Wednesday Morning, November 12, 2014

Energy Frontiers Focus Topic Room: 315 - Session EN+AS+EM+SE-WeM

Thin Film Photovoltaics

Moderator: Rachel Morrish, Colorado School of Mines

8:20am EN+AS+EM+SE-WeM2 Epitaxy and Nanochemistry of CdS on Cu(In,Ga)Se₂ for Photovoltaic Devices, X. He, University of Illinois at Urbana Champaign, H. Tellez, J. Druce, Kyushu University, Japan, K. Demirkan, Miasole, P. Ercius, Lawrence Berkeley National Laboratory, V. Lordi, Lawrence Livermore National Laboratory, J. Kilner, Imperial College London, UK, T. Ishihara, Kyushu University, Japan, Angus Rockett, University of Illinois at Urbana Champaign

Cu(In,Ga)Se₂ (CIGS) photovoltaics are very promising candidates for highperformance energy generation from sunlight. They typically include a heterojunction between CdS and CIGS. The nature of that heterojunction is critical to the performance of the devices. We present experimental results on the nanochemistry of CIGS and CIGS/CdS heterojunctions and the nanostructure of the junctions. In particular we present low energy ion scattering (LEIS) results on epitaxial single crystal CIGS and CIGS/CdS heterojunctions formed by chemical bath deposition of CdS. Also shown are results of high-resolution transmission electron microscopy (TEM) studies of the CIGS/CdS heterojunction where the junction is formed by physical vapor deposition. LEIS has single-atomic-layer chemical sensitivity that provides a unique ability to distinguish the nanochemical nature of CIGS surfaces and heterojunctions. TEM provides both nanostructural information and the possibility to determine the chemistry of the junction on the nanoscale by energy dispersive spectroscopy and energy filtered imaging. Complete epitaxy of the CdS throughout its ~50 nm thickness is observed in the physical-vapor-deposited CdS. Domains of cubic zincblende and hexagonal wurtzite structure CdS have been observed. Twins in the CIGS grains were found to propagate into and often through the CdS layer, resulting in a twin or grain boundary in the CdS. The CdS epitaxial relationship and the effect of surface steps on the CIGS surface are shown. The nanochemical analysis results show significant penetration of Cu into the CdS layer, although no alteration in the CdS nanostructure is observed. The other elements show an abrupt nanochemical junction. LEIS results show the presence of segregated layers on the CIGS surface and further refine the nature of the nanochemical intermixing across the interface.

8:40am EN+AS+EM+SE-WeM3 Microstructure Development in Cu₂ZnSn(S_xSe_{1-x})4 Thin Films During Annealing of Colloidal Nanocrystal Coatings, B.D. Chernomordik, M. Ketkar, K. Hunter, A.E. Béland, Eray Aydil, University of Minnesota

A potentially high-throughput and inexpensive method for making $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) thin film absorber layers for solar cells is annealing of coatings cast from colloidal dispersions of CZTS nanocrystals (NCs). The nanocrystal coatings can be annealed in sulfur or selenium atmosphere to make CZTS or CZTSSe, respectively. During annealing, the nanocrystal films can transform into polycrystalline thin films with micrometer size grains. Understanding the roles of key annealing parameters in the development of microstructure in CZTSSe thin films is critical for achieving inexpensive and high-efficiency CZTSSe solar cells. In this presentation, we will discuss the effects of parameters such as selenium vapor pressure, annealing temperature, substrate, and h eating ramp-rate on the microstructure development in CZTSSe films and contrast the results with films annealed in sulfur. By using a closed system, rather than a flow furnace, we can quantify and systematically control selenium pressure. Annealing films at high selenium pressure (450 Torr) leads to the formation of a layer of 2-5 µm size CZTSSe grains on top of a nanocrystalline layer that is rich in carbon. This segregation of carbon at the CZTSSe-substrate interface is commonly ascribed to the immediate formation of a capping/blocking layer of CZTSSe grains, which trap the carbon, originating from the ligands on NC surfaces, beneath these grains. However, we found that a continuous layer of CZTSSe grains is not necessary to observe carbon segregation to the film-substrate interface. In contrast, films annealed with sulfur do not show such distinct carbon-rich layers and most of the carbon volatilizes from the film during annealing. Increasing the heating ramp-rate to the annealing temperature eliminates the formation the carbon-rich layer and results in grains that are approximately 500 nm. We will discuss the results of a series of experiments which led us conclude that Se condensation during annealing may play a key role in grain growth and carbon segregation.

9:00am EN+AS+EM+SE-WeM4 Effect of Chemical Wet Cleaning on Surface Composition and Work Function of Thin Film CZTS, Se, Kasra Sardashti, University of California at San Diego, E.A. Chagarov, T. Kaufman-Osborn, University of California, San Diego, S.W. Park, University of California San Diego, R. Haight, W. Wang, D.B. Mitzi, IBM T.J. Watson Research Center, A.C. Kunnnel, University of California at San Diego

Polycrystalline Copper-tin-zinc-sulfide/selenide (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed earth-abundant elements. Photovoltaic devices fabricated on CZTS,Se has reached the highest (or record) conversion efficiency of the 12.6 %. One of the key parameters to further boost the conversion efficiency is to control the concentration of recombination sites at the surface, in the grain boundaries, and in the bulk. Surface states formed on the sample surface as a result of carbon and oxygen contamination can act as non-radiative recombination sites which limit the ultimate cell efficiency. Therefore, a surface-cleaning method which can effectively reduce the amount of surface oxygen and carbon is necessary for CZTS,Se processing. In this work, 2 µm thick CZTS,Se films were prepared by spin coating hydrazine-based precursor solutions onto Mo-coated soda lime glass substrates in a nitrogen-filled glove box. To clean the CZTS,Se surfaces, three different wet cleaning recipes were used: a) NH4OH only; b) HCl followed by NH4OH; 3) H2O2 followed by NH4OH. The effect of the wet cleaning on the surface composition including carbon and oxygen content has been studied via X-ray photoelectron spectroscopy (XPS) and femtosecond ultraviolet photoelectron spectroscopy (fs-UPS). Spatial variation of work function over the surface upon surface cleaning was measured via Kelvin Probe Force Microscopy (KPFM). The stability of the clean surface against reoxidation in ambient was modeled by density functional theory (DFT). The H2O2/NH4OH recipe showed the best result reducing the amount of surface O and C down to 5% and 20%, respectively. This is due to the oxidizing effect of H2O2 which converted the carbonaceous surfaces contaminants into oxides which were later removed by NH4OH. DFT calculations are consistent with a group VI surface being stable against oxidation by ambient moisture. KPFM measurements showed strongly non-homogeneous surfaces after both NH4OH-only and H2O2/NH4OH clean. Areas with work function different from CZTS could be the binary chalcogenides formed during the growth and were covered by the native oxide. NH4OH etch successfully removed the covering oxide and made those phases visible to KPFM.

9:20am EN+AS+EM+SE-WeM5 Phase Transformation, Surface States, and Electronic Structures of Pyrite Thin Films Under *In Situ* Heating and Oxygen Gas Exposure, *Yu Liu*, *N. Berry, Y.N. Zhang*, University of California Irvine, *C.-C. Chen*, Argonne National Laboratory, *H. Bluhm, Z. Liu*, Lawrence Berkeley National Laboratory, *R.Q. Wu*, *M. Law, J.C. Hemminger*, University of California Irvine

Iron pyrite (cubic FeS₂) with its exceptional optical absorption and suitable band gap is a promising earth-abundant semiconductor for thin film solar cells. Using ambient pressure synchrotron x-ray spectroscopies, we report the nanoscale depth profiles of surface and electronic structures for phasepure pyrite thin films under in situ heating and oxygen gas exposure. Polarized x-ray absorption spectra show that the absorption edge of Fe L_2 edge shifts closer to the Fermi surface with increasing temperature. The XAS line shapes of Fe and S L-edge provide the information of ligand crystal field environment and the phases of the FeS2 particles. We also report the non-destructive photoemission depth distributions of sulfur defects, vacancies, impurities and oxide as a function of temperature and oxygen dose. Valence band spectra indicate a band gap narrowing related to the creation of surface states at elevated temperature. An irreversible phase transition from pyrite (FeS₂) to pyrrhotites (Fe_{1-x}S) occurs above 430 °C. In addition, our results under in situ oxygen gas exposure suggest that the surface monosulfide species is oxidized first, and the reduction in the total density of states near the Fermi surface is caused by oxide layers of sulfate like and iron oxide products on the top ~2 nm.

9:40am EN+AS+EM+SE-WeM6 Improvement of SnS-based Photovoltaic Devices via Reverse Engineering of the V_{oc} and Study of Optimal n-Type Material, *Rona Banai*, *N.J. Tanen, J.J. Cordell, J.R. Nasr, R.E. Urena, H. Lee, J.R.S. Brownson, M.W. Horn*, Penn State University

Tin (II) Monosulfide (SnS) has theoretical promise as a new material for thin film photovoltaics (PV). Despite a full decade of rigorous research to develop SnS-based devices, improvement beyond single-digit percent efficiencies seems unattainable. Engineering this material into a usable device is crucial for future development. Our group has been investigating the optical and structural properties of magnetron sputtered SnS_x thin films [1,2,3]. This work will investigate the properties that govern open-circuit voltage, including band gap, series resistance, carrier concentration and built-in potential. Some of these parameters are directly related to the junction material paired with SnS. Several partner materials will be presented with p-SnS including, but not limited to highly doped n-ZnO and n-SnS. Current work is underway to produce n-type SnS as well which would have potential to produce a homojunction.

The optoelectronic properties of SnS make it a suitable material for PV. Its high absorption coefficient, greater than 10^4 cm⁻¹, and band gap near 1.3 eV are well matched with the solar spectrum. SnS also has a carrier concentration greater than 10^{15} cm⁻³ and potential to be both n-type and p-type. Our group is able to produce dense SnS thin films with optimal electronic properties. Sputtering the material gives great control over the material properties and recent work optimizing post-deposition heat treatment has shown great promise for improving the material.

Tin sulfide thin films were sputtered on glass and oxidized silicon substrates at varying substrate-to-target distances, substrate temperature, target power, and chamber pressure. The sputter target was a 3" SnS₂ with 99.999% purity (LTS Research Laboratories, Inc.). These sulfur-rich samples were then annealed under medium vacuum (<2x10⁻⁶ Torr) in the deposition chamber at 400°C to produce a uniform α -SnS, which is most likely to be p-type. Producing n-type SnS is possible via annealing of the films in a methanol/SnCl₄ solution. Production of homojunction SnS-based thin film devices is not found in the literature. Our work aims to produce these devices for the first time and compare them to a well-known partner material such as ZnO.

[1] R. E. Banai, et al., in *Proceedings of 2012 38th IEEE Photovoltaics Specialists Conference*, Austin, 2012, pp. 164-169.

[2] R. E. Banai, et al., *IEEE Journal of Photovoltaics*, vol. 3, no. 3, pp. 1084-1089, 2013.

[3] R. E. Banai, et al., in *Proceedings of 2013 39th IEEE Photovoltaic Specialists Conference*, Tampa, 2013, pp. 2562-2566.

11:00am **EN+AS+EM+SE-WeM10** Advanced Contacts for High Efficiency CdTe Solar Cells, *D. Meysing, J.J. Li, J. Beach, T.R. Ohno,* Colorado School of Mines, *M.O. Reese, T.M. Barnes,* National Renewable Energy Laboratory, *Colin Wolden,* Colorado School of Mines

Record CdTe device efficiency has recently surpassed 20%, and it is the leading thin film photovoltaic technology in terms of commercial installation with current manufacturing capacity exceeding 1 GW/year. However, with a Shockley-Queisser limit of \sim 33% there remains substantial room for additional improvements in efficiency. The quality of both the front and back contacts has substantial influence on CdTe solar cells device efficiency, impacting the current and voltage respectively. This talk will focus on recent work directed at understanding the materials science of both the front and back contact interfaces and optimizing their performance.

Cadmium sulfide is the most commonly employed window layer in the front contact, and its properties can greatly affect cell performance through optical absorption and the quality of the CdS-CdTe junction. In this work, we develop reactive sputtering as an alternative to chemical bath deposition (CBD) for the production of oxygenated cadmium sulfide (CdS:O) to enable high efficiency CdTe solar cells. The intrinsic properties of CdS:O as well as their impact on device performance were studied by varying the oxygen content in the Ar sputtering ambient over the range of 0-10%. XRD, RBS, XPS, and spectrophotometry were used to measure the crystal structure, composition, bonding, and optical properties, respectively. The variation in properties is unsurprisingly non-linear, and optimal performance is attributed to a compromise between optical transmission, which improve monotonically with oxygen content, and band alignment which sharply attenuates device performance beyond a critical threshold.

It is notoriously difficult to make a good ohmic contact to CdTe using conventional metals, because this requires a work function of greater than 5.7 eV. Copper-doped zinc telluride (ZnTe:Cu) is one of the most commonly employed buffer layers to mitigate this issue. ZnTe was identified due to its valence band alignment and compatibility with CdTe. Copper has both positive and deleterious effects and it is critical to precisely control both its amount and spatial distribution in order to obtain high efficiency. We have developed a back contacting procedure that employs rapid thermal processing (RTP) to deliver precise control over the activation and distribution of Cu. The RTP process is coupled with atom probe tomography and advanced optoelectronic characterization to improve our understanding of the structure-property-performance relationships in this system. The advances achieved here using commercially scalable processes are combined to produce devices with $V_{\rm oc} > 850$ mV and efficiencies exceeding 16%.

11:20am EN+AS+EM+SE-WeM11 Structural Variations and their Effects on the Fundamental Bandgap of ZnSnN₂. Nathaniel Feldberg, University at Buffalo-SUNY, Y. Yang, University of Michigan, W.M. Linhart, T.D. Veal, University of Liverpool, UK, P.A. Stampe, R.J. Kennedy, Florida A&M University, D.O. Scanlon, University College London, UK, L.F.J. Piper, Binghamton University, N. Senabulya, R. Clarke, University of Michigan, R.J. Reeves, University of Canterbury, New Zealand, S. Durbin, Western Michigan University

In recent years Zn-IV-N₂ compounds have seen increased interest as potential earth abundant element semiconductors for photovoltaic and solid state lighting applications. Several reports of successful growth for the Ge and Si containing compounds are extant as well as more recent publications on the Sn containing member of the family. This material offers a possible alternative to indium containing materials which have experienced large price fluctuations due to limited domestic supply, lack of recycling and heightened demand. Our films were grown by plasma assisted molecular beam epitaxy on (111)-yittria stabilized zirconia. In the case of an ordered lattice, density functional theory (DFT) predicts an orthorhombic structure; however, the disordered lattice is predicted to be pseudo-hexagonal. Reflection high energy electron diffraction patterns for these films indicate single crystal structure with hexagonal symmetry, consistent with X-ray diffraction measurements. Hall effect indicates carrier concentrations in the 3-10x10²¹ cm⁻³ range for which we would expect a significant Burstein-Moss shift. Contrary to expectations, optical measurements of absorption onset occur at higher energy in films with lower carrier concentrations. As in ZnSnP2, the bandgap is expected to narrow with the introduction of disorder for this material; this narrowing behavior is consistent with observed variations in absorption spectra. Of practical interest is the possibility of a material with a tunable bandgap without the need for traditional alloying. Zn-Sn-N₂ is expected to have a bandgap varying from 1.1 to 2 eV controlled by the continuous degree of order in the cation sublattice. Although hard X-ray diffraction measurements of these films do not show any variation from a hexagonal structure, Hall measurements of carrier concentrations compared with absorption data indicates that our samples vary their absorption onset, not as would be expected from Burstein-Moss Shift, but in a manner consistent with a variation in the lattice order. DFT calculations indicate that there is a variation in the Density of States between the ordered and disordered films. Films which were consistent with increased order absorption are also consistent with an increased order density of states measured by HAXPES.

This project is supported by NSF grant DMR1244887 (Program Director Charles Ying), and EPSRC grant EP/G004447/2.

11:40am EN+AS+EM+SE-WeM12 Inhomogeneity of *p-n* Junction and Grain Structure of Thin Film CdTe Solar Cells Studied by Electron Beams, *Heayoung Yoon*, *P. Haney*, NIST, *P. Koirala*, University of Toledo, *J.I. Basham, Y. Yoon*, NIST, *R.W. Collins*, University of Toledo, *N.B. Zhitenev*, NIST

Thin film CdTe solar cells are a promising photovoltaic (PV) technology in today's market due t o their high optical absorption and inexpensive fabrication processes . However, the current module efficiency is well below the theoretically estimated maximum efficiency (13 % vs. 30 %). Recent studies have suggested that inhomogeneity of the PV materials is mainly responsible for the low power conversion efficiency. In this work, we investigate the variation of local PV properties of CdTe solar cells, focusing on grain bulk, grain boundaries, and n-CdS / p-CdTe junctions. The window (≈ 120 nm thick CdS) and absorber ($\approx 2.2 \ \mu m$ thick CdTe) layers were sputtered on a TCO (transparent conductive oxide) coated glass substrate followed by CdCl₂ treatment. The back contact metals (3 nm Cu / 30 nm Au) were deposited and annealed, creating 256 devices in a 15 cm by 15 cm solar panel. Following light and dark current-voltage measurements, we performed local characterizations using electron beams for high (> 13 %) and low efficiency (< 6 %) devices within the panel. Electron beam induced current (EBIC) was used to measure the local carrier collection efficiency with a spatial resolution of ≈20 nm exciting carriers either from the top surface or the cross-sections of the devices. Cross-sectional EBIC data reveals that the peak of efficiency is in the middle of CdTe layer in the low efficiency devices, while the carrier collection is maximal near the p-njunction in the high efficiency devices. The EBIC contrasts at grains/grain boundaries in these devices are also compared. The measured local electronic properties are correlated to microstructural morphology (Transmission Electron Microscopy), orientation (Electron Back Scattered Diffraction), and chemical composition (Energy Dispersive X-ray spectroscopy). We perform 2D model drift-diffusion simulations to determine the magnitude of downward band-bending near grain boundaries (with typical magnitude of 0.2 eV). We will discuss the impact of carrier generation rate (high level injection vs. low level injection) in EBIC analysis.

12:00pm EN+AS+EM+SE-WeM13 Micro-Structural Activation Mechanisms in Thin Film CdTe Photovoltaic Devices, John Walls, A. Abbas, J.W. Bowers, P.M. Kaminski, Loughborough University, UK, K. Barth, W. Sampath, Colorado State University

Thin Film CdTe photovoltaics is a commercially successful second generation technology now used extensively in solar energy generation at the utility scale. Although the cadmium chloride treatment is a process that is essential to produce high efficiency devices, the precise mechanisms involved in the re-crystallization and associated improvement in electronic properties have not been fully understood. In this paper we report on the application of advanced micro-structural characterization techniques to study the effect of the cadmium chloride treatment on the physical properties of the cadmium telluride solar cell deposited by both close space sublimation (CSS) and magnetron sputtering and relate these observations to device performance. In particular, High Resolution Transmission Electron Microcopy (HRTEM) reveals that the untreated material contains high densities of planar defects which are predominantly stacking faults and that the optimized cadmium chloride treatment removes these completely with only twins remaining. Parallel theoretical studies using Density Functional Theory (DFT) shows that certain types of stacking fault are responsible for the poor performance of the untreated material. Extending the treatment time or increasing the annealing temperature above $\sim 400^{\circ}$ C improves the microstructure but results in lower efficiency devices. Composition -depth profiling using XPS and SIMS reveals that this deterioration in performance is linked with chlorine build up at the CdS/CdTe junction. These experiments and parallel theoretical studies have improved our understanding of the mechanisms at work in the cadmium chloride assisted re-crystallization of CdTe and could lead to further increases in device efficiency

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