# Wednesday Morning, November 6, 2002

## Organic Films and Devices
## Room: C-102 - Session OF+EL+SS+SC-WeM

### Metal-Organic Interfaces
### Moderator: L.J. Guo, University of Michigan

8:20am **OF+EL+SS+SC-WeM1 Interfaces between Metals and Conjugated Organic Materials: From Physisorption to Covalent Bonding**, ***N. Koch***, Princeton University, *J. Ghijsen,* Facultes Universitaires Notre-Dame de la Paix, Belgium, *A. Rajagopal,* Rutgers University, *C. Chan,* Princeton University, *J.J. Pireaux,* Facultes Universitaires Notre-Dame de la Paix, Belgium, *J. Schwartz*, *A. Kahn*, Princeton University **INVITED**

The electronic properties of interfaces formed between conjugated organic materials (polymers and small molecules) and other organic and inorganic materials are of paramount importance in terms of the performance of organic-based devices (e.g., light emitting diodes, thin film transistors). The alignment of energy levels at such interfaces is a direct consequence of the physical and chemical interactions between the materials. Using mainly photoemission spectroscopy (PES), we show that the nature of interaction between low work function metals and phenylene-based electroluminescent oligomers and polymers covers the whole range from physisorption (aluminum and samarium) to chemical reduction (calcium), and to charge transfer reactions (alkali metals). Although PES is a very powerful experimental tool to determine electronic properties of interfaces, great care must be taken in the interpretation of the data when wide band-gap materials, such as conjugated organic materials, are being investigated. We demonstrate that the observation by PES of a finite density of occupied states at the Fermi-level on an organic film in which alkali metal atoms have been intercalated does not necessarily imply metallicity nor the presence of negative polarons (radical anions), as previously proposed. From a combination of ultraviolet PES and Kelvin probe measurements, evidence is obtained that the substrate and the surface of the organic film are not necessarily in thermodynamic equilibrium, leading to potential misinterpretations of the Fermi level position at the surface of organic films.

9:00am **OF+EL+SS+SC-WeM3 Structural and Electronic Properties of the Interfaces between Au(111) and the Organic Semiconductors Pentacene and p-sexiphenyl**, ***C.B. France***, *P.G. Schroeder, B.A. Parkinson*, Colorado State University

Thorough understanding of the interface between organic semiconductors and metal contacts is important because of charge transfer events that take place in new devices based on organic semiconductors. Transistors[1] and photovoltaic devices[2] have been fabricated using pentacene as the organic semiconductor. In the interest of understanding the structural and electronic environments of these interfaces we have investigated thin films of pentacene and p-sexiphenyl on the Au(111) surface in ultrahigh vacuum using multiple characterization techniques. The entergetics of these heterojunctions have been measured using photoemission spectroscopy. Large interfacial dipole barriers exist at the interface of both systems. Temperature programmed desorption has been used to investigate the binding environment of the organic semiconductors on the metal substrate. Two different binding environments have been uncovered for both molecular semiconductors on the Au(111) substrate. Scanning tunneling microscopy has been used to investigate the coverage dependant structures that are formed by thin films of semiconductor molecules on the Au(111) surface. Pentacene was found to generate many overlayer structures at differing film thickness. Structures found on low coverage, monolayer and multilayer films will be discussed.

[1] Schön, J. H.;Berg, S.;Kloc, C.;Batlogg, B. Science 2000, 287, 1022.

[2] Schön, J. H.;Kloc, C.;Bucher, E.;Batlogg, B. Nature 2000, 403, 408. .

9:20am **OF+EL+SS+SC-WeM4 Growth of Organic Molecules on Ferromagnetic Substrates for Hybrid Organo-metallic Spintronic Devices**, ***M.V. Tiba***, *O. Kurnosikov, B. Koopmans, J.T. Kohlhepp, C.F.J. Flipse, W.I.M. de Jonge, U.S. Schubert,* Eindhoven U. of Technology, CNM, The Netherlands

Motivated by the success of polymer based- and molecular electronics, a challenging new field is emerging. Recent work has demonstrated the feasibility of hybrid organo-metallic spintronics, in which the spin degree of freedom is explicitly being used. Application in future magnetic sensor and memory technology has been proposed. Improved characteristics of such devices require very clean interfaces, therefore deposition of organic molecules in UHV environment is desirable. A severe complication of growing ordered structures of organic molecules on transition metal ferromagnetic substrates is their high reactivity. In this work we investigate the influence of substrate passivation on the bonding to the substrate (and hence the molecular ordering) for different organic molecules. Selection of the molecules is based on their electronic properties as well as their tendency to form well ordered layers. In the particular case of PTCDA molecules deposited on a Ni(111) substrate we show that quarter monolayer of oxygen reduces enough the reactivity of Ni to enable the molecules to form an ordered structure.[1] Current activities aiming at the fabrication of organo-metallic hybrid magnetic tunnel junctions having polycrystalline Co electrodes and organic barriers will be addressed as well.

[1] M.V.Tiba et al. Surf. Sci. 498 (2002) 161.

9:40am **OF+EL+SS+SC-WeM5 Controlling Metallic Contacts to Molecular Electronic Devices**, ***A.V. Walker***, *T.B. Tighe, O. Cabarcos, B.C. Haynie, D.L. Allara, N. Winograd,* Pennsylvania State University

In the development and design of molecular electronic devices, it is vital to understand the nature of the metal-organic monolayer interaction. To fully characterize these interactions, we employ a multi-technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations. Using an unfunctionalized molecular wire (4-[4?-(phenylethynyl)-phenylethynyl]-benzenethiol) monolayer on Au, we demonstrate that the metal-monolayer contact can be varied from complete destruction of the monolayer to contact formation at the monolayer terminus to complete penetration through the layer. For example, we show that upon deposition of Cu or Ag, the Cu and Ag atoms simultaneously interact with the terminal phenyl ring and penetrate to the Au/S interface. In contrast, Au penetrates through the monolayer at all coverages studied. By using metals specifically tailored for the chemistry of the device molecule as well as for electronic states, the characteristics of the metal-molecule contact can also be controlled. These types of data provide a foundation for rational design of contacts in molecular electronic devices.

10:00am **OF+EL+SS+SC-WeM6 DLC Thin Film as Electron Injection Layer in Organic LEDs**, ***M. Cremona***, Pontificia Universidade Catolica do Rio de Janeiro, Brazil, *R. Reyes,* Universidad Nacional de Ingeniería, Perú, *C.A. Achete, P.I. Guimarães, S.S. Camargo, Jr.*, Universidade Federal do Rio de Janeiro, Brazil

Recently, there has been an increased interest in organic light emitting diodes (OLEDs) due of their potential applications to color flat panel displays and in new optoelectronic components. These devices are assembled using three organic molecular materials: an electron injection layer, the emitting one and finally the hole injection layer. However, in most cases the electron injection is more difficult to achieve than hole injection. In this work two different diamond like carbon (DLC) thin films cathode were used to decrease the electron injection barrier. The first kind were nitrogen-doped amorphous hydrogenated hard carbon films deposited by rf glow discharge from methane-nitrogen mixtures onto the TPD/$Alq_3$ layer structure thermally deposited. DLC films were obtained for different $N_2$ partial pressures (bias voltage $V_b$=â€“370 V and total pressure P=8 Pa). Next, amorphous carbon nitride thin films (a-$CN_x$) have been deposited using a rf diode sputtering system onto the same organic structure. In this case the DLC films were deposited in reactive nitrogen-argon atmospheres. The partial pressure of nitrogen ranged from 0% to 100% at two different deposition pressures (P = 2 Pa and P = 8 Pa). In both cases a thick (150 nm) aluminum electrode were deposited onto the whole structure. The deposition process for the organic compounds is performed in high vacuum environment ($6x10^{-6}$ Torr) on glass substrates coated with an hole injecting ITO transparent layer. A preliminary investigation was conducted on the properties of the OLED device with the two DLC intermediate layers. The relationship between the properties of the DLC deposited films on the electroluminescent characteristics of the different devices are investigated. The refractive index of the DLC film deposited, their conductivity and optical absorption, the OLED I-V curves, a preliminary photoluminescent and electroluminescent OLED results are presented and discussed.

10:20am **OF+EL+SS+SC-WeM7 Self-assembly of Molecular 1D wires on Cu(110)**, ***Y. Naitoh***, *F. Rosei, P. Thostrup, M. Schunack, F. Besenbacher*, University of Aarhus, Denmark

The adsorption of a large organic $C_{90}H_{98}$ molecule, known as the Lander molecule, is studied by Scanning Tunneling Microscopy (STM) on a Cu(110) surface.[1] By exposing the surface to low doses of oxygen at elevated temperatures, we form a nanopattern of alternating bare Cu(110) regions and (2x1)-O reconstructed regions aligned parallel to the [001] direction. The oxygen-induced reconstruction reveals a long-range ordering of Cu-O rows 20-50 Å wide. When deposited on this template, Lander molecules adsorb preferentially on bare Cu regions. By tuning the oxygen dosing, thereby adjusting the lateral periodicity of the template, and by varying molecular coverage in a controlled manner we can form long 1D rows of molecular wires. This type of assembly opens new possibilities for ordering organic molecules on surfaces.

[1] F. Rosei et al., Science 296, 328 (2002).

### 10:40am **OF+EL+SS+SC-WeM8 Dip Pen Nanolithography on Insulating Substrates**, ***S.E. Kooi***, *P.E. Sheehan*, *L.J. Whitman*, Naval Research Laboratory

Methods of assembling nanoscale components at chosen locations on a surface are needed to produce nanoscale electronic and sensor devices. Dip pen nanolithography (DPN) has been successful in producing such features as small as ~10 nm wide and one monolayer thick in several different molecule - surface combinations. The most studied systems have been alkyl and aryl thiol depostion on gold surfaces; however, DPN has also been demonstrated for inorganic salts on silicon, biomolecules on gold, and silazanes on semiconductor surfaces. We explore the application of DPN to write functional molecules on a technologically important insulating surface, namely silicon oxide. We have written several different trichlorosilane molecules directly onto thermally-grown silicon oxide substrates. By choosing an appropriate trichlorosilane and post-deposition chemical modification of the written molecules, we can direct the deposition of other nanostructures (such as carbon nanotubes, semiconducting nanowires, or nanoparticles). For example, by writing 10-undecenyltrichlorosilane onto silicon oxide, we can create a terminal carboxylic acid group with a post-deposition chemical oxidation. Subsequent deprotonation of the patterned carboxylic acid groups produces a negative charge that directs the deposition of positively-charged nanostructures. The ability to place nanoscale components at chosen locations on a surface, in combination with traditional (e-beam) lithographic techniques, opens up the possibility of interfacing nanoscale components with traditional devices.

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