

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 alkyldenes) 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 alkyldene 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 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.

Author Index

Bold page numbers indicate presenter

— A —

Ahn, H.: OM-MoM5, **1**

— C —

Cahen, D.: OM-MoM1, **1**; OM-MoM9, **2**

Cohen, S.R.: OM-MoM9, **2**

— D —

Dutton, G.: OM-MoM3, **1**

— F —

Frisbie, C.D.: OM-MoM10, **2**

— H —

Haase, G.: OM-MoM9, **2**

— I —

Ivanco, J.: OM-MoM4, **1**

— M —

McBreen, P.H.: OM-MoM8, **2**

— N —

Netzer, F.P.: OM-MoM4, **1**

Nevo, I.: OM-MoM9, **2**

— O —

Oudghiri Hassani, H.: OM-MoM8, **2**

— P —

Paez, B.: OM-MoM6, **1**

— R —

Ramsey, M.G.: OM-MoM4, **1**

Robey, S.W.: OM-MoM7, **2**

— S —

Salvan, G.: OM-MoM6, **1**

Sengupta, S.K.: OM-MoM5, **1**

Siaj, M.: OM-MoM8, **2**

— V —

van Zee, R.D.: OM-MoM7, **2**

— W —

Whitten, J.E.: OM-MoM5, **1**

Winter, B.: OM-MoM4, **1**

— Z —

Zahn, D.R.T.: OM-MoM6, **1**

Zangmeister, C.: OM-MoM7, **2**

Zhu, X.-Y.: OM-MoM3, **1**