Monday Morning, October 19, 2015

Energy Frontiers Focus Topic
Room: 211B - Session EN+AS+EM+NS+SE+SS+TF-MoM

Solar Cells I
Moderator: Jason Baxter, Drexel University, Chintalapalle Ramana, University of Texas at El Paso

8:20am EN+AS+EM+NS+SE+SS+TF-MoM1 Elevated Temperature Phase Stability of CZTS-Se Thin Films for Solar Cells, *E. Chagarov, K. Sardashti*, University of California at San Diego, *D.B. Mitzi*, Duke University, *R.A. Haight*, IBM T.J. Watson Research Center, **Andrew C. Kummel**, University of California at San Diego
Density-functional theory simulations of CZTS, CZTSe and $CZTS_{0.25}Se_{0.75}$ photovoltaic compounds have been performed to investigate stability of $CZTS_{0.25}Se_{0.75}$ alloy vs. decomposition to CZTS, CZTSe and other secondary compounds. The Gibbs energy for vibration contribution was estimated by calculating phonon spectra and thermodynamic properties at finite temperatures. It was demonstrated that $CZTS_{0.25}Se_{0.75}$ alloy is stabilized not by enthalpy of formation but by vibration and mixing contributions to the Gibbs energy. A set of phase diagrams was built in multidimensional space of chemical potentials at 300K and 900K temperatures to demonstrate alloy stability and boundary compounds at various chemical conditions. The Gibbs energy gain/loss for several decomposition reactions was calculated as a function of temperature with/without Cu/Zn intermixing and vibration contributions to the Gibbs energy demonstrating $CZTS_{0.25}Se_{0.75}$ that even defect-free (no Cu/Zn intermixing) $CZTS_{0.25}Se_{0.75}$ can be stable at typical processing temperatures.

8:40am EN+AS+EM+NS+SE+SS+TF-MoM2 Chemical and Electrical Characterization of Polycrystalline CZTS,Se and CIGS,Se Grain Boundaries by NanoAuger and Kelvin Probe Force Microscopy (KPFM), *Kasra Sardashti*, UC San Diego, *P.D. Antunez, R.A. Haight*, IBM T.J. Watson Research Center, *A.C. Kummel*, UC San Diego
Polycrystalline Copper-zinc-tin-sulfide/selenide (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed of earth-abundant elements. Photovoltaic devices fabricated on CZTS,Se have reached conversion efficiencies of 12.6 %. One of the key parameters to further boost the conversion efficiency is to control the concentration of recombination sites at the surface, secondary phase interfaces and in the grain boundaries. To determine the presence of secondary phases on the surface and composition of grain boundaries, this work has employed Auger nanoprobe electron spectroscopy (NanoAuger) with 8nm lateral resolution combined with high resolution ambient Kelvin Probe Force Microscopy (KPFM) with dual-lock-in setup. NanoAuger was performed in planar and cross-sectional modes on CZTS,Se surfaces before and after top surface oxide removal by NH_4OH clean. Elemental maps before and after NH_4OH clean show Sn-/O-rich and Cu-poor grain boundaries suggesting that grain boundaries are terminated by tin-oxide (SnOx). Secondary phases such as SnSe and ZnSe were observed in the cross-sectional maps. Kelvin probe force microscopy (KPFM) on the cleaned surfaces showed that SnOx-terminated grain boundaries have 80-200 mV larger work function than grains, resulting in upward band bending between grains and grain boundaries. The upward band bending accompanied by the large valence band offset between the SnOx and CZTS,Se lead to relatively large energy barriers for both electrons and holes to travel into the grain boundaries and recombine. Comparison with the elemental maps for CIGSe (with device efficiencies as high as 18%) revealed the absence of the grain boundary oxide passivation.

9:40am EN+AS+EM+NS+SE+SS+TF-MoM5 Spin Coating Thin Film CZTS for Efficient, Low-Cost Solar Cells on Flexible Glass Substrates, *D. Kava, J. Galindo, C.O. Sana, S. Shahriar*, **Deidra Hodges**, University of Texas at El Paso
Photovoltaic's contribution to energy production continues to grow as costs continue to decrease. As silicon cells approach their limits, other materials are emerging. The development of Cu_2ZnSnS_4 (CZTS) thin film solar cells using non-vacuum liquid-based spin coating techniques have been previously investigated. The focus of this paper is the optimization of p-type CZTS thin film solar cells onto flexible substrates. Flexible solar panel costs are higher than their traditional counterparts. CZTS currently reports only a 3.2% efficiency on flexible glass, while the record for CZTS on non-flexible substrates is 12.6%. The cells are created using a single solution ink sol–gel method. All metals are dissolved in a single step prior to deposition onto substrates (nickel foil and corning willow glass) as a thin film. Corning

Willow glass is a new material introduced recently to the market, while nickel is a inexpensive flexible reflective foil. The Corning Willow glass is coated with a molybdenum layer as a reflective back contact layer. By using a single step and a solution deposition method, lower production cost are achievable. For thin film deposition, we used a non-vacuum spin coater (WS650 spin processor, Laurell Technologies) with an optimized spin coat programming. Annealing took place under vacuum in a RTP furnace while time, temperature and ramp functions were varied. The other layers of the device consists of cadmium sulfide n-type window layer and a zinc oxide doped with aluminum transparent top contact layer. Characterization and analysis of the thin films were performed using Raman spectroscopy, scanning election microscope (Zeiss NEON 40), X-ray diffraction (Philipps X'Pert), profilimeter (Veeco Dektak 150), UV-Vis-NIR Spectrophotometer (Carry 5000), Hall Effect measurement system (HMS3000) and 4 point probe (Lucas Labs) measurements. Results show CZTS thin film solar cells on flexible glass is obtainable.

10:00am EN+AS+EM+NS+SE+SS+TF-MoM6 Band Gap Profile of Cu(In,Ga)(Se,S) 2 Thin Films via High-Resolution Reflection Electron Energy Loss Spectroscopy, *Sung Heo*, *H.I. Lee, J.B. Park, G.S. Park*, Samsung Advanced Institute of Technology, Republic of Korea, *D.H. Lee, J.G. Nam*, Samsung, Republic of Korea, *H.J. Kang*, Chungbuk National University, Republic of Korea, *B.D. Choi*, Sungkyunkwan University, Republic of Korea
$Cu(In,Ga)Se_2$ (CIGS)-based solar cells was investigated with an aim of enhancing cell performance because these cells provided high conversion efficiency at relatively low cost. The efficiency of CIGS cells has recently approached 19.7% at small sizes. In general, $Cu(In_{1-x},Ga_x)(Se_{1-y}S_y)_2$(CIGSS) composition profiles are double-graded, and they can improve the open-circuit voltage (V_{OC}) and the efficiency of solar cells because band gaps increase toward both the surface (i.e., with the increase of sulfur) and the bottom (i.e., with the increase of gallium). It is important to accurately measure the band gap at the top and the bottom of the CIGSS cell. Nevertheless, the band gap profile measurement of the CIGSS as a function of depth is challenging.

In this study, we obtained the depth profile of the CIGSS cell using the quantitative Auger Electron Spectroscopy method, for which the relative sensitivity factor was corrected using the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. We also measured the band gap directly using high-resolution reflection electron energy loss spectroscopy (HR-REELS) with a monochromatic electron gun, which has low electron energy at 300 eV.

For the direct measurement of a band gap profile, HR-REELS spectra were obtained as a function of depth during Ar ion sputtering at 3.0 kV. The band gap profile shows a double-graded band gap as a function of depth. The band gap values are 1.32 eV at the surface (E_{g1}), 1.08 eV at the depth between 0.3 and 0.7μm ($E_{g\ min.position}$), and 1.50 eV at the depth of about 2.2 μm (E_{g2}), respectively. Our findings suggest a new analytical method which directly determines the band gap profile as function of depth.

10:40am EN+AS+EM+NS+SE+SS+TF-MoM8 Spatial Atmospheric ALD of Zinc Oxysulfide Buffer Layers for CIGS Solar Cells, *C. Frijters, P.J. Bolt, P. Poodt*, **Andrea Illiberi**, Solliance/TNO, Netherlands
Copper Indium Gallium di-Selenide (CIGS) solar cells are a promising approach in photovoltaic technology, having low production costs, high conversion efficiencies (> 20 %), as well as the possibility to manufacture them on flexible substrates. State-of-the-art in CIGS solar cells manufacturing is to use a stack of CdS, intrinsic ZnO (*i*-ZnO) and an Al-doped ZnO TCO on top of the CIGS film. Replacement of CdS by a non-toxic Cd-free layer with wider band gap (> 2.4 eV) would *a)* decrease the production cost by avoiding the expensive treatment of toxic wastes and *b)* increase the overall cell efficiency by enhancing the quantum efficiency in the blue range. Moreover, the use of a "soft" and highly conformal deposition technique is preferred to improve the electrical properties of the buffer layer/CIGS interface.

In this paper we present spatial atmospheric atomic layer deposition of a Zn(O,S) buffer layer as CdS replacement for CIGS solar cells. Spatial ALD is emerging as an industrially scalable deposition technique at atmospheric pressure which combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large area substrates, with high growth rates (up to nm/s). Films are grown by sequentially exposing the substrate to oxygen and sulfur precursors (H_2O, H_2S) and the zinc metal precursor (i.e., DEZn). By controlling the kinetics of surface reactions between evaporated precursors and reactive sites at the film surface, the composition of Zn(O,S) can be precisely tuned. The incorporation of S into

ZnO results in a bowing of the band gap in the range from 3.3 eV (ZnO) to 2.7 (S/O+S ~ 0.5) and 3.4 eV (ZnS), as measured by spectrophotometry. The morphology of the $Zn(O_{x-1},S_x)$ films varies from polycrystalline (for 0<x<30 and 70<x<100) to amorphous (30<x<70), as measured by X-ray diffraction. CIGS solar cells with a Spatial ALD Zn(O,S) buffer layer show an increased spectral response around 400 nm compared to solar cells with a CdS buffer layer. The solar cells with the Zn(O,S) buffer layer had an efficiency of 15.9 %, compared to 15.5 % for the reference solar cells with a CdS buffer layer.

11:00am EN+AS+EM+NS+SE+SS+TF-MoM9 Deep Level Electron Traps in Epitaxial $CuInSe_2$ Probed using Photo-Modulated X-ray Photoelectron Spectroscopy, *Nicole Johnson*, University of Illinois at Urbana-Champaign, *P. Aydogan*, Bilkent University, Turkey, *A. Rockett*, University of Illinois at Urbana-Champaign, *S. Suzer*, Bilkent University, Turkey

Performance in a variety of electronic devices is largely controlled by minority carrier charge capture on point defects. To date there is no experimental method to directly identify these point defects in a chemically specific fashion. Photo-modulated X-ray Photoelectron Spectroscopy (XPS) utilizes the chemical and charge sensitivity of XPS to identify changes in peak shape due to changing atomic charge state from capture of light-generated minority carriers. Epitaxial thin films of $CuInSe_2$ (CIS) were chosen as a case study for this technique because their defect chemistry is still relatively unknown as compared to traditional solar cell materials. The 500-1000nm thick films were grown by a hybrid sputtering and evaporation technique on GaAs(001) substrates at600-700°C. Aligned surface morphology features matching the substrate geometry in scanning electron microscopy (SEM) images indicate epitaxial growth, which was confirmed by x-ray diffraction (XRD).A layer of CdS was deposited on the CIS via chemical bath deposition to protect the CIS surface from oxidation in storage and to duplicate the heterojunction used in solar cells. Prior to loading in the XPS, the CdS was etched off to expose a Cd doped CIS surface for analysis. The photo-modulated XPS used monochromatic AlKα x-rays with a 532 nm laser as the illumination source. Under illumination, each film constituent was observed to exhibit unique binding energy shifts. Based on their peak shifts relative to the surface photovoltage profile, Cd and In were found to be right at the surface while Cu and Se were deeper into the film, consistent with a Cd-doped, In-rich surface. The technique is therefore shown to provide a chemically-sensitive depth profile non-destructively that can be obtained even on a relatively rough sample. Additionally, shape changes in the Se 3d doublet spectra indicate electron capture in a deep trap state that is likely due to cation vacancies. Measurements at varying temperatures indicate air-induced surface recombination states are passivated by annealing at 80C, allowing the surface photovoltage to persist. At 230C, an irreversible change happens in the surface properties such that the surface photovoltage gets much smaller and reverses sign. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

11:20am EN+AS+EM+NS+SE+SS+TF-MoM10 The Role of ZnTe Buffer Layers on the Performance and Stability of CdTe Solar Cells, *Jiaojiao Li*, Colorado School of Mines, *A. Abbas*, Loughborough University, UK, *D.M. Meysing, J.D. Beach, D.R. Diercks*, Colorado School of Mines, *M.O. Reese, T.M. Barnes*, National Renewable Energy Laboratory, *C.A. Wolden*, Colorado School of Mines, *J.M. Walls*, Loughborough University, UK

The use of ZnTe buffer layers at the back contact of CdTe solar cells has been credited with contributing to recent improvements in both record cell efficiency and module stability. To better understand the underlying reasons high resolution transmission microscopy (HR-TEM) and atom probe tomography (APT) were used to study the evolution of the back contact region before and after rapid thermal activation of this layer. During activation the 150 nm ZnTe layer, initially nanocrystalline and homogenous, transforms into a bilayer structure consisting of an amorphous region in contact with CdTe characterized by significant Cd-Zn interdiffusion, and a crystalline layer that shows evidence of grain growth and twin formation. This graded layer may passivate interface defects and account fo the improved open circuit voltage and fill factor that accompanies the RTP activation step. Copper, co-evaporated uniformly within ZnTe, is found to segregate dramatically after rapid thermal activation, either collecting near the ZnTe|Au interface or forming Cu_xTe clusters in CdTe at defects or grain boundaries near the interface. Further examination of the Cu_xTe clusters revealed that they are encased in a thin layer of Zn, and it is postulated that this structure may limit the extent of diffusion into CdTe and play an important role in device stability.

11:40am EN+AS+EM+NS+SE+SS+TF-MoM11 The Performance and Durability of Broadband Anti-Reflection Coatings for Thin Film CdTe Solar Cells, *G. Womack, P.M. Kaminski, **John Walls***, Loughborough University, UK

Light reflection from the glass surface of a photovoltaic (PV) module is a significant source of energy loss for crystalline silicon and all types of thin film PV devices. The reflection at the glass and air interface accounts for ~4% of the total energy. Single layer anti-reflection coatings using magnesium fluoride or porous silica with sufficiently low refractive index have been reported but these are only effective over a narrow range of wavelengths. In this paper we report on the design, deposition and testing of multilayer broadband anti-reflection coatings that reduce the weighted average reflection over the wavelength range used by thin film CdTe devices to ~1.22% resulting in a useful 3.6% increase in photocurrent. In this study we have used multilayer stacks consisting of silica and zirconia layers deposited using a reactive magnetron sputtering process. Details of the stack design, sputtering process parameters and the optical and micro-structural properties of the layers are provided.

Thin film CdTe devices pose a special problem because the anti-reflection coating is applied to one side of the glass while device layers are deposited directly on to the opposite glass surface in the superstrate configuration In thin film CdTe production, the glass is exposed to high temperature processes during the absorber deposition and during the cadmium chloride activation treatment. If glass pre-coated with a broadband anti-reflection coating is to be used then the coating must withstand temperatures of up to ~550°C. Surprisingly, our studies have shown that multilayer silica/zirconia anti-reflection coatings on soda lime glass remain unaffected by temperatures up to 600 °C at which point mild crazing is observed. This is an important observation since it means that low cost glass which is pre-processed with a broadband anti-reflection coating by glass manufacturers is potentially useable in thin film CdTe module production

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