

Tuesday Morning, October 30, 2012

Energy Frontiers Focus Topic

Room: 15 - Session EN+TF-TuM

Chalcogenide Solar Cells II

Moderator: H.W. Hillhouse, University of Washington

8:00am **EN+TF-TuM1 Thin Film Solar Cells: Present Status and Future Prospects.** *C.S. Ferekides*, University of South Florida **INVITED**

Thin film photovoltaics (TF PV) have long been viewed as a low cost option for solar electricity. Two very promising TF technologies are based on Cu(In,Ga)(S,Se)₂ (CIGS) and CdTe. The former has achieved the highest thin film laboratory efficiency (over 20%) and the latter is the lowest cost PV product on the market today (@ \$0.74/Watt). Recently, another thin film technology based on the kesterites Cu₂ZnSn(S,Se)₄ (CZTS) has received significant attention due to the abundance of the constituent elements, and small area cells have reached the 10% efficiency level. Despite all the successes achieved at the laboratory and manufacturing environments, TF technologies continue to face challenges some of which are unique to the specific material system. The presentation will provide an overview of thin film photovoltaics by comparing and contrasting the devices and technologies described above. Material, device and fabrication issues will be discussed with emphasis placed on some of the unique aspects of each technology: the need for sodium for CIGS and the importance of the co-evaporation process, the use of a chloride based treatment for CdTe and the challenge in forming back contacts to this device, and the loss of tin for CZTS.

8:40am **EN+TF-TuM3 Materials and Process Options for Cu(InGa)Se₂ Thin Film Solar Cells.** *W.N. Shafarman*, University of Delaware **INVITED**

Two approaches to depositing thin films of Cu(InGa)Se₂ and related alloys have been developed in the laboratory and are being implemented in large scale photovoltaics manufacturing. Precursor reaction processes use precursor films containing Cu, Ga, and In deposited by methods such as sputtering, printing, or electrodeposition chosen to provide potential manufacturing benefits. These are reacted in hydrogen selenide gas or elemental Se vapor to form the semiconductor absorber layer. Elemental co-evaporation is a single step process in which fluxes of all species are delivered to a hot substrate. Advantages and critical issues for these processing approaches will be compared. One of the materials options for Cu(InGa)Se₂-based absorber layers is the opportunity to alloy the film to increase its bandgap. This is desirable because the increased solar cell voltage can be advantageous for large scale module performance. Wider bandgap can be achieved by increasing the relative Ga content or by alloying with S, Al or Ag, but in all cases the cell efficiency decreases as the absorber layer bandgap increases beyond 1.2-1.3 eV. Alloying and composition control is generally straightforward using co-evaporation since these alloys form continuous solutions. With precursor reaction, however, chemical pathways to film formation are partly controlled by preferential reaction of Se with In instead of Ga, leading to aggregation of the Ga at the back of the film and, effectively, low bandgap. Multi-step reaction profiles can be used to control through-film composition in this case. For wide bandgap cells, recent results with the combination of Ag alloying and higher Ga content show promise. This includes improved optical properties, evidence of reduced structural disorder and improved performance with high open circuit voltage solar cells. The incorporation of Ag in both the precursor reaction and co-evaporation processes will be described.

9:20am **EN+TF-TuM5 Why Are We Making CIGS Solar Cells from Cu-poor Material?** *S. Siebentritt*, University of Luxembourg **INVITED**

CIGS can be prepared single phase in a large range of Cu-poor compositions. When prepared under Cu-excess a secondary phase of Cu selenide is formed which can be etched. Record solar cells as well as commercial modules are prepared from Cu-poor absorbers. However, the transport and recombination properties of material prepared under Cu-excess are superior. It has been known that the interface in cells with absorbers prepared under Cu-excess leads to increased recombination and thus limits the efficiency. The properties of the surface of CIGS absorbers prepared under Cu-excess is not well understood so far. We are preparing solar cells with absorbers grown under Cu-excess, where we make the surface Cu-poor to get the best from both worlds.

10:40am **EN+TF-TuM9 Zn_xCd_{1-x}S Thin Films for Chalcopyrite Solar Cells Deposited through Batch and Continuous-Flow Chemical Bath Deposition.** *B.S. Tosun, C. Pettit, S.A. Campbell, E.S. Aydil*, University of Minnesota

Copper indium gallium diselenide (CIGS) thin film solar cells already exceed 20 % overall power conversion efficiencies. These high efficiencies are achieved using an n-type cadmium sulfide (CdS) buffer layer deposited on the p-type CIGS absorber using chemical bath deposition. CdS buffer layers are also used in the emerging copper zinc tin sulfide/selenide (CZTSSe) based solar cells. In some cases, it is desired to grade and widen the band gap of the buffer layer away from the CdS-absorber interface by alloying CdS with Zn to form Zn_xCd_{1-x}S films. In this work, we demonstrate the ability to manipulate Zn fraction, x, as a function of distance from the absorber-buffer layer interface and investigate the fundamental factors that govern the evolution of the film composition as a function of depth. Specifically, Zn_xCd_{1-x}S films were grown from solutions containing cadmium sulfate ammonium hydroxide, ethylenediaminetetraacetic acid disodium, zinc sulfate and thiourea in two different types of chemical baths, a traditional batch-type chemical bath and a continuous-flow chemical bath. By changing the initial concentrations of Zn and Cd sulfate in the batch-type chemical bath deposition, the entire range of overall compositions ranging from primarily cubic ZnS to primarily hexagonal CdS could be deposited. Using Auger depth profiling, we show that a CdS rich layer forms at the film/substrate interface due to the faster reaction of Cd than Zn. The formation of Cd-rich Zn_xCd_{1-x}S layer at film/substrate interface followed by Zn-rich Zn_xCd_{1-x}S is favorable for solar cells. Thicker films with increasing band gap towards the surface can be deposited to increase the shunt resistance without sacrificing light transmission. In addition, we have developed a continuous chemical bath deposition system that allows deposition of Zn_xCd_{1-x}S films on 4-inch diameter substrates at temperatures as high as 80 °C without significant liquid temperature rise and without homogeneous nucleation and growth. Structure and composition of the films from the batch and continuous flow systems will be discussed and compared.

11:00am **EN+TF-TuM10 Selenization of Cu-Ga-In Precursors for Synthesis of CIGS Absorbers: Equilibrium and Kinetic Studies.** *C. Muzzillo, R. Krishnan*, University of Florida, *W.K. Kim*, Yeungnam University, Republic of Korea, *E.A. Payzant*, Oak Ridge National Laboratory, *Y.H. Sohn, B. Yao*, University of Central Florida, *J. Shen*, General Research Institute for Non-ferrous Metals of Beijing, China, *C. Campbell*, National Institute of Standards and Technology, *T.J. Anderson*, University of Florida

The emerging CuIn_xGa_{1-x}Se₂ (CIGS) PV industry is primarily differentiated on the basis of the process used to synthesize the CIGS absorber. The most common approach is a 2-step metal deposition/selenization with differentiation occurring on the method of metal deposition and Se source for selenization. Typical champion cell efficiencies, however, are slightly lower for 2-step processes as compared to co-evaporation. This has been attributed to difficulty in creating a 'U-shaped' Ga profile, void formation near the back contact, and differences in diffusion/reaction rates of Ga and In during synthesis. Furthermore, cost pressures are driving reduction of the selenization time (up to 8 hr) and thinning of the absorber layer. A better understanding of the thermodynamic and kinetic elements of the precursor Cu-Ga-In metal system offers the potential to exploit faster pathways, assist in scale-up, and ensure robust processing of CIGS. This study includes a critical assessment of thermochemical and phase equilibria data of the Cu-Ga-In ternary metal system. The calculated phase diagram includes 11 binary intermetallic phases and no ternary compounds. Of particular interest are the 4 phases which exhibit ternary solubility: α-Cu (fcc), γ-Cu₉(Ga_xIn_{1-x})₄ (sc), and η-Cu₁₆(In_xGa_{1-x})₉ (hcp) are all modeled with a sublattice formalism, and an ionic two-sublattice liquid model is employed. Time-resolved *in situ* high temperature X-ray diffraction data for selenization of metallic precursors have also been collected. Reaction pathways and kinetics of temperature ramp and isothermal anneal experiments have both been examined, and kinetic rate parameters for the Avrami and parabolic growth models have been estimated from the data. As examples, MBE deposited bilayer metal precursor structures (*e.g.* CuIn/CuGa) and elemental stacked layers (*e.g.* (Cu/Ga/In)_n) were selenized and the Ga distribution measured. The formation of Cu₁₁In₉, textured indium, and the solid solution γ-Cu₉(Ga_xIn_{1-x})₄ were also evident as well as formation of CuGaSe₂ and CIGS simultaneously for selected structures. Rietveld refinement of temperature ramped selenized samples was performed to estimate the Ga distribution. TEM-EDS results confirm that the Ga distribution after selenization depended on the order of deposition of the precursor structure. The samples were further characterized by SEM (microstructure) and ICP (final composition). The activation energy for formation of CIGS was

estimated from isothermal studies, and gave values of $76(\pm 14)$ for the glass/Mo/CuIn/CuGa and $93(\pm 4)$ and $101(\pm 9)$ kJ/mole for the glass/Mo/CuGa/CuIn precursor.

11:20am **EN+TF-TuM11 Fabrication of $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ Thin-Film Solar Cells on Single Layer Molybdenum**, *A. Kaul, E. Schmeller, N. Shiradkar, S. Pethe, N. Dhere*, Florida Solar Energy Center, University of Central Florida

Considering the various advantages of a single pass operation, efforts have been made to develop a recipe for device quality single layer molybdenum back contact film that has good adhesion to the soda-lime glass substrate and at the same time lower resistivity values. $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ (CIGS2) thin film solar cells with reasonable efficiencies were successfully fabricated on the single layer molybdenum film without any signs of peeling or back contact degradation during processing. The molybdenum films were also subjected to various processing conditions of temperature and gas ambient and the subsequent results from these tests are also being presented.

11:40am **EN+TF-TuM12 Investigation of Elemental Composition for $\text{Cu}(\text{InGa})\text{Se}_2$ Thin Films by Various Analytical Techniques**, *J.H. Lee, S.H. Kim, J.-H. Yoon, S.-O. Won, Y.H. Lee*, Korea Institute of Science and Technology, Republic of Korea

$\text{Cu}(\text{InGa})\text{Se}_2$ (CIGS) solar cells are very promising films for use in photovoltaic devices, as they feature a high absorption coefficient and a high conversion efficiency at a relatively low manufacturing cost. In order to develop an efficient CIGS solar cell, the relative ratio of the major elements should be determined quantitatively. In this study, a quantitative analysis of $\text{Cu}(\text{InGa})\text{Se}_2$ (CIGS) was performed using an electron probe micro analysis (EPMA), x-ray fluorescence (XRF), inductively coupled plasma-optical emission spectrometry (ICP-OES), Auger electron spectroscopy (AES), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and dynamic secondary ion mass spectrometry (dynamic SIMS). Surface roughness was observed by using atomic force microscopy (AFM) to identify the effect of the surface roughness on the reproducibility of the measurements. The relative sensitivity factors (RSF) of AES and SIMS were obtained by using ungraded CIGS thin film of known composition as the standard sample. Quantitative analysis of several CIGS samples were performed using the relative sensitivity factor (RSF) value calculated from the depth profile results of the standard film. The Cu/(In+Ga) ratio and the Ga/(In+Ga) ratio of SIMS results are relatively reproducible and close to those of the AES results. Overall, results from Composition of CIGS thin films by a variety of analytical methods were compared and their discrepancies were interpreted.

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