

Monday Afternoon, October 29, 2012

Energy Frontiers Focus Topic

Room: 15 - Session EN+TF-MoA

Chalcogenide Solar Cells I

Moderator: J. Luther, NREL

2:00pm EN+TF-MoA1 **Research Strategies and Results Toward Improving Thin Film CdTe Photovoltaic Devices Beyond 20% Conversion Efficiency**, T.A. Gessert, National Renewable Energy Laboratory **INVITED**

Recent studies of thin-film CdS/CdTe photovoltaic (PV) devices have suggested that significantly higher device performance will not be achieved unless recombination in the CdTe is reduced. Specifically, unless high recombination in the CdTe quasi-neutral region is reduced, benefits of increasing CdTe net-acceptor doping cannot be realized—because resulting higher open-circuit voltage will be accompanied by lower fill factor. Although some control of CdTe recombination has been achieved historically through the careful incorporation of oxygen, chlorine, and copper, many technologists believe a more promising avenue to higher device performance is by understanding and controlling the defects in the as-deposited CdTe. This is supported by theoretical studies that suggest much of the improvement associated with oxygen, chlorine, and copper is due to the interaction of these species with intrinsic defects related cadmium and tellurium (i.e., vacancies, interstitial, and anti-site defects). Although CdTe is a relatively simple semiconducting material that exists only near its 50%/50% composition, even at thermodynamic equilibrium, the material can sustain a small stoichiometric deficiency (~0.01%). Even this small extent of stoichiometry variation can produce intrinsic defects at a sufficient concentration to significantly alter device performance. Further, the typical techniques used in PV film deposition are not equilibrium processes, and so the extent of non-stoichiometry could be greater. Several research projects at NREL are currently focused on altering CdTe deposition and post-deposition processes to allow for an enhanced control of the as-deposited intrinsic defects. Related defect changes are being assessed using a combination of device analysis, time-resolved photoluminescence, low-temperature photoluminescence, and microscopic techniques. The presentation will discuss initial results where process changes expected to alter the as-deposited defects also affect junction evolution and device functionality. *This abstract is subject to government rights.*

2:40pm EN+TF-MoA3 **Nanocrystal-Ink and Soluble-Precursor Routes to Earth Abundant Element Kesterite Solar Cells**, H.W. Hillhouse, University of Washington **INVITED**

Given the terawatt scale of future energy needs, the most promising future photovoltaic materials should be Earth abundant with their primary mineral resources distributed across several geographic regions and their supply chains robust to reduce concerns of price volatility. In addition, the process of forming the solar cell should be scalable, low-cost, and not utilize dangerous or toxic materials. The strongest initial candidate appears to be kesterite structures of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and similar materials. The presentation will review the progress in developing photovoltaics devices based on these materials and our group's recent experimental and modeling results.

CZTS thin film solar cells have historically been synthesized by evaporating or sputtering metals (Cu, Zn, & Sn) followed by sulfurization or selenization. More recently, two potentially low-cost high-throughput approaches have been demonstrated that form the quaternary or pentenary chalcogenide directly from solution-phase processes. One is based on first synthesizing multinary sulfide nanocrystals and then sintering them to form a dense layer. The other approach utilizes molecular precursors dissolved in hydrazine. Both new approaches reach their highest device efficiencies by incorporating Se to form $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ devices, and each has yielded substantially higher efficiency devices than the best vacuum deposited absorbers. The hydrazine route has yielded the most efficient CZTS-based devices thus far. The presentation will highlight our recent progress in CZTS-based nanocrystal-ink devices. In particular, we have shown that germanium may be alloyed with CTZS (at least up to Ge/(Sn+Ge) ratios of 0.7) to form $\text{Cu}_2\text{Zn}(\text{Sn,Ge})\text{S}_4$ nanocrystals that have an increased bandgap. The defect chemistry is serendipitous, and yields devices at with greater than 8% power conversion efficiency. This exciting prospect may be used to create a back surface field and direct carriers in a similar manner to how gallium is used in high efficiency CIGS devices. In addition, we will report recent results from high throughput experiments focused on identifying doping and passivation agents.

3:40pm EN+TF-MoA6 **Developing Earth Abundant and Quantum Dot Materials for Thin-Film Photovoltaics**, M. Law, University of California Irvine **INVITED**

This talk describes projects in our group to develop thin-film photovoltaics based on earth-abundant iron pyrite (FeS_2) active layers and PbSe quantum dot (QD) solids. I will first introduce the promise and challenge of pyrite, describe solution- and gas-phase syntheses of pyrite films, and present preliminary electrical characterization of pyrite layers and device stacks. Then I will switch gears to highlight several projects focused on the chemistry/physics of QD solids, including our use of atomic layer deposition to produce environmentally-robust PbSe QD films with long carrier diffusion lengths for next-generation solar cells.

4:20pm EN+TF-MoA8 **Synthesis of Photovoltaic $\text{Cu}_2\text{ZnSnS}_4$ via Ex Situ Sulfidation of Co-Sputtered Cu-Zn-Sn Thin Films**, M. Johnson, M. Manno, X. Zhang, C. Leighton, E.S. Aydil, University of Minnesota

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is an emerging low-cost solar absorber for thin film photovoltaics based on non-toxic, high earth-abundance elements. While *ex situ* sulfidation of Cu-Zn-Sn precursor films in S vapor is a popular synthesis route for CZTS, much remains to be understood with regard to the sulfidation mechanisms, microstructural control, and structure-property relationships. In this work, DC magnetron co-sputtered Cu-Zn-Sn films, of varying composition, were sealed with 1.0 mg of S in evacuated (10^{-6} Torr) quartz ampoules, and then isothermally heat treated at sulfidation temperatures in the range $100^\circ\text{C} \leq T_S \leq 700^\circ\text{C}$. The films were then characterized structurally by scanning electron microscopy, Raman spectroscopy, and X-ray diffraction, and electrically via resistivity measurements between 4.2 K and 300 K. We find that the phase purity of the resultant films depends strongly on T_S , with complete conversion of the precursor film to CZTS occurring only at $T_S \geq 550^\circ\text{C}$. The final phase purity of *ex situ* sulfidized CZTS films is however remarkably insensitive to modest amounts of excess Zn and Sn in the Cu-Zn-Sn precursor film. Excess Zn or Sn in the precursor is readily ejected during sulfidation, via elemental or binary sulfide evaporation, respectively, while Sn-deficiency can also be corrected by introducing elemental Sn to the sealed quartz ampoule. However, due to the low melting point of Sn, and the absence of appropriate Sn-Zn alloys, the precursor composition *does* play a significant role in defining the final CZTS film microstructure, and the lateral homogeneity. In addition to detailed discussion of the physics and chemistry underlying the above observations we will also provide data on the transport properties of such films, including observations of hopping conduction.

Work supported by NSF (CBET-0931145) and IREE (RL-0004-11)

4:40pm EN+TF-MoA9 **Crossover from Intergranular Hopping to Conventional Charge Transport in Pyrite FeS_2 Thin Films**, X. Zhang, M. Manno, A. Baruth, M. Johnson, E.S. Aydil, C. Leighton, University of Minnesota

Pyrite FeS_2 is undergoing a tremendous resurgence of interest as a candidate thin-film solar absorber based on abundant, low-cost, non-toxic elements. Historically, FeS_2 -based Schottky solar cells have suffered from low open circuit voltages (~100 mV), and thus low efficiency, although the origins of this behavior are not entirely clear. In fact, even the electronic properties of FeS_2 are not well understood, including the conduction mechanisms and doping behavior. Understanding these issues could contribute significantly to improvements in FeS_2 -based solar cells, particularly if doping can be understood and controlled. In this work, we present a comprehensive study of the conduction mechanism in FeS_2 thin films synthesized via the *ex situ* sulfidation of Fe films in a S vapor at sulfidation temperatures in the range $100^\circ\text{C} \leq T_S \leq 700^\circ\text{C}$. The resultant films were characterized structurally, using X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, and confocal Raman microscopy; electrically, via transport and magnetoresistance measurements between 4.5 and 300 K; and magnetically with high-sensitivity dc magnetometry. At T_S around 500°C we observe a crossover in the conduction mechanism from some form of hopping conduction to a more conventional band transport-type mechanism. Through detailed analysis of the hopping parameters, measurement of the Fe spin-state, and simple calculations based on S diffusion in Fe, we demonstrate that intergranular hopping occurs via highly conductive, S-deficient, nanoscopic grain cores separated by nominally stoichiometric FeS_2 shells. We find that the approach towards more conventional band transport as T_S is increased above 500°C is due to an increase of S diffusion into the FeS_2 grains. Moreover, this conduction mechanism crossover is found to be accompanied by a sign reversal of the Hall coefficient, from hole-like (in the hopping regime) to electron-like. In addition to placing hard constraints on the conditions under which useful properties can be

obtained from FeS₂ synthesized under diffusion-limited conditions, these results also highlight potential problems with prior conclusions on the dominance of *p*-type behavior.

The work was supported by the Initiative for Renewable Energy & the Environment, IREE ((RL-0004-11) . Part of this work was carried out in the University of Minnesota Characterization Facility, a member of the NSF-supported Material Research Facilities Network.

5:00pm **EN+TF-MoA10 Plasma Assisted Synthesis of Pyrite Absorbers**, *R. Morrish, R. Silverstein, C.A. Wolden*, Colorado School of Mines

Pyrite (FeS₂) is a non-toxic, earth abundant chalcogenide with desirable characteristics for application as a photovoltaic absorber including a modest band gap of 0.95 eV and a large optical absorption coefficient ($>10^5 \text{ cm}^{-1}$). Although theoretically capable of >20% efficiency, to date pyrite devices have displayed poor performance. One key challenge has been the production of stoichiometric material that is free of impurity phases. Conventional approaches employ thermal sulfurization of iron-based films or precursors. These routes inherently produce contaminate phases (troilite, pyrrhotite, marcasite), that once formed, are difficult to completely remove. Thermodynamics suggests that hematite ($\alpha\text{-Fe}_2\text{O}_3$) may be directly converted to pyrite in the presence of sufficiently high sulfur activity. In this work, we demonstrate pyrite synthesis using a H₂S plasma to sulfurize hematite nanorods produced using chemical bath deposition. Conversion to pyrite was achieved by exposure to a 90% Ar-10% H₂S plasma at moderate temperature (350 - 450 °C). The application of plasma dramatically enhances both the rate of conversion and the quality of the resulting material. Composition analysis using both Raman and X-ray photoelectron spectroscopy confirm that the resulting pyrite is free of common impurity phases. The degrees of sulfur incorporation could be precisely controlled by plasma exposure, and the apparent optical band gap could be systematically reduced from 2.2 to 1.0 eV. Electron microscopy images showed the surface maintained a nanostructured architecture following sulfurization, and a 150 nm thick film was sufficient to absorb 99% of incident visible light. In this presentation we discuss the kinetics of this solid state transformation, as well as report on the optoelectronic properties of these materials.

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