

# Tuesday Afternoon, November 1, 2011

## Surface Science Division

Room: 110 - Session SS+EM-TuA

## Organic Electronic Interfaces

Moderator: J.R. Engstrom, Cornell University

2:00pm **SS+EM-TuA1 The Effect of Structure on Interfacial Energy.**  
*F. Stellacci*, EPFL, Switzerland **INVITED**

In this talk I will highlight recent result on solid-liquid interfaces where the solid has a nanostructure with a characteristic length scale that is only a few liquid molecule wide. The talk will start with the presentation of a new scanning probe technique able to measure interfacial energy (work of adhesion to be precise) with atomic/molecular resolution. It will then show how surfaces with alternating stripe-like domains a few nanometer thick have a structural component to their work of adhesion that can account for as much as 20% of the total energy. Finally novel self assembly approaches to achieve such surfaces will be discussed.

2:40pm **SS+EM-TuA3 Interfacial Electronic Structure of Dipolar Organic Semiconductors.** *O.L.A. Monti, M.P. Steele, N. Ilyas, L.L. Kelly, D.A. Rucke*, University of Arizona

We present an investigation of the evolution of the electronic structure at the interface of the dipolar organic semiconductor vanadyl naphthalocyanine with both highly oriented pyrolytic graphite and Au (111). Using angle-resolved two-photon photoemission and other photoelectron spectroscopies we observe both excitonic as well as strictly interfacial states in both ground and excited state manifolds, with large differences between the two surfaces. Simple electrostatic considerations provide a chemisorption model that is capable of quantitatively describing long- and short-range interface-mediated intermolecular coupling, significantly altering the molecular electronic structure. Additional insights are available from full-scale first-principles calculations at these interfaces. As a consequence, we show that electrostatic multipoles can significantly influence molecular and interfacial electronic structure, with direct and observable impact on interfacial charge-transfer dynamics. Interfacial electrostatic fields may therefore be used to manipulate in a concrete fashion processes of critical importance to solar energy conversion such as photoinduced interfacial electron transfer.

3:00pm **SS+EM-TuA4 Characterization of Quinonoid Zwitterion Molecular Films on Metal Surfaces.** *L. Routaboul, P. Braunstein*, Lab. de Chimie de Coordination (UMR 7177 CNRS), France, *B. Doudin*, Inst. de Phys. et Chimie des Mat. de Strasbourg, France, *J. Xiao, Z. Zhang*, Nebraska Ctr. for Mat. & Nanosci., *Y.B. Losvyj, O. Kizilkaya*, The J. Bennett Johnston Sr. Ctr. for Adv. Microstructures & Devices, *L.G. Rosa*, Univ. of Puerto Rico-Humacao, *P.A. Dowben*, Nebraska Ctr. for Mat. & Nanosc.

There is considerable interest in the functionalization of metal surfaces by molecules with large dipoles. For this purpose, *p*-benzoquinonemonimine-type zwitterions represent ideal candidates. These zwitterions can be anchored on gold surfaces where they form homogeneous thin films with the dipole preferentially oriented along the surface normal.<sup>[1]</sup> Some zwitterions will selectively adsorb on patterned gold substrates from solution while selective deposition of the zwitterions onto specific ferroelectric domains has been demonstrated. This represents an attractive approach to pattern molecular deposition on optically transparent planar substrates through electrostatic dipolar interactions or orientation dipole controlled surface chemistry. Taking advantage of the high solubility of two zwitterions in both organic solvents and water, we studied the influence of the solvent on the functionalization of surface.<sup>[2]</sup> The goal is to control both packing and selective deposition on a variety of substrates through zwitterion solvent combination.

**Acknowledgement.** This research was supported by the CNRS and the Ministère de la Recherche et des Nouvelles Technologies, the ANR (07-BLAN-0274-04), the National Science Foundation (grants CHE-0909580 and DMR-0851703), and the Nebraska Center for Materials and Nanoscience at the University of Nebraska-Lincoln.

4:00pm **SS+EM-TuA7 Directed Organization of C<sub>70</sub> Kagome Lattice by TiOPc-Monolayer Template.** *J.E. Reutt-Robey, Y. Wei*, University of Maryland

Abrupt molecular semiconductor interfaces between titanyl phthalocyanine (TiOPc) and C<sub>70</sub> were prepared by physical vapor deposition and characterized by UHV-STM. Molecular TiOPc is a highly anisotropic

molecule with a 3.5 dipole moment. Ordered TiOPc monolayer films of the honeycomb phase thus represent a regular 2-d dipolar lattice, which was investigated as an electrostatic template for the growth of the highly polarizable C<sub>70</sub>. Films of C<sub>70</sub> grown layer-by-layer revealed the directed formation of a Kagome lattice. Atomically detailed structural models were obtained for the 0-6 nm C<sub>70</sub> thickness (up to 5 ML) range over which the ordering influence of the TiOPc dipolar substrate persists. Unusually low-density C<sub>70</sub> molecular packing arrangements result from the ellipsoidal shape, curved surfaces and high polarizability of C<sub>70</sub>. While Kagome lattices have been frequently observed in colloidal and magnetic systems, this appears to be the first electrostatically-induced Kagome lattice involving a molecular film.

This work has been supported by the National Science Foundation under Surface Analytical Chemistry grant CHE0750203 and under the University of Maryland MRSEC DMR-05-20471

4:20pm **SS+EM-TuA8 Solvation - Assisted Growth of ZnPc and 4NO<sub>2</sub>-ZnPc Monolayer Films on Au(111).** *L. Tskipuri, Q. Shao, J.E. Reutt-Robey*, University of Maryland, College Park

The UHV spray-jet molecular beam deposition technique marries the chemical versatility and efficiency of solution-film processing with the atomic-level control and analytical tools of UHV surface science. Here we show how the solvent used in aerosol deposition can be used to fine tune film morphology. Thin films of ZnPc and 4NO<sub>2</sub>-ZnPc are grown on a Au(111) support with a newly developed spray-jet molecular beam deposition source and characterized in situ via UHV-STM. Phthalocyanines are delivered to the Au(111) surface in a series of N<sub>2</sub>-entrained μ-sized solvent droplets of variable surface residence time. The formation of submonolayer films with corresponding density variations demonstrates the impact of the ~nm-thick solvation layers on growth kinetics. Phthalocyanine film registration to the herringbone reconstruction of the Au(111) substrate, indicative of thermodynamically-favored structure, is observed only for aromatic solvents with long residence times. Vacancy cavities in monolayer films from solvent memory are eliminated with mild annealing, yielding film structures that rival PVD grown films. Results are interpreted through solvation-mediated kinetics.

4:40pm **SS+EM-TuA9 Direct Observation of NO<sub>2</sub> Adsorption onto CuPc Monolayers with STM.** *J.H. Park, J. Royer, S. Lee, T. Kent, W. Trogler, A.C. Kummel*, University of California San Diego

Copper phthalocyanine (CuPc) thin film devices have been widely studied for use as chemical vapor sensors; however, the molecular scale sensing mechanism remains undetermined. This study presents molecular scale observation of NO<sub>2</sub> adsorption onto CuPc monolayers using ultra-high vacuum (UHV) scanning tunneling microscopy (STM). CuPc monolayers were deposited on Au (111) surfaces by organic molecular beam epitaxy in ultra-high vacuum (UHV) and subsequently exposed to different NO<sub>2</sub> concentrations at atmospheric pressure. After annealing at 50 °C to improve STM imaging, for low NO<sub>2</sub> doses (1 ppm for 5min) the STM images reveal NO<sub>2</sub> molecules arranged as islands primarily along the domain boundaries. The NO<sub>2</sub> molecules almost completely desorb from the CuPc monolayer after annealing at 100 °C for 1 hr. Conversely, at high NO<sub>2</sub> doses (10 ppm for 5 min), the NO<sub>2</sub> exhibit irreversible reactions with the CuPc surface. After annealing at 50 °C, the domain boundaries act as nucleation centers for semi-ordered NO<sub>2</sub> adsorbates. As the annealing temperature is increased to 150 °C, the islands of NO<sub>2</sub> molecules diffuse from the domain boundaries to the CuPc terraces to form ordered structures on the terraces. After annealing at 250 °C for 1 hr, the CuPc monolayer becomes disordered and has numerous vacancies. The data is consistent with that NO<sub>2</sub> inducing CuPc decomposition. The behavior of NO<sub>2</sub> dosed CuPc monolayers suggests that NO<sub>2</sub> undergoes molecular chemisorption with the CuPc metal center at low exposures. However, at high exposures, NO<sub>2</sub> not only undergoes molecular chemisorption with the metal center, but also induces decomposition of the CuPc. This direct observation for NO<sub>2</sub> dosed CuPc monolayers with STM can give an insight into reversible versus dosimetric sensing in CuPc organic thin film chemical sensors (chemFETs). While nearly all weakly bonding analytes give reversible mobility sensor responses on CuPc chemFETs, some strong oxidants are observed to give reversible mobility responses at short exposures and dosimetric irreversible threshold voltage responses for longer exposures. This is consistent with the larger doses saturating the reversible chemisorption sites and inducing an oxidative decomposition of the CuPc which induces a dosimetric response via formation of uncompensated positive charge in the CuPc film. Therefore, the data is consistent with two chemisorption mechanisms of a strong oxidant on a single molecule given two different classes of sensor response.

5:00pm **SS+EM-TuA10 Tunneling Spectroscopy of Benzoic Acid Monolayers: The Role of the Metal-Molecule Interface.** *J. Kreil, P. LeClair, G.J. Szulczewski*, The University of Alabama

A series of self-assembled monolayers were prepared from para-substituted benzoic acids ( $X-C_6H_5CO_2H$  where  $X = H, F, Cl, Br, I,$  and  $CN$ ) onto oxidized Al films and characterized by x-ray photoelectron spectroscopy and contact angle measurements. The acids adsorb to the oxide as a carboxylate group with the plane of the aromatic ring largely perpendicular to the surface, which places the para-substituent away from the surface. Tunnel junctions were made by vapor deposition of Ag and Pb films as the top electrodes onto the monolayers. Four point probe electrical measurements were made from 4 to 300K. At 4 K the superconducting gap of Pb was observed and unequivocally demonstrates tunneling through a barrier without metallic shorts. When Ag was the top electrode, differential conductance [ $G(V) = dI/dV$ ] measurements at 4 K showed a quadratic dependence on the applied bias voltage and no zero-bias anomalies. These low temperature measurements suggest the monolayers form pin-hole free tunnel barriers. Two trends emerge when comparing  $G(V)$  versus bias voltage for junctions with Ag and Pb top electrodes. When Pb was the top electrode the minimum in  $G(V)$  versus bias voltage is offset from zero bias for each monolayer, which scales in a systematic manner with the polarity of the para C-X bond. However, when Ag was the top electrode there was no offset the tunneling conductance. The origin of the different tunneling behavior observed for Pb and Ag top electrodes will be discussed in detail.

5:20pm **SS+EM-TuA11 Interfacial Engineering of Organic Light Emitting Diodes with Sputter Treated Molybdenum Oxides as Hole Injection Layers.** *C.I. Wu, P. Wang, I. Wu*, National Taiwan University, Republic of China

In this paper, the mechanisms leading to the enhancement of organic light emitting diodes (OLEDs) with molybdenum oxide  $MoO_3$  incorporated in as hole injecting layers (HILs) will be discussed. The first one is the lowering of hole injection barrier between anodes and organic layers when a thin film of  $MoO_3$  is inserted. The high work function of  $MoO_3$  serves as a carrier ladder which decreases misalignment between the Fermi level of electrodes and highest occupied molecular orbital (HOMO) level of hole transport layers, such as  $N,N'$ -di(naphthalene-1-yl)- $N,N'$ -diphenyl-benzidine (NPB). The second model is the formation of gap states above the valence band edge of  $MoO_3$  to the Fermi level of electrodes when NPB molecules are deposited on  $MoO_3$  layers. These gap states enhance the conductivity of  $MoO_3$  and provide transition paths of carrier to assist the injection of hole from indium tin oxide (ITO) anodes to NPB layers. The third mechanism is the p-type doping effect of  $MoO_3$  doped in NPB layers. This p-type doping increases hole concentration in NPB layers and reduces the energy difference between the Fermi level of electrodes and the HOMO of NPB.

We will also demonstrate an effective method to improve the current injection efficiency of OLEDs by modifying the oxidation states of as-deposited  $MoO_3$  as HILs with in-situ argon ion ( $Ar^+$ ) sputtering. The injection current of devices incorporating this method is enhanced by one order of magnitude, as compared to that of devices without sputter treatment. The luminance of the devices is also improved. Beside device characterization, X-ray photoemission spectroscopy (XPS) and ultra-violet photoelectron spectroscopy (UPS) were carried out to obtain the chemical and electronic information of  $MoO_3$  thin films treated with  $Ar^+$  sputter and to unveil the origins of improvement in device performance. It is found that, with slight sputter treatments,  $MoO_3$  layers represent lower oxidation states and show metallic characteristics in energy band structure, which remarkably elevates the carrier injection efficiency from ITO to NPB.

5:40pm **SS+EM-TuA12 Probing Surface Photovoltage Development by Dynamical XPS Measurements.** *S. Suzer*, Bilkent University, Turkey

Various semiconducting, photoactive and insulating materials have been investigated using XPS where the data is collected in a dynamic mode. This is achieved by recording the spectrum while applying an electrical signal in the form of  $\pm 5$  or 10 V d.c. bias, and/or square-wave pulses, without and under photoillumination using different lasers. This method enables us to probe and sort out the effects and contributions of the three fundamental processes operating; *Charging, Photovoltage-Development, and Photoconductivity* in a *chemically specific fashion*. Accordingly, the chemical shift differences between the n- and p-doped semiconductors are amplified due to the effect of the photovoltage operating in the opposite directions. Time and/or frequency dependence of various processes adds a new dimension to XPS for sorting out the effects of external stimuli (electrons, ions, photons, etc.) as well as the chemical nature of the material under investigation. Experimental results and various applications will be presented and discussed.

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