

Monday Afternoon, November 9, 2009

Thin Film

Room: A8 - Session TF1+PV-MoA

Chalcogenide Photovoltaics

Moderator: A. Rockett, University of Illinois, Urbana-Champaign

2:00pm **TF1+PV-MoA1 Growth and Structure of RF Sputter-Deposited Cadmium Sulfide (CdS) Thin Films**, *R.S. Vemuri, D. Zubia, C. McClure, C.V. Ramana*, University of Texas at El Paso

Cadmium sulfide (CdS) is a group II-VI semiconductor, which finds many scientific and technological applications. CdS thin films are particularly interesting for application in large area photovoltaics in addition to field-effect transistors, visible spectral range photoconductors, optical filters and nonlinear integrated optical devices. However, growth and optimization of conditions to produce high-quality CdS layers is important for enhanced photovoltaic device performances. In the present work, ordered cubic structured CdS films for application in CdTe/CdS solar cells were produced using RF magnetron sputtering. Pure CdS target was employed for sputtering. Two sets of CdS films were deposited: (1) at varying powers, in the range of 70-130 W, at constant Ar pressure of 7 mTorr, and (2) at varying Ar pressures, in the range of 5-20 mTorr at a constant power of 100 W. A detailed structural characterization was made to understand the effect of processing conditions on the morphology evolution, grain size, and crystal structure of the CdS films. High-resolution scanning electron microscopy (HRSEM) measurements revealed the smooth surface morphology of the CdS layers both as a function of sputtering power and Ar-pressure. CdS films grown at 70-130 W were found to be nanocrystalline, exhibiting grain-size (L) dependence on the sputtering-power (W). L increased with W yielding the highest average L=145 nm at 105 W. Further increase in W resulted in decreasing L. Similarly, under varying Ar pressure, the highest L (~138 nm) values were found at 5 mTorr. X-ray diffraction (XRD) analysis indicated that the entire set of deposited CdS films exhibit highly oriented cubic structure. L values evaluated from XRD are in good agreement with the HRSEM results. The optical characteristics were evaluated and a functional relationship between growth conditions and band gap, useful to tailor the CdS films for desired solar-cell application, was found. The results obtained will be presented and discussed.

2:20pm **TF1+PV-MoA2 Characterization of Photovoltaic Thin Films Materials Using RF GD-OES and LA ICP-MS**, *F. Li, S. Anderson*, Air Liquide - Balazs, *P. Hunault*, HORIBA Jobin Yvon

Photovoltaic thin film materials have been characterized by a number of traditional vacuum techniques; Auger, XPS, SIMS, and GD-MS to name only a few. Depth profiles of solar cell modules, contamination in the sputtering targets or surface stoichiometry of photovoltaic thin films are specific application examples which predicate the technique best suited for the data requirement. The evolution of thin films with new chemistries and the importance of surface modification for photovoltaic applications provide a continuing need for thin film analyses along with an avenue for new analytical tools.

In this paper we will discuss the application of two non-traditional surface and material analysis techniques for the photovoltaic solar industry, glow discharge optical emission spectroscopy (RF GD-OES) and laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS). The RF GD-OES and LA ICP-MS techniques enable direct analysis and depth profiling of a variety of conductive and nonconductive materials and photovoltaic thin films such as SiO_2 , CdTe, CIGS, and TCO. With each technique, the ability to simultaneously depth profile more than 40 elements is possible. RF GD-OES and LA ICP-MS are much faster and more cost effective for depth profiling than SIMS. When using the techniques as an elemental survey technique, each analysis is more sensitive and also much faster than Auger and XPS.

Additional specific advantages of RF GD-OES and LA ICP-MS will also be discussed. Using radio frequency (RF) plasma for analytical signal generation, these techniques do not have the surface equilibrium issues seen with other surface analytical techniques such as SIMS. The charging effect that can cause issues with electron and ion beam techniques is also avoided. Additionally, there are no artifacts in their sputtering processes, especially on the top surface. Therefore, the surface stoichiometry of some solar thin films before and after chemical treatment can be reliably characterized. This feature is extremely important for surface modification projects in an effort to produce far more efficient photovoltaic thin films. Finally both RF GD-OES and LA ICP-MS don't require any sample preparation unlike GD-MS,

thin films and materials can be directly characterized in their natural states against NIST traceable standards.

2:40pm **TF1+PV-MoA3 Multi-technique Lateral and Vertical Surface Characterisation of Thin-film Photovoltaics**, *A.J. Roberts*, Kratos Analytical Ltd, UK, *C.J. Moffitt*, Kratos Analytical Inc., *J.W. Pankow*, National Renewable Energy Laboratory

Thin-film photovoltaic production is an important and fast growing field in energy technology. The most widely applied thin-film photovoltaic technology is based on the use of cadmium telluride / cadmium sulfide (CdTe/CdS) heterojunctions and although research in CdTe dates back to the 1950s the challenges associated with junction quality and electrical contacting have not been well addressed. Both vertical (depth) and lateral composition of thin film PV devices is of great importance for optimum performance.

The cadmium tin oxide (CTO)/zinc tin oxide (ZTO) bilayer structure is an alternative to traditional tin oxide front contacts and provides lower resistance and better light transmission. Modern multilayer stacks such as CdTe/CdS/ZTO/CTO/glass have lead to the best reported cell efficiencies of ~16.5% but disparate differences in efficiencies can be observed for devices made from films located within even a cm of each other and back contacted in identical fashion. This work presents the use of photoemission spectroscopies combined with Ar⁺ ion depth profiling to characterise a CdTe/CdS/ZTO/CTO/glass multilayer sample. X-ray photoelectron spectroscopy (XPS) depth profiling has been used to generate elemental and chemical information as a function of depth through the layer and interface regions using sputtering conditions chosen minimize surface roughening and knock on phenomena that can cause difficulties in discerning between true depth variations and sputter induced artifacts when analyses are done under traditional sputter conditions. In combination with XPS, ultraviolet photoemission spectroscopy (UPS) depth profiling has been used to measure the pseudo work-function of the layers and interface regions, allowing a pseudo work-function depth profile to be generated.

As well as vertical compositional characterisation the lateral composition has been investigated for a different thin-film PV system comprising Cu:In:Ga:Se (CIGS)/Mo/glass. Changes across the surface are undesirable in the manufacturing process as small differences in Cu/(In+Ga) or Ga/(In+Ga) can compromise ultimate device efficiency. These compositional changes typically occur over centimeter scales necessitating mapping over >5x5 cm. The multi-technique approach to surface characterisation of these thin film photovoltaics has provided chemical, elemental, pseudo work-function as a function of depth and lateral compositional information from two different thin film photovoltaic systems.

3:00pm **TF1+PV-MoA4 XPS Band Offset Measurements of ZnO, CdTe, and CuSCN for Application in Nanostructured Photovoltaics**, *T.C. Kaspar*, *T. Droubay*, *J.E. Jaffe*, *V. Shutthanandan*, *W. Jiang*, *S.A. Chambers*, *G.J. Exarhos*, Pacific Northwest National Laboratory

All photovoltaic devices require efficient electron-hole separation, transport, and collection. It is relatively straightforward to experimentally determine the charge transport properties of the individual component materials in a given cell design, allowing optimization. However, the charge transport across heterojunction interfaces between component materials is just as critical for overall cell performance. The electron or hole injection efficiency is determined by the band structure alignment at the interface; optimization of the interface for facile charge injection requires detailed knowledge of the band offsets, which cannot easily be determined by electrical transport measurements. We utilize high resolution x-ray photoelectron spectroscopy (XPS) to directly quantify the band offsets of heterojunctions relevant to photovoltaic cells. Nanostructured extremely thin absorber (ETA) photovoltaic devices have been proposed as an inexpensive alternative to current single-crystal device technology, although the devices reported thus far suffer from low conversion efficiency. Thus, materials relevant to ETA devices were chosen for study: n-ZnO as the electron transporter, solid-state p-CuSCN as the hole conductor, and CdTe as the photon absorber. High quality ZnO thin films were deposited by pulsed laser deposition (PLD) on F:SnO₂/glass substrates for XPS band offset measurements. The band offsets were determined as a function of ZnO conductivity, and strategies for improved electron conduction across the interface will be discussed. In addition, the materials properties of CuSCN were thoroughly characterized, and its electronic structure was compared to density functional theory (DFT) calculations. The calculations show an indirect bandgap of 2.7eV and highly anisotropic charge transport with the unusual prediction that hole mobility exceeds the electron mobility. Avenues to improve hole conduction through the introduction of defects in CuSCN were explored.

3:40pm **TF1+PV-MoA6 Effects of Cu Doping Level in ZnTe:Cu Back Contacts on Cu Diffusion and CdTe Solar Cell Performance**, *J.N. Duenow, R.G. Dhere, S.E. Asher, W.K. Metzger, J. Li, T. Moriarty, T.A. Gessert*, National Renewable Energy Laboratory

CdTe photovoltaic (PV) cells require a low-resistance back contact for optimal device performance. Cu-doped ZnTe (ZnTe:Cu) has been implemented successfully as an ohmic back-contact interface layer to CdTe, enabling PV cells with efficiencies of 14%. ZnTe:Cu offers the additional advantage of being easily manufactured by vacuum processing, which enables highly controlled, reproducible films. Although CdTe devices have been made without Cu-containing contacts, devices with Cu contacts have generally exhibited higher performance. Controlled Cu diffusion from the back contact is known to be critical for optimal performance. Sufficient Cu is required for doping the CdTe absorber to provide a strong electric field in the junction region. Excessive Cu, however, can lead to poorer collection by narrowing the depletion region to the extent that few minority carriers are generated within a diffusion length of the depletion region. Cu may also adversely affect the junction by diffusing into the CdS window layer.

Previous studies of Cu diffusion from ZnTe:Cu back contacts have been performed at NREL using a fixed doping level of Cu in ZnTe, but altering Cu diffusion by changing the deposition temperature or film thickness. In this study, we instead deposit ZnTe:Cu films from targets containing a range of Cu amounts—from 0.45 to 5 wt.%—while holding the temperature and film thickness constant. Capacitance-voltage, red-light-biased quantum efficiency, and secondary-ion mass spectrometry depth-profile measurements will indicate the net acceptor concentration in the CdTe and the degree of Cu diffusion as a function of the Cu density in the back-contact interface layer. Minority-carrier lifetime measurements will be used to correlate the effects of Cu density to the carrier recombination rate.

4:00pm **TF1+PV-MoA7 Surface and Interface Properties ZnTe-based Solar Cell**, *F. Fang, B.E. McCandless, R.L. Opila*, University of Delaware

In order to substantially reduce the capital costs of present crystalline silicon photovoltaics, alternative thin film solar cell (TFSC) devices are favored because of the inexpensive materials, simple material preparation, and low-cost large area fabrication. There is interest in growing polycrystalline thin films of II-VI direct band gap semiconductors, such as CdS/CdTe. TFSCs are well studied and currently being used for manufacture of commercial scale solar modules. Here, we are proposing a heterojunction system *n*-ZnSe/*p*-ZnTe as a wide band gap TFSC ($E_G > 2$ eV) for potential application in tandem cells. This provides an efficiency enhancement for future generation photovoltaics, provided the wide band gap cell efficiency can be increased. In addition, we are using Close Space Sublimation (CSS), which is a low-cost deposition method already demonstrated for high efficiency and commercial CdTe TFSC.

Our ZnSe/ZnTe TFSC is a heterojunction device with a high density of defect states at interfaces which can provide interface recombination centers; also the grain boundaries in polycrystalline semiconductor films act as shallow and deep defect levels within the bandgap and create different recombination mechanisms than radiative band-to-band recombination in ideal crystalline devices. As a result, minority carrier collection relies on the built-in electric field, and results in voltage-dependent collection of photo-generated current. Therefore, it is crucial to form a high quality diffused junction. Some earlier work reported a diffusion voltage of 1.70 eV for single crystal ZnSe/ZnTe structure, which suggests that open circuit voltage, $V_{oc} > 1$ V is feasible. We have used Al-K α X-ray photoelectron spectroscopy and Soft (Ultra-violet) X-ray photoelectron spectroscopy (Synchrotron Light Source) to investigate the surface chemistry and valence band structures of the as-deposited films, scanning electron microscopy (SEM) to investigate the surface and cross-section morphology, energy-dispersive X-ray spectroscopy (EDX) to verify the chemistry. Surface oxides on ZnSe have been identified and their effects on interface band offset are evaluated. A significant valence band maximum shift is also observed with UPS which indicates an increased maximum open circuit voltage of the junction. This result is consistent with our I-V testing. Better devices with $V_{oc} > 600$ mV and photocurrent $J_{sc} > 5$ mA/cm² were only obtained for films with ZnTe deposited immediately after ZnSe, i.e., no time for oxide formation. More detailed understanding of the chemistry and interfacial band structure are being investigated and used to guide a path to improved conversion efficiency.

4:20pm **TF1+PV-MoA8 Issues of Large-Scale Photovoltaic Energy Production from Thin-Film CdTe Devices**, *T.A. Gessert*, National Renewable Energy Laboratory **INVITED**

It is now widely accepted that thin-film photovoltaic (PV) devices will be important contributors of new US electricity generation. The annual production of PV devices needed to meet conservative U.S. Department of Energy goals for 2050 represents ~100 square miles of active module area (20 GW), or ~200 times the total area of photovoltaic modules installed in

the US by 2004. However, if the rate of growth observed in PV module production for the past eight years continues, 100 square miles of annual US PV production could be achieved as early as 2018. Further, the amount PV installed by 2036 could generate the entire 2004 US Total Energy Consumption (~100 Quadrillion BTU's, i.e., the combined energy consumed in the US from petroleum, coal, natural gas, nuclear, and all renewable sources). Regardless of what assumptions are made, PV represents a significant future market, especially for thin-film modules based on CdTe and related process technologies. This talk will discuss CdTe thin-film PV devices within the context of the major PV technologies in production today, and indicate areas where improved material and device understanding would be beneficial.

5:00pm **TF1+PV-MoA10 Novel Solar Cells based on a ZnGeAs₂ Absorber Layer**, *T.J. Peshek*, National Renewable Energy Laboratory and Arizona State University, *T.J. Coutts, T.A. Gessert*, National Renewable Energy Laboratory, *Z.Z. Tang, L. Zhang, N. Newman, M. van Schilfgaarde*, Arizona State University

We present the latest results on the development of a novel thin film solar cell based upon the direct gap chalcopyrite semiconductor ZnGeAs₂. This material has long been viewed as a promising solar material for high efficiency multijunction cells due to it being lattice matched to GaAs and having a band gap of about 1.1 eV. In light of recent advances in single junction solar cells based on chalcopyrite materials such as CuInSe₂ we have fabricated the first, to our knowledge, single junction cell based on ZnGeAs₂. Initial tests show the devices to have low conversion efficiencies because the photogenerated currents are low. However, we find that the open-circuit voltage in our first tests is approximately 0.135 V. It is our hypothesis based on the J-V curves that the current sourced by the cell can be improved significantly at this point by reducing the series resistance of the device and minimizing any shunts that seem to be present in these devices. The cell is structured according to the superstrate configuration using RF sputtered CdS as the n-type buffer layer. The p-type ZnGeAs₂ absorber was deposited at about 600 K by pulsed laser deposition.

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