SYMPOSIUM B
Compound Semiconductor Photovoltaics
April 22 – 25, 2003

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*Invited paper
mechanisms with different microscopic origin. There has been some
debate whether the prevailing one is the pair formation of the donor
with the metal vacancy (Acceptor-like) (The formation of an
acceptor-like site, accompanied by a large lattice relaxation
(DX-center). While the theory of the DX-center well explains
experimental observations such as persistent photocactivity,
the microscopic model is primarily based on theoretical
calculations. In order to characterize the local structure of
indium donor atoms in CdTe, radioactive \(^{111}\)In/\(^{111}\)Cd probe atoms are introduced
in-doped samples, and the electric field gradient (EFG) at the site of the probe atom is measured by means of the perturbed
\(\gamma\)-angular correlation (PAC) technique. Thus, the formation of A-centers
following in-doping is confirmed through the observation of the known
EFG for this defect, determined by the PAC. After removing the
vacancies by annealing the crystal under excess Cd vapor, however, a
different, relatively weak EFG of about \(V_\gamma =10^{-2}\) V m\(^{-2}\) is measured at the site of the \(^{111}\)Cd daughter nucleus. Attributing the observation of
this EFG to DX formation, the EFG signal corresponds to a
model of related configurations of \(^{111}\)Cd originating from the initially present DX-center configuration of the
\(^{111}\)In atom. This interpretation is supported by density functional
theory (DFT) based EFG calculation for the respective defect
configuration. The EFG is very sensitive to the strength of the lattice
relaxation and the detailed local arrangement of the lattice
atoms about the probe atom. Therefore, in combination with the DFT
calculations, the measured EFG is an experimentally obtained
confirmation for the microscopic model of the DX-center. Apart from
the EFG calculation, the DFT yields additional physical and chemical
information about both the metastable configuration of the Cd host
atom and the In related DX-center.

9:30 AM B1.4
HIGH-RESOLUTION ELECTRONIC STRUCTURE IMAGING ON
POLYCRYSTALLINE CdTe SOLAR CELLS BY SCANNING
TUNNELING MICROSCOPY. P. Satter, P. Zühl, E. Satter, V.
Kudrinov, T. Ohno, Department of Physics, Colorado School of
Miners, Golden, CO.

Scanning tunneling microscopy (STM) has become a standard
technique for atom-resolved imaging at conductor surfaces. A number
of STM-derived techniques exist that allow obtaining electronic
structure information with sub-nanometer spatial resolution. Scanning
tunneling spectroscopy (STS), for example, can be used to measure
variations in density of states, bandgap, and Fermi-energy, at the
atomic scale. We have successfully imaged polycrystalline CdTe cells
using STM. Both constant-current (cc) "topographic" images and
current images were obtained on devices with a thin ZnTe contact.
A close correlation is observed between features in cc STM and in
current maps. Intragrain material, identified via topographic maxima in
cc STM, carries significantly higher current than material near
grain boundaries. In addition, we find a highly non-uniform current
distribution within grains. Our high-resolution maps allow us to
relate these non-uniformities to the growth and processing conditions
of the devices, in particular the cooling of CdTe ingots during the
CdTe absorber and the ZnTe contact. In view of the wealth of
information contained in STM current images, it is likely that such
measurements will provide key data on electronic structure variations
at length scales far below the grain size.

9:45 AM B1.5
HYDROGEN AS A SELENIUM DOPANT CONCENTRATION
AND ACTIVITY AS A FUNCTION OF GROWTH CONDITIONS IN
POLYCRYSTALLINE CdSe/GROWN CdTe. A. Stafford, S.J.C.
Irving, Department of Chemistry, University of Wales, Bangor,
UNITED KINGDOM. K. Durrose, G. Zegg, Department of Physics,
University of Durham, UNITED KINGDOM.

Polycrystalline CdTe has considerable potential as a thin-film
photovoltaic absorber. However, control of the electrical properties
such that the grains are p-type with passivated grain boundaries,
a crucial in obtaining high-efficiency PV modules. It is well known
that doping in II/VI materials can be problematic due to compensation
from intrinsic defects and complex impurities. In this attempt to
obtain a better understanding of the behaviour of Selenium as an
dopant in CdTe, in order to maintain high concentration and thus
optimize photovoltaic performance, CdTe layers, 1-2 micron thick
were grown at different growth rates and V/II 1:1 selenium to
insulating sapphire substrates using the organometallic precursors
dimethylsila, disopropylethyl and tri-isopropyl selenides. The layers were electrically characterised using Van der Pauw (under both dark and illumination conditions) and Hall
measurements. Total dopant concentration was measured where
necessary using calibrated SIMS. SEM was used to check for
variations in grain size, and qualitative data on some intrinsic defects
were obtained using PL. Total ionization of the dopant was
measured to be higher at lower growth temperatures (350°C), but
electrical characterisation showed that the interface resistivity was
considerably
reduced at 400°C. At this temperature, for a given dopant flow, the resistivity under AM1.5 conditions was dependent upon constant V/I ratio, even though the conditions were approximately the same which would satisfy the highest efficiency CIGS devices. We have also studied three CIGS samples with Cu/(In+Ga) ratios ranging from 0.69 to 1.07. All of these films have been grown to thickness of approximately 0.2 μm on molybdenum-coated soda lime glass.

The ellipsometry spectra were measured at angles of incidence from 60° to 80° to ensure exact results. Spectra were measured over the energy range 0.7 to 5.0 eV. To avoid artifacts due to surface layers, analytical models use a surface roughness layer. Accurate values of real and imaginary parts of dielectric functions representative of CIGS absorber layer are obtained from the data. The structures observed in x-ray diffraction analysis were analyzed by fitting numerically the derived spectra of εr(ω)/ε0 to analytic line shapes using CPPB (Critical Point Particular Band Lineshape) fitting procedure to get the position of the energy, approximate amplitude and broadening of each oscillator. The overall energies are related to interband transitions based on the electronic band structure of the end-point compounds. Based on these results, we express the band gap energy, crystal-field splitting and spin-orbit splitting as a function of the gallium composition using the pseudobinary model.

We have used atomic force microscopy (AFM) to verify the surface roughness. Layer thickness determined from modeling of the VASE data. Scanning electron microscopy is used to determine grain size and microstructure of the films.

11:30 AM B1.10 EFFECTS OF Na ON Cu(In,Ga)Se2 THIN FILMS AND SOLAR CELLS. D. Rudman, M. Kaeding, F.J. Haug, H. Zieg, A. Tomassini, Physikalisches Institut, Universität Zürich, Zürich, SWITZERLAND. Also Electronic and Electrical Eng. Dep., Loughborough University, UNITED KINGDOM.

High efficiency Cu(In,Ga)Se2 (CIGS) solar cells generally need a small amount of Na incorporated into the absorber layer, which modifies layer growth and induces electronic changes. However, there is some discrepancy concerning the effects on the absorber microstructure. Some groups have reported a clear increase in grain size due to availability of Na during growth, others have found none and we have observed an unambiguous decrease. In all cases, CIGS layers were grown by physical vapour deposition. This indicates that the effects of Na on CIGS growth depend on the absorber preparation recipe and/or other parameters yet to be identified. Investigations about the impact of Na on CIGS grain growth will be presented for different CIGS growth procedures and incorporation techniques. The effects on photovoltaic performance of solar cells grown from such layers will be discussed.

SESSION B2: III-V PHOTOVOLTAIC MATERIALS

Chair: Daniel J. Friedman and Wuesth I. Simko-Davies Tuesday, April 22, 2003

Salon 10/11 [Marriott]

1:30 PM B2.1 EFFECT OF N ON THE DEFECT PROPERTIES IN GaAs. Su-Hui Wei, National Renewable Energy Laboratory, Golden, CO.

Unlike conventional isovalent semiconductor alloys A–xBx, C, where the physical properties change smoothly and continuously as a function of the composition x, for GaAs–xN–x, due to a large size and chemical mismatch between N and As, adding a few percent of N into GaAs can drastically change its electrical and optical properties. For example, its band gap can be significantly smaller than that of GaAs. As such, GaAs–xN–x has become a promising candidate as an absorber for high-efficiency tandem solar cells. Under thermal equilibrium, N solubility in bulk GaAs is very low [N] < 10¹⁸ cm⁻³. But, in epitaxial growth, a few percent of N can be mixed into GaAs. However, with high [N], one also see a considerable degradation of the minority carrier lifetime, indicating that [N] also affects significantly the properties of GaAs. Using first-principles total-energy calculations we show that N solubility in GaAs is controlled by the N chemical potential, μN. In bulk growth μN is limited by the formation of equilibrium bulk GaN, resulting low [N]. In epitaxial growth, however, strained GaN on the surface can lead to a much higher μN, thus significantly enhances [N] by eight orders of magnitude to about 4% at T = 650°C, in agreement with experiments. We also show that with high μN, low energy N-N and N-As split interstitials with deep levels will form, which are the likely sources of the nonradiative carrier killers in this system. Furthermore, we show that in the presence of the N, the character of the intrinsic and extrinsic defects in GaAs are qualitatively different from those without N. For example, we find that in GaAs–xN–x the N-related defects are electrically charged and acts as a donor in its own right, whereas in conventional III-V semiconductors H is an interstitial impurity causing passivation instead of doping. At high Fermi energy and H
concentration, we find that a N complex with two hydrogen (H2) is energetically more stable than the single-H configuration. This provides the formal proof that H2 cannot be stable in H V semiconductor. More surprisingly, we find that this H2 is electrically inactive and removes the effect of N on the band gap, i.e., restoring the gap of GaN. Effects of N on other defects (e.g., Vgr, Sgr) will also be discussed. This work was done with A. Janotti, S.B. Zhang, Sarah R. Kurtz, and C.G. Van de Walle and is supported by U.S. DOE under Contract No. DE-AC86-76FR04010.

2:00 PM B2.2 ELECTRONIC STRUCTURE OF HIGHLY MISMATCHED SEMICONDUCTOR ALLOYS. Wlodzimierz Walkiewicz, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

Highly mismatched alloys (HMA) are formed when the metallic ions in a semiconductor are replaced by more electronegative isoelectronic ions. The most extensively studied class of HMAS are group III-V homologous alloys in which metallic column V elements (e.g., As) are replaced by N. A striking feature of these alloys is a large reduction of the fundamental band gap with increasing N content. Special efforts have been devoted to GaAs-In,NAs alloys which, for x=5%, are lattice matched to GaAs and, for x>0.03, have a band gap lower than 1 eV. These alloys have considerable promise for optoelectronic applications. It has also been proposed that they could be useful to utilize the near infrared part of the solar spectrum in multijunction solar cells. We show that the electronic structure of InN, V,1-x alloys is accurately described by the Band Anticrossing (BAC) model as the bonding interaction between highly localized levels of substitutional N and the extended states of the host semiconductor matrix. The model has not only explained a large variety of effects observed in group III-V,1-x alloys but has also predicted new properties. For example, experiments have fully confirmed the theoretically predicted effective mass enhancement and the improved donor activation efficiency in GaNAs alloys as well as the N-induced transition from indirect to direct band gap in GaNP. We will also present our most recent results on mutual presence of the covalent electronic N and electrically active group IV donors impurities in GaAs In,NAs alloys. Finally, we will demonstrate that the BAC model is broadly applicable to other HMAs, most notably to the extreme case of CuSn,MnO Te2 alloys where highly electronegative O partially replaces metallic Te. In agreement with the BAC model we observe a large bandgap reduction in these alloys. Supported by US DOE under Contract No. DE-AC02-76SF00515.

2:30 PM B2.3 CHEMICAL AND ELECTRONIC CHARACTERIZATION OF GaSb/SURFACE PASSIVATION BY ALCOHOL-BASED SULFIDE SOLUTIONS. Zhiyan Liu and Shurti Prakash, University of Wisconsin-Madison, Department of Chemical Engineering, Madison, WI. David A. Shanks, University of Wisconsin-Madison, Department of Electrical and Computer Engineering, Madison, WI. T.F. Hubsch, University of Wisconsin-Madison, Department of Chemical Engineering, Madison, WI.

GaSb is an important III-V compound semiconductor for thermal photovoltaic applications. The performance of GaSb in such applications is sensitive to surface recombination and other surface chemical and electronic phenomena. GaSb surface is very chemical reactive surface and thick native oxides readily form on the surface at room temperature leading to a high density of surface states and high leakage currents. Therefore, control of GaSb surface or interface with desirable chemical and electronic properties is critical step in the GaSb-based device fabrication. It is found that sulfide-based treatments can reduce the surface states density and hence improve the performance of many III-V semiconductor devices. In this work, GaSb surfaces passivated by sodium sulfide in both alcohol-based solutions and dry conditions were studied. Alcohols, including ethyl, isopropanol and t-butyl alcohol, were compared to aqueous sulfide solutions in order to determine how solvent-based effects on the reactivity of the sulfide in the solution. Up to a seven-fold increase in PL intensity was observed for both n- and p-type GaSb after passivated with 2-propanol based sulfur solution, with the overall peak intensity of Sb/Ga being close to 1. Also the native oxides of gallium and antimony as well as elemental antimony on the surface are further reduced compared to the sample passivated by aqueous solutions. The chemical composition and bonding states of the surface atoms after sulfidation treatments were investigated by X-ray photoelectron spectroscopy (XPS). To investigate the thermal stability of sulfur bonds, the passivated sample was annealed to 600°C in vacuum. It is found that annealing at 300°C, all the surface Sb atoms are bulk-like, i.e., Sb-Ga bonded, and no Sb-S bonds could be detected. However, the amount of Sb-Ga bonds was increased with the temperature going up. After 600°C, all the Ga-S bonds were desorbed from the surface.


Radio-Frequency (RF) photoresponse measurements and one-dimensional device simulations have been used to evaluate bulk and surface recombination parameters in antimonide-based materials. The photoreconductivity response of antimonide-based substrates and doubly-capped epitaxial layers are simulated and used to extract the recombination parameters using experimental results. Excellent agreement has been obtained with a first-order model and test structure simulation when Shockley-Read-Hall (SRH) recombination is a key mechanism. When radiative and surface recombination are included, the simulation results show good agreement with the model. RF photoresponse measurements and simulations are compatible with a radiative recombination coefficient (B) of approximately 5 x 10^-12 cm^2/s. Auger coefficient (C) ~ 1 x 10^-23 cm^3/s and surface recombination velocity (SRV) ~ 400 cm/s for 0.50 - 0.55 eV doubly-capped InGaAsSb material with GaSb capping layers using the experimentally determined active layer doping of 2 x 10^17 cm^-3. Photon recycling, neglected in the analysis and simulations presented, will affect the extracted recombination parameters to some extent.

3:30 PM B2.5 MEYER-NELDEL RULE: CONSEQUENCES FOR PHOTOVOLTAICS. Richard S. Crandall, National Renewable Energy Laboratory, Golden, CO.

The Meyer-Nelddel rule (MNR) (compensation law) is ubiquitous in compound semiconductors and other materials. Data in this literature and to be presented at this meeting show emission rates of free carriers are proportional to trap density (D) and a characteristic cross-section (σ) for capture of carriers, respectively. The MNR is the result of a balance between emission and capture rates and is independent of the capture mechanisms. The MNR is also valid for more complex capture processes such as those due to non-radiative recombination centers.


We present data showing the potential adverse effects on photovoltaic device performance of all traps in InGaAsN. Deep-level transient spectroscopy measurements were performed on InGaAsN samples grown by both metal-organic chemical vapor deposition and RF plasma-assisted molecular-beam epitaxy. For each growth technique, we studied samples with various nitrogen composition ranging from 0.3% to 2.2%. A deep hole trap with activation energy ranging between 0.4 and 0.8 eV is observed in all samples. These data clearly obey the Meyer-Nelddel rule, which states that all traps have the same emission rate at the isokinetic temperature. A fit of our data gives an isokinetic temperature of 327 K, which means that both deep and shallow traps emit equally at the operating temperature of solar cells, the traps are recombination centers.

A new approach for high-efficiency thermophotovoltaic (TPV) systems using GaAs TPV cells on GaSb substrate is being investigated. The resulting structure consists of a back-band high-reflectivity mirror sandwiched between GaSb device layers and the handle substrate. Such a geometry provides several advantages for TPV cell performance enhancement and series interconnection of cells. The reflector 

Long-grained, polycrystalline, high efficiency, III-V photovoltaics grown on thin, flexible substrates are desired for powering satellites. However, such devices have proven to be elusive. All attempts thus far have resulted in small-grained material due to closely spaced, aperiodic nucleation sites, which prevent the formation of films with poor device quality due to carrier recombination at grain boundaries. To increase the grain size, the location and size of nucleation sites must be controlled. In this work, submicron islands of gallium metal were electrodeposited on n-type silicon from a solution of 0.1 M GaCl₃. Prior to the deposition, the silicon was patterned with photore sist to restrict the electrodeposition to defined regions. The electrodeposition was pulsed, with the potential stepped from -0.5 V to -1.8 V relative to the easy oxidation potential. The duration of the pulse ranged from 100 to 1000 ms, and the number of pulses ranged from 1 to 100. Longer and more pulses produced more gallium islands. After electrodeposition, the photoresist was removed and the samples were annealed in hydrogen (78 Torr, 6 atm) at 700°C for 10 minutes, after which anneal, AsH₃ was introduced to the gas flow and the anneal was continued for another 10 minutes. AFM images of the resulting material showed the dots to be 0.1 μm to 1 μm in diameter, with the large dots showing evidence of grain boundaries. SEM images showed similarly sized features, and EDX analysis indicated the dots were completely converted to GaAs by the anneal. This work was funded by grants from the Air Force Research Laboratory and the National Science Foundation.

4:45 PM B2.10 SCANNING TUNNELING SPECTROSCOPY OF NANOSCALE DOPANT-INDUCED DOTS IN GaAs. N.D. Jüger and K. Urban, Forschungszentrum Jülich GmbH, Jülich, GERMANY; E.R. Weber, Dept. of Materials Science, University of California, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA; Ph. Ebert, Forschungszentrum Jülich GmbH, Jülich, GERMANY.

We investigated the electronic structure and behavior of p-type nanoscale dopants induced in GaAs by conventional scanning tunneling microscopy and spectroscopy as a function of the number of dopant atoms within the dot. The dopant-induced dots are formed by fluctuations of the dopant atom distribution in sufficiently thin GaAs p+-layers. We find significant changes in the electronic conduction and transport characteristics of the nanoscale dots compared to spatially non-confined material. The differences in the electronic properties of the dots are found to arise from a reduced ability to screen the tip's electric field because of limitations to deplete the dots of free holes. The limited depletion is due to the presence of confining potentials surrounding the dopant-induced dots. The experiments highlight the effect of the discrete nature of dopant atoms and the resulting local variations of the potential on the conduction. The similarity of the dots' configuration with np-np transistors suggests that the physical mechanisms found here will also affect future miniaturized semiconductor devices, once they reach dimensions as small as those of the fluctuations of the dopant concentration.

SESSION D3: OLED INTERFACE CHARACTERIZATION
Chair: Victor Kuyashov and Vello Valdna Wednesday Morning, April 23, 2018 Salon 10/11 (Marriott)

8:30 AM • D3.1 THE DYNAMICS OF CADMIUM TELLURIDE ETCHING. K.D. Dobson, P.D. Pashan, B.E. McConnell, R.W. Birchmore, Institute of Energy Conversion, University of Delaware, Newark DE.

The inability to prepare stable ohmic contacts to p-GaTe has hindered the development of GaTe/Ch solar cells. Pseudomorphic back contacts to CdTe/CdS cells can be prepared by doping Te-rich CdTe surfaces with Zn. Oxidizing wet chemical etches are generally used to prepare Te-rich CdTe surfaces. However, despite the extensive use of wet etches in contacting CdTe, much is taken for granted regarding their action on polycrystalline CdTe films and possible effects on device performance. In this paper, recent in situ ellipsometric and transmission electron microscope details of CdTe etching will be presented. The use of variable angle spectroscopic ellipsometry, coupled with grazing incidence x-ray diffraction, has proven to be a very powerful approach for monitoring the nature of CdTe film surfaces following chemical treatments. Ellipsometric measurements have shown that etching polycrystalline-CdTe films with HNO₃/H₃PO₄ (NP) for 45 s produces a 180 nm crystalline-CdTe surface film, which is stable to


The formation of submicron GaAs islands on Si has been observed by in situ monitoring of epitaxial growth using monitoring of reflectance using Grazing Incidence X-ray Diffraction in the diffraction plane (GIXD) and in the plane normal (GIXN). It has been observed that, in the presence of Ga, the GaAs islands nucleate on the Si substrates and grow by island coarsening. The islands grow at a rate of several micrometers per second and eventually coalesce to form a continuous layer.
atmospheric oxidation for a number of hours. NP etches of 15.35s form thinner films with a significant amorphous-Te component, which significantly reduces the production of carriers following the etching step. NP etching is an aggressive reagent, which etches the CdTe surface and grain boundaries (GBs). Etching of GBs may affect device performance by increasing shunting, enhancing metal diffusion or passivating grain surfaces. Etching with Br2/methanol produces 1.2 nm amorphous-Te surface films, which begin to oxidize in air immediately following treatment. Br2 is less aggressive towards CdTe surfaces and GBs, however, GB diffusion of Br2 has been previously observed in CdTe/CdS films. Some of the etchants used within the cell structure may impact cell performance. To maximize the surface formation of Te while preserving GB integrity, the properties of a range of etch solutions were modified by varying concentration, viscosity and acidity. The effects of varying etch properties on CdTe surface chemistry and device performance will be discussed.

9:00 AM B3.2
FORMATION OF CdTe THIN LAYERS ON CdTe AFTER NP-ETCHING AND HgTe-GRAFITE PASTING. Yung-Yu, K. M. Jones, X. Wu, and M.M. Al-Jassim, National Renewable Energy Laboratory, Golden, CO.

It is well accepted that chemical etching of CdTe in NP solution (HNO3:H2PO4) improves back contact properties in CdS/CdTe solar cells. It is suggested that NP etching generates a Te-rich layer, which can be p+-, resulting in better back contact. Here we report our investigation of the microstructure and chemical composition at the CdTe/Te-rich interfaces generated by NP-etching polycrystalline and single crystalline CdTe and following with HgTe-graphite passivation. We find that after NP-etching, HgTe-graphite passivation and thermal annealing, a thin-layer (about 20 nm thick) of CdTe was formed between CdTe and Te-rich layers, giving the structure like CdTe/CdS/CdTe/graphite. Cross-sectional transmission electron microscope images show clearly that the CdTe layer has epitaxial relationship with the CdTe. Attempts were made to mimic the Te-rich CdTe layer by depositing a thin layer of Te on single crystalline CdTe. The samples were then applied with HgTe/graphite passives and annealed at different temperatures. However, no CdTe layer has been observed.

9:15 AM B3.3
CHEMICAL AND ELECTRONIC PROPERTIES OF CdTe/Se2Te3 CONTACTS FOR CdTe THIN FILM SOLAR CELLS STUDIED BY PHOTOEMISSION. D. Kraft, A. Thiesen, A. Klein, W. Jagermann, Darmstadt University of Technology, Institute of Materials Science, Darmstadt, Germany.

Formation of low resistance back contacts to CdTe thin film solar cells has been a research issue for many years. Ohmic contacts to solar cells are typically prepared by diffusion of dopants to form a thin space charge layer, which can be easily tunnelled. Unfortunately, further diffusion of dopants during solar cell operation may lead to a degradation of cell performance, which limits the use of Cu containing back contact materials. Stable CdTe solar cells with reasonable back contacts have been prepared using Sb2Te3/metal layer systems. We have investigated the chemical and electronic properties of such layer systems using a series of photoelectron spectroscopy. Sb2Te3 layers deposited onto CdTe were found to increase the substrate resistance to good back contact. By subsequent deposition of metal a chemical reaction is induced forming Sb and metal tellurides. The contact formation is related to diffusion of Sb into the CdTe leading to a stronger p-doped surface layer.

9:30 AM B3.4
ANALYSIS OF THE ZnTe-Cu CONTACT ON CdS/CdTe SOLAR CELLS. Tim Gesiers and Manuel Romero, National Renewable Energy Laboratory, Golden, CO.

The demonstration of a manufacturable, stable, low-resistance, ohmic contact for p-CdTe polycrystalline photovoltaic devices remains an important goal of the CdTe research community. Devices with fill factors approaching 77% have been demonstrated by incorporating a Cu-doped ZnTe contact interface layer between the CdTe absorber and a Ti metallization. This contact process uses ion-beam milling, instead of wet-chemical etching, to prepare the CdTe surface. In addition to potential manufacturing advantages, the high degree of control afforded by this approach has made it possible for this contact to enable systematic variation of critical aspects of the contact design. For example, changing only the thickness of the ZnTe-Cu layer affects the concentration within the CdTe and CdS layers but does not significantly change the electrical transport across the ZnTe/Cu interface barrier. Recently, spectroscopic cathodoluminescence (CL) has been added to our list of contact analysis tools. Depth-resolved CL studies reveal radiative recombination peaks at both ~1.57 eV and ~1.4 eV, and these two peaks are in different locations in the CdTe device. The higher-energy peak(s) are likely associated with excitons and shallow donor-to-acceptor transitions. Analysis of these peaks can provide clues to the evolution of the CdTe surface during the contact process. The broad group of peaks centered at ~1.4 eV has been described to a deep donor-acceptor pair (DDAP) in which the acceptor is believed to have an activation energy of ~150 meV. Analysis of CdTe bi-crystals indicates that this peak is not observed prior to typical CdTe contacts. Because CdTe/CdS contacts can incorporate both Cl and Cu into the CdTe, we believe analysis of the depth dependence of the 1.4 eV peak can assist with understanding the interference from the contact region into the CdTe device.

10:30 AM B3.5
Cu KEDGE EXAFS IN CdTe BEFORE AND AFTER TREATMENT WITH CHAs. Xiuzhen Liu and Alvin D. Carman, Department of Chemistry and Astronomy, University of Toledo, OH; Nadin Leyronovska, Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago, IL; Jeff Terry, Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago, IL, and Department of Physics, University of Notre Dame, Notre Dame, IN.

High performance CdS/CdTe thin film solar cells are usually completed with a Cu back contact. The copper appears to be critical for achieving heavy p-type doping of the CdTe at the contact. However, copper is also a fast diffusor and is suspected of playing a role in cell performance deterioration under certain conditions. Thus, we have used the fine structure in the Cu K-edge x-ray absorption spectrum to help elucidate the role of Cu in polycrystalline, thin-film CdTe solar cells. In particular, we have studied how the typical CdCl2 vapor treatment in an oxygen ambient – a critical step needed to improve the performance of CdTe thin film solar cells – alters the local environment of the Cu in CdTe. Samples were prepared through the same process as completed cells except without the SnO2 and CdS layers. The 325 micron CdTe film of each sample was sputtered at ~250°C onto either fritted silicon or Kapton substrates. Data were obtained at the MR-CAT beam-line at the Advanced Photon Source (Argonne IL). The Cu K-edge x-ray absorption spectra were collected in a fluorescence geometry with a 18-element Ge detector. We find the Cu absorption spectra to be similar to that of Cu2Te in the as-deposited CdTe film but with substantial changes after the vapor CdCl2 treatment. These changes are interpreted in terms of changes in the environment of the copper in the chloride treatment. This work was supported by NREL and the DOE.

10:45 AM B3.6
AFFECTING CdTe/CdS SOLAR CELL PERFORMANCE VIA GRAIN BOUNDARY AND SURFACE CHEMISTRY. Iris Vasily-Fisher, Amit Skt, David Calen, Weizmann Institute of Science, Rehovot, ISRAEL.

Chemical changes of external and internal surfaces (grain boundaries, GBs) can affect the electrical properties of grains, and thus affect the photovoltaic (PV) performance of thin film CdTe/CdS solar cells. As grain size decreases, the density of surface electronic states approaches that of the bulk. Thus, changes in the chemical and electronic properties of these surfaces can significantly change the materials carrier concentration and mobility. We used chemical treatments, such as surface etching, oxidation and the adsorption of series of molecules with different molecular moment, and different redox potentials, to study this. FTIR spectroscopy indicates adsorption of molecules with dicarboxylic acid and disulfide binding groups to CdTe and CdS. Surface photovoltage spectroscopy (SPS) indicates that adsorption of certain molecules changes the occupation of CdS surface states, due to changes in oxidation state, similarly to surface etch/ oxidation. Surface etch and oxidation also changed the surface band-bending in CdTe, and can therefore affect grain carrier concentration, and inter-grain carrier transport. SPS of cells show that adsorption of certain organic molecules changes the onset of cell photo-response, suggesting that chemical surface treatments can control PV cell performance. L-V measurements confirmed this: adsorption of molecules on CdTe before the back contact formation, changed Voc and Jsc compared to cells without molecules, indicating the molecules affect the CdTe / back contact interface. Molecule adsorption after contact formation, via the photo-CdTe, mainly changed Voc and Jsc, indicating the molecules affect the junction. This is explained by organic molecules affecting the cells PV behavior by their adsorption onto GBs close to, but not at the junction, i.e., action at a distance. These results thus indicate the potential of molecular treatments on ready-made polycrystalline devices. We thank USDOE/NREL for partial support.

11:00 AM B3.7
MAGNETIC SPATTERING FOR LOW-TEMPERATURE DEPOSITION OF CdTe-BASED PV. Alan D. Carman, Univ. of Toledo, Dept. of Physics and Astronomy, Toledo, OH.

Thin-film growth processes often rely on thermal energy to activate the surface mobility needed for developing good film properties. We
have used instead magnetron sputtering to provide additional energy to the incident species to control the film characteristics. RF magnetron sputtering work particularly with the heterojunction GdSi/GdTe thin-film solar cell in which both components are lightly doped with native defects. Recently we have used magnetron sputtering also to obtain 5-8/μm/° Al2O3/TiO2 films. Using this TCO we have incorporated cells with the following structure: sodiumaurateglass/ZnO/Al2O3/GdSi/GdTe/metal which had an NREL-confirmed 1.4% efficiency at AM1.5. (Voc = 847 mV, Jsc = 23 mAnm2, FF = 73%). We believe that keys to using the ZnO as the TCO and their cells hold all processing steps well below 400°C. First results also will be given for this cell structure on polymer superstructures. Additionally we will describe the use of reactive sputtering to deposit p-type ZnTe:N as part of the CdTe back contact and initial steps toward building a recombination junction based on ZnTe:N/ZnO:Al for possible use in tandem devices. Work supported in part by NREL.

11:30 AM B3.8 IMPROVEMENT OF CdS WINDOW LAYER FOR LARGE OPEN CIRCUIT VOLTAGES OF LOW ENVIRONMENTAL LOAD GdSi/GdTe SOLAR CELLS. T. Hayama, H. Odos, K. Nakamura, T. Fujihara, K. Shimizu, H. Okomato, Osaka University, Dept. of Physics, Graduate School of Engineering Science, Toyonaka, JAPAN.

Energy conversion efficiency of 16.6% has been realized in R&D level with the use of CdS/GdTe thin-film solar cells [1]. However, from a viewpoint of "environmental load" related to the Cd compounds, the thickness of the photovoltaic layer, which is usually 5-10 μm, must be reduced. We have proposed low "environmental load" CdS/GdTe thin-film solar cells with a photovoltaic thin-film layer thickness of < 3 μm, and already achieved a high conversion efficiency over 15% [2]. For the further improvement of the photovoltaic performance, control of CdS nanostructures including crystallinity of the CdS layer and interdiffusion at CdS/GdTe interface, one of the key issues because it has a large influence on growth of CdTe as well as interdiffusion at GdSi/GdTe interface. In this article, we show the results on the structural studies on CdS as a function of the deposition temperature in conjunction with the structural properties of CdTe deposited on the GdSi layers. Also shown are the electrical properties and photovoltaic performances of the CdS/GdTe solar cells made with the GdSi layers with different deposition temperatures. Fabrication methods of the CdS/GdTe solar cells including MOVCD for CdS deposition were almost identical with those in our previous reports [2, 3]. The preferential orientation of CdS layers as a function of the CdS deposition temperature were compared to the photovoltaic performance of CdS/GdTe solar cells with the GdSi layer. The solar cells on the GdSi layer with a well preferential orientation trend to obtain large Voc which would be related to change in the ionized charge distribution evaluated by CV measurements. Finally, we have achieved a conversion efficiency of 14.1% mainly due to an enhancement of Voc [1]. W. Wu et al., Abstracts of 29th IEEE PVSC (2002). [2] K. Nakamura et al., Jpn. J. Appl. Phys., 41 (2002) 4474. [3] K. Nakamura et al., Solar Energy Mater. & Solar Cells 75 (2003) 185.

11:45 AM B3.9 14% CdS/GdTe THIN FILM CELL WITH ZnO:Al TCO. Ashleah Gupta in collaboration with D. Compere, Department of Physics and Astronomy, University of Toledo, Toledo, OH.

We have used ZnO successfully for the first time as a window layer for high efficiency CdS/GdTe thin-film solar cells. A CdS/GdTe/Thin film ZnO front contact was deposited on sodiumaurate glass by RF sputtering from a ZnO-Al2O3 target. The ZnO:Al films have ~55% average transmission in the visible spectrum with <3 μm square sheet resistance. The GdSi and CdTe thin films were also deposited by RF sputtering and devices were completed with vapor CdCl4 treatment and evaporated Cu/Au back contact. No wet chemical processing was used during the fabrication. The highest processing temperature was 387°C, reached during the vapor CdCl4 treatment. These cells were tested at NREL, and an efficiency of 14% was confirmed, which is a record for a cell with ZnO:Al thin-film solar cell. The ZnO:Al-based cell had JSC of 36.6 mΑ/m2 compared to 20.7 mΑ/m2 for our recent NREL tested 12% cell on a commercial sodiumaurate/Al2O3 substrate. Other parameters of the 14% ZnO-based cell were FF = 73.2% and VOC = 814 mV. The improved performance is even more interesting in the current density increase due to the better transmission of the glass and the TCO. The devices on both kinds of TCO are being tested to determine their stability under simulated 1 sun illumination. Comparative stability data will be presented. This work was supported by NREL.

SESSION B4: CIS G SILICON INTERFACE CHARACTERIZATION

Chair: Wei Rui

Wednesday Afternoon, April 23, 2013
Salon 10/11 (Marriott)

1:30 PM B4.1 SOFT X-RAY SPECTROSCOPY OF BURIED INTERFACES IN CuIn(Se,S)2 BASED THIN FILM SOLAR CELLS: ALIGNMENT, INTERMIXING, AND HUMIDITY EFFECTS. C. Haske, L. Weinhardt, U. Groh, M. Merkel, E. Umbach, Experimentelle Physik II, Universitat Wurzburg, Wurzburg, GERMANY.

The main goal of this presentation is to demonstrate the unique capabilities of uranium and soft X-ray spectroscopies for the characterization of interfacial properties of CIS/GGS and p/n heterojunctions. Special focus will be on the influence of humidity on the electronic and chemical properties of the relevant surfaces and interfaces. The experimental necessities for such studies will be briefly reviewed, and an outlook on future technical and spectroscopic developments will be given.

2:00 PM B4.2 MICROSTRUCTURAL AND MICROCHEMICAL ANALYSIS OF CuIn(Ga)Se2/CIS HETEROFUCTIONS. Chan-Ming Lii, K. Robertson, A. Rockett, Univ. of Illinois, Dept. of Materials Science and Engineering, Urbana, IL.

The microstructure and microchemistry of Cu(In,Ga)Se2 (CIGS) layers have been analyzed by using transmission electron microscopy. Specimens were obtained from a number of groups producing high-performance solar cells from these materials. Both plan-view and cross-sectional TEM samples were prepared from these materials by mechanical grinding and ion milling. Energy dispersive x-ray spectroscopy was used to study the chemical composition of grains, grain boundaries, and CIGS/CIS heterojunctions. In addition, point defect superstructure ordering as in CuAu compounds, dislocations, stacking faults, and twins were examined and the results were correlated with the optical properties and in particular the phase transition and microstructure lifetime of the materials. In addition, correlations were drawn with device performances. Preliminary results suggest that minority carrier properties are directly correlated with disorder densities. Both Na and O have been found in grain boundaries along with changes in the ratio of Na to O for the matrix constituents. A detailed analysis of these observations is presented along with an analysis of the implications for optical, electronic, and solar cell property of the materials.

2:15 PM B4.3 CHEMICAL APPROACH TO MANEUVER THE DEFECT DENSITY IN CIS FILMS. S. Menezes, Y. Li, S.J. Menezes, InterPhases Research, Thousand Oaks, CA.

CIS layers are more sensitive to the deposition process and their environment than the CIS film. The higher sensitivity to the incidence is related to their Ga cofactor layer and is responsible for the stability of the CIS device performance. This paper investigates chemical methods to manipulate the defects in CIS films. The CIS films were characterized with photoelectrochemical and spectral measurements techniques. The effects of environment on specific chemical solutions and time, were monitored with photocurrent spectral response of the CIS films in an electrolyte medium. Based on the photocurrent output, specific surface treatment steps were devised for processing the CIS films. The surface modified films were fabricated into solar-grade devices, and device performance was assessed with certified reference untreated CIS films. The results reveal that the CIS films respond easily to a number of external stimuli with either positive or negative changes in the electrophysical properties. Strong time dependence of the photocurrent suggests a unique lifetime of the photoexcited carriers which makes the CIS film. The results provide new insights into the effects of stoichiometry, deposition method and oxidation effect on the defect chemistry of the CIS film. They are provided for tailoring surface treatments to engineer the defects in the CIS films for large-scale deposition of CIS films, without the need for the toxic etchants or buffer layers and the environmental hazards associated with these steps.

High efficiency thin film CuInSe₂ (CuInS₂-based) solar cells have been demonstrated in small [18.8%] and large area devices [12%]. Perhaps the most critical step in fabricating high efficiency devices is the formation of the metallurgical and related electrical junctions. The best results have been achieved by depositing a thin CdS layer on a CIGS absorber layer by Chemical Bath Deposition (CBD). Several explanations have been proposed to account for the positive role of CBD CdS in producing high efficiency cells. One hypothesis suggests that interdiffusion/reaction occurs between the metallurgical junction and chemically modifies the new surface region and shifts the electrical junction into the CdS. In this model, Cd diffuses into CIGS layers to form a high concentration of Cd on Cu site donor defects, which induces a type conversion [p to n] At sufficiently high substitutional Cd concentrations [e.g., CdSe, or CdIn(x)S(1-x)], which produces a graded interface structure [1]. The interdiffusion/chemical reaction proposed in this hypothesis appears to play a crucial role in determining the device performance.

Furthermore, the interplay between the In-rich compounds [e.g., CuInS₂] and CdS at this interface is suggested to be important to producing high efficiency cells by altering the junction between the CuInSe₂ and CuInS₂ phases. In support of this hypothesis, a recent study has demonstrated high efficiency CuInSe₂ cells using only a Cd electrode treatment [i.e., without growth of a CdS buffer layer] [2]. Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS) have provided evidence for Cd diffusion into the CIGS lattice. In this work CuK-edge XAFS, including XANES and EXAFS, was used to study the Cd atomic local structure on bulk CuInSe₂, CuInSe₅, and thin film Cu(In,Ga)Se₂ samples treated with an aqueous electrolyte solution containing Cd ions. The calculated K-edge EXAFS were used as structure references in the data analysis. The EXAFS results have shown that the nearest Cd atom neighbors in bulk CdSe and CdInSe₅ are almost identical. The Cd partial neighbor treatment calculated CuInSe₂ and CuInSe₅ samples, however, have very different local arrangements. A tetrahedral local structure with four Se nearest neighbors could not explain the data. The EXAFS results suggest that the Cd replacement of Cu or In atoms at tetrahedral sites is not the only mechanism of altering the new surface region with a Cd partial electron treatment. 1. K. Ramasubramanian, W. Wiesner, S. Asher, D. Niles, R.N. Bhatkar, K.R. Keneely, M.A. Contreras, and R. Nouri, Proc. 2nd WCPEC, Vienna, pp. 477-481 (1998). 2. J. Kessler, K.O. Véithans, M. Rudzik, R. Luscher, and H.W. Schock, Proc. 6th Int. PVSEC, New Delhi, p. 1005 (1994).

3:30 PM B4.5
ANALYSIS OF ZINC COMPOUND BUFFER LAYERS IN Cu(In,Ga)(S,Se)₂ THIN FILM SOLAR CELLS BY SYNCHROTRON-BASED SOFT X-RAY SPECTROSCOPY. L. Lauerhammer, M. Bür, A. Emmoni, U. Fiederle, Ch-H. Fischer, A. Grimm, T. Kotschnig, M. Ch. Lux-Steiner, J. Reichardt, B.R. Sankpal, S. Seibert, S. Schkol Pahl-Thelin-Institut, Berlin. Objective Zinc-containing buffer layers on Cu(In,Ga)(S,Se)₂ films for use as intermediate layers have been extensively studied over the last few years. In this contribution, we present a detailed analysis of these buffer layers by synchrotron-based soft X-ray spectroscopy. The experimental work is based on synchrotron radiation in the energy range of 10-20 keV. The measurements were performed at beamline BM 14 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were investigated using X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), and X-ray photoelectron spectroscopy (XPS). The XAS measurements were performed using a synchrotron radiation source with an energy resolution of 100 eV. The XES measurements were performed using a synchrotron radiation source with an energy resolution of 10 eV. The XPS measurements were performed using a synchrotron radiation source with an energy resolution of 1 eV. The results show that the Zn-containing buffer layers are characterized by a high content of zinc in the layers. The zinc content is highest at the interface between the buffer layer and the absorber layer. In addition, the XPS measurements show that the buffer layers are characterized by a high content of sulfur in the layers. The sulfur content is highest at the interface between the buffer layer and the absorber layer. In summary, the XAS, XES, and XPS measurements show that the Zn-containing buffer layers are characterized by a high content of zinc and sulfur in the layers. The results are important for the development of high efficiency thin film solar cells.
B5.3 HIGH RESOLUTION CHARACTERIZATION OF A SINGLE GRAIN BOUNDARY AND THE VARIOUS LAYERS IN CdTe/CdS SOLAR CELLS. Iris Vassy-Fisher, Sidney R. Cohen, David Cohen, Weizmann Institute of Science, Rehovot, ISRAEL.

We show that AFM-based methods can measure directly a single grain boundary (GB) and a single grain surface in solar cell-quality CdTe, deposited by closed-space vapor transport. Scanning capacitance microscopy (SCM) is shown to be a helpful tool in the study of point defects and electronic properties of these materials due to their strong topographical variations. SCM shows a barrier for hole transport across CdTe grain boundaries, with some variation in barrier height between boundaries. This conclusion was supported by the much more topography-sensitive scanning Kelvin Probe microscopy (SKPM). SCM was then used to follow effects of chemical changes of grain boundaries and surfaces on the electrical properties of grains with thin CdS films that do not receive CdCl2 treatment (annealing). It was found that CdS/CdTe solar cells with a difference in SCM signal between grain surfaces and GBs, possibly indicative of the low carrier concentration in the grain bulk. SCM (with SKPM) was also employed for high-resolution studies of the CdS/CdTe solar cell cross-section, to determine the location of internal junctions and to compare the electronic properties of the different layers. CdS and the high-resistance (HR)-CdS layer were found to be similar electronically. This explains the role of the HR-CdS as a supplement for the very thin CdS, without reducing the blue response of the cell. No buried homojunction in the CdTe is seen, contrary to what has been suggested in some recently published models. We thank USDOE/NREL for partial support, and Veeco-Orco for help in SCM, and I. Bar-Joseph (WIS) for use of his SCM.

B5.4 COMPOUND SEMICONDUCTORS AS THE MATERIALS OF MULTIBAND PHOTOVOLTAIC CELLS. Lianghuan Feng, Yaping Cui, Jingqum Zhang, Lili Wu, Wei Li, Wei Cai, Jianguo Zheng, Bing Li, Zhi Lei, Qiang Yan, Dept of Materials Science, Shenzhen University, Chengdu, CHINA.

Recently, A. Laguie et al and M. Green have proposed and discussed the concept of multiple-band photovoltaic cells (MBPV). They have shown efficiency advantages if a third band is included into the injection process, and mentioned two paths to establish the third band: impurity band and multiple quantum wells. In the paper, we have studied the applications of some compound semiconductors for MBPV, considering the direct band gap, with different widths of the semiconductors. For the impurity band MBPV, the minimal optical losses of some selected compound semiconductors of wide band gap, such as ZnTe, CdS, ZnSe, CdSe, Hg1-xCdxTe, Zn1-xMnxO2, ZnO and In2O3, are calculated in the conditions of A0 and AM1 when the impurity band is at an appropriate deepness inside the band gap. The optical loss decreases with an increase of gap wideness, for example, it is 32.8% for CdS and 21.6% for In2O3, which are much lower than 52% for standard polycrystalline silicon solar cells. The bandgaps of electron transition through the impurity band and carriers transportation in the third band have been investigated, and the minimal state density in impurity band and concentration of doping atoms have been obtained and discussed. In experiment, the doped ZnTe and ZnSe polycrystalline films have been deposited by coevaporation. For multiple quantum well MBPV, CdTe/ZnTe, ZnSe/CdTe and ZnS/CdS multiple quantum wells are interesting due to their small vertical or conduction band gap, and 0.05 eV, 0.11 eV or 0.0 eV, respectively, as well as the appropriate quantum well deepness of 0.77 eV, 0.86 eV and 1.28 eV, respectively. The excitation process of electrons and transportation mechanism of carriers in the multiple quantum wells have been analyzed. From the physics of MBPV, the results have been discussed.

B5.5 PHOTOLUMINESCENCE EXCITATION STUDIES OF CuGaSe2. I.E. Beckers, S. Sieberstetti, and M. Ch. Lux-Steiner, Hahn-Meitner-Institut, Berlin, GERMANY; M. Wagner, Dept. of Physics and Measurement Technology, Linkoping University, Linkoping, SWEDEN; R. Heitz and A. Hoffmann, Technische Universitat Berlin, GERMANY.

Photoluminescence excitation (PLE) spectroscopy at liquid-nitrogen temperature is used to study CuGaSe2 epitaxial films grown by metal organic chemical vapor deposition (MOVCD). The growth conditions are varied to obtain compositions with [Cu]/[Ga] = 0.8 - 1.2. The PL excitation is monitored during two decades at room temperature and their phonon replicas show a peak at 1.71 eV for Cu-rich films, which can be correlated to the excitation absorption. This peak vanishes for films grown by Ga-excess. For increasing Ga-excess an increasing overlap can be observed of the excitation and the peak energy in photoluminescence (PL) spectra. This is an indication for the occurrence of band tail states. With increasing laser excitation power this overlap decreases. In previous PL studies we have interpreted the broad emissions in Cu-rich material by potential fluctuations [1]. It has been noted that the concentration is lower in Ga-rich films due to a higher degree in compensation [2]. In this study, comparative results of PLE, PL and Hall measurements give an unequivocal evidence for the occurrence of potential fluctuations in Cu-rich CuGaSe2, this disagree for material with a lower degree of compensation (Ga-rich CuGaSe2) and high laser excitation power. [1] A. Beckers, S. Sieberstetti, J. Albert, and M. Ch. Lux-Steiner, J. Appl. Phys., 89 (2001) 4581. [2] S. Sieberstetti, A. Beckers, M. Wagner, T. Karg, U. Kärger, U. Keimer, M. Ch. Lux-Steiner, W. Harneit, S. Brebels, J. Albert, and M. Ch. Lux-Steiner, Solar Energy Mater. Sol. Cells, 67 (2001) 129.

B5.6 INFLUENCE OF NANOPORE TiO2 WITH CuInS2 USING ATOMIC LAYER DEPOSITION. TOWARDS A 3D SOLAR CELL. Marin Gnanou, Laboratory for Inorganic Chemistry, Faculty of Applied Sciences, Delft University of Technology, Delft, THE NETHERLANDS; Catelijne Grasso, Electronics and Information Systems, Ghent University, Gent, BELGIUM; Frank Lennemann, ECN Energy, Energy Research Center of The Netherlands, Petten, THE NETHERLANDS; Albert Goossens and Joep Schoonman, Laboratory for Inorganic Chemistry, Faculty of Applied Sciences, Delft University of Technology, Delft, THE NETHERLANDS.

This paper deals with the influence of nanoporous TiO2 with CuInS2 using Atomic Layer Deposition (ALD). This is a nanocomposite, in which a wide bandgap n-type semiconducting oxide and n-type visible light sensitive CuInS2 are combined on a nanometer scale, known as the Extremely Thin Absorber (ETA) solar cell concept, which may open a new horizon in the manufacture of future photovoltaic devices. First a dense film of TiO2 (~100 nm) is deposited onto TCO-glass (SnO2:F). On top of this, a nanoporous TiO2 film is applied with primary particles between 10 and 50 nm in diameter. Next these substrates are infiltrated with CuInS2 using ALD. The process conditions are: 2·10-3 Torr reactor pressure, temperature between 350 and 500°C, and CuCl, InCl3, and H2S as precursors. The influence of process conditions on the structure and the electrical properties of CuInS2 is examined. The growth temperature, the purge time, and the vapor pressure of the precursors are found to be the decisive parameters. Moreover, a thermal anneal in an H2S (500°C, 1 bar) and air (200°C, 1 bar) ambient after deposition appears to be vital to the quality of the nanostructured heterojunction. The thin films are investigated with X-ray diffraction, Raman spectroscopy, and photoluminescence spectroscopy. The photovoltaic response is also measured and indeed a photocurrent is generated along with a photovoltage. The fill factor, however, is rather poor and also the open-circuit voltage, Voc, and short-circuit photocurrent, isc, are moderate. To improve the performance a buffer film between the TiO2 and CuInS2 is necessary. There are several reasons for this improvement. The conduction bands of TiO2 and CuInS2 leads to significant energy loss. Also the band gap of current leads to a quantum efficiency difference out of CuInS2 into the TiO2 is also a problem as the deposition temperature must be above 350°C. A well-chosen buffer film can deal with these issues. Future investigations focus on new materials and new sources of production of CuInS2 and CdS, which are both deposited by ALD. A tunnel barrier can also improve the performance of the device. When a 1-2 nm thick Al2O3 films is applied buffer the Voc and the fill factor increases significantly. Future investigations will focus on the use of different ALD materials for CuInS2 and CdS in order to allow stepwise improvement of the energy conversion efficiency.

B5.7 PHOTOLUMINESCENCE FATIGUE IN CdTe PHOTOVOLTAICS. Diana Skvadija, C. Verella and V.G. Karpov, University of Toledo, Toledo, OH.

We found that in a polycrystalline CdTe/CdS solar cell, illuminated with a laser beam of constant power, junction photoluminescence (PL) intensity gradually decreased over time. This phenomenon is analogous to the PL fatigue in chlorophyllide glasses. In our work it was studied as a function of time at different laser beam intensities and temperatures. Both contact-free and metalized regions were investigated. We were able to discriminate between two independent mechanisms: short-time PL decrease due to local laser heating and more gradual change related to the material degradation (PL fatigue). PL fatigue was more profound at higher temperatures and higher laser beam powers. Its observed value in some cases was as large as 80% after 100 hours. However, at low temperatures and low beam powers it saturated rather quickly not exceeding 10 percent of the initial PL intensity. PL fatigue showed substantial variations between different spots on the sample. We attribute the observed phenomenon to defect creation by the light-generated electrons and holes. Defect concentration increases in the course of irradiation thereby providing additional non-radiative recombination channels for electrons and
holes. This negative feedback makes the defect-generation rate slowing down over time, so that the PL intensity saturates. We have worked out a simple model that may well fit our data. This work was supported by NREL and NSF-REU.

B5.8 ELECTRO-MODULATED PHOTOLUMINESCENCE IN CdS/CdTe SOLAR CELLS. A. Vasko and A. D. Compan, University of Toledo, Department of Physics and Astronomy, Toledo, OH.

We have performed electro-modulated photoluminescence (EMP) on polycrystalline thin-film CdS/CdTe solar cells, excited with HeNe and Ar lasers. The cells were fabricated from small-grain films produced by growth of CdTe by chemical transport (CdTe thickness is 0.15 μm, CdTe thickness = 2.3 μm) and larger-grain films from vapor-transport deposition with somewhat thicker layers. The effects of light soak on the EMP from these cells has also been studied. A typical peak-to-peak modulation voltage was 150 mV. EMP peaks as a function of hold time for different excitation wavelengths were similar to the first derivative of PL intensities as a function of offset bias, as expected. The 1.95 eV light excites EMP from the CdTe bandgap, while argon laser-excited EMP originates from a CdS defect band. Our previous studies on PL at various bias offsets [2] suggested that only the PL spectra height, not its shape, changed as the bias offset changed. This might suggest that the shape of the EMP spectrum should be identical to that of unmodulated PL. However, subtle differences have been noticed. There is a slight shift in the peak position, and there is a peak at about 1.65 eV in the 1.95 eV-excitation PL which does not respond to the modulation. This work has been supported by NREL.

B5.9 TEMPERATURE-DEPENDENT PHOTOLUMINESCENCE FROM CdTe/CdS SOLAR CELLS. K. J. Price1, L. Gorrell, A. Vasko, A. D. Compan, University of Toledo, Department of Physics and Astronomy, Toledo, OH. 1Summer Faculty Scholar from Morehead State University, Morehead, KY.

Photoluminescence (PL) from polycrystalline CdTe/CdS solar cells was studied over the temperature range 50 C to 50 C. We are able to observe above-background PL at forward current densities as low as 3 mA/cm2, allowing us to explore the behavior of current-voltage regimes within the normal operating parameters of the device. The EL spectrum is very similar to the photoluminescence (PL) spectrum, and is independent of applied voltage. We show that the EL most likely originates from injected electron-hole recombination at the CdTe/CdS junction. The total EL intensity is found to vary as a power-law function of current, EL ∝ Iγ, where I is the forward current density and γ is near 2. The exact value of γ varies with temperature and from sample to sample. The relationship of EL spectra before and after the presented. This work supported in part by a Faculty Summer Research Grant from Morehead State University, the NSF-REU program, and NREL.


A technique for spatially resolved optical characterization of CdS/CdTe thin film solar cells has been developed using electroluminescence (EL). In EL, excess minority carriers are injected via forward biasing. Light produced in radiative recombination is collected with a CCD camera. Because EL intensity depends upon radiative and non-radiative recombination lifetimes, it provides insight into material and structural resolution is a benefit of EL. It provides insight into the non-uniformities of polycrystalline CdTe. At high magnification the resolution is diffusion limited, but coarser measurements of several millimeters may also be made. Non-uniformities in emission have been observed throughout this range. Further benefits of EL as a characterization technique are as follows: EL probes the region of most interest, namely the CdTe near the main junction. Also, it is observable at room temperature and dose acquisition is fast. Finally, EL is observable at very low carrier injection rates, comparable to short circuit current. (Though more structure is often revealed at higher injection rates.) This low injection limit can be a negative. This fact, along with the aforementioned ease of observation, means that EL could possibly be used for quality control and in situ testing of modules. Data gathered from CdS/CdTe cells from various institutions deposited using different methods such as close spaced sublimation, vapor transport, and sputtering will be presented. In addition to changes in material, changes in processing was observed to affect EL emission. Furthermore, overall EL emission decreased noticeably with stress at various biases and elevated temperature, with non-uniformity increasing. Changes in EL became apparent before changes in parameters acquired with standard current-voltage measurements, suggesting that this technique can be used as an early indicator for degrading cells.

B5.11 CHARACTERIZATION OF DEEP DEFECTS IN CdS/CdTe THIN FILM SOLAR CELLS USING DEEP LEVEL TRANSIENT SPECTROSCOPY. P. V. Jong Versluis, Paul Clavins, Ghost University, Department of Solid State Sciences, Gent, BELGIUM.

The presence of deep defects levels in thin film solar cells can sharply affect the characteristics of the photocathodic energy conversion. Therefore, knowledge of the origin and nature of these defects is desirable. Deep level transient spectroscopy (DLTS) was performed on a series of CdS/CdTe thin film solar cells. Temperature scans between 5 and 350K revealed several small and midgap majority traps. These midgap traps were also investigated using isothermal DLTS (region 250 to 330K) where the temperature is kept constant and the rate window is varied. This way the midgap traps can be characterized completely. Optical DLTS has revealed the presence of minority carrier traps. Laser diodes with wavelengths of 850 and 635 nm were used for the optical excitation. These wavelengths were particularly chosen for their specific excitation region in the CdTe: 850nm excites the complete layer (sub-bandgap wavelength), whereas 635nm only excites the CdS/CdTe interface because of the high absorption. A complete characterization of the defect levels was made. The effect of these defects on the solar cell characteristics is discussed, and their origin and nature are assigned. The results are compared with literature data.


Oxidative etches, and specially those based on bromine water mixtures, enable preparation of planar, smooth, specular Cu(In,Ga)Se2 surfaces, whose chemical properties are well defined and have been studied previously. This etch, that leaves secondary phases on the surface can be followed by a second etch to prepare a surface devoid of elemental Se (using CN-) or of oxides (HCl, NIES), by both. First, we will present an overview the Cu(In,Ga)Se2/Se surface composition after such etches, and where it was possible (e.g., with Br), we will present a model of the etch mechanisms and kinetic. We will also compare those surface composition to the bulk ones and to those observed in vacuum just after film growth of coevaporated surfaces. Those well defined chemical etching procedures can then be used to prepare interfaces with the buffer layer that can also be investigated chemically, using high resolution XPS and angle resolved XPS. Finally, complete devices can be elaborated and characterized in terms of photovoltaic performance and in terms of electrically active defects (by admittance spectroscopy). Correlations between electrical and chemical properties at well defined CdS/CdS interfaces will be presented and discussed.

B5.13 TRANSFERRED TO B5.3

B5.14 THE LINEAR COMBINATORIAL STUDY ON CdO-SnO2 TERNARY COMPOUNDS. Xiaoshui Li, Tim Gesser, and Timothy Coutts, National Renewable Energy Laboratory, Golden, CO.

The linear combinatorial synthesis using low pressure metal organic chemical vapor deposition (CVD) has been used to prepare oxide oxide (CdO)x-tin oxide (SnO2) ternary compound thin films. The difference in decomposition temperature of Cd and Sn precursors was used to achieve the film composition variation. Because the Cd precursor has lower decomposition temperature, thus at leading end of the substrate, the films were Cd-rich. The cubic CdO structure was observed by XRD, and the SnO2 phase from XRD spectra along the reaction chamber, the amount of Cd precursor depleted. As a result, the Cd to Sn ratio in the films decreases. The crystal structure was mixed with cubic CdO and spinel CdSnO4. When Cd to Sn ratio close to 2/1, the films were dominated by cubic spinel CdSnO4. As Sn concentrations continue to increase, the films become amorphous and stayed as amorphous structure for a very wide composition range. Finally, the tetragonal SnO2 structure emerged and became dominate. The most interesting result from this combinatorial study is that the highest Hall mobility [50 to 60
\[ \text{cm}^{-2}\text{V}^{-1}\text{s}^{-1} \] have been achieved for this compound system were
reached with amorphous structure with Cd to Sn ratio of 2/1 to 1/1. Beyond this Cd to Sn ratio, the Hall mobility was low. The
carrier concentration of the films varied from the high \(10^{17} \text{ cm}^{-3}\) to the middle of \(10^{16} \text{ cm}^{-3}\). The optical band gap varied from 2.75 eV to 3.65 eV due to the changes of composition and carrier concentration.

**B.5.15** ALTERNATE CONFIGURATION AND METHOD FOR FABRICATING A FLEXIBLE CIS PV CELL. S. Makita, Y. Li, S. S. Natour, National Renewable Energy Laboratories, Golden, CO.

Flexible PV cells offer distinct advantages over conventional PV modules for space applications. Inexpensive roll-to-roll electrochemical processing could extend their applications for high volume terrestrial use. Adapting the CIS cell to roll-to-roll processing is complicated by specific material and processing requirements, which rule out high volume PV manufacturing. This paper presents an alternate PV cell configuration based on the n-type indium selenide and an electrochemical fabrication method that could potentially simplify the process steps, reduce the number of cell components and hence the costs. It investigates the effects of different substrates and alternate deposition sequences, using photolithography and surface analytical methods. Voltammetric techniques monitor the CIS electrodeposition process parameters for the film formation mechanism and its composition. X-ray diffraction and composition analysis provide insights into the CIS film morphology, growth mechanism and the role of the substrate. The results indicate a new route for controlling the grain growth on CIS films. They lead to a simple four-step method for roll-to-roll PV cell fabrication.

**B.5.10** TRANSPARENT CONDUCTING ZINC OXIDE FILMS PREPARED BY BIPOLAR PULSED BIASING TECHNIQUE. H. Y. Lee, S. P. Lau, Y. G. Wang, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

We report the deposition of highly conductive and transparent zinc oxide (ZnO) films by filtered cathodic vacuum arc in conjunction with bipolar pulsed biasing on glass and polyethylene naphthalate (PEN) substrates at temperatures as low as 80°C. A combination of 2×10⁷ V/cm and 500 W of the ratio of positive pulse duration to negative pulse duration at 90 percent, and these films exhibit transmittance above 80 percent and resistance as low as 5 × 10⁵ ohm cm which is comparable with good quality indium tin oxide (ITO) films. The high resistivity of the undoped films is attributed to zinc interstitial. ZnO doped with aluminum was also prepared by Al doped target, the conductivity of the ZnO:Al films increase further and also possess high transparency.

**B.5.17** DEFECT ESTIMATION OF CuGaSe2 ON PHOTOELECTRON SPECTROSCOPY AS THE END MATERIAL OF CuInGaSe2 alloy system is worthy to be investigated for advancement of the high-voltage solar cell performance. CuGaSe2 has been deposited by metal organic chemical vapor deposition (MOCVD) and characterized so far, but the identification of defect origins is still uncertain. In this work, samples were prepared by molecular beam epitaxy (MBE) to avoid effects of grain boundaries and impurities inherent to polycrystalline material. The PL spectrum was adopted to characterize because of its high sensitivity to a small amount of intrinsic point defects. Identification of the defect species was tried with the aid of PL spectrum transformation caused by annealing in vacuum. The high peak of CuGaSe2 films was grown on [111]-oriented GaAs substrates under Cu excess conditions to obtain nearly stoichiometric composition. [Cu]/[Ga] composition ratio of the as-grown samples measured by electron probe microanalysis was 0.06. The excitation voltage was from 1.1 to 1.4 due to existence of a CuSe surface phase. The surface phase was removed by etching in a potassium cyanide (KCN) aqueous solution. After KCN etching, the film compositions were confirmed by EPMA to be stoichiometric CuGaSe2. [Cu]/[Ga] ratio was close to unity and samples were measured at the temperature range from 30°C to 450°C in various atmospheres, argon, oxygen and with the intention of driving defects. Annealing of the samples changed greatly the PL spectra indicating that it had caused the defects that are also present in CuGaSe2 and/or to extinguish. Corroborated consideration on correlation between annealing atmosphere and PL spectra led a conclusion that each characteristic peak of the PL spectra can be attributed to a specific defect as Cu vacancy, Se vacancy and their complexes as well.

**B.5.10** CHARACTERIZATION OF TRANSPARENT AND CONDUCTIVE ZnO:Ga THIN FILMS PRODUCED BY HF SPUTTERING AT ROOM TEMPERATURE. E. Fontecchio, V. Ascione, A. Marques, H. Iguine, I. Ferreira, R. Martins, Department of Materials Science/CENIMAT, Faculty of Sciences and Technology, New University of Lisbon and CEMOP-UNINOVA, Caparica, PORTUGAL.

Transparent conducting oxide (TCO) with optical transmission more than 80% in the visible region and resistivity less than \(10^{-4} \text{ Ω cm}\) have been widely used as electrodes for optoelectronic devices. Most of previous research on TCOs has been focused on ITO and TEO. However, TCO films based on zinc oxide are taking an important role because of the advantages of low cost, resource availability (about a factor of 1000 more abundant than In), non-toxicity and high thermal/chemical stability. Al, In, and Ga have been reported as an effective dopant for zinc oxide based films. Most of the works related to zinc oxide use Al as dopant. Nevertheless, Al presents a very high reactivity leading to oxidation during the growth of the film, which may become a problem. Ga is less reactive and more resistant to oxidation compared to Al. On the other hand, the excellent bond lengths of Ga and ZnO are estimated to be 1.92 and 1.97 Å, respectively. The slightly smaller bond length of Ga-O than that of Zn-O offers an advantage since it prevents the polymorphic transformation of the ZnO lattice even in the case of high Ga concentrations. In this work Ga-doped polycrystalline zinc oxide (GZO) thin films have been deposited at high growth rates by rf magnetron sputtering. The dependence of electrical, optical and morphological properties on the rf power density were investigated. The lowest resistivity \(1.9 \times 10^{-4} \text{ Ω cm}\) was obtained for an rf power density of 9 W/cm² at RF. The films are polycrystalline with a hexagonal structure and a strong [010] type orientation (002) reflections present in all the visible spectra of about 85%. The low resistivity, accompanied with a high growth rate deposited at RF, enables the deposition of these films onto polymeric substrates for flexible applications.

**B.5.20** DESTRUCTION OF LIGHT/DARK SUPERPOSITION FAILURE IN CIGS SOLAR CELLS. Markus Glöckler, Carolyn R. Jenkins, and James R. Sites, Physics Department, Colorado State University, Fort
Collins, CO.

CIGS solar cells in many cases show a failure of light/dark superposition of the current-voltage (J-V) curve, which generally becomes more pronounced at lower temperatures. J-V measurements under red light may also show an additional distortion, known historically as long-term degradation. The long-term nature of the degradation indicates that a secondary barrier can result from the conduction band offset between CIGS and the commonly employed CdS window layer. This barrier acts similarly to a second diode with the same polarity and in series with the primary photodiode. The temperature dependence of the degradation is strong, suggesting that the CdS/CdTe interface is the dominant factor in the degradation process. Numerical modeling of the proposed explanation, including a band offset consistent with experimental and theoretical values, gives a very good fit to measured light and dark J-V curves over a wide temperature range. It also predicts the observed difference between illuminated J-V curves with photon energy above the CdS band gap, and those with photon energy below the band gap. The model assumes that the CdS/CdTe interface is the dominant factor in the degradation process, and that the CdS/CdTe interface is the dominant factor in the degradation process.

CIGS/CdS and CdTe/CdS devices have exhibited conversion efficiencies in excess of 21%, making them competitive with high-quality single-crystal silicon devices for these applications. However, CIGS/CdS devices are fabricated on substrates with a rougher texture. Unfortunately, the poor thermal conductivity of glass makes this an impractical approach for the fabrication of concentrator cells where thermal management is an important constraint. Therefore, we have been fabricating these devices on stainless steel substrates. These devices have lower conversion efficiency, but the difference between the performance of the glass and stainless steel-based devices decreases as the flux level increases. In the present work, we employ spectral response and drive-level capacitance profiling with high-flux white light bias, as well as photoluminescence (PL) and time-resolved minority carrier lifetime measurements, at varying flux levels, in an effort to better understand the primary non-radiative recombination mechanisms exhibited by these devices. We systematically investigate the observation that these inherently defect-laden photodiodes tend to behave more ideally as the flux level increases and examine the implications for their utilization in solar concentrator systems.

B.21
HIGH FLUX CHARACTERIZATION OF CIGS SOLAR CELLS.
J. R. Young, R. N. Koch, T. J. Duda, B. Reyes, S. Johnson, and J. Klehl, National Renewable Energy Laboratory, Golden, CO.

Cu(In,Ga)S_2 is one of the most promising materials used for making polycrystalline, thin-film solar cells. Conversion efficiencies of over 18% have been demonstrated in the laboratory under standard one-sun operating conditions. Recently, these devices have been investigated for their use in solar concentrator systems. Under one sun, Cu(In,Ga)S_2 devices have exhibited conversion efficiencies in excess of 21%, making them competitive with high-quality single-crystal silicon devices for these applications. Most high efficiency Cu(In,Ga)S_2 devices are fabricated on substrates with a rougher texture. Unfortunately, the poor thermal conductivity of glass makes this an impractical approach for the fabrication of concentrator cells where thermal management is an important constraint. Therefore, we have been fabricating these devices on stainless steel substrates. These devices have lower conversion efficiency, but the difference between the performance of the glass and stainless steel-based devices decreases as the flux level increases. In the present work, we employ spectral response and drive-level capacitance profiling with high-flux white light bias, as well as photoluminescence (PL) and time-resolved minority carrier lifetime measurements, at varying flux levels, in an effort to better understand the primary non-radiative recombination mechanisms exhibited by these devices. We systematically investigate the observation that these inherently defect-laden photodiodes tend to behave more ideally as the flux level increases and examine the implications for their utilization in solar concentrator systems.

B.22
VAPOR TRANSPORT DEPOSITION AND CHARACTERIZATION OF POLYCRYSTALLINE CdTe SOLAR ABSORBERS.
James M. Kennedy, Samuel A. Weller, Department of Chemical Engineering, Stephen Kelly and Tim R. Olson, Physics Department, Colorado School of Mines, Golden, CO; Lawrence M. Woods and Roseie Bibilie, ITN Energy Systems, Littleton, CO.

Cadmium telluride (CdTe) has been identified as a promising absorber layer for large-scale terrestrial thin film photovoltaics. High-throughput, low cost deposition techniques are therefore needed. Vapor transport deposition (VTD) is being investigated as an alternative technology to the high rate synthesis of polycrystalline cadmium telluride thin films. The VTD system operates in a chucked payload configuration, decoupling the source and substrate environments. By controlling the source independently of the substrate, high source vapor concentrations can be obtained. This results in VTD yielding higher growth rates than conventional CIGS technologies, making it a process more amenable to large-scale manufacturing. Additionally, the decoupling of source and substrate allows for a relatively large process window for CdTe deposition. Process variations investigated include source pressure, substrate temperature, source temperature, and chamber oxygen concentration. Film properties of interest included growth rate, uniformity, morphology, and crystal structure. Analytical techniques employed were profilometry, scanning electron microscopy (SEM), atomic force microscopy (AFM), and x-ray diffraction (XRD). Selected films were processed into photovoltaic devices and analyzed by current-voltage (IV).
0.12 to 0.03 eV. We also observed that NaNbN treatment eliminates a deep minority trap in the In(Ga)As photodiode. [2] For high-Ga content devices, only one intercarrier trap is detected. These traps arise from shallow to deep; (3) The carrier concentration (C–V) decreases as the CIGS becomes more In(Ga)As-rich. [4] All our data for low- and high-Ga devices show that the charge-carrier emission rate obeys the Shockley- Read rule. In this presentation, we will discuss our results in terms of the physics of this rule and correlate the defect densities in the films with device performance.

**D5.26**

INTEGRATION OF CHEMICALLY DEPOSITED SnS THIN FILMS INTO FOTOVOLTAIC STRUCTURES, M.T.S. Nair, P.R. Nair, J. Campos, O. Gonzalez-Aran, M. Sanchez, Universidad Nacional Autonoma de Mexico, Centro de Investigacion en Energia, Temoco, MEXICO.

SnS thin films of thickness up to 1000 nm are deposited from chemical baths containing Sn(II) chloride and thiourea. These films are slightly p-type and photoductive. By heating in air at 160-180 °C, the films are converted to SnO2, with x decreasing from the substrate towards the film surface, thereby creating a graded conductivity film. By depositing again an SnS thin film on such an SnO2 thin film, lateral heterostructures of the type, (SnO2)_{x}SnS_{1-x} are formed. With the addition of a chemically deposited top layer of CuS, SnS thin film on the SnS thin film, photovoltaic structures are produced. Optimization of the film thickness and process conditions to improve the open-circuit voltage above 400 mV is currently underway.

**D5.27**

OPTIMIZATION AND CHARACTERIZATION OF A PHOTOVOLTAIC DEVICE STRUCTURE UTILIZING FOTOVOLTAIC (FOTO) DETECTION, Ajay K. Kochhar, Univ of California Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Jing Tang, Univ of California Santa Barbara, Materials Department, Santa Barbara, CA; Eric W. McFarland, Univ of California Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Craig Struckey, Univ of California Santa Barbara, Dept of Chemistry & Biochemistry, Santa Barbara, CA.

Recent work has established the potential of a surface sensitized Schottky barrier solar cell device as a viable, inexpensive alternative to conventional solar cells. A photoreceptor (dye or quantum structure) is coupled to an ultra-thin [100 Å] layer of Au deposited on anodically formed TiO2 to form a Schottky barrier. Separation of the primary photocative subsystem and the system for charge energy storage in the device separates the tasks allowing flexibility in optimization and fabrication. Electrode-recombination in the Schottky barrier is eliminated, by restricting changes to the majority carriers, and band gap per se is no longer a constraint. Barrier height (photovoltaic) and photocatalysis for the solar spectrum are independently controllable. Methods for optimization of the Au and TiO2 interfaces and dye sensitization of the surface have been developed. Under simulated AM 1.5 illumination (100 mW/cm²), devices presently show open-circuit voltages of 0.34 V and short-circuit current densities of 0.12 mA/cm², with fill factor of 0.56. Complete IV, Characterization and fabrication characteristics of fully fabricated solar cell devices of varying metal layer thickness, surface sensitization, and semiconductor preparation have been performed.

**D5.28**

IN SITU CONTROL OF NANOSCALE TEXTURE FORMATION DURING DEPOSITION OF ZnO LAYERS FOR LIGHT TRAPPING IN THIN FILM SOLAR CELLS, Perla P. Cao, University of Alabama at Birmingham, Dept of Physics; Birmingham, AL.

Textured transparent conducting oxides (TCOs) are often integrated into solar cell structures as light trapping media to enhance device efficiency. Although many have been few studies attempting optimization of the film texture to achieve maximum performance for this application. One way of generating TCOs with improved texture control is pulsed laser deposition (PLD). This is due to the addition of a broad range of structural characteristics during PLD. Although these characteristics are undesirable in many cases, they are particularly suitable for creation of controlled nanoscale texture in TCOs. However, in order to control the incorporation of these structural variations into the resulting film it is necessary to understand their dynamic behavior before and after deposition. Few studies have concentrated on this problem. This is partially because there are few techniques capable of performing in-situ measurements on gas-suspended nanoscale particles during material deposition. In this work we have used low-pressure differential mobility analysis to perform high-resolution particle spectrometry in the 1-1000 nm size range and study the gas-phase dynamics of nanoparticles formed during PLD of a broad range of materials during nanoscale fabrication. In this work we have used low-pressure differential mobility analysis to perform high-resolution particle spectrometry in the 1-1000 nm size range and study the gas-phase dynamics of nanoparticles formed during PLD of pulsed laser deposition of films of ZnO films with sub-micron texture. ZnO targets were ablated in inert gas atmosphere with background pressures in the 7-400 Torr range and laser fluences of 1.5-3 J/cm². In-situ measurements reveal that during ZnO depositional conditions, the ZnO population is described by bimodal size distributions with a concentration peak in the 5-10 nm size regime and another around 200 nm. At low pressures (<150 Torr) and low laser fluences (<1 J/cm²), the population is dominated by nanoscale particles. For fluences above 3 J/cm², a surge of particles with sizes around 200 nm is observed. We will discuss how the interplay between these two size regimes affects the texture of the resulting film as determined by AFM analysis.

**SESSION B6: CIGS MATERIALS AND SYNTHESIS**

Chair: Yutaka Yae and Toshi Nakada
Thursday, April 24, 2003
Salon 10/11 (Marriott)

**8:30 AM B6.1**

IMPROVEMENTS IN CIGS SOLAR CELL PROCESSES – IN SITU DEPOSITION MONITORING AND SOFT WINDOW LAYER DEPOSITION TECHNIQUES, Shigeru Niki, Keisicho Sakurai, Akihisa Yamada, Paul Foss, Kiyuki Inoue, Koji Masubara, and Hirotaka Tanpa, Energy Electronics Research Institute, AIST, JAPAN; Ralf Hunger, University of Dortmund, GERMANY; Roland Scheer, Helm- Meitner-Institut, Berlin, GERMANY.

Refinement and innovation in the CIGS solar cell fabrication process further improvement in solar cell performance can be expected though high conversion efficiencies of φ >18% have already been achieved. In this paper, new in-situ characterization techniques which can improve process controllability during CIGS absorber layer deposition will be discussed. In addition, soft (damage-free) deposition of high-quality window layers will be introduced. For in-situ growth monitoring, a pyrometer was introduced for detecting changes in film composition. Use of a pyrometer was found to be more sensitive than a thermocouple. An oscillatory behavior in the pyrometer reading was observed in the initial stage of the three stage process, and was found to correspond to changes in film thickness, making it possible accurate thickness control of CIGS films. Spectroscopic light scattering techniques have also been applied. This technique was found to be much more sensitive to changes in composition than other techniques, and to be effective for real-time surface roughness measurement. For window layer growth, use of soft deposition technologies have also been explored. First, pulsed laser deposition technique has been investigated. High-quality ZnO transparent conducting oxide films with a resistivity as low as ρ = 2×10¹⁰Ωcm and a rms roughness below 1 nm have been demonstrated. A novel ion plating technique in the substrates of soft deposition technique providing both superb controllability of the high density plasma as well as ion beam sputter has been developed for large-area deposition of transparent conducting oxides. ZnO films have been deposited on glass substrate at 200°C as a growth rate of 0.8μm using a pulsed Nd:ZnO target. Resistivities of ρ = 2×10¹⁰Ωcm with carrier concentrations of n=1×10¹⁰cm⁻² have been demonstrated. Performance of CIGS solar cells using the above mentioned techniques will be also discussed.

9:00 AM B6.2

GROWTH MONITORING OF Cu(In, Ga)Se₂ BY GRAZING INCIDENCE X-RAY DIFFRACTION (GIXRD), L.M. Hahn, Meitner-Institut, Berlin, GERMANY; R.W. Schock, Institut für Physikalische Elektronik, Universität Stuttgart, GERMANY.

Grazing incidence X-ray diffraction (GIXRD) in conjunction with a layer absorption modelling algorithm is a powerful tool for studying the structural properties of polycrystalline thin films. A typical application is the refinement of compositional depth profiles. By variation of the incidence angle it is possible to obtain depth dependent structural information of Cu(In, Ga)Se₂ (CIGS) thin films up to a thickness of several microns. Of particular interest are changes of the In/Ga ratio or the S/Se ratio with depth of the as grown film. Compositional gradients of this kind can be included intentionally by a rate controlled single layer coevaporation process. However, many processes rely on sequential deposition of layers with different composition which are then converted to CIGSSe at high temperatures in a chalcogen atmosphere. Due to the sequence of Cu-poor and Cu-rich growth phases, significant compositional gradients may form unintentionally in CIGSSe thin films. At the end of a Cu-rich growth step a remarkable recrystallization of the entire film takes place and coincides with the formation of a secondary Cu-rich Cu₈In₅Se₁₇ phase. The recrystallization is believed to considerably improve the electrical properties of the material. A particular interesting sequential deposition technique is the three stage process, which currently leads to CIGSSe thin film solar cells with highest efficiencies. However, the implications for structural changes and the effect on compositional gradients of this recrystallization are yet not well understood. In this contribution we
use the GIXRD technique to monitor these structural changes by comparing spectra before and after the recrystallization of the film. By using GIXRD measurements it is therefore possible to delineate the elemental distribution with depth and to learn about structural changes which occur at various stages during film growth.

9:15 AM B6.3 DIFFUSION OF Ga AND In IN CuGaSe_2 THIN FILMS. Axel Neisser, Reiner Klenk, Marta Ch. Lux-Steiner. Technische Universität Berlin, GERMANY.

As reported earlier the growth of CuGaSe_2 absorber layers in a two step process is characterized by sequential segregation of two ternary phases leading to a phase of high Ga content at the bottom of the layer and a phase of high In content at the top. In a subsequent recrystallization phase Ga diffuses from the bottom phase into the top phase and In diffusion from the top phase towards the bottom. The degree of alloying of the resulting quaternary Cu(In_xGa_(1-x))Se_2 phase strongly depends on annealing temperature and time of the recrystallization phase. In order to quantify the diffusion process independently from the film growth process suitably designed CuGaSe_2/CuInSe_2 diffusion couples have been investigated by thermal annealing. Annealed samples have been performed in the temperature range from 500°C to 600°C. Annealed samples have been examined by XRD and SNMS depth profiling.

The experimental results the following characteristics could be deduced: - despite interdiffusion of Ga and In the bilayer retains its two phase structure of two layers of almost homogeneous composition, - the composition of these layers depends on the annealing temperature, - diffusion interdiffusion is much more effective if copper/sulfide is present in the sample. To quantitatively describe the interdiffusion process and the associated G3 depth profile a numerical simulation of the XRD spectra was combined with modelled G3 depth profiles based on the modelled Muller and others studies about G3 diffusion in CuGaSe_2 thin films the obtained experimental data could only be described when applying a 3-dimensional diffusion model which accounted for a bulk and a grain boundary diffusion process. The respective diffusion coefficients could be determined. The enhancement of grain boundary diffusion in the presence of copper sulfide indicates the role of the secondary phase as a high mobility path for cations.

9:30 AM B6.4 INVESTIGATION OF CuGaSe_2 GROWTH KINETICS USING TIME-RESOLVED HIGH TEMPERATURE X-RAY DIFFRACTION ANALYSIS. Suk Kim, Woo Kyung Kim, Timothy J. Anderson, Oscar D. Crimble, Department of Chemical Engineering, University of Florida, Gainesville, FL, E. Andrew Pugmire, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN, Sheng S. Li, Department of Electrical and Computer Engineering, University of Florida, Gainesville, FL.

The reaction kinetics for formation of CuGaSe_2 from precursor films consisting of stacked binary NaSe layers were studied by means of high temperature X-ray diffraction analysis. Different reaction paths and phase transformations were observed depending on the precursor film microstructure. For example, the isothermal phase evolution of the InSe/CuSe couple film was observed at different temperatures by in-situ time-resolved X-ray diffraction. The pathway produces a diffusion barrier layer that can be schematically represented as InSe/CuSe → InSe/(CuGaSe/CuSe). The shape of the fractional reaction (x) vs. time curve for a reaction is a decay consistent with a diffusion-controlled reaction mechanism. The rate constant and apparent activation energy for CuGaSe_2 formation were estimated.

9:45 AM B6.5 Cu(In_xGa_(1-x))Se_2 GROWTH STUDIES BY IN SITU SPECTRO-SCOPIC LIGHT SCATTERING. A. Neisser and A. Neisser. Fraunhofer-Institut, Institut für Solar-Energie, Berlin, GERMANY, K. Saurer, P. Bons, S. Kiki, Thin Film Solar Cells Group, Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

The growth of polycrystalline Cu(In_xGa_(1-x))Se_2 thin films using a 3-stage deposition process has been investigated by in situ diffuse spectroscopic light scattering in the wavelength range of 400-800 nm. The film formation, which is in progress for industrial solar cell production, is comprised of the stages InGaSe deposition, CuSe deposition, and InGaSe deposition. The development of surface roughness is monitored by the intensity of the diffusely scattered light. Differences in the time dynamics of the intensity at different wavelengths can be explained by the development of surface roughness at different length scales. Of specific interest is the development of roughness around the stoichiometric points of film annealing. It is shown that the measurement of the spectroscopic light scattering can be used for process control and for adjustment of the final film roughness.

10:30 AM B6.6 CuInGaSe_2-BASED DEVICES: FROM MATERIALS TO PRODUCTS. John Kessler, Angstrom Solar Center, Uppsala University, Uppsala, SWEDEN.

The goal of thin film CuInGaSe_2-based solar cell development is the establishment of a product, and a product is much more than the sum of its material components. Without being so complete as to cover the economic and market issues, the present contribution focuses on certain challenges concerning the application of CuInGaSe_2-based product. A first synergy, concerning synthesis, is found in the triangular relationship between materials, processes and device development. Designing such processes can be established that permit their synthesis, and are notably realistic if product size equipment can be defined to perform this synthesis. For example, the debate behind aspects such as co-sputtering versus selenization for the CuInGaSe_2 growth results from different optimism. This situation is not limited to the CuInGaSe_2 layer, but is applicable to all the other involved materials. As the understanding of the material systems and structures improve, and as the knowhow concerning their growth improves, large scale cost-effective equipment can be designed. Other synergies, such as that between devices, modules and their functionality will also be shown. For example, we will discuss how the present understanding of issues such as durability, may lead to a redifinition of the device and module structures, as well as of the involved materials. Less technical issues, such as market acceptance, can impose modifications, for example Cd-free devices. These issues require a better functional understanding of the interfacial issues and of the junction itself. Taking examples from the recent progress made in throughput (fast and thinner growth), process ease (simplicity and tolerance), and process control (as well as possible approach to each acceptability and functionality), we will discuss how the objective of a long term stable module can differ from that of a record laboratory device.

11:00 AM B6.7 MOLECULAR BEAM EPITAXY OF THIN CuInSe_2 FILMS ON Si. W. Calvet, H. Levenzen, C. Pottskofer, Fraunhofer-Institut SEI, Berlin, GERMANY.

CuInSe_2 layers were grown on Si single crystals of different orientation using molecular beam epitaxy (MBE). The stoichiometry was varied between 0.5 and 1.5 for the nominal CuIn ratio and the film thickness was varied between 150 and 200 nm. Boni et al. photoelectron spectroscopy (PES) was used to determine the surface stoichiometry whereas the volume composition was investigated by Rutherford backscattering (RBS). Strain analysis by x-ray diffraction (XRD) yields the lattice parameter of CuInSe_2. Cu-rich films a growth direction parallel to [112] in the In-rich films the growth direction is given by the substrate orientation with [112] microfacets detected by low energy electron diffraction (LEED). The surface morphology of the epitaxial films from the wafer instead of the expected orientation along the CuInS_2 binary, the presence of a strain field of CuInS_2 varied along the CuInS_2 cut through the Gibbs phase triangle yielding a (100) facet. The role of electronic effects on growth mode and phase formation is discussed.

11:15 AM B6.8 CuInGaSe S_2 ABSORBERS FORMED BY RAPID THERMAL PROCESSING OF ELEMENTAL PRECURSORS: ANALYSIS OF THIN FILM FORMATION AND IMPLEMENTATION OF LARGE AREA INDUSTRIAL PROCESS. Joerg Palm, Volker Probst, Rainer Toelle, Walter Stetter, Stefan Scholl, TCGIS, München, GERMANY.

Large area CuInGaSeS_2 films for solar modules are processed by rapid thermal processing of stacked elemental layers. A pilot line for 60x90 cm² absorbers and 30x30 cm² modules is now running. We will present the current status of our pilot line: Modules with efficiencies of 19% are fabricated with excellent structural and electrical uniformity. For the optimization of electrical performance the selenization and sulfurization process is analyzed by structural, compositional, and opto-electronic characterization tools: X-ray diffraction (XRD), x-ray fluorescence (XRF), secondary ion mass spectroscopy (SIMS), photo luminescence (PL) decay and spectral response (SR). Sequentially processed CIGS films show typical donut-like distribution profiles. For our previously published model obtained by In-Situ XRD analysis the Ga profile can be explained by the strongly inhibited formation of binary gallium-selenides. Ga stays in a selenium rich melt whereas the chalcogenide formation to bottom type materials are ruled out by the typical morphology and the segregation of Ga towards the bottom. The sulfur incorporation is investigated by comparing XRF data and
SIMS profiles of samples from different sulfurization recipes. Two different mechanisms for sulfur incorporation are proposed: If S is available before CIGS formation is complete, S diffuses first into the Cu-Se binary phase and is efficiently incorporated into the bulk of the film. A characteristic dependence of S on the Cu/(In+Ga) ratio is observed. If S is available only after CIGS formation is completed, a previously published diffusion and exchange process takes place. It will be shown that the accumulation of sulfur towards the back is predominantly due to the incorporation into an intermediate polyhydrosulfoselenide layer. Device characterization shows that the Ga and S profiles lead to a favorable double band gap grading structure.

11:30 AM B6.9
EFFICIENT LOW CIGS SOLAR CELLS PREPARED BY ELECTRODEPOSITION WITHOUT VACUUM POST
DEPOSITION STAGE. Denis Guimard, Nicolas Bodor, Jean Andraud, Jamal Kordi, Jean-Francois Guillemier, Daniel Llaure MA, CNRS, Paris, FRANCE; Pierre-Yves Huantier, Olivier Kerrec, EDF-R&D, FRANCE; Paul Mogensen, Saint-Gobain Archipanic, Aubervilliers, FRANCE.

CulnS2 and Culn(In,Ga)S2 layers have been prepared by an electrodeposition based process, with morphologies suitable for device completion, without any post-additional vacuum process. Several promising processes to elaborate high efficiencies cells from those electrodeposited precursors have been elaborated. Ammoniated films yield large grains and excellent morphology. Efficiencies above 8% are reproducibly obtained. The best cell yields an efficiency of 9.1% (no AR coating). To the best of our knowledge, this is a record efficiency for electrodeposited CIGS. Ga has been inserted within our CIGS films during the electrodeposition step. We have been able to insert up to 35% of gallium (vs. all elements). Films with gallium have very good morphology and are processible, after deposition without any post-additional vacuum process, for device completion. Results on first CIGS cells will be presented. Results on bigger substrates will be presented as well. For instance, electrodeposited 10 x 10 cm2 CIGS substrates have been obtained with very homogeneous composition and morphology. Material characterization has been performed on all the different elaborated substrates (XRD, SEM, EDX), as well as current-voltage, capacitance-voltage and spectral response analysis, which will be presented for process optimization. This will allow to evaluate the possibilities of these cells for a possible future low cost and efficient route for CIS Photovoltaics.

11:45 AM B6.10
EPITAXIAL-LIKE GROWTH OF CulnS2 FILMS ON SAPPHIRE BY RF REACTIVE SPUTTERING. Yumin He, I. Physikalisches Institut, Justus-Liebig University Giessen, GERMANY; Alain Krost, Institut fuer Experimentelle Physik, Otto-von-Guericke University Magdeburg, GERMANY; Thorsten Kramer, Anke Polisch, Bruno Meyer, I. Physikalisches Institut, Justus-Liebig University Giessen, GERMANY.

We demonstrate the first deposition of CulnS2 thin films on sapphire by radio frequency reactive sputtering with a CuxIn1-x alloy target and He+S. The RF power was kept constant at 200 W (24.27 W/cm2) and the target was rotated with 800 rpm. The H2 flow was varied from 28 to 35 sccm during the sputtering process. X-ray diffraction revealed that the sputtered films are mainly (112) oriented CulnS2 phase incorporating with a minor Culn2 phase, which is only visible by using x-ray powder diffraction. The substrate temperature was heated up to 500°C, while the H2 flow was varied from 28 to 35 sccm during the sputtering process. X-ray diffraction rocking curve measurements on (112) CulnS2 films on (001) sapphire. There are mainly six peaks shown in the x-ray scans of X-ray diffraction, which can be grouped into two sets. Each set consists of three peaks with an equal separation of about 120°, which is expected for a single crystalline CulnS2 layer. The two main reflection groups rotate by 180° with respect to each other, and lead to twins in the CulnS2 layers. Transmission electron microscopy was carried out to investigate further the microstructure and orientation of the nearly epitaxially sputtered CulnS2 layers. The surface morphology of the films was characterized by atomic force microscopy and scanning electron microscopy. Additionally, Hall effect measurements on the electrical transport properties of the films are currently underway.

SESSION B7: TRANSPARENT CONDUCTING OXIDES
Chair: Steven S. Hegedus Thursday, April 24, 2003 Salon 10/11 (Marriott)

13:30 PM B7.1
THE ROLE OF TRANSPARENT CONDUCTING OXIDES IN SOLAR CELLS. Timothy J. Coates, Timothy A. Gessert, David L. Young, J. Scott Ward, and Todd M. Neuf, National Renewable Energy Laboratory, Golden, CO.

Transparent conducting oxides (TCOs) are used in all thin-film solar cells and their properties, as well as the detail of their deposition, can adversely impact cell performance. There is a high free-carrier concentration of TCOs that can lead to excessive optical absorption, especially if the mobility is low, although this effect can be reduced using thinner films. Free-carrier absorption can adversely impact the single bandgap thin-film cells because the short wavelength portion of the absorption can extend into the response range of the cell. For tandem thin-film devices, being developed within the DOE High Performance Photovoltaics program, it will be even more likely that the TCO properties will influence cell performance, unless very high mobilities are maintained. However, mobilities as high as 75 cm2 V−1 s−1, together with concentrations of 1 x 1020 cm−3, have been achieved for CdSbO4 and other TCOs, which would be sufficiently high to reduce free-carrier losses. Although films of this quality have been made in the research laboratory, they require post-deposition annealing at high temperature (800°C). This may place restrictions on the range of possible designs for the new generation of cells. It seems likely that such a high temperature would necessitate the TCO being deposited as the first layer of the stack of thin films comprising the tandem cell, to avoid inter-diffusion and other possibly damaging effects at critical interfaces. In turn, this restricts possible designs to 'superstrate' cells. In this paper, we will review the magnitude of the free-carrier loss process, its potential impact on both single- and tandem junction thin-film solar cells, and possible designs of the latter.

2:00 PM B7.2

As the band lineup of Cu(In,Ga)Se2 (CIGS), CdS and ZnO is expected to effect the performance of CIGS thin film solar cells, bandgap engineering of ZnO films is important. Bandgap engineering of ZnO films using a solid solution of ZnO with other materials such as MgO has been studied by several groups. However, in these studies, ZnO was treated as semiconductors, not as transparent conducting oxides. We propose the use of the bandgap modified ZnO as transparent conducting film to control the band lineup in CIGS solar cells. As a first step, we have tried to produce low resistivity and transparent ZnMgO films by a pulsed laser deposition system. A mixture of ZnO, MgO, and Al2O3 powders was pressed into a pellet and sintered in the air. The sintered target was ablated in an oxygen ambient by a KrF excimer laser. Transparent and low resistivity Al-doped ZnMgO films were obtained on Corning 7059 glass substrates with a substrate temperature less than 200°C. Bandgap values of up to 4 eV were obtained with an electrical resistivity of the order of 104 Ω cm or less. A minimum resistivity of 7.8 x 10-4 Ω cm was obtained using a target with 10 mol% Mg content. The average optical transmittance of 0.3 µm thick films was more than 90% for wavelengths between 400 and 1100 nm.

2:15 PM B7.3

Transparent conducting oxides (TCOs) are an important component in a number of technologies including thin-film photovoltaics, smart windows, and flat-panel displays. Due to the increasing demand of TCOs, new multinary TCO materials have gained tremendous interest in recent years. Conductivities for ZnSn-O transparent conducting oxides (TCOs) are quite low compared with well known simple TCOs such as In2O3:Sn and SnO:Al. Nevertheless, our interest in ZnSn-O TCOs is two-fold: First, ZnSnO4 is an important interface layer in the CdS/CdTe world record polycrystalline solar cell [16.5% to date (2004)]; Second, ZnSnO4 is a very high reported electron work function of 5.3 eV, which makes it attractive as a hole extracting electrode in polymer photovoltaic. In particular, there is an interest in eliminating the CdSnO4/ZnSnO4 bilayer from the CdTe device if the conductivity of ZnSnO4 can be improved to be comparable to CdSnO4. We have deposited ZnSnO3 and Zn2SnO4 films were grown by Pulsed Laser Deposition (PLD). We explored various deposition conditions to optimise electrical and optical properties. The results showed that by changing the deposition parameters, we were able to grow conducting as well as insulating zinc stannate films. Interestingly, ZnSnO3 showed substantially better electrical properties than Zn2SnO4. All of the ZnSnO3 films deposited at 100°C and lower were amorphous. XRD on highly textured films indicated uniform composition and amorphous structure. Films
that were excited annealed in the 4% H₂ in argon at 400°C showed improved electrical properties. In most cases, the electrical properties of ZnO, converted to a conductivity of approximately 360 cm⁻¹ cm⁻¹. However the SnO₂ films decomposed after high temperature annealing (>350°C). Result on how crystal structure affects electrical properties will be discussed.

2:30 P.M. B7.4
HIGH QUALITY TRANSPARENT CONDUCTING OXIDE FILMS DEPOSITED BY A NOVEL ION PLATING TECHNIQUE. Kakoaya Ikoma, Koji Morihara and Hiroshi Kaneko, Energy Electronics Institute, AIEST, Himeji, Japan; Hiroshi Saeki, Sumitomo Heavy Industries, Ehime, Japan; Kyoichi Araki, Nissin Technical Center Co., Ltd., Ehime, Japan; Tetsuya Yamamoto, Kochi University of Technology, Kochi, Japan.

A novel ion plating technique which has the attribute of both superb controllability of the high density plasma as well as ion beam shape has been developed and applied for the deposition of transparent conducting oxides. Indium tin oxide (ITO) films have been deposited on 800 mm wide glass substrates at 150°C. Resistivities of ρ = 1.2x10⁻²Ω·cm and RA surface roughness of below 0.2 um with excellent uniformity over an 800 mm wide substrate have been demonstrated. The low ion energy and the uniform dispersion of ion atoms were considered to contribute in low resistivity in ITO films. ZnO films have been deposited on glass substrate at 200°C at a growth rate of 0.6um using Gd-doped ZnO target. Resistivities of ρ = 2x10⁻³Ω·cm with carrier concentrations of n = 1x10¹⁰ cm⁻³ have been demonstrated. Advantages of this technique include reduced ion damage, scalable capability, in-plane uniformity, low growth temperatures and fast deposition speed suggesting that the technique is very promising for solar cell applications.

2:45 P.M. B7.5
THE INFLUENCE OF SUBSTRATE AND CONCENTRATION ON CVD-GROWN p-TYPE Ga₂O₃ TRANSPARENT OXIDE SEMICONDUCTING FILMS. Jianliang Cai and Hai Geng, National University of Singapore, Department of Materials Science, Singapore.

Copper aluminum oxide films were grown by the use of metalorganic plasma enhanced chemical vapor deposition (MO-PECVD). It is observed that the film electrical and optical properties are significantly affected by substrates and film composition. Under the same growth conditions, films could be insulators when growing on amorphous quartz substrate but be semiconductors when growing on single crystal quartz. Different techniques, such as XRD, Seebeck, AFM, SEM, univis-visible spectroscopy, Hall effect measurements, were employed to study the structural, electrical, and optical properties of the films. Models and mechanisms of carrier transfer were proposed and discussed. We have also found that the film can be conductive for a range of film composition. The analysis suggests that the traditional interpretation of the p-type conduction can be extended to a wider range of systems.

3:30 P.M. DISCUSSION II
POLYCRYSTALLINE THIN FILM TANDEM CELLS: ARE THEY A Viable OPTION FOR High EFFICIENCY? Moderated by Tim Coats, National Renewable Energy Laboratory.

SESSION B8. POSTER SESSION
GROWTH AND JUNCTION FORMATION
Chair: Luis Stolti
Thursday Evening, April 24, 2008
8:00 P.M.
Salon L-7 (Marriott)

B8.1
THE EFFECTS OF SUBSTRATE ROUGHNESS ON CIS DEVICES DEPOSITED ON STAINLESS STEEL FOIL. Wendell K. Buschel and Ingrid Repins, ITN Energy Systems, Littleton, CO; Markus E. Beck, Global Solar Energy, Tucson, AZ.

Flexible substrates offer advantages for photovoltaic devices in terms of manufacturing costs and power to weight ratio when compared to the more traditional glass substrates. Efficiency differences between devices on glass and those on flexible substrates may be due to a variety of issues, such as surface roughness, impurity diffusion, and differences in thermal properties. This paper focuses on the effects of substrate roughness on device performance. A typical glass substrate has an average roughness of approximately 40 Å, while stainless steel foils can exhibit roughnesses varying from several hundred to thousands of Angstroms. It was previously demonstrated for a small sample set that low roughness correlates with higher efficiency. In this study, the sample set is expanded over an array of roughnesses for identical cells, and device results are compared with those on glass. It is possible to closely match the electrical properties of glass to bare substrate properties, and the present accurate comparison of devices if the substrate properties are thought fully chosen. For example, the use of stainless steel foil of various thickness helps to more closely match the thermal properties of glass, while use of molybdenum and chromium layers has been proven to act as an acceptable impurity barrier for iron. Variations in surface roughness of the stainless steel foils were achieved via mechanical or chemical treatment. Properties of completed devices, their contribution to solar cell performance, substrate preparation, and substrate treatments are discussed in this paper.

B8.2
CHEMICAL AND ELECTRONIC STRUCTURE OF THE ZnO/GOX INTERFACE IN Cu(In, Ga)S₂ THIN FILM SOLAR CELLS. L. Weinhardt, O. Fuchs, C. Heike, and E. Umbach, Experimentelle Physik II, Universität Würzburg, Germany; T.P. Nielsen, S. Vielbeck, and F. Karg, Shell Solar, Munich, Germany.

In solar cells based on Cu(In, Ga)S₂/Se/Ge (CIGS), one potential target for further optimization of cell performance is the commonly used ZnO window layer. Today, a n-ZnO/p-ZnO structure is generally used, separated from the CIGS solar absorber by a CdS buffer layer. Apart from important bulk parameters of the ZnO layer, such as window transmission and resistivity, particularly the properties of its interface to the CdS buffer layer represent a crucial component for the optimization of solar cells. For a further improvement of this interface, a detailed understanding of the chemical and electronic properties is needed. We have thus investigated the ZnO/CdS interface using X-ray photoelectron spectroscopy to probe its chemical properties, and we have used UV and inverse photoemission for a direct determination of the band gaps and band alignment at the heterojunction. The results will be discussed in view of a level alignment model for the complete CIGS thin film solar cell device, taking into account the previously found electronic and chemical structure of the CdS/CIGS/Se interface [1,2] as well as new results for absorbers with varied sulfur content at the surface. [1] L. Weinhardt et al., Proc. 17th EPS EC Munich 2001. [2] M. Merkle et al., Appl. Phys. Lett. 79 (2001) 4892.

B8.3

The built-in electric potential plays a major role in photovoltaic devices, because it collects photoexcited carriers and is a key factor in determining the open-circuit voltage of the device. However, characterization of the built-in potential has been limited to indirect ways such as current-voltage and capacitance-voltage measurements. We have recently employed scanning Kelvin probe microscopy to measure the electrical potential and measured distributions of the electrical potential on cross sections of the solar cells, quantitatively and with sub-micron spatial resolution. The measurements provide valuable information about the electrical properties of the devices and are useful for understanding the performance of solar cells. In this presentation, we will report on the electrical potential in epitaxial Hall and thin-film Cu(In, Ga)Se₂ solar cells. On a GaInP₂ single junction cell, two potential features were measured and were assigned to the p-n junction and the potential barrier at the interface between the GaInP₂ layer and the GaAs substrate. The potential on the p-n junction was photovoltaic and that on the GaInP₂/GaAs interface was photo-inactive. On a GaInP₂/GaAs tandem cell, two potential features were measured near the top and bottom p-n junctions. When the sample was under short circuit and illuminated with light with photon energies greater than the band gap of the top junction, the photovoltage signal from the bottom junction of the GaAs part was measured due to charge accumulations on the bottom junction in the condition of undiluted photocurrent between the top and bottom cells.

On a Cu(In,Ga)Se₂ thin film, profiles of the electrical potential demonstrate that the p-n junction is a buried homojunction. The built-in electric field terminates at the Cu(In,Ga)Se₂/CdS interface, indicating that the CdS and ZnO layers of the device structure are inactive for the collection of photo-generated carriers.
The quaternary GaAsSb alloys are attractive materials for thermophotovoltaic (TPV) devices because the energy gap can be varied from 1.5 to 2.5 eV by changing the As/Sb ratio while maintaining that the lattice is matched to the GaSb substrate. Significant progress has been made in the growth of epitaxial layers by organometallic vapor phase epitaxy (OMVPE), and high-efficiency TPV devices with spectral response out to 3 μm by device engineering were reported. To achieve further improvements in TPV device performance, detailed materials studies of the GaAsSb microstructure and minority carrier lifetime, along with device structure considerations are underway. Studies of the microstructure by transmission electron microscopy reveal the natural formation of a vertical superlattice due to phase separation of GaAsSb. Minority carrier lifetime measurements were performed by time-resolved photoluminescence to study bulk recombination and surface recombination velocity at various heterointerface interfaces. This paper reports the material characteristics of the superlattice and heterointerface device designs, and their implications on TPV device performance.

**BS.5 ELECTRODEPOSITION OF CIS ON METAL SUBSTRATES.**

Andrew Bongartz, Jano Baehr, Rudolf Thielen, Sonja Wolff, Andreas Krattinger, Marcel Mikolaiczak and Klaus Kalberla, CIS Solartechnik Ltd, Hamburg, GERMANY.

The development of a low cost role to role production process for CIS remains an attractive goal. In the present approach, the absorber is prepared by an electrodeposition technique, where copper or stainless steel have been chosen as flexible substrates. During the actual R&D phase feasibility investigation is performed which should prove the viability of the deposition process at the yield levels of 8% in efficiency. This approach poses two major challenges. The first one is related to the metal substrate. Here, the adhesion of the CIS absorber layer has to be realized, and at the same time the metal substrate is not allowed to act as a source for poisoning impurity diffusion into the absorber. Secondly, the question has to be answered if the desired minimum efficiency can be reached by electrodeposition of the CIS absorber layer. Adhesion problems occur mainly for the copper substrate. They could be overcome by an electrodeposition layer of Ni. This, however, requires an additional diffusion barrier against Ni. Layers of Cr, Ti, Ta and the corresponding nitrides have been used for this purpose. The degree of impurity diffusion is analyzed by EDS and SIMS measurements. Up to now best results are obtained with a Ta barrier layer. For R&D electrodeposition is carried out on rotating disc electrodes with a surface area of about 60 cm². Two electrodeposition routes are evaluated. Sequential plating of Cu, In, Ga and Se is compared to simultaneous electrodeposition. For Ni/molybdenum substrates, which have been used for comparison reasons, the actual best efficiency of the sequential process is 7.1%, while 5.0% have been obtained with the simultaneous plating process on 0.25 cm² aperture area.

**BS.6 INTERFACE FORMATION BETWEEN POLYCRYSTALLINE Cu(In,Ga)Sb and HVI COMPOUNDS.** T. Schumeney, Frank Stiehler, A. Klein, R. Hunger, W. Joegermann, Darmstadt University of Technology, Institute of Material Science, Darmstadt, GERMANY.

The interface between Cu(In,Ga)Sb (absorber) and CIS (buffer) is crucial for the performance of CIS solar modules containing CdS-free CIS layers. High performance of ordered defect compounds (ODC) and interdiffusion is known at these interfaces, their impact on interface band alignment and interface defect states is not clear. The outstanding cell performance of CdS buffer layers, in comparison to other buffer materials, is also not resolved. We have performed systematic studies of interface formation between Cu(In,Ga)Sb and HVI semiconductors: GaxNi1-xSe and Zn(x=S,Se,Te) using m- and w-photocurrent photoelectrochemical techniques. Copper indium diselenide surfaces were prepared by heatingoff of Se layers, which were deposited onto the absorber layers in the deposition chamber directly after absorber deposition. Interfaces with HVI compounds were prepared by deep annealing. The determined band alignments are compared to theoretical calculations.

**BS.7 NUCLEATION AND GROWTH OF Cu(In,Ga)Sb ON MOLYBDENUM SURFACES.** T. Schlenker, K. Orgassa, H.W. Schott, J.H. Werner, Institute of Physical Electronics, University of Stuttgart, GERMANY.

Our research on thin film Cu(In,Ga)Sb solar cells shows a strong dependence of solar cell efficiency and yield on deposition rate and substrate temperature during the nucleation phase of the absorber growth. Thus, the present work investigates the growth mechanism of Cu(In,Ga)Sb on Mo films on glass, as the typical back contact for Cu(In,Ga)Sb absorber cells. Mo films are either fabricated by a sputter process or by electron beam evaporation. Each technique results in a different morphology of the absorber surface. We deposit Cu(In,Ga)Sb films of nominal 2.9 to 29 nm thickness using a thermal evaporation process with varying rates at constant substrate temperature of 530°C. An ultra-high resolution scanning electron microscope serves to analyze the samples. For polycrystalline Mo substrates, that were fabricated by a sputter process, the theory of homogenous nucleation (i.e. no special sites or point defects) explains Cu(In,Ga)Sb cluster formation and island density. According to this theory, the relationship between the island density and the evaporation rate is found. The "critical island size" (cluster size that is more likely to grow than decay) is 4 to 10 atoms (depending on formation of the nucleation step). For the growth on Mo, fabricated by evaporation, strong island density fluctuations occur as well as deviations from the correlation between the nucleation density and the evaporation rate of the Cu(In,Ga)Sb absorber. Most probably, on these substrates, in addition homogenous nucleation takes place. In this case, different nucleation steps are generated by randomly distributed mesoscopic defect sites with high trapping energy. At high growth stages the transition from isolated islands to closed films takes place in the coalescence regime.

**BS.8 ROLE OF SURFACE BAND-GAP WIDENING IN Cu(In,Ga)Se2 THIN FILMS FOR THE PHOTOVOLTAIC PERFORMANCE OF ZnO/CoS/Cu(In,Ga)Se2 HETEROJUNCTION SOLAR CELLS.** Uwe Rieg and Mirco Turco, Institute of Physical Electronics, University of Stuttgart, GERMANY.

The Cu(In,Ga)Se2/ZnO interface and the surface region of the Cu(In,Ga)Se2 absorber film are the most important part of the ZnO/CdS/Cu(In,Ga)Se2 heterojunction solar cell. Despite the importance of this part, its electronic properties are not satisfactorily understood. This contribution discusses different proposed models for that close-to-interface region and their implications for electronic losses in the device. The theoretical part of this study uses numerical simulations as well as analytical considerations of the device properties. The outcome of the theoretical work is compared to experimental results on a wide variety of Cu(In,Ga)Se2 heterojunction solar cells. Our main conclusion from our experiment and theoretical studies is that: the conduction band offset at the Cu-poor prepared Cu(In,Ga)Se2 absorber layer is the surface band gap that is increased with respect to the bulk value, eliminating recombination at the buffer/absorber interface. In turn, this process is the limiting factor for all devices that are prepared with a Cu-rich absorber composition.

**BS.9 OXYGENATED CIS WINDOW LAYER FOR SPUTTERED CdS/CdTe SOLAR CELLS.** Aklesh Gupta, Karthikeyan Allada, Sung Hyun Lee, and Alvin D. Compaan, Department of Physics and Astronomy, University of Toledo, Toledo, OH.

The conventional polycrystalline CdS heterojunction window layer used in CdS/CdTe thin-film solar cells has a bandgap of ~2.4 eV which causes absorption in short wavelength region resulting in reduced short-circuit current (Jsc). The device efficiency can be improved if bandgap of CdS is increased. Wu, et al [1] have demonstrated improved current using CdS:O reactively sputtered at room temperature with CdTe subsequently deposited at high temperature (~500°C). The alloying of CdS with oxygen increases the absorption edge of the layer, and hence the blue response of CdTe-based cells. Here we report similar reactive sputter deposition of CdS in mixtures of Ar/O2 at various substrate temperatures, and the use of these films in sputtered cells. At a substrate temperature of 250°C the addition of O2 to the sputter gas results in a red shift of the absorption edge (from 2.35 eV to 1.9 eV), which is opposite to the one observed for room temperature deposition which gives a blue shift (2.95 eV to 2.72 eV). Room temperature deposited films show a considerable broadening of LO phonon peaks indicating nanocrystallinity as the O2 fraction increases. XRD measurements of these films showed the formation of an amorphous structure at high O2 fractions. We shall report on the electrical and compositional properties of the films. Preliminary CdS/CdTe device results have demonstrated an improvement in Jsc and increased blue response but not yet higher efficiency. This work was supported by NREL. [1] X. Wu et al "High efficiency polycrystalline CdTe thin film solar cells with oxygenated amorphous CdS (O×CdS:O) window layer" presented in 29th IEEE photovoltaics specialist conference, 20-24 May 2002, New Orleans.

**BS.10 FORMATION AND IONIZATION ENERGIES OF POINT DEFECTS IN COPPER MALLEABLE ALLOYS USING AB INITIO METHODS.** C. Dominik, S. Laribi, J.M. Raoult, S. Tournier, EDF R&D, Departement MNC, Les Renardieres, Moret sur
Loi: J.F. Guillelmoles, Ecole Nationale Superieure de Chimie Paris, LECA, PARIS, FRANCE.

The opto-electronic properties of Cu(In,Ga)Se_2 and related compounds depend on their defect chemistry in a way that is far from being understood and in which ab initio calculation could help by providing deeper insights as shown previously. ab initio calculation of energy and electronic structure of various intrinsic (including defect pairs) and extrinsic (including potential dopants such as Cd or Zn) point defects have been performed in chalcopyrite semiconductors Cu_xSe_y and CuGa_xSe_2 and their alloys, some of them being computed for the first time by advanced ab initio techniques. The influence of the local order, chalcopyrite or CuAu, is also considered. The simulation methods are based on density functional theory within the framework of pseudo-potentials and plane wave basis. The results will be discussed in view of the existing data, models and calculations.

**BS.11**
SPUTTERED ZnTe:N AND ZnO:Al FOR SOLAR CELL ELECTRODES AND RECOMBINATION JUNCTION
Jennifer Drage, V. Brabec, C. Humbert, C. Travers, Y. Yu, R.G. Beal, A.D. Compan, University of Toledo, Department of Physics and Astronomy, Toledo, OH; T. Osborn, University of Toledo, Department of Chemistry, Toledo, OH; B.E. McCandless, P.D. Paulson, University of Delaware, Institute of Energy Conversion, Newark, DE.

We have used sputtered ZnTe:N and ZnO:Al as transparent electrodes for Cu(In,Ga)Se_2 based solar cells. ZnTe is a reactive sputtering target that provides excellent Zn:Te ratios. Our ZnTe films have shown 85% above 750 nm and resistivity as low as 10 ohm cm with fine grains of approximately 30 nm diameter. ZnO:Al is sputtered from a ZnO:Al_2O_3 target. The ZnO:Al films have resistivity as low as 4 x 10^{-4} ohm cm with 85-90% transmission over the visible spectrum. To test the stability of the films, ZnTe:Al films were annealed in argon, dry air, and nitrogen at a range of temperatures from 200°C to 500°C. Resistance decreased with annealing temperatures less than 392°C and increased with annealing temperatures above 392°C. ZnO:Al films were annealed in dry air and nitrogen at temperatures from 300°C to 500°C. Though the resistivity increased at higher temperatures, there was no change in the transmission. It is important to the function of a tandem solar cell is a transparent contact, like ZnTe:N/ZnO:Al, to replace the traditional metal contact to the CIS/CIGS solar cell. We investigate the ZnTe:N/ZnO:Al bilayers as recombination junctions and how they are affected by the thickness of the ZnTe:N and ZnO:Al. The sputtered ZnTe:N and ZnO:Al films were characterized by AFM, STEM, XRD, transmission, 4-probe, and Hall measurements. This work is supported by the NREL High Performance Photovoltaics Project.

**BS.12**
REAL-TIME FAULT DIAGNOSIS OF SENSORS FOR FAULT TOOLS: CONTROL OF CIS (CIGS) PHOTOVOLTAIC PROCESS.
Shahriar S. Joshi, Nick Gomez, Michael Chaffin, ITN Energy Systems, Inc., Littleton, CO; Scott Weidman, Markus Beck, John Maiba, Jeff Britt, Global Solar, Tucson, AZ.

One of the important features of real-time control of thin-film deposition processes is the ability to measure in-situ variables that are closely related to the quality of the film. Ultimately, the quality of the process control is dependent on the quality of information that can be extracted from sensor measurements. It is not unusual to hear about production runs being aborted due to sensor failures especially when the sensors are exposed to harsh environments. Thus sensor reliability has a direct impact on product yields. Faulty sensors need to be identified in real-time in order to ensure that the manufacturing process does not continue with incorrect process settings, and if possible, the sensing process should be reconfigured so that the control can continue with accurate information. In this paper, real-time sensor fault diagnosis strategies developed by ITN Energy Systems, Inc. (ITN) and Global Solar (GSE) to enable fault-tolerant controllers for thin-film CIGS deposition processes are presented. The results suggest that these strategies are very effective. Also, sensing process reconfiguration methodologies that lead to fault-tolerant controllers will be discussed.

**BS.13**
EFFECTS OF ZnTe/ZnS/Cu COMPLEX BACK-CONTACT ON DEVICE CHARACTERISTICS OF Cu(In,Ga)Se_2 SOLAR CELLS.
Lili Wei, Daolin Cai, Lianghuan Feng, Yaping Cai, Wei Cai, Jingui Zheng, Qing Yang, Sinchan Univ, Dept of Materials Science, Chengdu, CHINA.

Zinc telluride is an ideal back-contact material for Cu(In,Ga)Se_2 solar cells due to the small band gap of CuTe and possibility of heavily p-doped by Cu, which means that a thin interlayer of Cu-doped ZnTe between p-CdTe and metal back electrode of high function can make a stable and low ohmic contact. In order to prevent the diffusion of Cu into CdTe layer and decrease the interface state densities between p-CdTe and Cu-doped ZnTe layers, we have proposed to introduce an undoped ZnTe film as a buffer between both layers. In this paper, Cu-In-Ga layers have been deposited by vacuum co-evaporation, and the Cu-In-Ga/CdTe, Cu-In-Ga/CdTe/Cu-In-Ga-ZnTe, and Cu-In-Ga/CdTe/Cu-In-Ga-ZnTe/Cu-In-Ga films were deposited by three kinds of back contact, i.e. complex ZnTe/ZnS/Cu layer, single ZnTe/Cu layer and no buffer layer, have been fabricated. The influence of Cu concentration in the doped ZnTe layer as well as the thickness of undoped ZnTe layers on CdTe/CIGS photo-voltaic devices and the optimization of these devices have been studied. Considering the abnormal temperature dependence of dark conductivity in ZnTe-CdTe films, we have investigated the effects of annealing temperatures on the performance of the cells. The results show that the cell over- and cross over phenomena of dark and photo-LVC curves can be eliminated by use of the complex back contact layer. In general, the performance of the cells with a complex layer is better than that with a single layer and much better that without back contact layers. It has been demonstrated that the diode quality factor has decreased to 1.8 and the fill factor has increased to 23% for Cu-In-Ga/CdTe/Cu-In-Ga-ZnTe/Cu-In-Ga cells, in which there is no high resistance transparent layer. The relative reasons have been discussed.

**BS.14**
OPTIMIZED GROWTH CONDITIONS FOR Cu(In,Ga)Se_2 LAYERS GROWN BY CO-EVAPORATION AT HIGH DEPOSITION RATES.
O. Lundberg, M. Edoff, J. Lu, L. Stolt, Uppsala University, Ångström Solar Center, Uppsala, SWEDEN.

A high deposition rate (equivalent to a short deposition time) of Cu(In,Ga)Se_2 (CIGS) layer, while maintaining high material quality, is desired for low cost fabrication of CIGS based solar cells. In this study, solar cell devices were fabricated from CIGS films grown by co-evaporation at high deposition rates. It was found that devices with CIGS layers grown at higher deposition times are more sensitive to the final Cu/(In+Ga) composition. As the Cu/(In+Ga) ratio decreases, the performance of these devices decreases more rapidly than that of devices with CIGS layers grown at lower deposition times. Thus, higher growth rates the composition process window is smaller. The effect of the higher growth rate on the CIGS material quality is investigated by transmission electron microscopy. CIGS layers with evaporation times longer than 15 minutes resulted in compact films with some continuous grains, extending from bottom to top. For evaporation times under 15 minutes the grain size is reduced and voids are introduced into the films, which could be detrimental for the device performance. Nevertheless, even an evaporation time of 3.75 minutes a 12.8% efficient device, without interfacial coating, has been fabricated. [1] O. Lundberg, M. Bodegard and L. Stolt, Rapid Growth of Thin Cu(In,Ga)Se_2 Layers for Solar Cells, EMRS 2002, Strasbourg.

**BS.15**
HIGH-PERFORMANCE BARRIER LAYERS FOR FLEXIBLE CIGS THIN-FILM SOLAR CELLS ON METAL FOILS.
Dirk Herrmann, Friedrich Kessler, Konrad Herz, Axel Ecke, Michael Pohl, Zentrum für Sonnenenergie, und Wasserstoff-Forschung Baden-Württemberg (ZSW Stuttgart, GERMANY; Andreas Schönhuber, Uwe Schumacher, Institut für Photovoltaik [IPV], University Stuttgart, GERMANY.

Commonly CIGS (Cu(In,Ga)Se_2) based thin-film solar cells are deposited on sulfur containing glass substrates at temperatures around 550°C. Highly efficient CIGS modules fabricated on thin and flexible non-glass substrates would on the other hand open entirely new application areas. Many research groups are currently working toward cost, flexibility and conversion efficiency are metallic foils. On the way towards a monolithically integrated high efficiency CIGS module on metal foils three distinct problems have to be solved: (1) reduction of diffusion of substrate elements into the CIGS absorber, (2) Na-doping of the absorber, necessary to attain high efficiencies and (3) electrical isolation between substrate and metal substrate. These issues have been addressed in this paper. Preferred foils with regard to costs and physical properties were ferritic steel, stainless and Fe/Ni/Co-alloys (e.g. Kovar). SiO_x- and Al_2O_3-based barriers were fabricated by different deposition methods (sagel, PECD and sputtering). Sodium was added using SIMS and SNMS depth profiles revealed the various suitable of the diffusion barriers and the effectiveness of Na-doping. For example, the SiO_x barrier deposited by the sagel method proved to be a suitable candidate for diffusion barrier. On ferritic steel a decrease in content in the CIGS absorber of up to two orders of magnitude could be achieved. Due to the rough surfaces of the metal
foils, perfect electrical solution with these layers is a big challenge. With the help of a newly implemented measurement technique, based on electron microscopy combined with SEM images, pinholes in the barrier layers could be localized and correlated with growth failures. Best suitability for high efficiency CIGS solar cells were provided by the combination of two layers with distinct properties (e.g., isolation/diffusion barriers plus sodifying smoothing layer). For CIGS solar cells on metal substrate foils including Na-containing diffusion barriers efficiencies of 12.9% (AM 1.5, 1000 W/m²) could be achieved. In this paper we will present results on various barrier layers as well as on CIGS mini-modules (5 cm²) on flexible metal foils.

**BS.16**  CURRENT STATUS AND FUTURE PROSPECTS OF CISCuT BASED SOLAR CELLS AND MODULES. Olaf Tober, Michael Winkler, Jürgen Persdorf, Joachim Griesche, ISE - Institut für Solare Energiesysteme, Potsdam, GERMANY. "ECN - Energy research Centre of the Netherlands, Petten, THE NETHERLANDS.

CISCuT - CIS on Cu-Tape - has been established as a new thin film technology in which Cu(In,Ga)Se₂ based solar cells are continuously fabricated on a Cu-tape in a series of consecutive roll-to-roll processes. Flexible modules encapsulated into polymer foils are assembled by interconnecting strips of this tape in a roof tile manner. This process technology also provides light and spectral responses that show efficiencies of 9% so far that have been certified by the Fraunhofer Institute Solare Energiesysteme. Suitability tests over more than 3000 hours show promising results. Furthermore, we changed from cell and from module to large flat modules that have automatically been assembled to different areas are compared. This comparison gives insight into how the different roll-to-roll processes including the assembling of the module influence the overall quality of the modules. Furthermore, the mechanical properties and the stability of the CISCuT-based solar cells and modules are compared. An outlook on the future prospects of this exciting technology is given.

**BS.17**  MODIFICATION OF Cu(In,Ga)Se₂ SURFACE BY TREATMENT IN CADMUM SOLUTIONS. Q. Nguyen Hong and H.W. Schock, Institute of Physical Electronics, University of Stuttgart, GERMANY.

We introduce Cd into Cu(In,Ga)Se₂ (CIGS) absorber by wet chemical treatment in Cd⁺⁺ solution with varying NH₃ concentration and investigate the role of modified CIGS surface on the cell performance of ZnO/CdS/CIGS heterojunction. Current-Voltage (I/V) measurements show reduction of the open circuit voltage depending on the NH₃ concentration: a slight reduction in the case of solution without NH₃ and much stronger with a solution containing 1 mol/L NH₃. X-ray photoelectron spectroscopy (XPS) reveals the presence of Se atom in metal (Cd, Cu, In, Ga) oxides on the CIGS surface after treatments. The oxidation products on CIGS surface are decreased with increase of the NH₃ concentration and disappear in the case of solution containing 1 mol/L NH₃. The decrease in the open circuit voltage is related to the redox potential. Secondary Ion Mass Spectroscopy (SIMS) shows that treatment of the CIGS layer in solution with NH₃ introduces more Cd into the CIGS absorber than non-NH₃ solution. Thus, the diffusion of Cd into the CIGS absorber is intimately tied to the CIGS surface redox interaction process which is controlled by the NH₃ concentration. We conclude that Cd-diffusion and the reaction of oxidized surface layer are competitive. Comparing the XPS, SIMS and I/V results, we propose that the degradation of cell performance is due to surface oxidation and Cd-diffusion, where the effect of Cd-diffusion is dominating. The results point to a "defected near-surface layer" created by Cd-diffusion which introduces additional defects.

**BS.18**  IN SITU XRD STUDIES OF SEQUENTIAL CuIn(S,Se)₂ FORMATION. Jorma Djordjevic, Eveline Rudiger, Roland Scheer, Hahn-Meitner Institut, Berlin, GERMANY.

The formation of CuInSe₂-CuInS₂ alloy films from chlorination of different precursors is investigated by in situ energy dispersive x-ray diffraction (EDXRD). A sequential synthesis procedure was used. Copper and indium (Cu/In in 1:1.8) were evaporated onto molybdenum coated soda-lime glass and selenium was introduced as a layer of elemental selenium or as a InSe₃ layer. Such prepared precursor films were then fired in elemental sulfur or in Se. The effects of the selenium precursors and the influence of sulfurization conditions on the resulting absorber film composition and properties were investigated. It is shown that the ternary phases in the final film were CuInSe₂, CuInS₂ and CuIn(S,Se)₂ in the case of the elemental selenium precursor deposition and CuInS₂, CuInSe₂ in the case of InSe₃ precursors. The difference in the formation pathway is investigated in detail.
Deposition processes of the Cd-free buffer layer (ZnS, InS) and the transparent conducting oxide layer (ZnO:Al) were studied by the MOCVD method and further improvements were implemented by an extra Cu-rich growth stage, since we did not observe the existence of the so-called quasi-liquid Cu-S binary phase which is known as a flux for large scale growth. [1] K.K. Banger, J. Current and A.F. Hepp, 27th IEEE Photovoltaic Specialists Conference, 2P.5 (2002).

**BS.24 QUANTUM DOT SENSITIZED SCHOTTKY BARRIER SOLAR CELLS.** J. Zhang, D.B. V. University of California Santa Barbara, Materials Dept., Santa Barbara, CA; Ajay K. Kashyap and Eric W. McFarland, University of California at Santa Barbara, Dept. of Chemistry, Santa Barbara, CA; Gideon D. Stucky, Univ. of California at Santa Barbara, Materials Dept and Dept of Chemistry and Biochemistry, Santa Barbara, CA.

A solar cell device structure has been investigated which utilizes photovoltaic excitation of CdS/CdTe semiconductor quantum dots (QD) for photon-to-electron conversion and subsequent injection and transport of ballistic electrons through a sub-band in a film on a Au/TiOx/Ti multi-layered Schottky barrier structure. Fundamental issues involve the photon-to-electron conversion efficiency of the QD's, the electron coupling of the QD excited state to the metal conduction band, hot electron transport in the noble metal film and over the Schottky barrier, and the charge separation by the semiconductor device structure. The thickness of the Au layer must be kept below the mean free path of a hot electron in the metal to allow efficient electron transport from the semiconductor quantum dots to the Au layer. We have improved the electrical coupling between the quantum dots and Au layer by surface morphology modification. This complete inorganic, solid-state device configuration has the advantage of eliminating the electron-hole pair recombination in the semiconductor and the need for significant minority carrier transport. A typical device has an open circuit voltage of 340 mV and a short circuit current density of 0.05 mA/cm² with a fill factor of 0.46 under AM1.5 broadband illumination (100 mW/cm²). This work demonstrates an alternative approach for the fabrication of low cost and durable solar cells.

**BS.25 FABRICATION AND PROPERTIES OF CdTe/ZnTe THIN FILMS FOR TANDEM SOLAR CELL APPLICATION.** Ramesh Desai, Tim Geertsz, Sally Asher, and Helio Mattinson, National Renewable Energy Laboratory, Golden, CO.

Modeling of two-junction tandem devices shows that for optimal device performance, the bandgap of the top cell should be around 1.8 eV. CdZnTe alloys can be tailored to yield bandgaps in the desired range. In this study, three approaches were used to fabricate these films, using close-spaced sublimation (CSS) and radio-frequency sputtering (RFS) techniques. In the first approach, we used mixed precursor of CdTe and ZnTe to achieve the desired composition. In the second approach, we used precalcined CdTe and ZnTe powders (obtained from CDE Materials Inc.) as the source. In the last approach, we used Zn, even for the source composition of 75% Zn, these films contained very low quantities of Zn (~2%). We tried unsuccessfully, to increase the Zn content in the films by confining Zn vapor by enclosing the region between the source and substrate, reducing the substrate temperature to 400°C and adjusting the source-substrate distance. Finally, we used thin film couples, consisting of 300-nm thick CdTe deposited by CSS and 300-nm thick ZnTe deposited by RFS, and the samples were then heat-treated in cadmium chloride vapor. Secondary Ion Mass Spectrometry analysis of the samples showed extensive interdiffusion of Cd and Zn for the annealed samples. We will present the data on the various stack configurations of CdTe and ZnTe and the effects of different post-deposition processes such as thermal annealing and alloy formation, as well as the results from the first two approaches.


Several structural and electrical properties have been studied in semiconductor bilayers and especially in heterojunction solar cells of the type CdS/CdTe, however the possible influence of the different grain sizes mismatch between layers on the properties of the heterojunction has not carried over to our knowledge. By patterning in large area grown CdS or by CSV/T grown CdTe. We present in this paper a study on the influence of the grain size mismatch on the diode...
characteristics. Particularly the efficiency the solar cells, Voc, Jae, ideal diode factor and saturation current are reported and the results are presented and discussed.

**BS. 27**

**NON-VACUUM THIN-FILM CIGS PV MODULES**

Chris Ebengreuther, Karen Pauls and John Serra, Unisun, Newbury Park, CA.

One of the most promising strategies for lowering the cost of photovoltaics is to replace vacuum deposition in the thin-film technology, and one of the most promising thin-film PV absorber materials is copper indium gallium selenide (CIGS). CIGS thin films are typically deposited by vacuum-based techniques, but the complexity and cost of vacuum deposition equipment limit cost savings. Non-vacuum deposition techniques can provide substantial operational and cost advantages relative to vacuum deposition, including lower capital equipment costs, lower operational complexity, lower skilled labor costs, lower raw material costs, and higher overall return on investment. This work is aimed at developing low-cost, non-vacuum techniques for fabricating monolithic CIGS PV modules. CIGS films are formed using novel nanoparticle materials. Homogeneous CIGS layers are formed by incorporating the desired materials (e.g. Cu, In, Ga, etc.) into phase-stabilized, sub-micron particular metal/oxide precursor materials. Layers of particles are deposited using spraying and printing methods, and particular layers are converted into solid CIGS films by reactive sintering at atmospheric pressure. Sprayed or pre-coated layers typically exhibit non-planar morphologies and low particle packing, and CIGS films made from sprayed layers typically exhibit related non-planar morphologies and residual void space. The surface roughness of spray- or slip-derived CIGS films results in the average sheet conductivity of overcoating coatings; thin coatings of transparent conductors deposited on rough CIGS films exhibit sheet resistances on the to two orders of magnitude higher than equivalent coatings on planar surfaces. Nano additives can improve layer morphology and sintered film properties, but organic additives can cause carbon contamination of the sintered CIGS films. Results with low-residue additives will be discussed. The fabrication of monolithic multi-cell modules imposes additional constraints on transparent conductor sheet conductance. Alternative module designs will be discussed that can accommodate the impact of non-planar CIGS films.

**BS. 28**

**REDUCTION OF m-CrO2-CRACKS IN LARGE DIAMETER In-Ga-Sb BULK CRYSTALS**

K. Juliet Vogel, Dept. of Engineering Science, Purdue University, West Lafayette, IN.

The ternary alloy, In-Ga-Sb, is a compound semiconductor of tunable bandgap in the range of 0.18 - 0.72 eV, with promising applications in photovoltaic (PV), photodetector (PD), and other high-efficiency opto-electronic devices in the infrared regime. Bulk crystal growth followed by ingot diffusion to form p-n junctions is a well-established process for low cost, large volume devices using diffusion Ge or binary InH and InLI compounds. However, similar research and development on bulk ternary and quaternary compounds has not been as successful, primarily due to experimental difficulties in growing single-homogeneity multi-component semiconductor alloys. The large separation between the liquidus and solidus phases leads to compositional segregation which, coupled with differences in the lattice parameters and thermal expansion coefficients of the constituent binaries, causes excessive strain in the solid lattice, often resulting in mechanical cracking of the crystals. However, by combining precise temperature regulation with advanced fluid mixing schemes during solidification, it may be possible to synthesize large diameter bulk material from ternary alloy InH-V mixtures.

Utilizing a unique system based upon vertical Bridgman technique, large diameter (50 millimeter) In-Ga-Sb polycrystalline ingot of high compositional uniformity and remarkable quality have been grown. Novel methods of improving the melt during solidification have been used in conjunction with optimization of the furnace temperature gradient profiles to significantly reduce or remove micro-cracking in the crystal boules while reducing the growth time from several months to a few days. In this paper, the experiments will be reviewed, detailing the system and crystal growth parameters. Electron probe microanalysis (EPMA) data of vertical and horizontal cross-sections will be presented to examine the compositional variations throughout grown crystals. Further, the potential evidence for stressinduced cracking resulting from specific melt mixing schemes will also be presented.

**8:30 AM **

**B9.1**

**NEW JUNCTION CAPACITANCE METHODS FOR THE STUDY OF DEFECT DISTRIBUTIONS AND CARRIER PROPERTIES IN THE COPPER INDIUM DISELENE ALLOYS**

J. David Cohen, Jennifer T. Hecht, Department of Physics and Materials Science Institute, University of Oregon, Eugene, OR; William N. Shafranek, Institute for Energy Conversion, University of Delaware, Newark, DE.

Junction capacitance methods are routinely applied to the study of new semiconductor materials to learn about deep defect states within the semiconductor bandgap. In studies of thin-film CIGS materials, related methods such as admittance spectroscopy and DLTS have been used quite successfully over the past decade for this purpose. However, these methods have potential difficulties: First, such measurements are not simple to interpret when the deep defect densities become comparable to or exceed those of the free carrier densities. Second, it is hard to distinguish distributions of defects within the bulk interior of microcrystalline semiconductor films from surface and higher concentration near the carrier junction, particularly when both may contain defect bands with broad energy distributions. Third, it is extremely difficult to obtain accurate distributions of minority carrier traps and for defect levels near midgap, although these are likely to have the greatest impact on photovoltaic device performance. Finally, the interpretation of all such studies is made even more problematic by the presence of metastable defect phenomena in these materials. We have recently been quite successful utilizing two methods which are new to the study of such CIS alloys: drive-level capacitance profiling, and transient photocapacitance spectroscopy. In this talk I will explain the principles behind these techniques and the advantages and disadvantages of these methods have compared to the more traditional methods mentioned above. I will then review several of the key results that we have obtained by applying these methods to the study of the CIS alloys over the past 2 years. This has resulted not only in new information concerning the deep defects and their spatial distributions in these materials, but also to more accurate determinations of free carrier densities, and of minority carrier trapping dynamics within the junction region.

**9:00 AM **

**B9.2**

**DEFECTS IN COPPER INDIUM ALUMINUM DISELENE FILMS AND THEIR IMPACT ON PHOTOVOLTAIC DEVICE PERFORMANCE**

Jennifer T. Hecht, Department of Physics, Linfield College, McMinnville, OR; J. David Cohen, Department of Physics, University of Oregon, Eugene, OR; William N. Shafranek, Institute for Energy Conversion, University of Delaware, Newark, DE.

We have characterized the thermal and optical transitions associated with electronically active defects in CuIn1-xAlxSe2 (CIAS) films. The films studied were incorporated as the absorber layer in high efficiency photovoltaic devices, which have the structure Mo/CIS/CdS/ZnO/ITO. In this series of devices, the Al fractions range from x=0 to 0.5, resulting in absorber bandgaps varying from 1.0 eV to 1.67 eV. The device efficiencies range from 7% to 13%; however, for devices with x>0.3, the open circuit voltage is limited at 0.74 V, and does not increase with increasing Al content and bandgap. This limits the device performance for the higher bandgap CIAS devices. These devices were studied using admittance spectroscopy, drive level capacitance profiling, transient photocapacitance spectroscopy, and transient photocurrent spectroscopy. These measurements, performed on the completed devices, create a picture of the electronic density of states in the bandgap of the CIAS layer and its uniformity through the thickness of the device. They also give information about the activation energy of conduction and the minority carrier mobility in each film. These studies have shown that films with x=0.35 typically have an activation energy of conduction near 0.4 eV. This is at least 0.3 eV higher than that of analogous CuIn1-xGa2xSe2 (CIGS) films. We believe the more intrinsic nature of the CIAS films is a result of a prominent deep acceptor band (with a density near 10^17 cm^-3), which effectively pins the Fermi level. This may also account for the open circuit voltage being limited at x=0.35. In addition, the Urbach energy, 43 meV, is roughly double that of corresponding CIGS films. Thus, our measurements indicate that these CIAS films with x=0.35 are significantly more disordered than corresponding CIGS films, which likely negatively impacts the resulting photovoltaic device performance.

**9:15 AM **

**B9.3**

**MESOSCOPIC POTENTIAL FLUCTUATIONS AND PASSIVATION OF GRAIN BOUNDARIES IN Cu(In,Ga)Se2 THIN FILMS**

Manuel J. Remiro, Jehad Altashami, Chun-Sheng Jiang, Sewail M. Al-Jaisme, Remmel Noawi, National Renewable Energy Laboratory, Golden, CO.

Thin-film solar cells are promising for future, cost-effective, terrestrial photovoltaics. So far, the recent efficiency for these solar cells has been demonstrated by thin films of Cu(In,Ga)Se2 (CIGS) deposited by the three-stage process. However, the full potential of CIGS in
The radiation hardness of Cu(In,Ga)Se	extsubscript{2} based thin-film solar cells is outstanding among all photovoltaic materials as proven by many terrestrial irradiation experiments. In addition, recent post-irradiation annealing experiments demonstrate that irradiation-induced defects anneal out at relatively moderate temperatures between 330 and 400 K or even at ambient temperature if the devices are illuminated. However, not in all situations the recovery of the device performance is complete, i.e., some part of the radiation damage is irreversible. Whereas a 1-MeV electron irradiation the initial device performance is fully re-established by thermal annealing, the damage after 3-MeV electrons as well as after any kind of proton irradiation is not completely reversible. We further observe, that the loss of minority carrier lifetime leading to a degradation of the open circuit voltage of the devices, in general, tends to anneal out, whereas the loss of net doping density, the so-called carrier removal effect, is not reversible. The contribution will summarize our irradiation and annealing experiments. We will discuss our experimental results, especially the consequences of reversibility and irreversibility of specific kinds of radiation damage, with respect to the forecast of device performance under space conditions.

10:05 AM **B9.5**
PHOTOCONDUCTIVE CIS IN CdTe/CIS SOLAR CELLS
Steven E. Shaheen, Kevin D. Dobson, Brian E. McCandless, Darshini Dhasn, Dan Hynes, Institute of Energy Conversion, University of Delaware, Newark, DE.

The impact of photoconductive CIS (PC-CIS) in CdTe/CIS solar cell modules can be significant. Different methods have been suggested using spectral response (SR) with spectrally filtered bias light; i.e., dual beam photon response measurements, along with photocurrent and current-voltage (J-V) measurements. Cu-compensated CIS is a well-known photocouider. One manifestation of PC-CIS is a large crossover between light and dark J-V curves where the dark curve has a larger resistance than the light J-V curve due to a large decrease in CIS dark conductivity. Another signature of PC-CIS in this work is a significant increase in blue SR as well as an increase in red SR with bias light. The SR often exceeds unity for wavelengths less than 520 nm. This is explained by the blue-chopped light modulating the field and allowing collection of carriers generated by the bias light during the ac cycle. The enhancement of blue SR increases following thermal and electrical stress of the device, and increases when the CdS is intentionally Cu-doped prior to CdTe deposition, and is correlated with the increased J-V crossover. It is present in some degree in nearly all devices we have examined from different deposition processes containing Cu. The PC-CIS signature is not present in the absence of the CIS layer. The PC spectrum was extracted from the low Sr at wavelengths less than 515 nm by dividing the bias light spectrum with bandpass filters. This spectrum is similar to the PC-CIS response data of Shainov (1998) for Cu-compensated CIS, peaking around 700 nm. We conclude that Cu-compensated CIS is responsible for the increased dark resistance of the stressed CIS/CdS solar cells suggesting that Cu in CdS has changed the doping hence field profile in the devices. This has implications for stability.
Nanostructural and diffusion properties at the CIGS/TCO interface of these devices have been investigated using transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and secondary ion mass spectroscopy (SIMS). CuIn_{0.2}Ga_{0.8}Se_{2} (CIGS) thin films were deposited by the modified three-stage process onto the TCO-coated glass substrates at deposition temperatures of 500\textdegreeC. CuIn_{0.2}Ga_{0.8}Se_{2} (CIGS) thin films were deposited by the method similar to CIGS deposition excluding the In evaporation step. All TCO films showed the sheet resistance of around 10 ohm/sq and optical transmission of more than 85% at 550 nm. The cell structure in this experiment was a substrate type such as a ZnO:Al/ZnO/CdS/CIGS/TCO/glass structure. Almost no intermixing at the CIGS/ITO. CIGS/ITO. CIGS/SnO\textsubscript{2}-F, and CIGS/SnO\textsubscript{2}-F interface boundaries fabricated at a deposition temperature of 550\textdegreeC was found by SIMS and EDX analyses. The lattice image revealed that the CIGS and CIGS grains grew epitaxially (grain by grain) onto SnO\textsubscript{2}-F or ITO thin layers. On the other hand, a considerable amount of interdiffusion at the absorber/TCO interface occurred at higher substrate temperatures, resulting in a low cell performance. In contrast, large amount of Zn-diffusion was found for the CIGS/ZnO and CIGS/ZnO interface boundaries even at relatively low substrate temperatures. The excess Zn-diffusion resulted in the serious deterioration of the cell performance. Dark current-voltage-temperature characteristics for the CIGS and CIGS devices fabricated on the TCO back contacts are also discussed in connection with the diffusion behavior at the CIGS/TCO interface.

11:30 AM B9.9
ON A BETTER UNDERSTANDING OF RECORD EFFICIENCY DNY CIGS-FREE CIGS SOLAR CELLS USING ATOMIC LAYER DEPOSITED INDUM SULFIDE BUFFER LAYERS
Negar Naghavi, Jean-François Guilleminot, Daniel Lincot, Laboratoire Dielectri chrome et de Chimie Analytique, UMR 7575 CNRS, ENSCP, Paris, FRANCE; Bruno Carreau and Arnaud Echegocory, Institut Lavoisier/REMI, Université de Versailles-Saint-Quentin, Versailles, FRANCE; Stepanie Spiering and Micheal Powalla, Zentrum für Sonnenenergie-und Wasserstoff-Forschung, Stuttgart, GERMANY.

Thin film solar cells based on Cu\textsubscript{(In,Ga)}Se\textsubscript{2} (CIGS) are entering the industrial period. At present high efficiency devices and modules use thin CdS interfacial buffer prepared by chemical bath deposition. Alternatively to CdS buffer layers, especially cadmium-free materials are expected for next generations of CIGS modules. ZnS based buffers are the most advanced option via the chemical bath deposition route. Indium sulfide buffer layers are emerging on the other side as the most promising option via dry deposition processes. The interest of the dry option is the possibility of a complete integration of the production line with vacuum processes. The breakthrough of the indium sulfide route has been related to the use of the atomic layer chemical vapour deposition (ALCVD) which first allowed to reach a 13.5% cell with very interesting features with respect to the cell parameters, especially a very good collection in the UV range. Recently new record efficiencies in cells (about 16%) have been obtained and efficient modules modules have been fabricated. There is now a great interest for characterizing in detail these new devices. This presentation will be devoted to the characterization of high efficiency ALCVD indium sulfide/CIGS cells mostly by optical, XRD, SEM, and XPS techniques. First results on the characterization of these devices open important new views on interface formation processes in CIGS cells related to the use of indium sulfide buffers.

11:45 AM B9.10
INTERFACE FORMATION OF CONDUCTING OXIDES.

Oxide conductors as ZnO, In\textsubscript{2}O\textsubscript{3} or TiO\textsubscript{2} are important as contacts in different thin film solar cells. Nevertheless their electronic interface properties are hardly studied so far. For this reason we have prepared several interfaces between such oxides and chalcogenide semiconductors as CdS and Cd\textsubscript{2}Se and investigated their electronic properties using in - situ photoelectron spectroscopy. All interfaces exhibit large interface dipoles of 0.5 – 1.0 eV. The dipoles are oriented with their positive end towards the oxide, indicating a charge transfer from the oxide to the chalcogenide semiconductor. In addition to the interface dipoles the deposited films show a characteristic thickness dependent cation to anion core-level binding energy difference, independent of whether the deposition sequence is oxide on chalcogenide or reverse. A theoretical calculation of the band alignment at the CdS/ZnO interface [1] agrees with our experimental determination. This indicates that the band alignment and the large interface dipoles are governed by intrinsic material properties. [1] S-H. Wei and A. Zunger, Appl. Phys. Lett. 72, 2011 (1998).