

Wednesday Afternoon, November 12, 2014

Energy Frontiers Focus Topic

Room: 315 - Session EN+AS+EM-WeA

Organic-Inorganic Interfaces for Energy

Moderator: Ramana Chintalapalle, University of Texas at El Paso

2:20pm **EN+AS+EM-WeA1 Towards Efficient Solution Processed Organic Photovoltaic Devices**, *Elsa Reichmanis*, Georgia Institute of Technology **INVITED**

Solution-processed π -conjugated semiconductors exhibit potential in the development of low-cost, light-weight and large-area flexible plastic optoelectronics, particularly photovoltaics (OPVs). However, one drawback to current OPVs is their limited efficiency. We have explored the use of donor-acceptor (D-A) hybridization to tailor HOMO/LUMO energy levels and thus the band gap. Materials exhibiting high charge carrier mobility and strong low-energy absorption profiles have been synthesized and characterized. Coupled with materials structure, the performance of devices fabricated using polymeric semiconductors depends critically upon alignment of the polymer chains at the nano- through meso- and macro-scales. Significant structure-process-property relationships that allow for enhancement of long-range order will be discussed. For instance, a lyotropic liquid crystalline (LC) phase has been observed in poly-(3-hexylthiophene) (P3HT) via solvent-evaporation induced self-assembly. The lessons learned through these studies may allow for simple, controllable, and cost-effective methodologies for achieving high performance flexible plastic electronic devices.

3:00pm **EN+AS+EM-WeA3 Understanding Carrier Dynamics in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ Using Time-Resolved Terahertz Spectroscopy**, *G.W. Guglietta*, Drexel University, *K. Roy Choudhury*, *J.V. Caspar*, DuPont Central Research and Development, *Jason Baxter*, Drexel University

We have used time-resolved terahertz spectroscopy (TRTS) to measure lifetimes and determine recombination mechanisms in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) thin films fabricated from nanocrystal inks. TRTS probes photoconductivity on femtosecond to nanosecond time scales that are relevant for recombination in thin film photovoltaics. Terahertz frequencies (0.2-2.5 THz) correspond to typical scattering rates in semiconductors, enabling determination of carrier density and mobility. Ultrafast time resolution permits tracking the evolution of carrier density to determine recombination mechanisms. By manipulating the photoexcitation wavelength and fluence, we can tailor the generation profile of photoexcited carriers to distinguish between surface, Shockley-Read-Hall (SRH), and Auger recombination mechanisms and determine rate constants.

TRTS experiments and modeling were used to understand the role of recombination mechanisms and their contribution to CZTSSe photovoltaic performance. TRTS photoconductivity shows an instrument-limited onset within 1 ps of an ultrafast pump pulse, followed by a slow decay over nanoseconds. Photoconductivity decay kinetics were fit with a bi-exponential model with two time constants and a weight fraction. The short time constant is typically ~200 ps and roughly corresponds to diffusion to and recombination at the surface. The long time constant is typically ~2 ns and is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the pump wavelength. As the excitation wavelength is shifted towards the blue, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

3:20pm **EN+AS+EM-WeA4 Comparative Study of the Doping Effects of Titanium and Nitrogen into Tungsten Oxide (WO_3) Thin Films for Photovoltaic Device Applications**, *Mirella Vargas*, *C.V. Ramana*, The University of Texas at El Paso

Tungsten oxide (WO_3) is a technologically important n-type semiconductor that is extensively studied in the fields of electronic and opto-electronic

devices. Due to its unique properties such as a high work function and high-coloration efficiency, WO_3 is attractive for electrochromic and memory devices including large area information displays, smart-windows, and optical heat-mirrors. Low-dimensional structures of WO_3 coupled with an ideal band gap ($E_g \sim 2.8$ eV) have been employed as materials for the photocatalyst driven by visible light irradiation in dye-sensitized solar cells. In addition, WO_3 has also become a strong contender to replace indium-doped tin oxide or ITO thin films in transparent electrode applications. The present work is focused on WO_3 thin films characterized as promising transparent conducting oxide (TCO) materials by investigating doping effects on the structural, chemical, and optical properties. The incorporation of titanium (Ti) was achievable by depositing the films through co-sputtering of W and Ti metal targets. The sputtering powers to the W and Ti were kept constant at 100 W and 50 W, respectively, while varying the growth temperature (T_s) in the range of 25-500 °C. While all the samples are optically transparent, the structural quality of Ti-doped WO_3 films is dependent on T_s . Ti-doped WO_3 films grown at $T_s < 400$ °C were amorphous. A temperature of 400 °C is critical to promote the structural order and formation of nanocrystalline films in the monoclinic phase. The optical constants and their dispersion profiles determined from spectroscopic ellipsometry indicate that there is no significant inter-diffusion at the film-substrate interface for W-Ti oxide film growth of ~40 nm. The index refraction (n) at $\lambda = 550$ nm vary in the range of 2.15-2.40 with a gradual increase in growth temperature. Nitrogen (N_2) incorporation was made through a post-deposition anneal in an ammonia environment on WO_3 films. The un-doped WO_3 films grown by variable growth temperature will be annealed at high temperatures for various rates to accommodate a strong N_2 incorporation. The tungsten oxynitride films will be characterized by various analytical techniques to compare the doping effects of Ti and N_2 on the structural, electronic, and optical properties of WO_3 thin films.

5:00pm **EN+AS+EM-WeA9 Engineering Exciton Recombination in Organic Light-Emitting Devices**, *Russell Holmes*, University of Minnesota **INVITED**

While capable of realizing very high peak efficiency, many organic light-emitting devices (OLEDs) suffer a significant reduction in efficiency under large injected current densities. This efficiency roll-off can limit device brightness and potentially compromise operational stability. Much previous work has identified the key contributing factors to the efficiency roll-off in phosphorescent OLEDs as triplet-triplet annihilation and triplet-polaron quenching. Here, the parameters associated with these quenching processes are independently measured, and the impact of the exciton recombination zone width on the quenching processes in various OLED architectures is examined directly. In high efficiency devices employing a graded-emissive layer (G-EML) architecture the roll-off is due to both triplet-triplet annihilation and triplet-polaron quenching, while in devices which employ a double-emissive layer (D-EML) architecture, the roll-off is dominated by triplet-triplet annihilation. Overall, the roll-off in G-EML devices is found to be much less severe than in the D-EML device. This result is well accounted for by the larger exciton recombination zone that is experimentally measured in G-EML devices, serving to reduce exciton density-driven loss pathways. Indeed, a predictive model of the device efficiency based on the quantitatively measured quenching parameters shows the role a large exciton recombination zone plays in mitigating the roll-off.

5:40pm **EN+AS+EM-WeA11 Interface Engineering to Control Magnetic Field Effects of Organic-based Devices by using a Self-Assembled Monolayer**, *Hyuk-Jae Jang*, NIST & WFU, *S.J. Pookpanratana*, NIST, *A.N. Brigeman*, Wake Forest University, *R.J. Kline*, NIST, *J.I. Basham*, NIST & PSU, *D.J. Gundlach*, *C.A. Hacker*, *O.A. Kirillova*, NIST, *O.D. Jurchescu*, Wake Forest University, *C.A. Richter*, NIST

Magnetic field effects (MFEs) in non-magnetic organic semiconductors provide a non-contact approach to control electronic and optoelectronic properties of organic-based devices by using a sub-tesla magnetic field and thus they have been of great interest to industry as well as academia around the world.^{1,2} However, there is no consensus on the physical mechanism(s) causing the MFEs in organic semiconductors even though a variety of fundamental models have been proposed to explain the effects.² Studies on many different organic semiconductors and organic-based structures have shown that the magnitude and even the sign of the MFEs can vary by changing the measurement and fabrication conditions such as bias voltage, film thickness, and temperature. Therefore, it is suggested that there can be multiple origins inducing the MFEs and the outcome may result from a competition between different MFE mechanisms.²

In this presentation, we report a novel method of manipulating the MFEs on electrical resistance of organic semiconductors, namely organic magnetoresistance in Alq_3 (tris-(8-hydroxyquinoline) aluminum) – based devices by simply adding a molecular self-assembled monolayer (SAM) between a metal electrode and an organic semiconductor. SAMs have been known for their versatile use in various technological applications.³ Particularly, SAMs can alter the physical property of an inorganic solid surface and thus modify the interface between an electrode and an organic thin film when a SAM is inserted between them.³ We show for the first time that the interfacial modification by simply inserting a fluorinated SAM (heptadecafluoro-1-decanethiol [$\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$] or F-SAM) in organic-based devices changes the sign of organic magnetoresistance due to the change in relative strength of different MFE mechanisms coexisting in organic-based devices. In addition, we utilize different MFE mechanisms coexisting in organic-based devices by adding a thin TPD (N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine) layer to create a system whose organic magnetoresistance can be tuned by an external bias voltage.

References

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2. W. Wagemans, P. Janssen, A. J. Schellekens, F. L. Bloom, P. A. Bobbert, and B. Koopmans, *SPIN* vol. 1, pp. 93-108, 2011.
3. J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides, *Chem. Rev.* vol. 105, pp. 1103-1169, 2005.

6:00pm **EN+AS+EM-WeA12 Study on the Correlation between Electrode-Active Layer Interfaces and Performance of Polymer Solar Cells**, *Huanxin Ju, J.F. Zhu*, University of Science and Technology of China

The PSCs were fabricated with different cathodes (Ca/Al and Al) as the electron-collection layers and with PCDTBT (poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]) and PC70BM ([6,6]-phenyl-C71-butyric acid methyl ester) as the active layers. The Ca/Al interlayer significantly improves the open circuit voltage (VOC), short circuit current (JSC), fill factor (FF) so as to improve the PCE in comparison with Al as the cathode. In order to understand how the electrodes affect the device performance, the Ca/PCDTBT and Al/PCDTBT interfaces were investigated by transient photovoltage (TPV), charge extraction (CE) and synchrotron radiation photoemission spectroscopy (SRPES). The TPV and CE measurements were used to determine the charge carrier lifetime and density. Charge carrier recombination rate constant was found to be much smaller in the device with Ca/Al cathode as compared to that with Al cathode. Energy band diagrams and interfacial chemical reactions were characterized using high-resolution SRPES. The results indicate that the Ca interlayer can induce the stronger dipole moment, which facilitates electrons collection and drives holes away at the cathode/polymer interface. The device performance was improved because of the lower recombination.

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