Wednesday Morning, October 20, 2010

Energy Frontiers Topical Conference
Room: Pecos - Session EN+TF-WeM

CIGS, CZTS and Chalcopyrite Films & Solar Cells
Moderator: E.S. Aydil, University of Minnesota

8:00am **EN+TF-WeM1 CIGS and CZTS Nanocrystal-Ink Solar Cells**, *H.W. Hillhouse*, *R. Agrawal, Q. Guo, G.M. Ford*, Purdue University
INVITED
The development of suitable colloidal nanocrystal inks are a key step in the development of low-cost solar cells since they enable the use of fast and inexpensive coating processes such as spray coating and roll coating to form a thin film photoabsorbing layer. Chalcopyrite structure copper indium gallium diselenide (CIGSe) and stannite or kesterite copper zinc tin sulfides (CZTS) are key photoabsorbing materials for thin film solar cells due to their near ideal band gap and their serendipitous defect chemistry (CIGSe) and Earth abundance (CZTS). Although several methods have been reported that describe the synthesis of CIGSe and related nanocrystals, precise control of the composition for these ternary and quaternary compounds has been problematic [1]. We have reported the solution-phase synthesis of stoichiometric chalcopyrite structured CuInSe2 nanocrystals [2], Cu(In,Ga)S2 [3], and the very first synthesis of Cu2ZnSnS4 nanocrystals [4]. The syntheses proceed rapidly from elemental and halide reagents via a simple batch reaction without "hot injection" in a single component coordinating solvent. We have demonstrated the use of these nanocrystals for low-cost solar cells by fabricating devices without using any oxygen-free techniques (after NC synthesis) and employing a scalable roll coating method. The nanocrystal inks are first coated on a back contact (Mo coated sodalime glass in this case). The nanocrystal layer is then easily consolidated into large crystalline domains by a brief thermal treatment in a selenium rich atmosphere to prevent selenium loss or to replace sulfur with selenium. The fabricated cells are robust and increase in efficiency with time, exhibiting similar serendipitous defect chemistry as layers formed by vacuum co-evaporation. We have fabricated solar cells by roll coating CIGS or CZTS nanocrystal-inks over large areas. CIGS devices fabricated by roll coating over large areas with a device architecture of Mo/CIGSSe/CdS/i-ZnO/ITO/Ni/Al are (at the time of the abstract submission) 12.0% efficient under standard AM1.5G illumination. The presentation will focus on the key aspects of the nanocrystal synthesis, ink coating, nanocrystal consolidation, and device fabrication and characterization for both CIGS and CZTS solar cells.

[1] Hillhouse H.W. & Beard M.C., Current Opinion in Colloid & Interface Science, 14, 245 (2009).

[2] Guo, Q.J., Kim, S.J., Kar, M., Shafarman, W.N., Birkmire, R.W., Stach, E.A., Agrawal, R., Hillhouse, H.W., Nano Letters 8, 9, 2982 (2008).

[3] Guo, Q.J., Ford, G.M., Hillhouse, H.W., Agrawal, R., Nano Lett. 9, 8 3060 (2009).

[4] Guo, Q.J., Hillhouse, H.W., Agrawal, R., J. Am. Chem. Soc. 131, 11672 (2009).

8:40am **EN+TF-WeM3 Compositional (non)Uniformity and its Effect on CIGS Solar Cell Performance**, *W. Li*, *S.R. Cohen, K. Gartsman, P. von Huth, R. Popovitch-Biro*, Weizmann Institute of Science, Israel, *Th. Rissom*, Helmholtz Zentrum Berlin, Germany, *D. Cahen*, Weizmann Institute of Science, Israel
CIGS is a promising material for solar cell applications. Uniformity of the polycrystalline composition and structure is an important factor in the solar cell performance. This work is an attempt to study CIGS (non)uniformity systematically as a function of depth, employing independent, complementary high resolution techniques which also reveal inter- and intra-grain compositional, structural, and electronic nonuniformities. In particular, thin cross-sections, prepared by field ion beam (FIB), were studied using TEM-based techniques to achieve higher spatial resolution of the composition than is normally possible. It was found that the Ga/In ratio in the devices drops initially with depth, then rises sharply again near the Mo contact. Furthermore, large variations of this ratio are observed from grain to grain. This variation is even observed within individual single crystal grains along their growth direction. Our measurements confirm the formation of a $MoSe_2$ phase at the Mo – CIGS interface. The lattice constant, measured by selected area diffraction (SAD), varies with the Ga composition, in agreement with Vegard's law. The extent of compositional variation was found to vary inversely with the temperature of sample preparation. Additionally, our measurements confirm the formation of a $MoSe_2$ phase at the Mo – CIGS interface.

A series of scanning probe (SPM)-based techniques, including scanning capacitance microscopy (SCM) and conducting probe atomic force microscopy (CP-AFM) were applied to correlate local device performance and doping concentration with the composiitonal (non)uniformity revealed in these TEM results and will be presented here.

This compositional non-uniformity may well be of relevance for the properties and performance of solar cells made with such films, and this issue will be addressed in the talk.

9:00am **EN+TF-WeM4 Combinatorial $Cd_{1-x}Zn_xS$ Thin Films Deposited with a Continuous Flow Microreactor**, *K.M. McPeak*, Drexel University, *H.P. Bui, T.P. Beebe*, University of Delaware, *J.B. Baxter*, Drexel University
Chemical bath deposited CdS thin films are commonly used as buffer layers in CdTe and CIGS photovoltaics because they form a high quality *p-n* junction with the absorber. However, light absorption by the CdS reduces solar cell efficiency. $Cd_{1-x}Zn_xS$ has a wider band gap than CdS, offering the potential to reduce deleterious absorption of light in the 300-550 nm range and improve current densities by over 2 mA/cm^2. To maximize energy conversion efficiency, the $Cd_{1-x}Zn_xS$ should be a single-phase ternary alloy and the stoichiometry should be optimized to ideally position the conduction band edge for increased transmissivity while retaining good junction properties.

We report on chemical bath deposition of combinatorial $Cd_{1-x}Zn_xS$ thin films using a continuous flow microreactor. The microreactor uses a sub-millimeter reaction channel, with the substrate acting as one reactor wall. The microreactor behaves like a plug flow reactor whereby the bath composition changes as flowing material is deposited on the substrate. While the bath composition changes with respect to position down the reaction channel, the composition at any position is time-invariant. The graded bath composition results in deposition of graded thin films whose stoichiometry and optoelecronic properties change significantly over length scales of millimeters to centimeters. Spatially resolved characterization of the substrate enables rapid and direct correlation of material properties to growth conditions, which is not possible with a batch reactor where bath composition changes with time.

Graded $Cd_{1-x}Zn_xS$ films grown with 1:200 Cd:Zn bath composition at the inlet had composition that varied from x=0.0 to x=0.17 over a distance of 12 mm on a single substrate. Film stoichiometry was determined by x-ray photoelectron spectroscopy (XPS) mapping. Stoichiometry changes because of differences in speciation and reaction kinetics of the cation species as they flow down the channel. XPS and XRD confirm that CdZnS is a single phase material. Deep level emission in photoluminescence and XPS indicate that O and OH is also incorporated into the film and is bound to Zn, with amount increasing further down the reaction channel. The graded stoichiometry causes the absorption edge to blue-shift by over 80 nm, as determined by UV-vis transmission and reflectance measurements. Blue-shifting band edge and changes in defect density are also seen by photoluminescence. The continuous flow microreactor offers new potential for deposition of graded thin films that act as combinatorial libraries for high throughput screening and accelerated materials discovery.

9:20am **EN+TF-WeM5 A Chemical Bath Process for Depositing Cu_2ZnSnS_4 Photovoltaic Absorbers**, *A. Wangperawong, J.S. King, S.M. Herron, B.P. Tran, K. Pangan-Okimoto, S.F. Bent*, Stanford University

9:40am **EN+TF-WeM6 Synthesis Routes for $CuIn_{1-x}Ga_xSe_2$ Thin Film Absorbers**, *R. Krishnan*, *T.B. Song, V.U. Chaudhari,* University of Florida, *E.A. Payzant,* Oak Ridge National Laboratory, *R. Noufi,* National Renewable Energy Laboratory, *T.J. Anderson*, University of Florida
Chalcopyrite Cu(In,Ga)Se$_2$ is one of the most promising absorber materials for high efficiency thin film solar cells with reported conversion efficiency exceeding 20%. The National Solar Technology Roadmap for CIGS PV specifically calls for deposition rates of *"30–40 μm/h and <1 μm CIGS absorber thickness"* by 2015. This is compared to the current estimate in the Roadmap of *"5 μm/h and 1.25–3 μm CIGS absorber thickness."* The comparison translates into a reduction of the absorber synthesis time from ~15 to 36 min to ~1.5 to 2 min. The challenge is to get high throughput and yield with columnar grain growth while retaining the high efficiency. In this work *in-situ* high temperature X-ray diffraction with and without selenium overpressure is used to determine absorber synthesis mechanisms for various precursors structures. Qualitative analysis of the data gives information on the reaction pathway and quantitative analysis of the data yields rate constants.

This presentation summarizes studies on the selenization of elemental stacked layers of copper, indium, gallium and selenium in two different

configurations. In the first configuration (sample A), copper was first deposited on glass/Mo substrates, followed by gallium, indium and selenium. In the other configuration (sample B), gallium was first deposited followed by indium, copper and selenium. ICP results showed that both the samples were copper poor. Reaction pathways were followed with and without selenium overpressure and isothermal soaking experiments were performed to obtain the kinetic parameters using the Avrami growth model to reduce the data. The reaction pathways were similar for both the configurations, showing formation In, Cu_9Ga_4, and Cu_2Se initially, followed by Se crystallization and formation of the intermediates In_4Se_3, $CuSe_2$, $CuSe$ and CIS, and finally yielding product $CuIn_{1-x}Ga_xSe_2$. The value of x computed from Vegard's law yielded 0.35 for sample A and 0.37 for sample B. The activation energy computed from the Avrami model yielded 88.4($\pm$12) and 125.1(($\pm$9) kJ/mole for samples A and B, respectively. The decrease in the local Avrami exponents (0.21-0.26) suggests the existence of an inhomogeneous distribution of nuclei during growth or interdiffusion of gallium and indium with simultaneous grain growth. Additional characterization such as SEM and TEM were performed to provide physical and compositional support of the pathway.

10:40am **EN+TF-WeM9 Atmospheric Processing Approaches to Low Cost Scalable Photovoltaics**, *M.F.A.M van Hest, A. Miedaner, C.J. Curtis, J. Leisch, P. Hersh,* National Renewable Energy Laboratory *, K. Steirer, R.M. Pasquarelli, J.A. Nekuda, R.P. O'Hayre,* Colorado School of Mines*, **D.S. Ginley***, National Renewable Energy Laboratory   **INVITED**

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