

# Monday Afternoon, October 19, 2015

## Energy Frontiers Focus Topic

Room: 211B - Session EN+AS+EM+NS+SE+SS+TF-MoA

## Solar Cells II

Moderator: Adrie Mackus, Stanford University

2:20pm EN+AS+EM+NS+SE+SS+TF-MoA1 **Influence of Annealing Temperature in the Bulk Defect Formation in Perovskite Thin Films.** Weina Peng, B.X. Anand, L.-H. Liu, S.C. Sampat, B.E. Bearden, A.V. Malko, Y.J. Chabal, University of Texas at Dallas

Perovskites are emerging as front-runners for solar cell applications because of their superior optoelectronic properties. Over the past few years the grain size of perovskites has been continuously improved from several hundred of nanometers to a few millimeters which resulted in better solar conversion efficiencies. In addition to surface and grain boundary related defects, perovskites are prone to the formation of bulk defects as well. However the role of bulk defects in the determination of photovoltaic performance of perovskites is rarely explored. To this end we investigate the impact of annealing temperature on the defect density in polycrystalline  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films of  $\sim 1$  micron average grain size prepared using vapor assisted solution process (VASP). The photoluminescence (PL) intensity and lifetime show systematic reduction when the annealing temperature is increased from  $150^\circ\text{C}$  to  $200^\circ\text{C}$ . A rough estimate of the defect state density obtained using fluence dependent PL measurements reveal a 5 fold increase in defect density for a  $25^\circ\text{C}$  increase in annealing temperature although the average grains size stays unchanged. Furthermore, surface passivation of perovskite films using  $\text{Al}_2\text{O}_3$  via atomic layer deposition leads to an improvement in PL intensity and lifetime. But the PL quantum efficiency, as well as the lifetime, of the surface passivated  $200^\circ\text{C}$  annealed sample remains significantly lower than that of the un-passivated  $150^\circ\text{C}$  annealed sample indicating that the majority of the defects states we observe in the high temperature annealed samples originate from bulk defects. Thus the present study shows that minimizing the number of bulk defects, in addition to surface defects, is very important in the realization of highly efficient perovskite solar cells.

3:00pm EN+AS+EM+NS+SE+SS+TF-MoA3 **Tandem Solar Cells Using Perovskites, Silicon and CIGS.** M.D. McGehee, Tomas Leijtens, Stanford University **INVITED**

The efficiency of perovskite solar cells has soared from a few percent to over 20% in the last 3 years. They are very attractive for multijunction solar cell applications because the bandgap of perovskite semiconductors can be easily tuned in the range of 1.55 to 2.2 eV and the open circuit voltage of the cells is large. We have made highly efficient semitransparent perovskite solar cells using silver nanowire meshes as the top electrode. These cells can be used in combination with either silicon or copper indium gallium diselenide solar cells to make four-terminal and two-terminal tandems. We will also present detailed characterization of perovskite semiconductors made with different processing conditions to show what needs to be done to minimize recombination and make the solar cells stable.

3:40pm EN+AS+EM+NS+SE+SS+TF-MoA5 **Lifetime, Mobility, and Diffusion of Photoexcited Carriers in Ligand-Exchanged Lead Selenide Nanocrystal Films Measured by Time-Resolved Terahertz Spectroscopy.** G.W. Guglietta, Drexel University, B.T. Diroll, E.A. Gaulding, J.L. Fordham, University of Pennsylvania, S. Li, Drexel University, C.B. Murray, University of Pennsylvania, Jason Baxter, Drexel University

Colloidal semiconductor nanocrystals have been used as building blocks for electronic and optoelectronic devices ranging from field effect transistors to solar cells. Properties of the nanocrystal films depend sensitively on the choice of capping ligand to replace the insulating synthesis ligands. Thus far, ligands leading to the best performance in transistors result in poor solar cell performance, and vice versa. To gain insight into the nature of this dichotomy, we used time-resolved terahertz spectroscopy measurements to study the mobility and lifetime of PbSe nanocrystal films prepared with five common ligand-exchange reagents. Non-contact terahertz spectroscopy measurements of conductivity were corroborated by contacted van der Pauw measurements of the same samples. The films treated with different displacing ligands show more than an order of magnitude difference in the peak conductivities and a bifurcation of time-dynamics. Inorganic chalcogenide ligand-exchanges with sodium sulfide ( $\text{Na}_2\text{S}$ ) or ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) show high THz mobilities above  $25 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is desirable for transistors, but nearly complete decay of transient

photocurrent within 1.4 ns. The high mobility with  $\text{NH}_4\text{SCN}$  and  $\text{Na}_2\text{S}$  exchanges is more than offset by their short lifetimes and results in diffusion lengths of only  $\sim 200$  nm. In contrast, ligand exchanges with 1,2-ethylenediamine (EDA), 1,2-ethanedithiol (EDT), and tetrabutylammonium iodide (TBAI) show  $\sim 5\times$  lower mobilities but much longer carrier lifetimes, with  $\sim 30\%$  of photoexcited carriers remaining for  $>10$  ns. The long lifetimes with EDA, EDT, and TBAI yield diffusion lengths of at least 500 nm, which is approaching the film thickness desired for strong light absorption in solar cells. This bifurcated behavior may explain the divergent performance of field-effect transistors and photovoltaics constructed from nanocrystal building blocks with different ligand exchanges.

4:00pm EN+AS+EM+NS+SE+SS+TF-MoA6 **iCVD Synthesis and Integration of Poly(vinylpyrrolidone) and Poly(4-vinylpyridine) as Polymer Electrolytes in Dye Sensitized Solar Cells.** Yury Y. Smolin, S. Janakiraman, A.J. Sauter, M. Soroush, K.K.S. Lau, Drexel University

Initiated chemical vapor deposition (iCVD) is used to synthesize and integrate poly(4-vinylpyridine) (P4VP) and polyvinylpyrrolidone (PVP) as polymer electrolytes within the mesoporous  $\text{TiO}_2$  photoanode of dye sensitized solar cells (DSSCs). DSSCs with conventional liquid electrolytes are prone to leakage and evaporation, which hinders DSSC durability and field implementation. In addition, liquid electrolytes lead to significant electron recombination within the cells that limit DSSC performance. In contrast, polymer electrolytes do not suffer from the practical disadvantages and could potentially enhance the cell's I-V behavior.

However, in order to enable good contact between the  $\text{TiO}_2$  electrode and the polymer electrolyte, a major obstacle is the difficulty in achieving good pore filling of the polymer into the mesoporous  $\text{TiO}_2$  layer. Mesoscale pore diameter, high aspect ratio, and tortuous pore structure of the photoanode along with liquid surface tension, poor wettability, and solute steric hindrance make pore filling extremely limited when using liquid techniques. This leads to poor electrical contact and lower efficiency. To overcome the challenges of pore filling, we directly synthesized polymer electrolytes inside the pore volume of the photoanode using the solvent-free technique of iCVD. iCVD relies on the vapor delivery of monomer and initiator, which facilitates infiltration into the porous  $\text{TiO}_2$  substrate, and by controlling the relative rates of diffusion and surface polymerization through iCVD process parameters, uniform and conformal growth of polymer is achieved. The pore filling of the polymer electrolyte into 5–10  $\mu\text{m}$  photoanodes using iCVD is typically 90–100% which is significantly better than that achievable with liquid techniques like spin coating.<sup>1</sup>

In this work, we will show that iCVD P4VP and PVP polymer electrolytes can be effectively integrated within  $\text{TiO}_2$  mesoporous photoanodes to produce enhanced DSSCs. By varying the polymer electrolyte chemistry including the use of a crosslinking agent during iCVD to stabilize the resulting polymer structure, DSSC I-V characteristics, such as open-circuit voltage, short-circuit current density and fill factor, are tuned.<sup>2</sup> To gain a better understanding on the effect of the polymer electrolyte, experimental techniques such as linear sweep voltammetry, intensity modulated spectroscopy, and impedance spectroscopy are used. Mathematical modeling of DSSC behavior is also performed to relate these experimental observations with the dynamics of the operation of the cell.

1. S. Nejadi and K. K. S. Lau, *Nano Lett.*, 2010, 11, 419-423.

2. Y. Y. Smolin et al., *J. Power Sources*, 2015, 274, 156-164.

4:20pm EN+AS+EM+NS+SE+SS+TF-MoA7 **Interfacial Effects on Device Performance in Organic Solar Cells.** Huanxin Ju, J.F. Zhu, University of Science and Technology of China, D.S. Ginger, University of Washington

The better understanding of the underlying mechanisms is essential for the further development of highly efficient organic photovoltaics (OPVs) devices. In this paper, the transient photovoltage (TPV) and charge extraction (CE) measurements in combination with the synchrotron radiation photoemission spectroscopy (SRPES) were used to gain insights into the correlation between the microscopic interfacial properties and macroscopic device performance. The OPV devices based on PCDTBT:  $\text{PC}_{70}\text{BM}$  with Ca interlayer were studied as a reference system to investigate the interfacial effects on device performance. The charge carrier decay dynamics demonstrated that the device with the Ca interlayer exhibited a lower recombination constant ( $k_{\text{rec}}$ ) than that only with the Al cathode at a given charge carrier density ( $n$ ). In addition, the interfacial energy band structures indicated that the strong dipole moment produced by the Ca interlayer can facilitate electron extraction as well as drive hole away at the cathode/polymer interface, resulting in retarding interfacial recombination losses. Finally, we examined the device performance with the Ca interlayer to find that the efficiency is improved by 28% as compared to that without

the Ca interlayer, which shows good correlation with the observed interfacial properties.

4:40pm **EN+AS+EM+NS+SE+SS+TF-MoA8 Tungsten-Titanium Mixed Oxide Thin Films for Improved Structural and Optical Properties for Solar Driven Applications**, *Mirella Vargas*, The University of Texas at El Paso, *N.R. Murphy*, Air Force Research Laboratory, *R.V. Chintalapalle*, The University of Texas at El Paso

Tungsten oxide ( $\text{WO}_3$ ) is a well-established n-type semiconductor possessing unique optical and electronic properties.  $\text{WO}_3$  has become the most interesting inorganic material for electrochromic applications due to the reversible spectral absorption properties associated with  $\text{WO}_3$ .  $\text{WO}_3$  thin films and nanostructures exhibit an optical band gap that permits efficient use of the solar spectrum including absorption in the blue part of the visible region and the ultraviolet region, as well as a high transmission region that extends from the near-infrared (IR) to the visible spectrum. Coupled with good electronic transport properties, photosensitivity, and chemical integrity,  $\text{WO}_3$ -based materials are attractive for applications related to sustainable energy production including energy efficient windows and architecture, photoelectrochemical (PEC) water-splitting, photocatalysis and solar cells. Anion or cation doping into  $\text{WO}_3$  has been extensively studied as this offers the opportunity to tailor the transport properties that may influence the efficiency of solar driven devices. Titanium doping into  $\text{WO}_3$  has proven to enhance the electrochromic response and the cyclic lifetime by a factor of five in PEC devices. In the present case a systematic investigation of progressively increasing the Ti content in the W-Ti target for reactive sputtering has been employed to tune the structure, chemistry, and properties of the films. Tungsten-titanium (W-Ti) mixed oxide thin films were fabricated using reactive sputtering of W-Ti alloy targets with Ti content ranging from 0 to 30 wt.%. X-ray photoelectron spectroscopy confirms the existence of W and Ti in their highest oxidation states of +6 and +4, respectively. Quantification of binding energy shifts for W and Ti core-level transitions confirms the formation of  $\text{WO}_3$ - $\text{TiO}_2$  composite oxide films. Optical analyses made from spectrophotometry measurements indicate a decrease in band gap with a discrete amount of Ti incorporation. The band gap decreases with increasing Ti from 3.0 eV to 2.5 eV. Such films are expected to have the possibility for tuning the electrical conductivity while retaining the optical transparency to make them efficient for photoelectrochemical cells and photovoltaics.

5:00pm **EN+AS+EM+NS+SE+SS+TF-MoA9 Potential Resolution to the "Doping Puzzle" in Pyrite  $\text{FeS}_2$** , *X. Zhang, M. Li, L. O'Brien, J. Walter, M. Manno, F. Mork, J. Kakalios, Eray Aydil, C. Leighton*, University of Minnesota

In principle, pyrite  $\text{FeS}_2$  is one of the most suitable photovoltaic materials for sustainable low-cost, large-scale solar cell manufacturing because it has high absorbance in the visible and comprises earth-abundant inexpensive elements. However, current efficiencies of solar cells based on pyrite  $\text{FeS}_2$  have not exceeded 2.8%. Early research on this material concluded that unintentionally doped  $\text{FeS}_2$  thin films are p-type and subsequent solar cell work evolved based on this presumption. In fact, it is now widely accepted that  $\text{FeS}_2$  thin films almost always exhibit p-type conduction even though single crystals are typically found to be n-type. This discrepancy between single crystals and thin films is perplexing and to date this puzzle remains unexplained. In this talk we reexamine the conclusion that undoped  $\text{FeS}_2$  films are predominantly p-type and provide an explanation for this "doping puzzle" in pyrite. Using a combination of Hall effect, thermopower, and temperature-dependent resistivity measurements on a large set of well characterized single crystals and thin films, we show that the widely accepted predominant p-type behavior in pyrite films may, in fact, be an artifact of hopping conduction and should be revisited. Specifically, both Hall effect and thermopower measurements establish that all of our high-mobility ( $>1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) films and single crystals are n-type. Temperature-dependent resistivity measurements on these high mobility films and crystals establish diffusive electronic transport. We find that films with lower mobility ( $4 \times 10^{-2} - 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) also show n-type Hall effect but exhibit a p-type Seebeck coefficient, leading to a discrepancy in the measured carrier type. Temperature-dependent resistivity measurements on these intermediate mobility films show a transition from diffusive to hopping transport. Finally, both Hall and Seebeck coefficients are strongly suppressed and invert in the lowest mobility thin films ( $<4 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) indicating apparent p-type conduction. Temperature-dependent resistivity measurements establish unambiguous hopping behavior in these lowest mobility films. Based on this evolution of Hall and Seebeck coefficients with carrier mobility, and the well-known suppression of the Hall and Seebeck effects in conductors with hopping electronic transport, we conclude that the apparent crossover from n-type to p-type with decreasing mobility is, in fact, an artifact of hopping conduction.

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5:20pm **EN+AS+EM+NS+SE+SS+TF-MoA10 Interparticle Contact Radius and Electron Transport in Thin Films Comprised of Nanocrystals**, *Elijah Thimsen, D. Lanigan*, Washington University, St. Louis

Thin films comprised of nanocrystals are being explored for a variety of applications that involve electron transport. For traditional applications such as photovoltaic solar cells, the goal is often to utilize solution processing to make an inexpensive thin film that essentially behaves as a bulk material with diffusive transport. For other applications, such as neuromorphic computing, variable range hopping (VRH) transport is more desirable because it enables a given nanocrystal to have orders of magnitude more nearest neighbors than it physically touches. It is of paramount importance that the structure-property relationships that control electron transport mechanism be elucidated. Previous work has demonstrated that interparticle separation distance affects charge carrier mobility. However, for films comprised of nanocrystals that are physically touching, what is the effect of contact radius? In this work, we present a systematic experimental study of the effect of interparticle contact radius on the electron transport mechanism in thin films comprised of heavily-doped ZnO nanocrystals embedded in  $\text{Al}_2\text{O}_3$ . As the contact radius increased, the electron transport mechanism crossed over from VRH to diffusive conduction. For large contact radius between nanocrystals, the room-temperature electron mobility in the film approached the local mobility within a nanocrystal, approximately  $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . The conclusion is that for nanocrystals that are physically touching, the interparticle contact radius determines the transport mechanism. With the ability to control the electron transport mechanism in films comprised of ZnO nanocrystals, we performed an exploratory study of the Hall effect in these materials. Hall effect measurements are of great utility and are routine for determining charge carrier mobility and type, but the interpretation of data for materials that exhibit VRH has been difficult in the past. For well-connected ZnO nanocrystals that exhibit diffusive conduction, the Hall coefficient was independent of temperature, as expected for the high doping level. Alternatively, for films with small contact radius between nanocrystals, which exhibited a VRH transport mechanism, we observed an anomalous behavior of the Hall coefficient at low temperature (100 to 200 K). Surprisingly, for films that exhibited VRH, the magnitude of the Hall coefficient increased exponentially with decreasing temperature, in stark contrast to the conventional wisdom that the Hall effect is suppressed for VRH.

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