

Monday Morning, October 28, 2013

Energy Frontiers Focus Topic

Room: 101 A - Session EN+PS+TF-MoM

Thin Film, Organic, and Chalcogenide Solar Cells

Moderator: Y. Xu, Oak Ridge National Laboratory

8:20am EN+PS+TF-MoM1 Understanding (?) Solar Devices through Soft X-Ray and Electron Spectroscopy, C. Heske, UNLV and KIT

INVITED

The purpose of this talk is to demonstrate how a tool chest of soft x-ray and electron spectroscopies (in particular using high-brilliance synchrotron radiation) is uniquely suited to unravel the electronic and chemical properties of surfaces and interfaces in thin film solar cells. We will show how photoelectron spectroscopy (PES), Auger electron spectroscopy (AES), inverse photoemission (IPES), x-ray emission spectroscopy (XES), and x-ray absorption spectroscopy (XAS) can be suitably combined to derive band gaps, study local chemical bonding and electronic level alignment, and derive insights into chemical stability at surfaces and interfaces. As examples, Cu(In,Ga)(S,Se)₂ and CdTe thin films and devices will be discussed.

9:20am EN+PS+TF-MoM4 Continuous-Flow Chemical Bath Deposition of Zn_xCd_{1-x}S Thin Films For Chalcopyrite Solar Cells, B.S. Tosun, J.T. Abrahamson, A.A. Gunawan, K.A. Mkhoyan, S.A. Campbell, E.S. Aydil, University of Minnesota

Kesterite and chalcopyrite thin film solar cells have an n-type metal sulfide (e.g., CdS, ZnS or Zn_xCd_{1-x}S) buffer layer deposited on the p-type absorber. This buffer layer is typically grown using chemical bath deposition (CBD) from metal salts and thiourea in basic aqueous solutions. In a typical CBD system, the entire solution, including the substrate, is heated. This leads to homogeneous nucleation of the metal sulfide particles in addition to the heterogeneous reaction that deposits the desired buffer layer on the substrate. This homogeneous nucleation and growth of particles wastes chemicals and causes problems with solar cells when the particles stick on the absorber surface. To solve these problems we have developed a continuous chemical bath deposition (CF-CBD) system that allows the deposition of Zn_xCd_{1-x}S films on 4-inch diameter substrates at temperatures ranging from 50 to 85 °C without significant solution temperature rise and without homogeneous nucleation and growth. Only the substrate is heated to the deposition temperature while the CBD solution is rapidly circulated between the bath and a chilled reservoir. The key features of the design are easily scalable and adaptable to roll-to-roll deposition. We have demonstrated that the CF-CBD system can be used to deposit uniform thickness and composition Zn_xCd_{1-x}S films across 4-inch diameter substrates for a variety of x values by changing the concentrations of the Zn and Cd salts in the bath. Addition of ethylenediaminetetraacetic acid disodium to the chemical bath deposition is the key to preventing deposition on surfaces other than the heated substrate surface and key to obtaining films with uniform composition and structure across the film's thickness. Films were characterized using x-ray diffraction, Auger depth profiling, spectroscopic ellipsometry, transmission electron microscopy and Kelvin probe force microscopy. The effect of deposition parameters such as temperature, bath stirring rate and bath composition on the structure and composition of the films will be discussed.

9:40am EN+PS+TF-MoM5 Development of Plasma-Enhanced Vapor Transport Deposition of CdTe Absorbers, J. Beach, C.A. Wolden, J.J. Li, Colorado School of Mines

Development of plasma-enhanced vapor transport deposition of CdTe absorbers

Jiaojiao Li, Joseph Beach, and Colin A Wolden

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Cadmium telluride is a leading absorber material for thin-film solar cells. However, state-of-the-art open circuit voltages (V_{oc}) of CdTe thin film solar cells fall ~350 mV below the value expected based on the band gap of CdTe. V_{oc} is mainly compromised by the structural defects, low carrier density and low recombination lifetime. Conventional methods to eliminate defects require the use of high temperature deposition or annealing processes which are incompatible with low cost soda-lime glass. The low hole density is because CdTe is difficult to dope due to numerous self-compensation mechanisms. CdCl₂ treatment is always used to passivate the grain boundaries and increase carrier lifetime, but additional Cd may induce Te vacancies. In this work we introduce plasma-enhanced vapor transport deposition (PEVTD) as an alternative technique for thin film CdTe

synthesis. The viability of vapor transport deposition (VTD) is demonstrated by First Solar's use of this approach to produce both the lowest cost modules. Plasma deposition techniques are able to introduce energy to films at low thermal budget. PEVTD is a hybrid of these two technologies, and we expect it to also be amenable to scale-up. In this method, high energy electrons dissociate Te₂ dimers into reactive Te species, so a high quality Te rich film may be achieved at low temperature. Moreover, plasma enhancement may activate group V dopants to dope CdTe at a higher concentration. Finally, active gases such as H₂S or SO₂ are added to the carrier gas stream to passivate interface defects and increase minority carrier lifetime. In this talk we discuss the design, construction, and operation of this reactor. We describe the dependence of the CdTe film quality on the kind of gases we use, plasma power, and substrate temperature. Films are characterized using XRD, SEM, UV-Vis-NIR spectrophotometry, Hall and light and dark current-voltage measurements.

10:00am EN+PS+TF-MoM6 Self-Limiting Growth of Pyrite Solar Absorbers using Pulsed PECVD, C. Sentman, Colorado School of Mines, M. O'Brien, Trinity College Dublin, Ireland, C.A. Wolden, Colorado School of Mines

Pyrite, FeS₂, is a non-toxic, earth abundant semiconductor that offers several potential advantages as a photovoltaic material, including low cost, large absorption coefficients and a band gap that is suitable for the harnessing of solar energy. Conventional thin film deposition techniques typically require the use of a post-deposition annealing step in elemental sulfur in order to achieve stoichiometric material. This cumbersome step is usually conducted in sealed quartz ampoules, requiring precise control over sulfur mass, time, and temperature. In this talk we introduce pulsed plasma-enhanced chemical vapor deposition (PECVD) as an alternative technique for thin film pyrite synthesis. In pulsed PECVD a mixture of iron pentacarbonyl (IPC, Fe(CO)₅) diluted in H₂S is delivered continuously to the reactor while the plasma is pulsed using square wave modulation at low frequency (~1 Hz). The concept is that IPC absorbs during the plasma off step, and that it is fully sulfurized *in situ* during the plasma on step. The process offers digital control over thickness with control on the order of ~1 Å/pulse. In this work we demonstrate the conditions required to achieve self-limiting growth of pyrite thin films. The dependence of pyrite deposition rate and material quality as a function of relevant variables such as H₂S:IPC ratio, plasma duty cycle, plasma power, pressure and substrate temperature is described. Films are characterized using a suite of analytical techniques including Raman, XRD, FESEM, and UV-Vis-NIR spectrophotometry. Through appropriate control of deposition parameters stoichiometric FeS₂ could be deposited at controllable rates between 0.1 – 1 Å/pulse without the need for post-deposition annealing. The onset of thermal CVD between these precursors was found to be ~300 °C, and it is shown that this process leads to the formation of undesirable sulfur-deficient phases. Processing could also be used to tune the pyrite to marcasite ratio. Films display expected absorption coefficient (~10⁵ cm⁻¹) and optical band gap (~1 eV). We are currently analyzing their optoelectronic properties and will report on the process-structure-property relationships in this system.

10:40am EN+PS+TF-MoM8 Surface Energetics of AgInSe₂ Thin Films, P. Peña Martin, A. Rockett, University of Illinois at Urbana Champaign

The chalcopyrite system has contributed the top performing absorber layer for thin film photovoltaic devices, Cu(In,Ga)Se₂, but the surface properties of these compounds are not well understood. While CuInSe₂ (CIS) has proven difficult to obtain atomically resolved surface images, the AgInSe₂ (AIS) surface has been recently observed. Study of the surface structure, growth mechanics and defects of AIS can provide important details of its behavior, as well as yielding insight into other chalcopyrites, like CIS, by comparison of the results. This work presents the results of growing epitaxial AIS films and studying their surface morphology to help understand its growth behavior and to transfer this knowledge to help understand the growth of chalcopyrites in general.

Thin films of AIS were grown by hybrid sputtering and evaporation technique on (110), (110), (111), and (-1-1-1) GaAs substrates. Film thicknesses were around 500 nm, and the substrate temperature was varied from 500-700°C. Their microstructures were characterized by a variety of techniques including scanning electron (SEM), scanning tunneling (STM), and atomic force (AFM) microscopies, as well as x-ray diffraction (XRD). SEM shows that the films all exhibit facets or features that are aligned across the sample, indicating that the films are epitaxial, confirmed by x-ray diffraction.

AIS was found to show a similar preference as does CIS for polar facets. The films grown on GaAs (111) and (-1-1-1) are very smooth with

individual atomic steps resolvable, while growth on GaAs (110) results in films that spontaneously facet to two polar faces with roughnesses that differ dramatically. AFM line profiles indicate an angle of $\sim 68^\circ$ between the faces, as expected for the angle between polar (112) planes. One side of the facets is stepped, with triangular features pointed toward the "peak" of the facet. The other side shows fewer features, with occasional triangular terraces pointed toward the "valley" instead. This is consistent with a chemical difference between these two surfaces. The films grown on (100) GaAs are highly featured, with rectangular pits that are likely (111) terminated. The features on films grown on both (100) and (110) substrates both show smaller size than films grown on CIS, even with a higher homologous temperature for AIS.

11:00am **EN+PS+TF-MoM9 Microstructure Evolution During Annealing of Copper Zinc Tin Sulfide Colloidal Nanocrystal Coatings to form Large-Grain Polycrystalline Thin Films**, *B.D. Chernomordik, A.E. Béland, D.D. Deng, A.A. Gunawan*, University of Minnesota, *D.J. Norris*, ETH Zürich, Switzerland, *E.S. Aydil*, University of Minnesota

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, or CZTS), copper zinc tin selenide ($\text{Cu}_2\text{ZnSnSe}_4$, or CZTSe), and their alloys are candidates for environmentally sustainable light absorbing materials for thin film solar cells because they are composed of abundant elements. In one potentially low-cost approach to making solar cells, coatings drop-cast from colloidal dispersions of CZTS nanocrystals (NCs) (inks) are annealed to form 1-3 micron thick polycrystalline films with 1-3 micron grains. We synthesize CZTS NC inks using rapid thermal decomposition of copper, zinc, and tin diethyldithiocarbamate precursors in presence of hot (150-300 °C) oleylamine. The synthesis temperature determines the NC size, which can be tuned from 2 to 25 nm. The formation of CZTS is confirmed using X-ray diffraction (XRD), Raman spectroscopy, and energy dispersive X-ray spectroscopy (EDS). Following synthesis, the NCs are dispersed in toluene and NC films are cast on various substrates including quartz and soda lime glass. One micron or thicker films cast from <10 nm NCs crack due to capillary forces during drying. Cracks are reduced significantly when films are cast from 25 nm nanoparticles. The NC films are then placed in quartz tubes with pure S, Se, or a mixture of the two, evacuated to 10^{-6} Torr, sealed, and then heated for the desired times (1-8 hours) at the desired temperatures (500-800 °C). This annealing approach provides excellent and very reproducible control of the annealing temperature and S and/or Se pressure over the film. The resulting films are characterized using a suite of techniques, including XRD, electron microscopy, EDS, and Raman scattering. We have explored the extent to which vapor species, vapor pressure, substrate choice, carbon content in the NC film, annealing time, and annealing temperature affect the mechanisms by which the polycrystalline films form and how their microstructure evolves. Depending on the annealing conditions, the CZTS NCs sinter and grow to sizes ranging from a hundred nanometers to a few microns. In addition to sintering, we observe abnormal grain growth, which, if encouraged, can lead to formation of single-crystal CZTS grains up to 10 microns in size. Raman scattering spectra collected from these large CZTS crystals show that the crystals have texture, preferring two orientations. The surface energy difference between the NCs and the large grains is the driving force for abnormal grain growth, which appears to be enhanced at high temperatures but reduced significantly on SLG and at high S pressures. The abnormal grain growth can be turned on or off via control of these variables.

11:20am **EN+PS+TF-MoM10 Enhanced Grain Growth in $\text{Cu}_2\text{ZnSnS}_4$ Thin Films via Vapor Transport of Alkali Metal Impurities**, *M. Johnson**, University of Minnesota, *S. Baryshev*, Argonne National Laboratory, *E. Thimsen, M. Manno, X. Zhang, C. Leighton, E.S. Aydil*, University of Minnesota

While power conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) based solar cells have increased relatively rapidly, very little research has been focused on the effects of the substrate on CZTS films. To date, the best performing CZTS solar cells have been deposited on Mo-coated soda lime glass (SLG), a carryover from $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ (CIGS) solar cells where Na diffusion from the SLG into the CIGS layer enhances the power conversion efficiency. Impurity diffusion is also expected when CZTS is deposited on Mo-coated SLG, but SLG hosts many other impurities including K, Ca, Mg, and Al and a systematic investigation of whether these impurities diffuse into CZTS and what effect they may have on the film properties has not been conducted. To this end, we have investigated the effects of these impurities on the microstructure of CZTS films. Thin CZTS films were synthesized via *ex situ* sulfidation of Cu-Zn-Sn films co-sputtered on a variety of substrates, including, SLG, quartz, and Pyrex. The metallic precursor films were loaded into a quartz ampoule with 1 mg of S, evacuated to 10^{-6} Torr, sealed and sulfidized at 600 °C for 8 hours. The

sulfidized films were then characterized using X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Concentration depth profiles were examined using time-of-flight secondary ion mass spectrometry (TOF-SIMS). CZTS films synthesized on SLG have significantly larger grains than films grown on other substrates. We have conducted experiments where identical Cu-Zn-Sn precursor films on quartz were sulfidized both in the absence and in the presence of a bare additional piece of SLG in the sulfidation tube. Remarkably, the grain sizes ($>1 \mu\text{m}$) in CZTS films sulfidized with SLG present are dramatically larger than the grain sizes (100's of nm) in CZTS films sulfidized without SLG. This demonstrates conclusively that impurities in SLG volatilize in a S atmosphere and incorporate into nearby CZTS films synthesized on a quartz substrate. Of all the impurities present in SLG, the TOF-SIMS experiments implicated Na, K and Ca as possible elements responsible for enhanced grain growth. To investigate the effects of these impurities individually, we then introduced very small and controllable amounts of Na, K, or Ca into the ampoule during sulfidation of the CZTS. Impurity amounts as low as 10^{-6} moles of Na or 10^{-7} moles of K loaded into the sulfidation tube resulted in a dramatic increase in grain size for films deposited on quartz, while Ca loading had little effect on the final microstructure. The results presented will demonstrate that subtle changes in impurity types and compositions lead to drastic changes in CZTS films.

* TFD James Harper Award Finalist

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