

# Wednesday Afternoon, November 2, 2011

## Energy Frontiers Focus Topic

Room: 103 - Session EN1+TF-WeA

### Thin Film Chalcogenide Solar Cells (CIGS, CZTS, CdTe and Related Materials)

Moderator: L.W. Rieth, University of Utah

2:00pm **EN1+TF-WeA1 Comparative Study of Structure and Morphology of  $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$  and  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  Thin Film Absorbers Using EBSD**, A. Kaul, E. Schneller, N.G. Dhere, Florida Solar Energy Center, H.R. Moutinho, National Renewable Energy Laboratory

Electron backscatter diffraction (EBSD) in scanning electron microscopy (SEM) is a powerful technique that allows crystallographic information such as the grain orientation, grain boundaries and also the grain size to be obtained. Crystalline maps are formed in EBSD while the electron beam of a SEM scans the sample surface providing information about crystalline orientation of individual grains as well as features such as twin boundaries. This study relates to EBSD investigation of  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGSe) and  $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$  (CIGS2) samples that were prepared by a two stage process which is easily scalable to large area manufacturing. Since sample polishing is very critical for generation of very good quality Kikuchi pattern formed by back scattered electrons, the earlier work was focused on optimizing the sample polishing technique. Efforts were also made to develop a database to facilitate proper indexing and corresponding accurate determination of preferred orientation of the pseudo-quaternary compound absorber films. Eventually, high quality Kikuchi patterns and EBSD maps have been obtained. It is essential for the research and development of the chalcopyrite thin film absorbers to elucidate the effect of variation of processing conditions (temperature, time and composition) on the growth and development of microstructure. Therefore, in the current work, CIGSe and CIGS2 absorber films were synthesized under different processing conditions and their EBSD maps and patterns are being compared in terms of grains size, grain orientation and grain boundaries as a necessary and vital step prior to undertaking the study of the still more complex compound  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2-y}\text{S}_y$  (CIGSeS) being used in large-volume production of photovoltaic solar cells and modules.

2:20pm **EN1+TF-WeA2 Improving the Damp-Heat Stability of Copper Indium Gallium Diselenide Solar Cells**, B.S. Tosun, University of Minnesota, R.K. Feist, The Dow Chemical Company, S.A. Campbell, E.S. Aydil, University of Minnesota

While copper indium gallium diselenide (CIGS) thin film solar cells with laboratory efficiencies exceeding 20 % have been reported, these high efficiencies may degrade with time as the devices are exposed to humid environments. It is well known that grain boundary diffusion of water through the ZnO to the CIGS-CdS interface is implicated in long-term degradation of the solar cell performance.<sup>1</sup> This penetration must be reduced or stopped to increase the solar cell lifetime. Herein, we show that amorphous tin dioxide ( $\text{SnO}_2$ ) layers deposited by radio frequency (RF) magnetron sputtering on top of the completed CIGS solar cells can significantly increase the device lifetime by forming a barrier against water diffusion. Specifically, with approximately 0.2 micron and thicker  $\text{SnO}_2$  layers deposited on top of the completed CIGS solar cells we have demonstrated that initially 11.1 % efficient CIGS solar cells lose less than 7 % of this peak efficiency and still exhibit efficiencies greater than 10 % (factor of 10%) after 150 hours at 85 °C and 85 % relative humidity. In comparison, under identical test conditions, the solar cells without the  $\text{SnO}_2$  layer lost nearly 80 % of their initial efficiency within 24 hours after commencing the test. We studied the effects of deposition conditions and film thickness for different film structures on the solar cell stability in damp-heat tests. The deposited  $\text{SnO}_2$  films tend to be amorphous when deposited at room temperature or when the films are thin, but show increased crystallinity for thicker films and films deposited at 150 °C. We found that solar cells coated with polymorphous  $\text{SnO}_2$  films exhibit better damp-heat stability than those coated with polycrystalline films. By polymorphous we mean films that consist of nanocrystalline  $\text{SnO}_2$  embedded in amorphous  $\text{SnO}_2$ . We attribute this difference to the lack of grain boundary diffusion in polymorphous  $\text{SnO}_2$  films. Replacing the crystalline ZnO window layer with a  $\text{SnO}_2$  film can provide further protection of the CIGS solar cells. We demonstrate a 8.2±0.2 % efficient CIGS solar cell with a  $\text{SnO}_2$  window layer. Same solar cell fabrication process and CIGS film with ZnO window layer resulted in 8.2±0.6 % overall efficiency. The open circuit voltages of the two cells were the same indicating that the band alignment with the  $\text{SnO}_2$  film is suitable for CIGS. These  $\text{SnO}_2$  films were deposited using magnetron sputtering at 5 mTorr

and 150-250 W RF power using Ar as the sputtering gas without substrate heating.

<sup>1</sup>R. Feist et al, IEEE Photovoltaic Specialist Conference, 2009.

2:40pm **EN1+TF-WeA3 Progress Towards a High-Efficiency Cu-Zn-Sn-S-Se Thin-Film PV Technology**, D.B. Mitzi, O. Gunawan, T.K. Todorov, D.A.R. Barkhouse, S. Bag, R. Haight, T. Gokmen, T. Goisard de Monsabert, S.J. Chey, S. Thiruvengadam, IBM T.J. Watson Research Center

**INVITED**

A key criteria for achieving terawatt-compatible photovoltaic (PV) technology is the ability to fabricate high power conversion efficiency (>10%) solar cells using a low-cost process (< \$1/watt) and readily available, abundant and preferably non-toxic materials. The kesterites,  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTSSe), are considered a promising PV technology for meeting this goal because of similar electronic properties to the two leading thin-film chalcogenide technologies, CdTe and  $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$  (CIGSSe), achieved while employing low-cost, readily-available constituents. This talk will discuss recent developments that have enabled the demonstration of the first CZTSSe solar cells with certified power conversion efficiencies of over 10%, using a glass/Mo/CZTSSe/CdS/i-ZnO/ITO structure and a simple liquid-based deposition approach. We also present a device characterization study that compares the CZTSSe devices with higher-performing CIGSSe analogs, elucidating some of the key performance bottlenecks in CZTSSe cells, including dominant buffer-absorber recombination, high series resistance and a relatively short minority carrier lifetime. These studies help to elucidate key areas for improvement for the CZTSSe cells in the effort to develop a high performance pervasive technology.

4:00pm **EN1+TF-WeA7 Solar Cells from Colloidal Dispersions of  $\text{Cu}_2\text{ZnSnS}_4$  Nanocrystals**, A. Khare, Y. Li, B. Chernomordik, B.S. Tosun, A.W. Wills, D.J. Norris, E.S. Aydil, University of Minnesota

Copper zinc tin sulfide ( $\text{Cu}_2\text{ZnSnS}_4$  or CZTS) is emerging as a promising photovoltaic material for thin film solar cells. CZTS has a band gap of ~1.4 eV, the ideal value for converting the maximum amount of energy from the solar spectrum. In addition, CZTS has a high absorption coefficient ( $> 10^4 \text{ cm}^{-1}$  in the visible region of the electromagnetic spectrum) and its constituent elements are all abundant in the earth's crust and are non-toxic. We have synthesized CZTS nanocrystals from metal dithiocarbamate complexes. The diameter of the nanocrystals can be varied from 2-7 nm by changing the temperature and synthesis time. A suite of methods including Raman spectroscopy, optical absorption, electron energy loss spectroscopy and X-ray diffraction were used to characterize these nanocrystals and show that they are phase-pure CZTS. Nanocrystals with diameters less than 3 nm exhibit quantum confinement. These quantum dots were used to assemble quantum dot solar cells. In a second approach to making solar cells, thin films of CZTS nanocrystals are annealed to form thin films with large grains. Nanocrystals melt at temperatures much less than the bulk temperature and recrystallize to yield larger CZTS grains. These films were then used for making conventional thin film solar cells.

4:20pm **EN1+TF-WeA8 Surface Structure of Pyrite Thin Films Grown by MOCVD**, M. Cheng, Y. Liu, N. Berry, A. Margarella, J.C. Hemminger, M. Law, University of California, Irvine, H. Bluhm, Z. Liu, Lawrence Berkeley National Laboratory

Iron pyrite ( $\text{FeS}_2$ ) has been considered one of promising materials for use in solar cells due to its large absorption coefficient, suitable band gap and elemental abundance. In-lab X-ray photoelectron spectroscopy and tunable-energy synchrotron X-ray photoelectron spectroscopy were used to explore the surface structure of pyrite thin films grown by metal organic chemical vapor deposition (MOCVD). The influence of sodium diffusion on the growth of pyrite thin films on glass substrates was examined. By using synchrotron X-ray photoelectron spectroscopy, the different types of sulfur chemical states on the surface of pyrite thin films were resolved. The mechanism of pyrite oxidation after exposure to different oxidizing environments indicated that the surface monosulfide species were oxidized first. In addition, the band gap of pyrite thin films was determined by combining valence band spectroscopy with X-ray absorption spectroscopy compared to traditionally ultraviolet-visible absorption spectroscopy. The discrepancy between the two measurement techniques will be discussed.

4:40pm **EN1+TF-WeA9 Effect of the Use of a c-CdS Nanocrystalline Layer on the Photovoltaic Characteristics of the Screen Printed CdS/CdTe Heterostructure**, *L.G. Rangel-Chavez*, UAM-Azcapotzalco, Mexico, *M. Garcia-Aguirre*, *F.A. Cuevas-Ortiz*, Cinvestav-IPN, Mexico, *M.I. Neria-Gonzalez*, Instituto Tecnológico de Estudios Superiores de Ecatepec, Mexico, *M.A. Melendez-Lira*, Cinvestav-IPN, Mexico

The fact that the efficiency for the CdS/CdTe system has remained without any change for several years until now requires employing new approaches in order to increase it. In this work it is reported the effect on the photovoltaic characteristics of the CdS/CdTe system by employing as source of the CdS the one obtained as a by-product from bio-remediation of heavy metals in residual waters. By using a novel sulfate-reducing bacterium (*Desulfovibrio alaskensis* 6SR) particles of the CdS semiconductor are obtained. Structural and optical characterization by XRD, UV-vis, Raman and photoluminescence spectroscopies shown that nanoparticles of cubic CdS are obtained. The nanoparticles of cubic CdS are deposited on CdTe films by screen printing and then subject to a mild thermal treatment. It is expected that the employment of CdS with cubic rather than hexagonal crystal structure will reduce the number of defects at the CdS/CdTe interface improving the transport of minority carriers through it. We will report the effects on the spectral response and filling factor obtained for the CdS/CdTe heterostructure by employing nanostructured cubic CdS as compared to those obtained employing hexagonal CdS.

\*: Work partially supported by CONACyT-Mexico.

5:00pm **EN1+TF-WeA10 Surface Structure and Chemistry of AgInSe<sub>2</sub> Studied by Scanning Tunneling Microscopy**, *P. Peña Martin*, *J.W. Lyding*, *A. Rockett*, University of Illinois at Urbana-Champaign

Chalcopyrite semiconductors such as  $(\text{Cu,Ag})(\text{In,Ga})(\text{S,Se})_2$  show great promise in thin film solar cells as they exhibit high optical absorption and excellent performance even as polycrystalline layers. The alloy  $\text{AgInSe}_2$  (AIS) is a promising candidate for solar applications, as it has a nearly ideal energy gap (1.2 eV), high absorption coefficient, and shows sharper photoluminescence emissions than do the Cu-containing alloys. The surface of the material forms the heterojunction and determines many aspects of device performance. These semiconductors also contain a large number of intrinsic point defects, which are probably responsible for minority carrier recombination in the depletion region. Therefore understanding the surface and near surface nanostructure and nanochemistry are critical to device optimization. To characterize the structure and buried point defects near the surface, we used ultra high vacuum scanning tunneling microscopy (UHV-STM) to obtain atomic-scale topographic and electrical information.

We report the first atomically-resolved STM images and current-voltage profile measurements of AIS. Epitaxial layers were grown on epi-ready substrates of p-GaAs(111)A by hybrid technique, in which Ag and In are sputtered concurrently with effusion cell evaporation of Se. The resulting film was transported in a N<sub>2</sub> ambient to the STM laboratory, mounted under normal lab air as quickly as possible, and introduced to vacuum, with a total atmosphere exposure of about 20 minutes. The sample was degassed at ~100°C to drive off water and other contaminants. Electrochemically-etched W tips were used for scanning. The STM measurements were carried out in a home-built system with a base pressure of  $1.2 \times 10^{-8}$  Pa ( $9 \times 10^{-11}$  Torr). Topographic images reveal atomically-resolved regions on the surface with the periodicity expected for the polar metal-terminated [112] plane, 0.34 and 0.36 nm along rows oriented 60° from each other. This indicates that the surface does not reconstruct, unless by swapping one type of metal atom for another. Current-voltage spectra confirm that the material exhibits n-type behavior with an energy gap close to the bulk value of 1.2 eV. Some regions exhibit more fluctuations in the bandgap for a series of current spectra taken along a different line, indicating that there are variations in the electronic properties due to defects. We attempt to correlate these with topographic features in order to identify the defect responsible. Understanding and controlling these defects should lead to improved device performance, and some of the results may even carry over to CIGS devices.

5:20pm **EN1+TF-WeA11 Imaging and Phase Identification of Cu<sub>2</sub>ZnSnS<sub>4</sub> Thin Films using Confocal Raman Spectroscopy**, *A.-J. Cheng*, *M. Manno*, *A. Khare*, *C. Leighton*, *S.A. Campbell*, *E.S. Aydil*, University of Minnesota

Copper zinc tin sulfide (Cu<sub>2</sub>ZnSnS<sub>4</sub> or CZTS) is a potential candidate for next generation thin film solar cells because it contains abundant and nontoxic elements and exhibits high light absorption. Thin films of CZTS are typically synthesized by sulfidizing a stack of zinc, copper and tin films. In addition to CZTS, a variety of binary and ternary metal sulfides can form and distinguishing among phases with similar crystal structure can be difficult. Herein, we show that confocal Raman spectroscopy and imaging can distinguish between CZTS and the other binary and ternary sulfides [1]. Specifically, Raman spectroscopy was used to detect and distinguish between CZTS (338 cm<sup>-1</sup>), Cu<sub>2</sub>SnS<sub>3</sub> (298 cm<sup>-1</sup>) and Cu<sub>4</sub>SnS<sub>4</sub> (318 cm<sup>-1</sup>)

phases through their characteristic scattering peaks. Confocal Raman spectroscopy was then used to image the distribution of coexisting phases and is demonstrated to be a useful tool for examining the heterogeneity of CZTS films. We show that, during sulfidation of a zinc/copper/tin film stack, ternary sulfides of copper and tin, such as Cu<sub>2</sub>SnS<sub>3</sub> form first and are then converted to CZTS. The reason for formation of Cu<sub>2</sub>SnS<sub>3</sub> as an intermediary to CZTS is the strong tendency of copper and tin to form intermetallic alloys upon evaporation. These alloys sulfidize and form copper tin sulfides first, and then eventually convert to CZTS in the presence of zinc. As a consequence, films sulfidized for 8 hours at 400 °C contain both CZTS and Cu<sub>2</sub>SnS<sub>3</sub> while films sulfidized at 500 °C contain nearly phase-pure CZTS. In addition, using Cu K $\alpha$  radiation, we identify three CZTS X-ray diffraction peaks at 37.1° [(202)], 38° [(211)] and 44.9° [(105) and (213)], which are absent in ZnS and very weak in Cu<sub>2</sub>SnS<sub>3</sub>.

[1] A.-J. Cheng, M. Manno, A. Khare, C. Leighton, S. A. Campbell, and E. S. Aydil, *J. Vac. Sci. Technol. A*, in press (2011).

5:40pm **EN1+TF-WeA12 Synthesis of CZTS Solar Cells using Non-Toxic Sulfur Precursor**, *P. Vasekar*, *L. Ganta*, *D. Vanhart*, *T. Dhakal*, *C.R. Westgate*, The State University of New York at Binghamton

Thin film solar cells based on Cu(In,Ga)(S,Se)<sub>2</sub> and CdTe have demonstrated significant improvement in last few years and they are also being transferred to production level. However, both CIGS and CdTe based thin film solar cells are hindered by potential environmental hazard issues and scarcity issues associated with the constituent elements, mainly Te, In, Ga and to some extent Se. Recent research trends are moving towards finding alternatives based on earth-abundant and non-toxic elements. An alternative material Cu(Zn,Sn)(S,Se)<sub>2</sub> is being explored these days by the thin film photovoltaics community which contains earth abundant materials like Zn and Sn. CZTS structure can be derived from CuInS<sub>2</sub> chalcopyrite structure by replacing one half of the constituent indium atoms by zinc and other half by tin. The resulting bandgap varies in the range of 0.8 eV for a selenide structure to 1.5 eV for a sulfide structure. Copper and sulfur in earth's crust are 50 and 260 ppm respectively and while abundance of zinc and tin is 75 and 2.2 ppm in respectively. As compared to this, indium in earth's crust is 0.049 ppm and selenium 0.05 ppm. CZTS also has a large absorption coefficient in the order of 10<sup>4</sup> cm<sup>-1</sup>. There are vacuum-based as well as non-vacuum based approaches for the synthesis of CZTS solar cells. Among vacuum based approaches, generally sulfurization in H<sub>2</sub>S atmosphere is carried out on sputtered CuZnSn precursors. However, there are toxicity issues involved with the use of H<sub>2</sub>S gas. We subscribe to the philosophy of sticking to a non-toxic approach of synthesizing thin film solar cells and for the first ever time introduced a non-toxic sulfur precursor called di-tertiray-butyl-disulfide (TBDS) for the sulfurization of CZT layer. Initial results are quite encouraging and device quality CZTS cells are already being synthesized. The CZTS cells are characterized using materials characterization techniques such as SEM, XRD, XPS and photovoltaic parameters are being extracted under AM 1.5 conditions and also analyzed using quantum efficiency measurement. This is the very first attempt to successfully synthesize CZTS solar cells using a non-toxic sulfur source.

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