

Wednesday Morning, November 2, 2011

Energy Frontiers Focus Topic

Room: 209 - Session EN+NS-WeM

Organic Photovoltaics

Moderator: R.A. Quinlan, Naval Surface Warfare Center, Carderock Division

8:00am **EN+NS-WeM1 Sol-gel Prepared Ca Doped ZnO and Its Application in Polymer-Oxide Bilayer Hybrid Solar Cells, M. Wang, I. Hill, Dalhousie University, Canada**

Conjugated polymer/metal oxide hybrid photovoltaic devices have received considerable attention in recent years due to their potential for scalable, low-cost manufacturing. To improve device efficiency, most research has focused on increasing the fill factor and short circuit current. In this article, calcium doped zinc oxide ($Zn_xCa_{1-x}O$) is used as electron acceptor in the hybrid poly(3-hexylthiophene) / $Zn_xCa_{1-x}O$ bilayer solar cells to modify the band offsets and increase the open circuit voltage. XRD results show the sol-gel prepared Ca doped ZnO films have a hexagonal wurtzite phase with no indication of calcium separation. Atomic force micrographs indicate the $Zn_xCa_{1-x}O$ surface becomes decorated with interconnected ridges approximately 100 nm in height. The rms surface roughness increases with increasing Ca. The band gap obtained from UV-vis absorption spectra widens from 3.20 to 3.60 eV as the Ca concentration increases from $x=0$ to $x=0.12$. The work function of the $Zn_xCa_{1-x}O$ films measured by Kelvin probe is seen to decrease with increasing Ca composition for values of x up to 0.12, which indicates a decrease in electron affinity. The open circuit voltage of hybrid P3HT/ $Zn_xCa_{1-x}O$ devices increases from 570 mV at $x = 0$ up to 800 mV for $x = 0.10$. Work is under way to incorporate Ca doped ZnO nanoparticles into bulk heterojunction solar cells to optimize device efficiency.

8:20am **EN+NS-WeM2 The Influence of ITO Surface Treatments on Spatially Localized Photocurrent Variation in Organic Photovoltaic Devices, B.J. Leever, Air Force Research Laboratory, I.P. Murray, Northwestern University, M.F. Durstock, Air Force Research Laboratory, T.J. Marks, M.C. Hersam, Northwestern University**

The fabrication process for bulk heterojunction (BHJ) organic photovoltaic (OPV) devices nearly always includes anode modification steps ranging from solvent cleaning to haloacid treatments to the deposition of interfacial layers such as polymer blends or transition metal oxides. The role of these treatments is not yet fully understood, but they are thought to modify the anode work function, contribute to electron-blocking, alter the anode surface energy, and prevent shunts among other functions. In separate work, conductive atomic force microscopy (AFM) and derivative techniques have been used to simultaneously probe both the morphological and electrical properties of BHJ photovoltaic layers. Previous work has demonstrated a correlation between BHJ nanostructure and properties such as photocurrent at the same scale (~ 20 nm) as the phase separation in these films. Photocurrent variability has also been observed at a length scale orders of magnitude larger than the domains in the BHJ layer, and this variation has been speculated to have an origin in the anode or interfacial layers in the OPV architecture.

In this work, a correlation between indium tin oxide (ITO) surface treatment and spatially localized photocurrent variation has been found in OPV devices with a poly(3-hexylthiophene)-[6,6]-phenyl-C-61-butylric acid methyl ester (P3HT:PCBM) BHJ layer. Atomic force photovoltaic microscopy (AFPM) was used to scan arrays of functioning $2 \mu\text{m}$ solar cells with varied ITO surface treatments. The standard deviation of the average photocurrent was found to be 11.4% for devices fabricated on untreated ITO, 8.6% for devices with a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) interlayer, and 6.7% for devices with a HCl-treated ITO surface. These results suggest that conductive non-uniformity in the ITO surface is transferred through the P3HT:PCBM film and that improving the anode conductive uniformity could be an important role of OPV interfacial layers or anode surface treatments.

8:40am **EN+NS-WeM3 Electronically Monodisperse Single-Walled Carbon Nanotube Thin Films as Transparent Conducting Anodes in Organic Photovoltaics, T.P. Tyler, R.E. Brock, H.J. Karmel, T.J. Marks, M.C. Hersam, Northwestern University**

Carbon nanomaterial thin films are being increasingly investigated for use as transparent electrodes in a variety of optoelectronic devices [1-3]. These flexible and solution-processible films are ideal candidates for organic electronics, including organic photovoltaics (OPVs), where low production

costs and mechanical robustness are essential. While carbon nanotube networks have begun to be explored in such devices, the inherent polydispersity of the samples—namely the mix of both semiconducting and metallic species—has prevented the realization of their full potential in these devices and convoluted a complete understanding of their implications on device operation. Herein we report the use of single-walled carbon nanotubes (SWNTs) sorted by electronic type via density gradient ultracentrifugation as the transparent anode in poly(3-hexylthiophene) (P3HT) [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) organic photovoltaic devices. Through a combination of dip coating and nitric acid treatment we achieve film roughnesses comparable to typical transparent oxides such as indium tin oxide. While carbon nanotube films are often electronically doped during processing, either intentionally or as a byproduct of roughness-reducing acid treatments, we find that the application of the quintessential electron-blocking interlayer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) removes sufficient adsorbed dopant groups to return the semiconducting nanotubes to their original state, vastly reducing their contribution toward current collection and transport. This is observed by both sheet resistance increases and UV-vis-NIR spectrophotometry. Further investigation using X-ray photoelectron spectroscopy reveals that the weakly-bound nitric oxide groups on the surface are almost entirely removed by PEDOT:PSS. By varying the semiconducting and metallic content in the electrodes, we find that metallic content greater than 70 percent yields devices with efficiencies 50 times greater than those comprised of almost entirely semiconducting SWNTs. This observation is counterintuitive considering that freshly acid-treated semiconducting SWNT films often possess a lower sheet resistance than their metallic counterparts [4]. This underscores the advantage of using metallic-enriched populations for transparent conductors, where unstable doping of semiconducting carbon nanotubes complicates processability and ultimately reduces device performance.

[1] T. M. Barnes; et al. *Appl. Phys. Lett.* **2010**, *96*, 243309.

[2] S. Kim; et al. *Adv. Funct. Mater.* **2010**, *20*, 2310.

[3] J. Li; et al. *Nano Lett.* **2006**, *6*, 2472.

[4] J. L. Blackburn; et al. *ACS Nano* **2008**, *2*, 1266.

9:00am **EN+NS-WeM4 In Situ Characterization of Lifetime and Morphology in Operating Bulk Heterojunction Organic Photovoltaic Devices by Impedance Spectroscopy, B.J. Leever, C.A. Bailey, Air Force Research Laboratory, T.J. Marks, M.C. Hersam, Northwestern University, M.F. Durstock, Air Force Research Laboratory**

Numerous reports have established that improving the performance of bulk heterojunction (BHJ) organic photovoltaic (OPV) devices requires not only the development of materials systems with improved spectral response and higher charge carrier mobility but also the ability to understand and tailor the morphology of these systems. Approaches for morphological characterization have included microscopic techniques such as scanning electron microscopy, transmission electron microscopy, and various atomic force microscopy techniques. Other methods have provided indirect information about active layer morphology by enabling the determination of charge carrier lifetimes. These approaches have included transient absorption spectroscopy, transient photovoltage, and time-of-flight techniques among others. While these methods have proven quite informative, the relationships between nanoscale morphology, device performance, and the underlying electrical characteristics of functioning devices are not yet fully understood.

Recently, impedance analysis has begun to be applied to BHJ OPV devices. These reports demonstrate that the impedance analysis framework established for dye-sensitized solar cells can, to some extent, be extended to bulk heterojunction devices in order to calculate average charge carrier lifetime, electron densities-of-states, and charge carrier concentrations. However, a detailed analysis of the impedance response of active devices, and its dependence on device processing history, morphology, and operating conditions is still needed. In this work we acquire and analyze the impedance behavior of operating P3HT:PCBM bulk heterojunction devices and its dependence on illumination and bias conditions, active layer composition, and annealing history. We also report a simplified equivalent circuit model that successfully describes bulk heterojunction devices over a range of illumination conditions and applied biases. We use this model to extract relevant device performance characteristics such as average electron lifetime and find, in agreement with other reports, that bimolecular recombination losses play a significant role in these devices. To this end, we demonstrate a correlation between device efficiency and lifetime, and describe how values extracted from the present equivalent circuit model can be used to optimize device performance with new materials systems.

9:20am **EN+NS-WeM5 Singlet Exciton Fission in Tetracene and Diphenyltetracene**, *P. Jadhav, A. Mohanty, J. Sussman, M. Baldo*, Massachusetts Institute of Technology

INVITED

Singlet exciton fission is a process by which a high energy singlet spontaneously decomposes into two low energy triplets. It is an example of a multi-exciton generation process that could allow the efficiency of solar cells to reach beyond the Shockley-Queisser limit. In this talk we examine singlet exciton fission in solar cells based on tetracene and diphenyltetracene (DPT). Notably we find that the photocurrents in each cell have opposite dependencies on the application of a magnetic field, suggesting that fission increases the photocurrent in tetracene-based solar cells, but decreases the photocurrent in DPT-based solar cells.

We report an organic semiconductor solar cell using tetracene and CuPC (Copper Phthalocyanine) as donors, and C60 as the acceptor. Tetracene absorbs photons in the 450-550-nm region, generating high energy singlets which split into two lower energy triplets, potentially doubling the photocurrent in this part of the spectrum. CuPC extends the absorption of the solar cell to the red part of the spectrum. We also demonstrate bulk heterostructure tetracene-C60 devices and tested them for singlet exciton fission.

We observe that: (i) The addition of the CuPC layer does not affect the flow of excitons from tetracene to the CuPC – C60 junction significantly because of similarities in triplet energies of tetracene and CuPC, (ii) The application of a .5T magnetic field shows ~1.5% change in photocurrent, confirming singlet fission, (iii) Low temperature quantum efficiency measurements show a drop in the tetracene IQE (internal quantum efficiency), and a singlet fission yield of 72% at room temperature. The drop in performance at low temperature is expected since singlet exciton fission in tetracene is a thermally activated process. (iv) Singlet exciton fission has a very high yield even in bulk heterostructure devices and can be potentially used to improve the performance of polymer solar cells.

In comparison, we observe that solar cells consisting of DPT-C60 exhibit a large positive (+5%) effect of the magnetic field on the photocurrent, +5% at ~4T. We explain the anomalous magnetic field effect and demonstrate that it can be increased beyond 100% by biasing the device close to open circuit, potentially leading to applications as an anisotropic magnetic field detector.

10:40am **EN+NS-WeM9 Charge Separation and Relaxation in Phthalocyanine-C₆₀ Photovoltaic Systems**, *G.J. Dutton*, University of Maryland -College Park, *S.W. Robey*, National Institute of Standards and Technology

Organic photovoltaic (OPV) structures depend on charge transfer processes occurring within 10's of nanometers of donor-acceptor interfaces. Charge generation in these devices involves successive steps of (1) optical absorption to create excitons, (2) diffusion of the exciton population to the donor-acceptor interface, (3) exciton dissociation and charge transfer at the interface and (4) charge transport and collection at electrodes. The charge separation step depends critically on electronic level alignment between the donor and acceptor. Also, because exciton diffusion to the interface occurs on timescales of several to 10's of picoseconds (ps), relaxation processes occurring on sub-ps and ps timescales as the exciton diffuses can impact the energy available for charge separation at the interface. We have investigated the exciton relaxation and charge separation processes close to phthalocyanine (Pc)-C₆₀ interfaces by combining time-resolved two-photon photoemission (TR-2PPE) with organic MBE to form donor-acceptor interfaces layer-by-layer. Pc $\pi \rightarrow \pi^*$ transitions are excited by a pump pulse to generate singlet (S₁) excitons. The resulting population dynamics are then probed with a time-delayed UV pulse to follow the relaxation and charge separation as a function of energy. For CuPc /C₆₀ interfaces, we compared the decay dynamics as a function of CuPc thickness, and thus distance from the C₆₀ interface, to allow determination of the rate of charge transfer at the interface. We find a charge transfer rate of $\approx 8 \times 10^{12} \text{ sec}^{-1}$ for the initial exciton population formed immediately after pumping. For CuPc, the exciton population also undergoes vibrational relaxation and intersystem crossing (ISC) on a timescale of $\approx 1-2 \text{ ps}$, ultimately resulting in the production a triplet exciton population at significantly lower energy. By again comparing results for thin and thick Pc layers we estimate that the charge transfer rate of this lower energy triplet population is reduced by at least a factor of ≈ 1000 , giving charge transfer rates closer to $8 \times 10^9 \text{ sec}^{-1}$. We will also discuss measurements for the case of H₂Pc and C₆₀ where ISC of the Pc singlet excitons to triplet levels is negligible. Our results will be discussed within the context of the Marcus theory of charge transfer and connections will be made to calculated charge transfer rates for similar donor-acceptor interfaces.

11:00am **EN+NS-WeM10 Low Energy Ion-Assisted Modification of PbS Nanocrystal-Sexithiophene Composite Films**, *F.D. Pleticha*, University of Illinois at Chicago, *L. Donghwa*, University of Florida, *I.L. Bolotin*, University of Illinois at Chicago, *S.R. Phillipot*, *S.B. Sinnott*, University of Florida, *L. Hanley*, University of Illinois at Chicago

The properties of semiconductor nanocrystal-organic films are of interest for applications in photodetectors, light-emitting diodes and photovoltaics. The versatility of these films arises from the ability to tune the bandgaps by adjusting the PbS nanocrystal size. Nanocrystalline photoelectric properties are also strongly affected by the chemical environment presented to them and by their bonding to the surrounding organic films. PbS nanocrystals are simultaneously deposited under vacuum into an organic matrix of evaporated α -sexithiophene while concomitantly modulating the film interface with 50 eV acetylene ions. Cluster beam deposition has been shown to allow the preparation of PbS nanocrystals that are surface terminated with either Pb or S [1]. Surface polymerization on ion assisted deposition (SPIAD) has shown an ability to increase the conjugation of oligothiophenes and otherwise lead to their chemical modification [2-4]. Cluster beam deposition and SPIAD are combined here to modulate the interface between the PbS and the organic matrix by introducing acetylene ions during the formation of the film. X-ray photoelectron spectroscopy analysis shows chemical shifts indicative of acetylene ion modulated interaction between the nanocrystals and sexithiophene. The deposition process was also simulated by a linearly scaled density functional theory method. These computer simulations indicate chemical bonding between the nanocrystals and sexithiophene, which is consistent with the chemical shifts observed by XPS.

1. A. M. Zachary, I. L. Bolotin, D. J. Asunskis, A. T. Wroble, and L. Hanley ACS Appl. Mater. Interf. 1 (2009) 1770

2. S. Tepavcevic, A. M. Zachary, A. T. Wroble, Y. Choi, and L. Hanley, J. Phys. Chem. A 110 (2006) 1618

3. S. tepavcevic, Y. Choi, and L. Hanley, Lang. 20 (2004) 8754

4. W. -D. Hsu, S. Tepavcevic, L. Hanley, and S. B. Sinnott, J. Phys. Chem. C 111 (2007) 4199

11:20am **EN+NS-WeM11 Molecular Modulation of Solar Cells: Where Inorganic, Molecular and Organic Electronics Meet**, *D. Cahen, R. HarLavan, O. Yaffe*, Weizmann Institute of Science, Israel

Organic materials present a promising direction for potentially cheaper solar cells. One way to use them and increase our understanding (e.g., define basic physical cell performance limits), is hybrid, organic / inorganic photovoltaics (PV). We explore 2 main directions to hybrid PV - with molecules as dipolar films, i.e., use electrostatics

- with molecular monolayers as electronic transport medium.

While we find that incomplete partial dipolar monomolecular films can control solar cell behavior for /single, poly- and nano-crystalline cells, for current to pass through the molecules, we need dense monolayers. Alkyl chain monolayers help form near-ideal Metal-Insulator-Semiconductor (MIS) diodes, with significant PV activity. Surprisingly, though we can actually make *MIS* cells without a separate *I*(nsulator) layer, suggesting that 'MIS' effects are at least partly more "chemical than is often thought.

In this way we demonstrate a near-ambient, simple, potentially low-cost approach to make and modify semiconductor solar cells, using a monolayer of molecules, as short as two carbons, that self-assembles onto the semiconductor (absorber) surface, passivating and buffering it. Good passivation is necessary to express the molecule-induced interface dipole, which can change the semiconductor electron affinity by up to 1 eV.

Good, stable interface passivation along with strong inversion allows minority carriers, generated by absorbed light, to move laterally within the semiconductor top layer, for collection by a minimal-area grid, deposited on the conducting polymer and also minimizes photo-current losses, due to sheet resistance. Thus, $\leq 1 \text{ nm}$ thick organic molecules appear to convey a unique advantage over inorganic passivation or buffer layers.

11:40am **EN+NS-WeM12 Correlation of Interfacial Electronic Structures and Open Circuit Voltages in Organic Solar Cells**, *M.H. Chen*, National Dong Hwa University, Taiwan, Republic of China, *W.H. Tseng, J.Y. Wang, C.T. Tseng, C.I. Wu*, National Taiwan University

In this study, the interfacial electronic structures and energy band diagrams of polymer/fullerene bulk heterojunction (BHJ) solar cells are investigated. To study the device performance influenced by the interlayer, poly(3-hexylthiophene) (P3HT) mixed with 6,6-phenyl C61-butyric acid methylester (PCBM) are used as an active layer and bathocuproine (BCP) and calcium (Ca) are incorporated respectively with the cathodes. Since the mechanisms leading to the improvement of power conversion efficiency are more chemically and electronically complicated and have not been

understood, the ultraviolet and x-ray photoemission spectroscopy (UPS and XPS) are used to investigate the properties of energy band, electronic structures and the interface chemistry at the interface. For the devices incorporated with BCP, the highest occupied molecular orbital (HOMO) level of PCBM is pulled down about 0.3 eV with respect to the Fermi level after the deposition of BCP. It indicates that the BCP layer could modify the energy band by shifting the energy level of acceptors, causing the increase of built-in potential (V_{bi}). Thus, the open circuit voltage (V_{oc}) attributed to the increase of V_{bi} resulted from BCP could be enhanced. Moreover, AFM image indicates that BCP molecules cannot form a uniform layer on the active layer surface, pointing out that band modulation is the key reason to the V_{oc} improvement. For the devices with Ca as cathodes, the UPS results with deposition of Ca illustrate a 0.8 eV-downward shift in energy levels of P3HT, but not in those of PCBM. Therefore, the energy difference between the HOMO of P3HT and the LUMO of PCBM is widened, resulting in the increase of V_{oc} and the enhancement of device efficiency. Moreover, from the XPS spectra, there is an extra new peak appearing at the lower binding energy about 162 eV, which suggests that the addition of electrons around the reactive sulfur (S) atoms in P3HT molecules after Ca deposition. The combinations of S and Ca spectra imply that the formation of Ca-S bonding at the Ca/P3HT interface, which is in good agreement with the findings of UPS spectra.

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