UV-photoemission and workfunction measurements. The substrate used was the oxygen reconstructed Cu(110) surface. This surface reconstructs to form a mesoscopically patterned surface consisting of alternating stripes of clean Cu(110) and passive Cu(110)-(2x1)O, with stripe widths in the range of several nanometers depending on oxygen exposure. The bonding interaction of the probe molecule bithiophene is very different on the two surfaces resulting in band alignment differences of 1 eV for films grown on these surfaces. On the Cu(111)-(2x1)O striped surface for coverages of bithiophene up to two monolayers, the photoemission spectra is a result of the superposition of spectra offset by this difference in band alignment clearly indicating local differences in the charge injection barrier. However, beyond two monolayers the valence band spectra clearly indicate a single emitting species whose energy position is determined by the average interface dipole. The results thus show that inhomogeneities of the substrate surfaces will lead to local differences in the charge injection barrier which are invisible to area averaging techniques if the molecular film thickness are greater than the lateral dimensions of the inhomogeneities. Acknowledgments: Supported by the Austrian Science Foundation SFB Electroactive Materials

5:00pm **OM-MoA10 A General Soft Contact Evaporation Method for Molecule-Based (Opto) Electronic Devices**, *H. Haick, J. Ghabboun, D. Cahen*, Weizmann Institute of Science, Israel

Hybrid devices, in which molecular functionality is used to influence the characteristics of established electronic devices, but that do not require electronic charge transfer through the molecules, is an alternative approach to more established ones to molecule-based electronics. It is worth pursuing because of stability issues and the ability to use established technology as much as possible at this stage of molecule-based electronics. One such hybrid approach is based on controlling electronic properties of semiconductor devices by placing molecules, whose dipole can, synthetically, be changed systematically, at the device interface. Because mostly one can not insert molecules into a ready-made device interface, constructing such device structures requires device completion by making

a solid electrical contact to a surface with the organic molecules on it. This is problematic because a process such as thermal evaporation or sputtering easily damages the molecules, especially molecules that have sensitive functional groups exposed. Earlier we overcame this by successful use of soft, alternative methods. Still, the clear technological advantages of vacuum evaporation led us to search for ways to adapt this method to meet the challenge. The result, which we will present here is Indirect, Collision-Induced, Cooled Evaporation (ICICE), with which we prepared, among others, GaAs/molecule/Au diodes. ICICE decreases drastically the temperature and, thus, the kinetic energy of the evaporated particles/atoms arriving at the surface and assures that irradiation emitted from the crucible does not reach the modified samples. Based on TOF SIMS, XPS, STM and (I-V) electrical measurements, we find that ICICE provides intimate contacts without damaging the (~ 1-3 nm wide monolayer of) organic ligands and their functional groups. This is best expressed by the clear molecular effect on the resulting Au/GaAs barrier heights; they vary with the functionality of the adsorbed molecules. To understand the limiting steps for contacting by means of metal evaporation, we compared results obtained in our experimental system with ICICE, and another popular one, known as Direct Evaporation Under Cryogenic Cooling (DEUCC). While, indeed use of the DEUCC mode leaves the organic ligands beneath the metal contacts, it does damage their functional groups. This finding, for which we will present an explanation, has very significant implications as it shows that while the often-used criterion of absence of shorts in metal/molecule/metal junctions is indeed a necessary condition for successful contacting molecules, it is not a sufficient one. We thank the Israel Ministry of Science (Eshkol fellowship to HH and tashtyoth project and the Israel Science Foundation (Jerusalem) for partial support.

# Tuesday Evening Poster Sessions, November 4, 2003

## Contacts to Organic Materials Topical Conference Room Hall A-C - Session OM-TuP

### Poster Session

#### OM-TuP1 Study of Surface Photovoltage Effects in Doped Organic Molecular Thin Films, *C. Chan, W. Gao, A. Kahn*, Princeton University

We investigate photoemission-induced surface photovoltage (SPV), i.e. non-equilibrium resulting from photoexcitation and separation of carriers, in organic films. We focus on electrically doped molecular films that exhibit interface depletion regions<sup>1</sup> and can sustain charge separation and SPV. We combine ultraviolet photoemission spectroscopy (UPS) to measure the HOMO and vacuum levels under illumination, and contact potential difference (CPD) measurement with a Kelvin probe to measure the vacuum level in the dark. Zinc phthalocyanine (ZnPc) and N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine ( $\alpha$ -NPD) p-doped with the acceptor molecule, tetrafluorotetracyanoquinodimethane (F<sub>4</sub>-TCNQ), are investigated.<sup>1,2</sup> UPS and CPD measurements are performed as a function of film thickness deposited on Au. CPD measurements reproduce with excellent accuracy the UPS-observed shifts of the molecular energy levels, in particular through a depletion region ~30-50 Å near the metal-organic interface of the doped organic films. The excellent agreement shows that: (1) efficient p-doping occurs even in the dark in these two organic systems; (2) SPV is negligible in both doped and undoped organic films. The undoped films do not have depletion regions where charge separation can occur. In the doped films, electrons separated in the interface depletion region recombine in the metal before generating significant SPV, whereas the holes readily recombine throughout the film.<sup>1</sup> W. Gao and A. Kahn, *Organic Electronics* 3, 53 (2002)<sup>2</sup> W. Gao and A. Kahn, *J. Appl. Phys.* (accepted for publication; July 1, 2003).

#### OM-TuP2 Adsorption of PTCDCA on Si(100), *B. Grandier, T. Soubiron, J.P. Nys, M. Dubois, C. Delerue, D. Stievenard*, IEMN-CNRS, France

Submonolayer coverages of perylene-tetracarboxylic-dianhydride (PTCDA) molecules have been investigated with scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). At low coverage, comparisons between the STM images and calculations of the electronic structure of the molecule show that the molecule adsorbs mostly in a planar configuration with its axis parallel to the Si dimers. Different configurations are observed and associated with physisorbed and chemisorbed states of the adsorbates. At higher coverage, X-ray measurements indicate that only a fraction of the molecules are chemisorbed and that the bonding occurs through the dicarbonyl functional groups, preserving the pi-conjugation of the molecules. While PTCDA selectively reacts with the Si dimers, steric hindrance is found to be the major cause to hamper the formation of an ordered film.

#### OM-TuP3 Potential Imaging of Metal-organic Semiconductor Interfaces using Kelvin Probe Force Microscopy, *O. Tal*, Tel Aviv University, Israel; *W. Gao, L. Friedman, A. Kahn*, Princeton University; *Y. Rosenwaks*, Tel Aviv University, Israel

Understanding and improving the performance of organic electronic devices depends, to a great extent, on the elucidation of organic materials interfaces with inorganic and organic solids alike. Therefore these interfaces are the focus of this work. We present a study of two dimensional (2-D) potential profiles across metal-organic film interfaces (metal- Au or Al, organic film - tris(8-hydroxyquinolino) aluminum [Alq<sub>3</sub>]) with nanometer spatial resolution provided by Kelvin probe force microscopy (KPFM) in a nitrogen environment. The contact potential difference (CPD) is measured across Al/Alq<sub>3</sub>/Al, Au/Alq<sub>3</sub>/Au and Au/Alq<sub>3</sub>/Al sandwich-like structures following cleavage under the inert atmosphere. The CPD profiles are in a very good agreement with vacuum level profiles estimated by calculation, which are based on ultraviolet photoemission spectroscopy (UPS) measurements. Preliminary measurements of these structures and "device-type" structures under operating conditions will be presented and discussed. This work is the first step in providing a new and unique type of information on the electronic structure of metal-organic and organic-organic interfaces, as determined by KPFM and additional techniques.

#### OM-TuP4 Conductive Core-Shell Nanoparticles: An Approach to Self-Assembled Mesoscopic Wires, *G. Kaltenpoth, M. Himmelhaus*, Universität Heidelberg, Germany; *L. Slansky*, Daimler-Chrysler AG, Germany; *F. Caruso*, University of Melbourne, Australia; *M. Grunze*, Universität Heidelberg, Germany

Conductive core-shell nanoparticles were prepared by coating negatively charged monodisperse polystyrene (PS) latex spheres with a thin layer of polyethyleneimine (PEI). Subsequently, gold colloid with 3 nm in size was electrostatically adsorbed onto the PEI-coated spheres, and finally, an electroless gold plating step was repeatedly carried out to yield a high gold coverage and thus a conductive gold shell. The metallic behavior was investigated by XPS and UV-vis. In the XPS Au4f peak, a shift due to charging effects was observed at low metal coverage, which decreased with increasing gold decoration, and vanished with the formation of a conductive metal shell. The UV-vis spectra show a coverage-dependent shift and broadening of the Au plasmon resonance. The self-assembly of the metal coated spheres into continuous lines was investigated to explore the applicability of such particles to realize self-assembled electrical circuits. It was found that the particles selectively adsorb to the carboxyl-terminated areas of line patterns fabricated by microcontact printing of alternating carboxyl- and methyl terminated alkanethiolates on gold.

#### OM-TuP5 The Enhancement of Passivation Effect and Long Time Stability on Aluminum Cathode Deposited by Adatom Mobility Enhancing Technique in Organic Electroluminescent Display, *S.M. Jeong, W.H. Koo, S.H. Choi*, Yonsei University, Korea; *S.J. Lee*, Kyung Seong University, Korea; *K.M. Song*, Kon Kuk University, Korea; *H.K. Baik*, Yonsei University, Korea, South Korea

Highly stable and electroluminescent devices based on spin-coated PPV thin films have been achieved. The improvement of lifetime is derived from aluminum cathode deposited by adatom mobility enhancing technique. There are much less pinhole defects because of fine grain size caused by high surface mobility and contact area between Al and PPV increase. It is believed that the passivation effect and minimizing thermal degradation is induced by much less pinhole defect and large contact area between Al and PPV.

#### OM-TuP6 Hole-injection and Transport in Arylamines Films Sandwiched between Metal Contacts, *G. Szulcowski, J. Li, K.-Y. Kim, J. Sun, S.C. Blackstock*, University of Alabama

We have synthesized a series of electron-rich arylamines to systematically control their electronic properties, i.e. dipole moment and ionization potential. Films of these molecules were made by solution and/or vapor deposition techniques on Ag and Au substrates and characterized by cyclic voltammetry and x-ray photoelectron spectroscopy. We have measured current-voltage curves of monolayer and multilayer films to study hole-injection and transport. We find that these molecules rectify current under forward bias above a threshold voltage. A plot of the threshold voltage against the measured electrochemical oxidation potential yields a straight line with an excellent correlation coefficient,  $R = 0.98$ , and slope greater than unity. We will discuss how the molecular properties influence charge-injection at the metal-molecule interface. We acknowledge the National Science Foundation for support of this work through the Materials Research Science and Engineering Center grant # DMR0213985.

## Surface Science

### Room 327 - Session SS+OM-ThA

#### Self-Assembled Monolayers

Moderator: L. Hanley, University of Illinois at Chicago

2:00pm **SS+OM-ThA1 Non-dissociative Chemisorption of Methanethiol on Ag(110)- A Critical Result for Self-assembled Layer Formation, J.-G. Lee, J. Lee, J.T. Yates, Jr.,** University of Pittsburgh

Three definitive experiments have been performed which show that CH@sub 3@SH does not dissociate upon chemisorption on clean Ag(110). On the clean Ag(110) surface, the adsorption in the first layer occurs at 0.5 ML, producing a (2x1) LEED structure. The undissociated molecule desorbs at ~140 K. Using a 50%-50% mixture of CH@sub 3@SD and CD@sub 3@SH, no evidence of S-H or S-D bond scission by isotope mixing between these molecules is found upon desorption. And finally, when the CH@sub 3@SH molecule is incident on clean Ag(110) surface in the temperature range from 240 K to 400 K, less than 1% of the incident molecules dissociate to produce adsorbed S. In contrast, when a sulfur-poisoned Ag(110) surface is exposed to CH@sub 3@SH, autocatalytic dissociation occurs below 240 K, producing CH@sub 4@, H@sub 2@S and adsorbed S atoms. These results are in striking contrast to the behavior of Cu(110) where CH@sub 3@SH dissociation occurs below 320 K leaving S. These results are of importance in understanding the self assembly of alkanethiol layers on silver where it has been commonly assumed that S-H bond scission occurs at room temperature. This work was supported by DOE-BES.

2:20pm **SS+OM-ThA2 Spectroelectrochemical Studies of Self-Assembled Monolayers of Thiols, I. Thom,** St Andrews University, Scotland; *M. Buck,* St Andrews University, Scotland, UK

Thiol SAMs provide a convenient route to modify electrodes and to serve as templates for directing electrochemical processes. Towards a rational design of thiol SAMs for electrochemical applications the electrochemically induced desorption and adsorption of thiols are studied in-situ using the combination of electrochemistry and non-linear optical techniques. Potential dependent capacitive and faradaic currents are correlated with the second harmonic signal which probes the S-Au bond formation. Studies of alkane thiols and biphenyl based thiols reveal that this correlation is strongly dependent on the electrolyte, i.e. both the penetration of ions into the layer and the desorption mechanism are affected by the electrolyte. In the ethanol case, a change in the desorption mechanism during multiple potential cycling is observed. While the current continuously decreases with increasing number of cycles, the change of the SHG signal remains essentially unaltered and indicates a change in the faradaic process. This change is explained by a transition from thiolate to disulfide formation upon the desorption of thiols.

2:40pm **SS+OM-ThA3 Photoemission Study of Dodecanethiol on Ag(111) and Au(111), H. Geisler,** Xavier University; *J.M. Burst, S.N. Thornburg, C.A. Ventrice,* University of New Orleans; *Y. Losovyj, P.T. Sprunger,* Louisiana State University

Self-assembled monolayers show great promise for use in many technological applications such as in chemical and biological sensing, chemical resists in lithography, corrosion protection, and molecular electronics. However, there are several fundamental properties of these systems that are not well understood. For instance, the adsorption of alkanethiols on Au(111) results in a (@sr@3 x @sr@3)R30° overlayer; whereas, adsorption on Ag(111) results in an incommensurate overlayer even though Au and Ag are isoelectronic and are lattice matched to 0.3%. Although there have been several studies of the geometric structure of thiols on Au(111) and to a lesser extent on Ag(111), there have been very few studies of the electronic structure of these films. Angle-resolved ultraviolet photoelectron spectroscopy studies of the growth of dodecanethiol on Au(111) and Ag(111) have been performed in UHV by vapor deposition. By using vapor deposition, the submonolayer striped phase, full monolayer upright phase, and the multilayer phase can be studied. The monolayer coverage of thiol results in peaks at binding energies of 20 eV, 14 eV, 10 eV, and 7 eV. By comparing the dispersion of the Ag(111) d-band emission for the clean surface to the surface after deposition of a monolayer of thiol, it was determined that there is a loss of order of the Ag surface atoms. Similar measurements for Au(111) reveal that the Au(111) surface remains in an ordered state. This result provides a mechanism for the different adsorption geometries of alkanethiols on Au(111) and Ag(111). Since there is no ordered template of Ag atoms after thiol adsorption, the van der

Waals interaction between the CH@sub 2@ chains dominates, resulting in an ordered, incommensurate overlayer. Measurements of the thiols in the multilayer regime reveal a uniform shift of the thiol peaks to higher binding energy, presumably due to sample charging effects from the insulating nature of these films at 150 K.

3:00pm **SS+OM-ThA4 Short Aromatic Thiols on Cu(111): Initial Adsorption Configuration and the Formation of an Ordered Monolayer, B.V. Rao, K.-Y. Kwon, J. Zhang, A. Liu, L. Bartels,** University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial orientation of di-chloro-thio-phenol (DCTP) and S-phenyl-thio-acetate (SPTA), a thio-phenol whose sulfur-bound hydrogen is replaced by an acetyl group. The latter is a common practice in order to protect the thiol group during the synthesis of poly-functional organic molecules. This poster compares the impact of the acetyl substitution on the initial steps of the molecules interaction with a Cu(111) surface. DCTP adsorbs at low temperatures (15K) with the sulfur atom at an on-top site and is able to rotate around it. This results in the observation of a flower shaped species on STM images. There are two chiral adsorption configurations which can be distinguished by STM. In contrast, SPTA adsorbs in a position in which both the phenyl and the second carbon of the acetyl group point upward resulting in a double protrusion in STM images. While tunneling electrons of less than 500meV of either bias can cause the abstraction of hydrogen from the thiol group of DCTP, SPTA is stable beyond 1V in tunneling bias. Increasing the coverage by adsorption at nitrogen temperatures, DCTP forms an ordered monolayer consisting of dimers, both of which have the phenyl group lying flat on the surface. The formation of extended islands of the ordered monolayer requires annealing of the sample beyond liquid nitrogen temperatures. Further increase of the coverage results in pronounced protrusion at defect sites of the ordered monolayer, which we interpret as molecules that point the phenyl ring away from the surface. STM resolution on a film consisting entirely of such species is poor; however, it can confirm that an ordered film is formed.

3:20pm **SS+OM-ThA5 Balance of Structure-building Forces in Monomolecular Films: Terphenyl-substituted Alkanethiolates on Noble Metal Substrates, A. Shaporenko,** Universität Heidelberg, Germany; *M. Brunnbauer, A. Terfort,* Universität Hamburg, Germany; *L.S.O. Johansson,* Karlstad University, Sweden; *M. Zharnikov,* Universität Heidelberg, Germany

The design of versatile monomolecular films relies on detailed knowledge of basic rules governing the packing density and exact arrangement of the molecular constituents in these systems. The most important issue in this connection is the understanding of the interplay between the structure-building headgroup-substrate and intermolecular interactions. To address this issue we have studied self-assembled monolayers (SAM) formed from terphenyl-substituted alkanethiols C@sub 6@H@sub 5@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (TPn, n = 1-6) on Au and Ag substrates. In these systems, strongly interacting terphenyl backbones force a dense molecular packing, which does not fit to the geometry of the metal-S-C bond at certain length of the aliphatic part. We used several complementary experimental techniques such as x-ray photoelectron spectroscopy (XPS), high-resolution XPS, near edge X-ray absorption fine structure spectroscopy, infrared absorption spectroscopy, ellipsometry, and water contact angle measurements to characterize the TPn SAMs. Odd-even changes in the packing density, the tilt angle of the terphenyl moieties, etc have been observed and considered in detail. These changes could be clear correlated with the geometry of the metal-S-C bond, which assumed to be different on Au and Ag. The results imply a predominant role of the headgroup-substrate interaction in the balance of structure-building forces in the aliphatic SAMs and give a practical tool for the fabrication of monomolecular films with desired properties.

3:40pm **SS+OM-ThA6 Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Based Thiol SAMs: A Combined STM and LEED Study, P. Cyganik, M. Buck,** University of St Andrews, UK; *W. Azzam, G. Witte, Ch. Woell,* Ruhr Universitaet Bochum, Germany

Self-assembled monolayers (SAMs) of thiols are promising candidates for nanolithographic applications. Towards a rational design and control down to the length scale reaching molecular dimensions we study SAMs a particular type of thiols which is characterized by a biphenyl unit and an alkane spacer of varying length (CH@sub 3@ (C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH, BPn, n = 2, 3, 4, 5). SAMs adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Our results demonstrate

# Thursday Afternoon, November 6, 2003

that preparation at elevated temperature results in highly ordered layers with large domains. Whereas the (2@sr@3x@sr@3) structure of the BP3 and BP5 SAMs is similar to that reported previously for other aromatic thiols, SAMs made from BP2 and BP4 exhibit a very different structure. A (5@sr@3x3)rect unit cell containing 8 molecules is found which corresponds to a packing density reduced by 25 % compared to BP3 and BP5. The odd-even effect observed in the molecularly resolved STM images of BPn, therefore, confirms the pronounced influence of the spacer chain on the structure of these biphenyl based SAMs.

**4:00pm SS+OM-ThA7 Mechanism of Nanomolecular Motion Induced by Polarity Change of the Electric Field in the Self-Assembled Monolayers, T. Ishida,** AIST, Japan; *H. Fukushima*, TPRC, SEIKO EPSON Corporation, Japan; *T. Tamaki*, AIST, Japan

We have successfully observed the nanoscale molecular motion induced by polarity change of the electric field by STM, when small amounts of asymmetrical disulfides containing mobile terphenyl moieties were embedded into pre-assembled dodecanethiol SAMs. Taking the direction of the dipole moment into account, the thickness of embedded molecular protrusions became larger at the positive bias. However, STM experiments revealed that the thickness of the molecular protrusions was larger at the negative bias, contrary to this prediction. STS revealed the higher rectification property at the area of the terphenyl terminated monolayer where also showed the higher electrical conduction at the negative tip bias compared to positive one. The higher electrical conduction at the negative tip bias was likely to retract the STM tip, showing the apparent nanomolecular motion by the polarity change. Next, we investigated the relationship between the higher rectification property and real conformational change. When symmetric disulfide which is not easy to change molecular conformation are embedded into pre-assembled dodecanethiol SAMs for the comparison, both the rectification property and apparent molecular motion were not observed. In addition, when the STM tip was directly attached to asymmetric disulfides, rectification property was not observed in STS. Thus, we concluded that the conformational change is the influential factor to induce the higher rectification property. @FootnoteText@@footnote 1@ T. Ishida, H. Fukushima, T. Tamaki and H. Tokumoto, Jpn J. Appl. Phys. in press. @footnote 2@ H. Fukushima and T. Tamaki J. Phys. Chem. B106 7142(2002).

**4:20pm SS+OM-ThA8 The Reaction of Tetrakis(dimethylamino)titanium with Self-Assembled Monolayers Possessing -OH, -NH@sub2@ and -CH@sub3@ Terminal Groups, A.S. Killampalli, P.F. Ma, J.R. Engstrom,** Cornell University

Organic materials are playing an increasing role in modern microelectronic devices--beyond their traditional role as photoresists. New areas include their application as low-@kappa@ dielectrics. Interfaces between organics and metals are also of interest, including in fields such as molecular electronics. To date, almost all work concerning the formation of organic-metal interfaces on pre-existing organic layers has involved metal thin films deposited by (elemental) evaporation. In the work described here we examine an alternative approach to the formation of inorganic-organic interfaces, namely, via the use of organo-transition metal complexes. Here we study the reaction of the titanium precursor, tetrakis(dimethylamino)titanium (TDMAT), with model organic surfaces [self-assembled monolayers (SAMs) terminated by -OH, -NH@sub2@ and -CH@sub3@ groups] using X-ray photoelectron spectroscopy (XPS). Trichlorosilane self-assembled monolayers have been formed on SiO@sub2@ surfaces that, in selected cases, were subjected to additional chemical conversion steps. Prior to insertion into vacuum these layers were characterized using AFM, ellipsometry and contact angle measurements. Exposure of these surfaces to TDMAT was carried out in a custom-designed ultrahigh vacuum chamber equipped with facilities for XPS and quadrupole mass spectrometry (QMS). In selected cases, angle resolved XPS (ARXPS) was used to probe the spatial extent of reaction of the precursor. Among the SAM surfaces studied, the -OH terminated SAM exhibits the highest reactivity, followed by the -NH@sub2@ and -CH@sub3@ terminated SAMs, in that order. ARXPS results reveal that TDMAT reacts primarily at the top of the -OH terminated SAM, while the reaction on the -CH@sub3@ terminated SAM is actually with underlying reactive regions at the SAM/SiO@sub2@ interface. Additional results concerning the reaction of TDMAT with these monolayers, including modeling of the adsorption kinetics, will be presented.

**4:40pm SS+OM-ThA9 Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using Near-Edge X-ray Absorption Fine Structure, T.M. Willey<sup>1</sup>,** University of California, Davis and Lawrence Livermore National Lab; *A.L. Vance, T. van Buuren, C. Bostedt, B.R. Hart, R.W. Meulenberg, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Laboratory; *C.S. Fadley,* Lawrence Berkeley National Laboratory

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on Au(111) have become increasingly important to achieve surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful in functionalizing surfaces for surface attachment and immobilization of proteins, DNA, viruses, as well as using the charged state of the endgroups in switchable surfaces. We are also using such functionalization in surface attached interlocking molecules to attempt to induce and measure reorientation (switching) within interlocking molecules. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, NEXAFS results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH@sub 2@)@sub 15@COOH) a long-chain molecule with strong chain-chain interactions and thioctic acid (S@sub 2@(CH@sub 2@)@sub 2@CH(CH@sub 2@)@sub 4@COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO- vs. COOH.) In addition, we will present initial results on ordering and attachment in amino-terminated alkanethiols on gold, and preliminary results using functional groups in switching interlocking molecules on surfaces.

**5:00pm SS+OM-ThA10 Self Assembled Monolayers on Microelectronic Copper Thin Film for Prevention of Corrosion, Y.S. Tan,** National University of Singapore, Singapore; *M.P. Srinivasan, S.O. Pehkonen,* National University of Singapore; *Y.M. Chooi,* Chartered Semiconductor Manufacturing Ltd., Singapore

Abstract: Self-assembled monolayers of dodecanethiol (DT), Mercaptobenzothiazole (MBT), Benzotriazole (BTA) and Imidazole (IMD) were formed by adsorption on the surface of copper thin film used in the ultra large-scale integrated circuits. The films were characterized by X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared (FTIR) Spectroscopy and contact angle measurements. The corrosion inhibitive behaviours of these organic monolayers were investigated in aerated 0.5 moldm@sup -3@ H@sub 2@SO@sub 4@ solutions by means of Electrochemical Impedance Spectroscopy (EIS) and polarization techniques. The presence of the monolayers reduced corrosion by blocking the copper surface from the dissolved oxygen in the acid medium. The relative inhibition efficiencies of these inhibiting agents in preventing copper oxidation is found to be in the order of: DT > MBT > BTA > IMD. The effectiveness of the inhibitors increased with temperature, concentration of the inhibitors and immersion time in the solution. An adsorption model was proposed on the basis of the variation of impedance with inhibitors' concentration.

<sup>1</sup> Morton S. Traum Award Finalist

## Author Index

### Bold page numbers indicate presenter

— A —

Ahn, H.: OM-MoM5, 1  
Azzam, W.: SS+OM-ThA6, 6  
— B —  
Baik, H.K.: OM-TuP5, 5  
Bartels, L.: SS+OM-ThA4, 6  
Blackstock, S.C.: OM-TuP6, 5  
Bostedt, C.: SS+OM-ThA9, 7  
Bredas, J.L.: OM-MoA1, **3**  
Brunnbauer, M.: SS+OM-ThA5, 6  
Buck, M.: SS+OM-ThA2, 6; SS+OM-ThA6, 6  
Burst, J.M.: SS+OM-ThA3, 6  
— C —  
Cahen, D.: OM-MoA10, 4; OM-MoM1, **1**;  
OM-MoM9, 2  
Caruso, F.: OM-TuP4, 5  
Chan, C.: OM-TuP1, **5**  
Choi, J.W.: OM-MoA7, 3  
Choi, S.H.: OM-TuP5, 5  
Choi, Y.M.: SS+OM-ThA10, 7  
Cohen, S.R.: OM-MoM9, 2  
Cyganik, P.: SS+OM-ThA6, **6**  
— D —  
Delerue, C.: OM-TuP2, 5  
Dubois, M.: OM-TuP2, 5  
Dutton, G.: OM-MoM3, 1  
— E —  
Engstrom, J.R.: SS+OM-ThA8, 7  
— F —  
Fadley, C.S.: SS+OM-ThA9, 7  
Friedman, L.: OM-TuP3, 5  
Frisbie, C.D.: OM-MoM10, **2**  
Fukushima, H.: SS+OM-ThA7, 7  
— G —  
Gao, W.: OM-MoA3, **3**; OM-TuP1, 5; OM-  
TuP3, 5  
Gao, Y.: OM-MoA8, 4  
Geisler, H.: SS+OM-ThA3, **6**  
Ghabboun, J.: OM-MoA10, 4  
Grandier, B.: OM-TuP2, 5  
Grunze, M.: OM-TuP4, 5  
— H —  
Haase, G.: OM-MoM9, 2  
Haick, H.: OM-MoA10, **4**  
Han, M.: OM-MoA7, 3  
Hart, B.R.: SS+OM-ThA9, 7  
Himmelhaus, M.: OM-TuP4, 5

— I —

Ishida, T.: SS+OM-ThA7, **7**  
Ivanco, J.: OM-MoM4, 1  
— J —  
Jeong, S.M.: OM-TuP5, **5**  
Johansson, L.S.O.: SS+OM-ThA5, 6  
— K —  
Kafafi, Z.H.: OM-MoA6, 3; OM-MoA8, 4  
Kahn, A.: OM-MoA3, 3; OM-TuP1, 5; OM-  
TuP3, 5  
Kaltenpoth, G.: OM-TuP4, **5**  
Killampallij, A.S.: SS+OM-ThA8, **7**  
Kim, K.-Y.: OM-TuP6, 5  
Koller, G.: OM-MoA9, **4**  
Koo, W.H.: OM-TuP5, 5  
Kwon, K.-Y.: SS+OM-ThA4, 6  
— L —  
La Rosa, S.: OM-MoA4, 3  
Lee, J.: OM-MoA7, 3; SS+OM-ThA1, 6  
Lee, J.-G.: SS+OM-ThA1, **6**  
Lee, S.J.: OM-TuP5, 5  
Li, J.: OM-TuP6, 5  
Liu, A.: SS+OM-ThA4, 6  
Long, J.P.: OM-MoA6, 3  
Losovjy, Y.: SS+OM-ThA3, 6  
Lozzi, L.: OM-MoA4, **3**  
— M —  
Ma, P.F.: SS+OM-ThA8, 7  
Madey, T.E.: OM-MoA5, 3  
Makinen, A.J.: OM-MoA6, **3**; OM-MoA8, 4  
McBreen, P.H.: OM-MoM8, **2**  
Meulenberg, R.W.: SS+OM-ThA9, 7  
— N —  
Nelson, A.J.: SS+OM-ThA9, 7  
Netzer, F.P.: OM-MoA9, 4; OM-MoM4, 1  
Nevo, I.: OM-MoM9, **2**  
Nys, J.P.: OM-TuP2, 5  
— O —  
Oudghiri Hassani, H.: OM-MoM8, 2  
— P —  
Paez, B.: OM-MoM6, 1  
Park, Y.: OM-MoA7, **3**  
Pehkonen, S.O.: SS+OM-ThA10, 7  
— R —  
Ramsey, M.G.: OM-MoA9, 4; OM-MoM4, **1**  
Rao, B.V.: SS+OM-ThA4, **6**  
Robey, S.W.: OM-MoM7, 2

Rosenwaks, Y.: OM-TuP3, 5

— S —

Salvan, G.: OM-MoM6, 1  
Santucci, S.: OM-MoA4, 3  
Sengupta, S.K.: OM-MoM5, 1  
Shaporenko, A.: SS+OM-ThA5, **6**  
Siaj, M.: OM-MoM8, 2  
Slansky, L.: OM-TuP4, 5  
Song, K.M.: OM-TuP5, 5  
Soubiron, T.: OM-TuP2, **5**  
Sprunger, P.T.: SS+OM-ThA3, 6  
Srinivasan, M.P.: SS+OM-ThA10, 7  
Stievenard, D.: OM-TuP2, 5  
Sun, J.: OM-TuP6, 5  
Szulczewski, G.: OM-TuP6, 5

— T —

Tal, O.: OM-TuP3, **5**  
Tamaki, T.: SS+OM-ThA7, 7  
Tan, Y.S.: SS+OM-ThA10, **7**  
Terfort, A.: SS+OM-ThA5, 6  
Terminello, L.J.: SS+OM-ThA9, 7  
Thom, I.: SS+OM-ThA2, **6**  
Thornburg, S.N.: SS+OM-ThA3, 6

— U —

Uchida, M.: OM-MoA8, 4

— V —

van Buuren, T.: SS+OM-ThA9, 7  
van Zee, R.D.: OM-MoM7, 2  
Vance, A.L.: SS+OM-ThA9, 7  
Ventrice, C.A.: SS+OM-ThA3, 6

— W —

Watkins, N.J.: OM-MoA6, 3; OM-MoA8, **4**  
Whitten, J.E.: OM-MoM5, **1**  
Willey, T.M.: SS+OM-ThA9, 7  
Winter, B.: OM-MoM4, 1  
Witte, G.: SS+OM-ThA6, 6  
Woell, Ch.: SS+OM-ThA6, 6

— Y —

Yates, Jr., J.T.: SS+OM-ThA1, 6  
Yu, X.: OM-MoA5, **3**

— Z —

Zahn, D.R.T.: OM-MoM6, **1**  
Zangmeister, C.: OM-MoM7, 2  
Zhang, J.: SS+OM-ThA4, 6  
Zharnikov, M.: SS+OM-ThA5, 6  
Zhu, X.-Y.: OM-MoM3, **1**