

Wednesday Morning, October 20, 2010

Energy Frontiers Topical Conference
Room: Mesilla - Session EN+NS-WeM

Organic Photovoltaics

Moderator: R.J. Holmes, University of Minnesota

8:00am **EN+NS-WeM1 Interface Properties between Organic Blend Films and Metallic Substrates for Solar Cell Applications.** *L. Lozzi, S. Santucci*, University of L'Aquila, Italy

In the last years a strong effort has been devoted to develop new solar cells based on organic compounds. These organic compounds can be mixed with other molecules, as, for example fullerene or its derivatives, forming a blend film to increase the charge separation efficiency. An important issue to evaluate the properties of these devices is to investigate the interface properties between these films and the metallic substrates generally used to realize the contacts.

In this work we have analysed, by using the photoemission spectroscopy (X-ray, Soft X-ray and Ultraviolet photons) the core levels and the valence band structures, in particular the HOMO states, of copper phthalocyanine (CuPc) and fullerene (C₆₀) blend films, composed by different CuPc:C₆₀ concentrations, deposited onto several metallic substrates (Au, oxidized Al and ITO), generally used as metallic contacts.

The molecular levels show, as a function of the blend film thickness and composition, a different behaviour depending on the substrate type. On Au the organic molecular level show, as the blend film thickness increases, a shift towards high binding energy. This shift depends on the organic composition. Depositing the blend film onto oxidized Al, a small shift in the opposite direction, i.e. towards lower binding energy, has been observed. Instead, when ITO substrate have been used, no shift have been observed.

The core levels generally show a different behaviour with respect to the molecular levels suggesting that no strong interaction with the substrates exist but a small redistribution of the molecular levels is present.

8:20am **EN+NS-WeM2 Energy Level Alignment at Conductive Polymer/Metal Interfaces.** *M.M. Beerbom, W. Wang, R. Schlaf*, University of South Florida

8:40am **EN+NS-WeM3 Electronic Structure of Key Interfaces in Organic Photovoltaic Cells.** *A. Kahn*, Princeton University **INVITED**

This talk reviews recent work on two types of interfaces that are important for organic photovoltaic cells. In the first part, we present the first direct determination via ultra-violet and inverse photoemission spectroscopy (UPS, IPES) of molecular level alignment between donor (D) and acceptor (A) in a bulk heterojunction.[1] We take the example of the interface between poly(3-hexyl thiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). The P3HT/PCBM blend is a standard, prototypical system for bulk heterojunction organic photovoltaic (OPV) cells. In question here is the relative position of the molecular levels of the donor (D) and acceptor (A) materials in the blend, given that LUMO(D) - LUMO(A) is linked to the charge separation process, and LUMO(A) - HOMO(D) is linked to the open circuit voltage (V_{oc}) of the OPV cell. A precise measurement of these molecular level offsets provides a firm basis for the accurate modeling of V_{oc} produced by these cells. The second part of the talk looks at the electronic structure of transition metal oxide films, such as MoO₃ or WO₃, and their role as hole-collecting electrode or central element of a charge recombination layer (CRL) in a tandem solar cell. Recent work has shown that these compounds exhibit exceptionally large electron affinity and work function.[2,3] N-doped by oxygen vacancies, they can act as efficient high work function hole-extractor (via electron injection through their conduction band) on the anode side of the solar cell. Similarly, combined with a low work function interlayer electrode, they form the central element of a CRL in a tandem cell.

[1] Z. Guan, J. Kim, Y.-L. Loo, and A. Kahn, *Org. Electr.* (submitted)

[2] M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, and A. Kahn, *Appl. Phys. Lett.* **95**, 123301 (2009)

[3] J. Meyer, M. Kröger, S. Hamwi, T. Riedl, W. Kowalsky and A. Kahn, *Appl. Phys. Lett.* (in press, 2010)

9:20am **EN+NS-WeM5 Photocarrier Generation and Transport Characteristics in Organic Heterojunction Solar Cells.** *J.D. Myers, W.T. Hammond, J.P. Mudrick, J. Xue*, University of Florida

There have been many recent advances in improving the efficiency of organic photovoltaics (OPVs) by using new organic active materials and/or

employing improved device architectures. However, our understanding of fundamental OPV device operation principles is still incomplete. A new measurement technique for OPVs, synchronous photocurrent measurement, can give insight into the generation and transport characteristics of photogenerated charge carriers. In synchronous photocurrent measurements, a device is illuminated with chopped monochromatic light in addition to a constant white light bias with an intensity close to 1 sun. With the device biased at any given voltage, the current of the OPV is fed into a lock-in amplifier, which extracts the relevant photocurrent response to the monochromatic light with a varying wavelength.

With this technique, we have shown the bias dependence of the photocurrent for various small-molecule device structures. In planar (or bilayer) and planar-mixed organic heterojunctions (HJs), the photocurrent under forward bias is negative (flowing from the cathode to the anode, opposite to the direction of the dark current), up to high forward biases (~1 V), well in excess of the built-in potential. This reveals the surprisingly dominant nature of the diffusion photocurrent in these architectures. However, for mixed HJ cells, the photocurrent reverses direction at a certain forward bias with the reversal of directions for the electric field and the drift current inside the active layer. There exists a strong correlation between the zero-photocurrent voltage and charge generation profile in mixed HJ OPVs.

This technique can also determine the relative contributions of field-induced exciton dissociation and donor-acceptor interface exciton dissociation in planar HJ cells. Traditionally, exciton dissociation in planar HJ cells is assumed to occur almost exclusively at the donor-acceptor interface; field-induced dissociation is taken as a negligible contributor to the photocurrent in these devices. However, as the thickness of an active layer (either donor or acceptor) increases, field-induced dissociation becomes more important. The field-induced contribution increases as the average location of exciton generation moves greater than one exciton diffusion length away from the interface, as demonstrated by using optical field simulations.

We have further used photocurrent measurements as an instrument in analyzing the recombination behavior in planar organic HJs utilizing different materials. Synchronous photocurrent measurement is a useful technique in determining the photocarrier behavior in organic HJ solar cells.

9:40am **EN+NS-WeM6 Interface Engineering for Improved Organic Photovoltaic Performance.** *C.K. Chan, D.S. Germack, P. Haney, L.J. Richter, D.M. DeLongchamp, D.J. Gundlach*, National Institute of Standards and Technology

Organic photovoltaic (OPV) cells are attractive for flexible, low-cost, large-area, and lightweight solar conversion applications. Despite this demand, robust and efficient devices have been limited by the quality of organic semiconductor materials and by the poor understanding and control of their interfaces. Interface modification using self-assembled monolayers or conducting polymers can be leveraged to tune the composition and phase segregation in binary bulk heterojunction photovoltaic cells. In this work, the interface composition of a 1:1 mixture of poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric-acid-methyl-ester (P3HT:PCBM) was characterized using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy as a function of surface energy. The substrates consisted of a low surface energy Nafion-based copolymer, 4-phenylbutyltrichlorosilane or octyltrichlorosilane self-assembled monolayers on SiO₂, or high surface energy native SiO₂. It was observed that while the free surface of the film was always P3HT-rich (7:3 P3HT:PCBM), the bottom interfacial composition varied from P3HT-rich (4:1 P3HT:PCBM) to PCBM-rich (1:4 P3HT:PCBM) as the surface energy of the substrate increased from 20 mN/m² to 80 mN/m². These observations were further supported by electrical characterization of bulk heterojunction films deposited on thin-film transistor structures where the surface energy of the gate dielectric was modified with self-assembled monolayers. The transistor performance exhibited higher hole mobility at P3HT enriched organic-dielectric interfaces (low surface energy substrates), while ambipolar transport was observed in devices with a PCBM enriched interface (high surface energy substrates). These observations of surface energy dependant interfacial composition should have clear implications for optimizing photovoltaic cell design in regards to "conventional" and "inverted" device architectures. However, P3HT:PCBM bulk heterojunction solar cells constructed on low and high surface energy substrates in conventional and inverted device structures exhibit nominally identical performance. Early efforts at modelling the effect of compositional gradients on photovoltaic performance suggest that this is expected given that current densities increase in constricted percolation pathways to maintain constant overall current. Although this may have little impact on initial device performance, the effects of higher current densities in the constricted interfacial regions on device lifetime are currently being investigated.

10:40am **EN+NS-WeM9 Experimental and Theoretical Investigation of Excitonic Energy Transfer in Organic Photovoltaic Cells**, *W.A. Luhman, R.J. Holmes*, University of Minnesota

This work demonstrates a novel approach for measuring the Förster radius of energy transfer between electron donating and accepting materials commonly used in organic photovoltaic cells (OPVs). Typically an exciton must diffuse to an electron donor-acceptor interface in order to be dissociated and contribute to photocurrent. Alternatively, if an exciton in the donor layer is instead able to undergo long-range energy transfer to the acceptor layer, diffusion is no longer required, and dissociation occurs from the acceptor layer. While such processes are surprisingly common in OPVs, they are often incorrectly ignored in measurements of the exciton diffusion length and in models of device performance. In this work, the efficiency of energy transfer between an emissive donor and an absorptive acceptor is investigated using complementary experimental and theoretical techniques. This is accomplished by spatially separating the donor and acceptor materials using a wide energy gap spacer layer to suppress charge transfer, and tracking the donor photoluminescence as a function of spacer layer thickness. Fitting experimental data obtained for a variety of small molecule and polymer donor materials allows for the extraction of Förster radii that correlate very well with predicted values. The effect of energy transfer on device performance and on measurements of the exciton diffusion length is also investigated using the archetypal small molecule donor material boron subphthalocyanine chloride (SubPc). An exciton diffusion length of (7.5 ± 0.4) nm is extracted from photoluminescence quenching experiments that carefully account for the role of energy transfer. These results will ultimately provide insight into the fundamental processes of exciton diffusion and dissociation in OPVs.

11:00am **EN+NS-WeM10 Molecular Architecture and Charge Separation at Abrupt Donor-Acceptor Interfaces**, *G.J. Dutton*, NIST, *W. Jin*, University of California at San Diego, *D.B. Dougherty*, North Carolina State University, *W.G. Cullen*, University of Maryland, *S.W. Robey*, NIST, *J.E. Reutt-Robey*, University of Maryland

Photocurrent production in organic photovoltaic structures differs fundamentally from current generation in inorganic semiconductor solar cells. Dissociation of excitons formed by optical absorption in organic materials requires heterointerfaces between electron donor and acceptor components. The extent to which molecular architecture, particularly along the donor-acceptor interface, impacts electronic level alignment and charge separation is of fundamental interest. In this work, we prepare well-defined molecular interfaces by the physical vapor deposition of select donor (MPc, Pn) and acceptor (C_{60}) components under UHV conditions. We determine the detailed structure of the donor-acceptor interface with Scanning Tunneling Microscopy and establish a correlation with electron band alignment (PES) and exciton dynamics (2PPES).

For technologically relevant interfaces between C_{60} and donors such as pentacene (Pn) or phthalocyanines (Pc), distinct structures/molecular orientations can be selectively engineered by organic MBE through deposition sequence and flux. For the case of C_{60} and Pn, "co-facial" C_{60} -Pn interfaces are formed by C_{60} deposition on crystalline Pn bilayer films supported by Ag(111), whereas "edge-on" C_{60} -Pn interfaces result from Pn deposition on hexagonal close-packed C_{60} monolayers supported by Ag(111). Such "edge-on" interfaces expand into large dendritic islands, as per reported "thin-film" phases, and support C_{60} cluster formation under subsequent C_{60} deposition. We show how electronic level alignments critical to V_{oc} and charge separation efficiency are impacted by these structural changes, and extend this information to other small-molecule cases, ZnPc: C_{60} and perfluorinated ZnPc, as time permits.

Finally, for interfaces between CuPc and C_{60} , we will present the first studies of charge separation at well-characterized organic donor-acceptor interfaces using TR-2PPE. By pumping the CuPc Q-band at 1.65eV, a time-delayed UV pulse then probes the excited state population. We identify dominant relaxation processes on timescales from 100fs to >100ps. By varying the CuPc film thickness, we observe significantly enhanced charge transfer of the singlet exciton at the interface with C_{60} . Following the population dynamics as a function of energy also provides evidence for recombination from charge transfer states back to the low-lying CuPc triplet.

This work has been supported in part by the NSF under the UMD MRSEC (DMR0520471) and the Surface & Analytical Chemistry Program (CHE0750203).

11:20am **EN+NS-WeM11 Hybrid Organic/Inorganic Solar Cells Based on Silicon Nanowires**, *M. Pietsch*, Max Planck Institute for the Science of Light, Germany, *V.A. Sivakov*, *B. Hoffmann*, *G. Broenstrup*, *F. Talkenberg*, Institute of Photonic Technology, Germany, *T. Seyller*, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany, *T. Fritz*, *B. Schroeter*, Friedrich-Schiller University Jena, Germany, *S.H. Christiansen*, Max Planck Institute for the Science of Light, Germany

Organic polymer solar cells have received a lot of attention as a promising approach to future photovoltaic energy sources due to their mechanical flexibility and their potential for low cost mass production, high open-circuit voltage values. From another side the hybrid organic/inorganic solar cells containing nanocrystals/nanowires of inorganic semiconductors (e.g. silicon) are promising for several reasons: (i) inorganic semiconductors have a much broader absorption spectrum than organic semiconductors; (ii) nanostructures can be doped to a specific *n*- or *p*-type doping level; (iii) nanostructures provide a large interface to the organic counter part due to their high surface to volume ratio.

The main topic of our research is focused on the formation of the hybrid organic/inorganic solar cells based on the silicon 1D nanostructures. The hybrid solar cells (presented here) are based on silicon nanowires (SiNWs) performed by two different approaches. A Vapor-Liquid-Solid (VLS) mechanism in a conventional chemical vapor deposition (CVD) chamber or electrodeless wet-chemical etching procedure was applied for the SiNWs realization. As-grown SiNWs are single crystalline and have a smooth (VLS SiNWs) or rough (etched SiNWs) surface covered with a thin oxide layer. Both types of SiNWs show enhanced absorption compared to bulk silicon in the visible spectrum and best results were achieved with etched arrays exhibiting absorption of 90 % over a broad spectral range (300-2000 nm). In a further step the huge nanowire surface was functionalized into a charge separation interface for solar cells by the depositing of semiconducting polymers upon them. To get a detailed picture of charge carrier separation at the organic/inorganic interface XPS/UPS measurements were performed to estimate band alignment between SiNWs and different polymers like PEDOT:PSS or P3HT. The Al:ZnO transparent conductive oxide (TCO) as a contact to the polymer coated SiNWs was realized by applying atomic layer deposition (ALD) technique which allowed us to cover SiNWs with precisely uniform Al:ZnO thin layer. For all device concepts based on SiNWs, the crystal structure, geometry (alignment of SiNW with respect to the substrate), interfacial properties between the SiNW and polymers are a key of importance for functioning of the PV devices. For this reason, the microstructure and optoelectronic properties (optical, microstructure) of the organic/inorganic solar cell will be presented and discussed in details during our presentation.

11:40am **EN+NS-WeM12 Influence of UV Radiation on Charge Injection Barriers in Dye-Sensitized Solar Cells**, *S. Gutmann*, *M.A. Wolak*, *M.M. Beerbon*, *R. Schlaf*, University of South Florida

The electronic structure of the interfaces in dye-sensitized solar cell structures was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). Electro spray thin film deposition in high vacuum was used to build the interfaces of interest directly in vacuum without exposure to the ambient. Electro spray enables the fabrication of clean, essentially uncontaminated thin films of organic molecules and nanoparticles directly in vacuum.

The experiments focused on the investigation of the indium tin oxide (ITO)/nanocrystalline TiO_2 interface, as well as the characterization of the $TiO_2/RuL_2(NCS)_2$ [cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)-ruthenium(II)] ("N3", a prototypical dye used in many currently pursued device structures)-dye interface. Both TiO_2 and N3 films were built up in several steps. After each step, characterization by XPS and UPS was performed. The resulting sequence of spectra allowed the determination of charge injection barriers and interface dipoles at the ITO/ TiO_2 and $TiO_2/N3$ interfaces. Our experiments revealed a strong influence of the UV radiation during UPS measurements on the band line-up at these interfaces. This was revealed through low intensity x-ray photoemission spectroscopy (LIXPS) measurements, which allow the measurement of the work function prior to UV exposure. These results suggest that even low-level UV radiation, such as encountered in an encapsulated solar cell, may lead to cell degradation over time due to a re-alignment of the electronic structure with detrimental effect on charge transport.

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