

Wednesday Afternoon, October 22, 2008

Surface Science

Room: 209 - Session SS2-WeA

Electrons and Electronic Spectra at Surfaces

Moderator: R.M. Osgood, Columbia University

1:40pm **SS2-WeA1 Electron Dynamics at a Metal-Organic Interface**, *C.H. Schwab, M. Marks*, Philipps University Marburg, Germany, *S. Sachs, A. Schöll, F. Reinert*, University Würzburg, Germany, *E. Umbach*, Forschungszentrum Karlsruhe, Germany, *U. Höfer*, Philipps University Marburg, Germany

The injection of charge carriers at a molecule-metal interface plays a decisive role in the performance of organic semiconductor devices. Especially new electronic states that may develop due to the interaction of the adsorbed molecules with the metal substrate can alter the injection mechanisms drastically. We present a recent study for a well characterized model system of epitaxial 3,4,9,10-perylene tetracarboxylic acid dianhydride (PTCDA) thin films on a Ag(111) substrate. Two-photon photoemission (2PPE) displays a dispersing unoccupied state between the metallic Fermi level and the lowest unoccupied molecular orbitals (LUMO) of PTCDA with an effective electron mass of 0.39 m_e at the Γ -point. Its energetic position in the band gaps of both the Ag(111) substrate and the PTCDA overlayer identify it as a genuine interface state, a result that is corroborated by model calculations. Time-resolved measurements show that the lifetime of electrons excited into this interface state is 55 fs. This is a relatively small value for an unoccupied state located only 0.6 eV above the Fermi level and is indicative for a large penetration of the wavefunction into the projected sp-gap of Ag(111). In order to investigate the role of the interface state for carrier transport between the organic semiconductor and the metal we populate the LUMO of PTCDA by absorbing 2.4 eV photons in films of varying thickness up to 100 ML and simultaneously record fluorescence and angle-resolved photoemission spectra. We observe a long lived component in the 2PPE intensity close to the Fermi level which clearly correlates with film thickness and fluorescence lifetime.

2:00pm **SS2-WeA2 Electronic Structure and Charge Separation at a Planar Molecular Heterojunction Probed by Two-Photon Photoemission**, *G. Dutton, D.B. Dougherty, S.W. Robey*, National Institute of Standards and Technology, *W. Jin, W.G. Cullen, J.E. Reutt-Robey*, University of Maryland, College Park

The molecular donor-acceptor interface performs a critical function in the operation of organic photovoltaics as the sole site of charge separation. Understanding the electronic structure and exciton/polaron dynamics at these interfaces is crucial for developing the understanding of the relevant diffusion, dissociation and recombination processes necessary for achieving enhanced efficiencies. We have employed photoemission techniques, primarily two-photon photoemission spectroscopy (2PPE) and time-resolved pump-probe measurements, to examine these issues for thin organic films and heterointerfaces of pentacene and copper phthalocyanine with C60 fullerene. This talk will concentrate on results for interfaces between copper phthalocyanine and C60 formed on Ag(111). Using a combination of visible 1.75eV pump, corresponding to the phthalocyanine Q-band absorption maximum, and 5.25eV UV probe, we observe the ultrafast population dynamics of the C60 LUMO electron-polaron at 0.3 eV above the Fermi level. Preliminary analogies of corresponding physical molecular structures at this interface will also be presented based on STM results for the similar zinc phthalocyanine:C60 interface.

2:20pm **SS2-WeA3 Quantitative Three-dimensional Spin-Polarimetry in ARPES**, *J. Osterwalder*, University of Zurich, Switzerland, *H. Dil, F. Meier*, University of Zurich and Paul-Scherrer-Institut, Switzerland, *J. Lobo*, University of Basel, Switzerland, *L. Patthey*, Paul-Scherrer-Institut, Switzerland

INVITED

An angle-resolved photoelectron spectrometer has been equipped with a full three-dimensional spin polarimeter by using two orthogonal Mott detectors.¹ The unique capability of the instrument has made it possible to introduce a new two-step fitting routine that provides absolute spin polarization vectors for each individual band intersected in a particular ARPES spectrum or momentum distribution curve.² This procedure is crucial when analyzing strongly overlapping peaks or weak signals sitting on a large unpolarized background. It is robust against strong intensity variations due to matrix element effects because it references the spin polarization contribution of each band to the measured peak intensity. The method is applied to two-dimensional systems where spin-orbit effects lead to complex momentum-dependent spin structures.³ Two prototypical

systems, Bi/Ag(111) ($\sqrt{3}\times\sqrt{3}$)R30° and Pb/Ag(111) ($\sqrt{3}\times\sqrt{3}$)R30° were investigated. We confirm that the surface states experience a large spin splitting. Moreover, we find that all surface states are 100% spin polarized, and that for some states, spin polarization vectors rotate out of the surface plane. With the photoelectron spin as an additional tag in the measurement, spin-split bands with splittings far below the measured line width can be resolved. This has allowed us to see such splittings in quantum well states within ultrathin Pb layers on Si(111). Comparable to surface states, the space inversion symmetry is broken in these films, and the spin degeneracy of the valence electrons is lifted. The effect is much smaller though, and we measure energy splittings as small as 15 meV.

¹ M. Hoesch et al., J. Electron Spectrosc. Relat. Phenom. 124, 263 (2002).

² F. Meier et al., Phys. Rev. B 77, 165431 (2008).

³ S. LaShell et al., Phys. Rev. Lett. 77, 3419 (1996); M. Hoesch et al., Phys. Rev. B 69, 241401 (2004).

3:00pm **SS2-WeA5 A New Spin on Chirality: Reactions Induced by Polarized Secondary Electrons from a Magnetic Substrate¹**, *R.A. Rosenberg, M.J. Abu Haija*, Argonne National Laboratory, *P.J. Ryan*, MUCAT, Ames Laboratory

Since nearly all biological compounds are homochiral, any model of the origin of life must be able to incorporate a mechanism that could lead to preferential chirality. Since chiral molecules have a certain handedness, many researchers have investigated the possible influence of circularly polarized UV photons and longitudinal spin-polarized electrons in creating an enantiomeric excess.²⁻⁴ However, in general the demonstrated effects have been small and/or on the order of the experimental error. In the present work we hypothesize that a previously unappreciated source may play a role in chiral-selective chemistry: low-energy (0-20 eV) spin-polarized secondary electrons, produced by photon,⁵ electron,⁶ or ion⁷ irradiation of a magnetic substrate. To test this theory we have performed detailed x-ray photoelectron spectroscopy measurements of the reaction rate for x-ray induced, secondary electron photolysis of a model chiral compound, R- or S-2-Butanol, adsorbed on a magnetized permalloy (Fe_{0.2}Ni_{0.8}) substrate. Our results show an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chirality of the molecule and the spin polarization of the secondary electrons. Not only do our results demonstrate a chirality enhancement well above that of most previous work, but, since this mechanism only requires a magnetic substrate and ionizing radiation, it should be viable in a wide variety of possible prebiotic environments.

¹This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357.

²M. Avalos et al., Chem. Rev. 98, 2391 (1998).

³W. A. Bonner, Orig. Life Evol. Biosph. 25, 175 (1995).

⁴P. Ehrenfreund et al., Rep. Prog. Phys., 1427 (2002).

⁵E. Kisker, W. Gudat, and K. Schroder, Solid State Comm. 44, 591 (1982).

⁶J. Unguris et al., Phys. Rev. Lett. 49, 72 (1982).

⁷R. Pfandzelter et al., Phys. Rev. B 68, 165415 (2003).

4:00pm **SS2-WeA8 The Temperature-Dependent Dynamic Solvation of Excess Electrons at the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide/Ag(111) Interface**, *M.L. Strader*, Max Planck Institut für Metallforschung, Germany

Interest in room temperature ionic liquids (RTIL's) has increased rapidly in the last decade, fueled by the potential of RTIL's as environmentally friendly 'designer solvents'. The unusual, highly ionic character of RTIL's has motivated study of their fundamental physical properties. The dynamic solvation responses of various RTIL's have been studied in bulk, and extension of study to the interface could prove useful to electrochemical applications. Two-color, angle-resolved, two-photon photoemission (AR-2PPE) has been used to study interfacial solvation dynamics in ultrahigh vacuum (UHV) for a number of systems. Thin films of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide were epitaxially grown on Ag(111) and studied with AR-2PPE. The well-known low vapor pressures of RTIL's afford the rare opportunity to study interfacial solvation dynamics at electrochemically relevant temperatures in the liquid phase. A pronounced increase in solvation at elevated temperatures is observed.

4:20pm **SS2-WeA9 Novel Acoustic Plasmons on Metal Surfaces**, *K. Pohl, B. Diaconescu*, University of New Hampshire, *G. Vercelli, L. Vattuone, M. Rocca*, CNISM, IMEM-CNR and Università di Genova, Italy

The recent discovery of a fundamentally new sound-like plasmon on a bare metal surface of beryllium may introduce a new research direction in the area of plasmonics.¹ While conventional surface plasmons are optical modes and have a finite excitation energy of a few eV, the novel acoustic mode can be excited with very low energies of a few meV. This allows, in principle, for a coupling with visible light for signal processing and

advanced microscopies as well as new catalysts on metallic surfaces. In order to show that this novel excitation is a general phenomenon on closed-packed noble metal surfaces, as predicted by our theoretical collaborators,² we have measured the dispersion of the acoustic surface plasmon on Cu(111) by electron energy-loss spectroscopy for a parallel momentum-transfer range from 0 to 0.20 1/Å. We can report that the dispersion is indeed linear (acoustic) with a slope (sound velocity) in good agreement with theory,² and energy values that extend up to 1 eV. We will show that the novel acoustic surface plasmon, ASP, is a general phenomenon on metal surfaces that support a partially occupied surface state within a wide bulk energy gap. It is caused by the non-local screening of the surface electrons due to bulk electron. The adsorption of about 0.25 ML of oxygen on the surface removes the surface state on Cu(111) and indeed destroys the ASP.

This work was supported in parts by the NSF under Grant No. DMR-0134933 and DMR-0753467, by the visiting scholar program of CNISM and by Compagnia S. Paolo.

¹B. Diaconescu, K. Pohl, L. Vattuone, et al., *Nature* 448, 57 (2007).

²V.M. Silkin, J.M. Pitarke, et al. *Phys. Rev. B* 72, 115435 (2005).

4:40pm SS2-WeA10 Exploring Adsorption through Surface Resistivity Measurements, *C. Liu, R.G. Tobin*, Tufts University

Surface resistivity – the increase in the electrical resistivity of a thin metal film due to surface defects or impurities – is a simple and readily measured property that provides a window into complex nonequilibrium surface processes. It originates in the diffuse scattering of the metal's conduction electrons by the localized potential created by the surface modification, and depends in complicated fashion on the local electronic structure of the scatterer. The variation of surface resistivity with coverage, for both single adsorbates and coadsorption systems, gives insight into the effects of surface defects and neighboring adsorbates on the electron-scattering probability. We report on several surface resistivity studies that reveal different aspects of adsorption. All are carried out on 50 nm thick epitaxial Cu(100) films grown on H-terminated Si(100) substrates. CO adsorption on these films exhibits striking differences in electron-scattering cross section for adsorption on different sites, with CO on defect sites exhibiting near-zero net scattering.¹ Studies of oxygen and sulfur adsorption reveal the effects of interadsorbate interactions. Individually adsorbed oxygen and sulfur show very different coverage-dependences, with oxygen atoms acting as independent non-interacting scatterers while at high coverages sulfur strongly suppresses scattering by nearby sulfur atoms.² Sulfur has a similar effect on coadsorbed oxygen, reducing its effective scattering cross-section essentially to zero when the two atoms are adsorbed on adjacent lattice sites.³ We suspect that the apparently zero differential resistivity observed for defect-bonded CO and for adsorption of O or S near a pre-adsorbed sulfur atom results not from zero electron scattering by the added adsorbate but from cancellation of the new adsorbate's added scattering by a reduction in scattering from the defect site or preadsorbed sulfur. These results can be analyzed qualitatively in terms of the behavior of adsorbate-derived orbitals near the Fermi level.

¹ C. Liu and R.G. Tobin, *J. Chem. Phys.* 126, 129705 (2007).

² R.G. Tobin, *Surf. Sci.* 524, 183 (2003).

³ C. Liu and R.G. Tobin, *J. Chem. Phys.*, in press.

5:00pm SS2-WeA11 Dependence of Surface Properties on Adsorbate-Substrate Distance: Work Function Changes and Binding Energy Shifts for I/Pt(111), *P.S. Bagus*, University of North Texas, *Ch. Wöll*, Ruhr Universität Bochum, Germany, *A. Wieckowski*, University of Illinois at Urbana-Champaign

A detailed analysis of the character of the bond of I adsorbed at on-top and three-fold sites of Pt(111) is presented. At both sites, the bonding is dominated by an ionic interaction supplemented with some covalent character due to donation from the adsorbed I anion to Pt. The way in which the I-Pt interaction affects observed properties, including the anomalous work function changes induced by the adsorption of I and the shifts of I core level binding energies, will be described. The surprising fact that a negatively charged adsorbate leads to a work function decrease, rather than the increase expected solely due to the charge of the adsorbate, arises from electronic reorganizations that cancel the dipole due to the charged adsorbate.¹ Furthermore, the contributions that lead toward an interface dipole that lowers the work function are larger as the adsorbate moves closer to the surface. Thus, the magnitude of the change in the interface dipole can be directly correlated with the distance of the I adsorbate from the Pt surface. A similar distance dependence is also found for the shifts of the I core level binding energies. In effect, these shifts can be interpreted to indicate adsorbate height. In particular, the shifts provide a new way to distinguish I adsorption at on-top and three-fold sites of Pt(111) since the distance of I from Pt(111) is different for these two sites. Furthermore, the effects important for the shifts of the interface dipole in the simpler case of I/Pt are also relevant for the charge transport barrier between a metal substrate and an organic adsorbate.² Thus the distance dependence demonstrated here for I/Pt may also provide information helpful for understanding these more complex systems.

¹ P. S. Bagus, D. Käfer, G. Witte, and C. Wöll, *Phys. Rev. Lett.*, 100, 126101 (2008).

² G. Witte, S. Lukas, P. S. Bagus, and C. Wöll, *Appl. Phys. Lett.*, 87, 263502 (2005).

5:20pm SS2-WeA12 Influence of Quantum Well States on Apparent Tunneling Barrier Height in Ultra Thin Pb Films, *J.D. Kim, S.Y. Qin, C.K. Shih*, The University of Texas at Austin

The thickness dependence of tunneling decay constant (κ) for ultra thin Pb films is studied with various sample biases by using low temperature STM. It is found that quantum well states (QWS) have a strong influence on κ . While the decay constant versus layer thickness (κ vs. L) clearly shows bilayer oscillations, we found that the apparent contrast in κ vs. L also show strong bias dependence. This result shows that κ -oscillation does not necessarily imply the work function oscillation. We further show that in this case, the parallel component of crystal momentum plays a critical role in tunneling process and is largely responsible for the observed phenomena. On the other hand, at large negative sample bias, the measured decay constants show less bias dependent. Nevertheless, at small negative biases (less than 0.3 V below), the measured κ is strongly influenced by location of QWS near Fermi energy.

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