

# SYMPOSIUM B

## Compound Semiconductor Photovoltaics

April 22 – 25, 2003

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SESSION B1: DEFECTS AND MATERIAL  
CHARACTERIZATION

Chairs: Shigeru Niki and Wolfram Jaegermann  
Tuesday Morning, April 22, 2003  
Salon 10/11 (Marriott)

**8:30 AM \*B1.1**

**THEORETICAL ASPECTS OF DOPING OF PHOTOVOLTAIC MATERIALS.** H. Katayama-Yoshida, Department of Condensed Matter Physics, and Department of Computational Nanomaterials Design, Nanoscience and Nanotechnology Center, The Institute of Scientific and Industrial Research (ISIR), Osaka University, Ibaraki, Osaka, JAPAN.

The low-resistive p- and n-type transparent conductors are necessary for the efficient photovoltaic (PV) solar cells. We propose a new valence control method of codoping for the fabrication of a low-resistive p-type ZnO based upon the ab initio calculation. We compare our prediction for the design of a low resistive p-type ZnO with the recent successful codoping experiment. The Delafossite structure of CuAlO<sub>2</sub> has great potentiality for p-type transparent conducting oxide to apply the high efficient photovoltaic solar-cells combined with n-type transparent conducting oxides such as ITO (indium tin oxides), SnO<sub>2</sub> or ZnO. We have calculated the electronic structure, impurity levels, and formation energy of Cu-vacancy, Al-vacancy, Be, Mg, Ca acceptors at the Al-site, and Be, Mg, Ca donors at the Cu-site. Calculated acceptor energy levels are as follows; Cu-vacancy (-300meV from the VBM [valence band maximum]), Al-vacancy (671 meV from the VBM), Be-acceptor (85 meV from the VBM), Mg-acceptor (200 meV from the VBM), and Ca-acceptor (960 meV from the VBM). We find that the Mg impurity at the Cu-site is more stable than the Al-site. Therefore, Mg impurity acts as donors at the Cu-site in the CuAlO<sub>2</sub>. This is the reason why Mg doping reduces the p-type conductivity in CuAlO<sub>2</sub>. We propose the following valence control method for the fabrication of p-type CuAlO<sub>2</sub>; (i) we should dope the high concentration of Cu-vacancy in order to form the impurity band with reducing the Cu vapor pressure during the PLD or MBE crystal growth method, or (ii) we dope the Mg or Be acceptors at the Al-site with reducing the Al vapor pressure and increasing the Cu vapor pressure during the thermal non-equilibrium crystal growth method such as MBE or MOCVD. We will compare our materials design with the available experimental data. Finally, I will discuss the valence control method of p-type CuInS<sub>2</sub> or CuInSe<sub>2</sub> based upon ab initio electronic structure calculation.

**9:00 AM B1.2**

**DEFECT PHYSICS ANALYSIS OF CHALCOPYRITE SEMICONDUCTOR CuInSe<sub>2</sub> USING EXAFS.** Theanne Schiros, Hunter College of the City University of New York and SSRL; P.E. Stallworth, S.G. Greenbaum, M.L. den Boer, Faisal Alamgir, Hunter College of the City University of New York; Scott Calvin, Naval Research Laboratory; J.-F. Guillemoles, Laboratoire dielectrochimie et de Chimie Analytique ENSCP.

CuInSe<sub>2</sub> is one of the most promising materials for thin film photovoltaic solar energy conversion. Its conductive properties are largely controlled by intrinsic structural defects (vacancies, anti-sites, and interstitials, etc.). Despite analysis with a variety of probes, controversy still exists as to the nature and origin of the defects in this compound. A better understanding of the native point defects occurring in CuInSe<sub>2</sub> is indispensable for thin film applications and of great value to basic science. Extended X-ray Absorption Fine Structure analysis is particularly well suited to this material, as it provides element specific structural information for each atom in the compound. From an analysis of the sinusoidal modulation of the absorption coefficient as a function of energy, one can quantitatively assess the number, type, and bonding of the neighboring atoms as well as their distances away from each other and the absorber. When compared with a reference model, this information can be used to identify and characterize the extent of vacancies, interstitials, and anti-sites present in a given material. We have used EXAFS to identify the defects likely to be present in our Bridgman grown, multi-crystalline samples of CuInSe<sub>2</sub>, constructed ab initio theoretical models of these defects, and fit multi-edge data to these models. As expected, a model of our measurements based on pure compounds with no defects was unable to fit the data. We find that a best fit requires a significant population of defects. The most likely configuration is a 12% vacancy in Cu, an 8% population of Cu-Se anti-sites, and a 5-6% population of In-Se anti-sites.

**9:15 AM B1.3**

**DX-CENTERS IN CdTe OBSERVED BY LOCALLY SENSITIVE PROBE ATOMS.** S. Lany, H. Wolf, and Th. Wichert, Technische Physik, Universitaet des Saarlandes, Saarbrücken, GERMANY.

The limited donor doping efficiency in II-VI compound semiconductors (e.g. ZnTe and CdTe) is usually blamed on two

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 (A-center) or the transition of the donor into an acceptor-like state, accompanied by a large lattice relaxation (DX-center). While the theory of the DX-center well explains experimental observations such as persistent photoconductivity, the microscopic model is primarily based on theoretical calculations. In order to characterize the local structure of Indium donor atoms in CdTe, radioactive <sup>111</sup>In/<sup>111</sup>Cd probe atoms are introduced into In-doped samples, and the electric field gradient (EFG) at the site of the probe atom is measured by means of the perturbed  $\gamma\gamma$ -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  $V_{zz} = 10^{21} \text{V/m}^2$  is measured at the site of the <sup>111</sup>Cd daughter nucleus. Attributing the observation of this EFG to DX-center formation, the PAC signal corresponds to a metastable, relaxed configuration of the <sup>111</sup>Cd probe atom, originating from the initially present DX-center configuration of the <sup>111</sup>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 MAPPING ON POLYCRYSTALLINE CdTe SOLAR CELLS BY SCANNING TUNNELING MICROSCOPY.** P. Sutter, P. Zahl, E. Sutter, V. Kaydanov, T. Ohno, Department of Physics, Colorado School of Mines, 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 device, in particular the presence of a Cu interlayer between the CdTe absorber and the ZnTe contact. In view of the wealth of information contained in STS 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**

**A STUDY OF ARSENIC DOPANT CONCENTRATION AND ACTIVITY AS A FUNCTION OF GROWTH CONDITIONS IN POLYCRYSTALLINE MOCVD-GROWN CdTe.** A. Stafford, S.J.C. Irvine, Department of Chemistry, University of Wales, Bangor, UNITED KINGDOM; K. Durose, G. Zoppi, 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, is 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 complexes. In this study we have attempted to gain a better understanding of the behaviour of Arsenic as an acceptor dopant in CdTe, in order to maximise hole concentration and thus optimise photovoltaic performance. CdTe layers, 1-2 microns thick, were grown at different temperatures and VI/II ratios on insulating sapphire substrates using the organometallic precursors dimethylcadmium, diisopropyltellurium and *tris*-dimethyl-aminoarsenic. The layers were electrically characterised using Van der Pauw (under both dark and AM1.5 conditions) and Hall measurements. Total dopant concentration was assessed where necessary using calibrated SIMS. SEM was used to check for variations in grain size, and qualitative data on some intrinsic defects was obtained using PL. Total Arsenic concentration was found to be higher at lower growth temperatures (350°C), but electrical characterisation showed that the lateral resistivity was considerably

reduced at 400°C. At this temperature, for a given dopant flow, the resistivity under AM1.5 conditions was dependent upon reactant VI/II ratio, exhibiting a minimum at Te: Cd  $\sim$  1.2 (Te-rich growth). Lateral resistivities as low as 100-200  $\Omega$ -cm were obtained, and compared with those previously measured for undoped p-type material. In all cases dark resistivities were several orders of magnitude higher. This is attributed to the presence of high grain-boundary potentials which become partially collapsed in the light. Results are discussed in the context of Marfaing's analysis of doping and compensation in CdTe, where hole concentration is thought to depend upon a balance between dopant acceptors and various compensating donor species, such as  $V_{Te}^{2+}$ ,  $(V_{Te}-As_{Te})^+$  or  $Cd_I^{2+}$ .

#### 10:30 AM \*B1.6

MATERIAL RELATED PREREQUISITES FOR HIGH EFFICIENCY CHALCOPYRITE BASED THIN FILM SOLAR CELLS. Hans-Werner Schock, University of Stuttgart, Institute of Physical Electronics, Stuttgart, GERMANY.

In this contribution we review the present state of understanding of material properties of chalcopyrite based thin films in respect of application in solar cells. Specific properties of the surface and grain boundaries as well as the back contact have direct consequences for device operation. Surface reconstruction is accompanied by a Cu depletion of the surface and provoke formation of a buried junction resulting in intrinsically graded structures. New information about the depth of Cu depleted surface layer is derived from grazing incidence x-ray diffraction. The origin of the charge necessary for an inversion of the surface is still open. In this context we summarise and evaluate controversial discussions about extrinsic doping by diffusion of donors from partial electrolytes or from the buffer layer. Further open questions are the reasons for low recombination velocity at grain boundaries and favourable properties of the back contact and its relation to the interface with back contact materials. Finally we will draw a comprehensive picture related to the boundary conditions of the material and their consequences for device performance.

#### 11:00 AM B1.7

STRUCTURE AND OPTOELECTRONIC PROPERTIES OF CuGaSe FOR PHOTOVOLTAIC APPLICATIONS. Marinus Kunst, Alexander Meeder, Hahn-Meitner Institut, Section of Solar Energy, Berlin, GERMANY.

Thin film solar cells, based on CuGaSe<sub>2</sub> absorber layers, are still limited by the poor optoelectronic properties of these layers. Using non-contact techniques, transient photoconductivity measurements in the microwave frequency range (TRMC measurements), photoluminescence spectroscopy (PL) at ambient temperature as well as sub gap absorption spectroscopy techniques, we present a systematic study on the optical and electrical properties of single crystal and polycrystalline CuGaSe<sub>2</sub> (CGSe) thin films. The single crystals were grown by chemical vapour transport (CVT) in a closed system using iodine as transport agent and polycrystalline CGSe as the raw charge. The thin films were deposited in two stages by an open-tube chemical vapor deposition process. The first stage leads to a nearly stoichiometric polycrystalline CGSe film of approximately 1.5 mm thickness. During the second stage the film is annealed in a Ga- and Se-rich atmosphere leading to a non-stoichiometric (slightly Ga-rich) film. PL measurements of nearly stoichiometric CGSe, single crystals and thin films; from 10K-300K show the presence of one main recombination path (about 1.3eV), dominant over the whole temperature range. After Ga and Se annealing this recombination path vanishes. For such annealed samples hardly any PL is observed at room temperature. Besides, in the nearly stoichiometric also excitonic PL at low temperatures was found in contrast to the annealed samples. A large difference in excess charge carrier kinetics between stoichiometric and annealed samples is observed: -Stoichiometric films show a very fast decay where after the excitation pulse excess charge carriers decay quasi instantaneously. -Annealed films show an extended photoconductivity decay over several orders of magnitude in time characterized by a power law. These results are attributed to the higher density of deep recombination states in stoichiometric CGSe, also revealed by sub gap absorption spectroscopy. This explains the apparently paradoxical result that the solar energy conversion efficiency is considerably higher in solar cells with annealed CGSe absorbers than in those with stoichiometric absorbers.

#### 11:15 AM B1.8

OPTICAL FUNCTIONS OF CHALCOPYRITE CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>. S.-H. Han<sup>a,b</sup>, D.H. Levi<sup>b</sup>, H.A. Al-Thani<sup>b</sup>, F.S. Hasoon<sup>b</sup>, K. Jones<sup>b</sup>, and A. Herman<sup>a</sup>; <sup>a</sup>Department of Physics, University of Colorado, Boulder, CO; <sup>b</sup>National Renewable Energy Laboratory, Golden, CO.

Key factors in determining the efficiency of photovoltaic devices are the optical properties of the absorber material. The highest efficiency CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGS) solar cells use thin-film polycrystalline CIGS absorber layers. We have applied variable angle spectroscopic

ellipsometry (VASE) to characterize the dielectric functions of samples with Ga: (In+Ga) ratios from 0 to 1.0. Cu : (In+Ga) ratios in these films are approximately 0.90, which is the ratio that yields the highest efficiency CIGS devices. We have also studied three CGS 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  $\mu$ m 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 included a surface roughness layer. Accurate values of real and imaginary part of dielectric functions representative of CIGS absorber layer are obtained from the data. The structures observed in  $\epsilon$  are analyzed by fitting the numerically differentiated spectra of  $d^2\epsilon(\omega)/d\omega^2$  to analytic lineshapes using CPPB (Critical-Point Parabolic-Band Lineshape) fitting procedure to get the position of the energy, approximate amplitude and broadening of each oscillator. The obtained energies are related to given inter-band transitions based on the electronic band structures of the ternary end-point compounds. Based on these results we express the bandgap energy, crystal-field splitting and spin-orbit splitting as a function of the gallium composition using the quasicubic 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 \*B1.9

EFFECTS OF Na ON Cu(In,Ga)Se<sub>2</sub> THIN FILMS AND SOLAR CELLS. D. Rudmann, M. Kaelin, F.-J. Haug, H. Zogg, A.N. Tiwari<sup>†</sup>; Thin Film Physics Group, Lab. for Solid State Physics, ETH Zürich, Zürich, SWITZERLAND. <sup>†</sup>also Electronic and Electrical Eng. Dep., Loughborough University, UNITED KINGDOM.

High efficiency Cu(In,Ga)Se<sub>2</sub> (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 on 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 Na incorporation techniques. The effects on photovoltaic performance of solar cells grown from such absorber layers will be discussed.

SESSION B2: III-V PHOTOVOLTAIC MATERIALS  
Chairs: Daniel J. Friedman and Martha I. Symko-Davies  
Tuesday Afternoon, April 22, 2003  
Salon 10/11 (Marriott)

#### 1:30 PM \*B2.1

EFFECT OF N ON THE DEFECT PROPERTIES IN GaAs. Su-Huai Wei, National Renewable Energy Laboratory, Golden, CO.

Unlike conventional isovalent semiconductor alloys A<sub>1-x</sub>B<sub>x</sub>C, where the physical properties change smoothly and continuously as a function of the composition  $x$ , for GaAs<sub>1-x</sub>N<sub>x</sub>, 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 even than GaAs. As such, GaAs<sub>1-x</sub>N<sub>x</sub> has become a potential candidate as an absorber for high-efficiency tandem solar cells. Under thermo equilibrium, N solubility in bulk GaAs is very low ( $[N] < 10^{14} \text{ cm}^{-3}$ ). But, in epitaxial growth, a few per cent of N can be mixed into GaAs. However, with high [N], one also see a considerable degradation of the minority carrier lifetimes, indicating that N also alters significantly the defect properties in GaAs. Using first-principles total-energy calculations we show that N solubility in GaAs is controlled by the N chemical potential,  $\mu_N$ . In bulk growth  $\mu_N$  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  $\mu_N$ , 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  $\mu_N$ , low energy N-N and N-As split interstitials with deep gap levels will form, which are the likely sources of the minority carrier killers in this system. Furthermore, we show that in the presence of N, the character of the intrinsic and extrinsic defects in GaAs are qualitatively different from those without N. For example, we find that in GaAsN a H atom bonds preferentially to the more electronegative N and acts as a donor in its own right, whereas in conventional III-V semiconductors H is an amphoteric impurity causing passivation instead of doping. At high Fermi energy and H

concentration, we find that a N complex with two hydrogens ( $H_2^*$ ) is energetically more stable than the single-H configuration. This provides the first theoretical proof that  $H_2^*$  can be stable in III-V semiconductors. More surprisingly, we find that this  $H_2^*$  is electrically inactive and removes the effect of N on the band gap, i.e., restoring the gap of GaAs. Effects of N on other defects (e.g.,  $V_{Ga}$ ,  $Si_{Ga}$ ) will also be discussed. \*This work was done in collaborations 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-AC36-99-GO10337.

#### 2:00 PM \*B2.2

ELECTRONIC STRUCTURE OF HIGHLY MISMATCHED SEMICONDUCTOR ALLOYS. Wlodek Walukiewicz, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

Highly Mismatched Alloys (HMAs) are formed when the metallic anions in a semiconductor are replaced by more electronegative isoelectronic atoms. The most extensively studied class of HMAs are group III $_x$ V $_{1-x}$  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 Ga $_{1-y}$ In $_y$ N $_x$ As $_{1-x}$  alloys which, for  $y=3x$ , 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 used to utilize the near infrared part of the solar spectrum in multijunction solar cells. We will show that the electronic structure of III $_x$ V $_{1-x}$  alloys is accurately described by the Band Anticrossing (BAC) model that considers an 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 the group III $_x$ V $_{1-x}$  alloys but has also predicted new phenomena. For example, experiments have fully confirmed the theoretically predicted effective mass enhancement and the improved donor activation efficiency in GaInNAs 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 passivation of the isoelectronic N and electrically active group IV donor impurities in Ga $_{1-y}$ In $_y$ N $_x$ As $_{1-x}$  alloys. Finally we will demonstrate that the BAC model is broadly applicable to other HMAs, most notably to the extreme case of CdS $_{1-y}$ Mn $_y$ O $_x$ Te $_{1-x}$  alloys where highly electronegative O partially replaces metallic Te. In agreement with the BAC model we observe a large O-induced reduction of the band gap in these alloys. Supported by US DOE under Contract No. DE-AC03-76SF00098.

#### 2:30 PM B2.3

CHEMICAL AND ELECTRONIC CHARACTERIZATION OF GaSb SURFACE PASSIVATED BY ALCOHOL-BASED SULFIDE SOLUTIONS. Zhiyan Liu and Shurti Prakash, University of Wisconsin-Madison, Department of Chemical Engineering, Madison, WI; Dovas A. Saulys, University of Wisconsin-Madison, Department of Electrical & Computer Engineering, Madison, WI; T.F. Kuech, 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 a 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 aqueous solutions were studied. Alcohol-based solutions, including ethyl, isopropyl and t-butyl alcohols, were compared to aqueous sulfide solutions in order to determine any solvent-based effects on the reactivity of the sulfur 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 photoemission spectroscopy (XPS). To investigate the thermal stability of sulfur bonds, the passivated sample was annealed to 600°C in vacuum. It is found after 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 Ga-S bonds was increased with the temperature going up. After 600°C, all the Ga-S bonds were desorbed from the surface.

#### 2:45 PM B2.4

RECOMBINATION PARAMETERS FOR ANTIMONIDE-BASED SEMICONDUCTORS USING RF PHOTOREFLECTION TECHNIQUES. R.J. Kumar, R.J. Gutmann, J.M. Borrego and P.S. Dutta, Center for Integrated Electronics, Department of Electrical, Computer and Systems Engineering, Rensselaer Polytechnic Institute, Troy, NY; C.A. Wang, Lincoln Laboratory, Lexington, MA; R.U. Martinelli, Sarnoff Corporation, Princeton, NJ; G. Nichols, Lockheed Martin, Schenectady, NY.

Radio-Frequency (RF) photoreflection measurements and one-dimensional device simulations have been used to evaluate bulk and surface recombination parameters in antimonide-based materials. The photoconductivity 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-Reed-Hall (SRH) recombination is the bulk recombination process. When radiative, Auger and surface recombination are included, the simulation results show good agreement with the model. RF photoreflection measurements and simulations are compatible with a radiative recombination coefficient (B) of approximately  $5 \times 10^{-11} \text{ cm}^3/\text{s}$ , Auger coefficient (C)  $\sim 1.0 \times 10^{-28} \text{ cm}^6/\text{s}$  and surface recombination velocity (SRV)  $\sim 600 \text{ cm/s}$  for the 0.50 - 0.55 eV doubly-capped InGaAsSb material with GaSb capping layers using the experimentally determined active layer doping of  $2 \times 10^{17} \text{ cm}^{-3}$ . 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 PHOTO-VOLTAICS. Richard S. Crandall, National Renewable Energy Laboratory, Golden, CO.

The Meyer-Neldel rule (MNR) (compensation law) is ubiquitous in compound semiconductors and other materials. Data in the literature and to be presented at this meeting show either emission rate prefactors or capture cross sections varying over 18 orders of magnitude. Without an understanding of the physical basis of the MNR these variations would appear ridiculous. However, they are a direct consequence of the multiphonon nature of the emission and capture processes. It is the large entropy change for a multiphonon transition that compensates for the large Debye-Waller factor that would otherwise preclude multiphonon transitions. A direct consequence of the MNR is that the distinction between shallow and deep traps is murky and no longer depends on only the activation energy but the free energy must be considered as well. Since experiments show that the isokinetic temperature for II-VI and III-V photovoltaic alloys is in the vicinity of the operating temperature, all traps have nearly the same carrier emission rates. Because these emission rates are low, the traps are recombination centers. In this presentation I will give an overview of the MNR, outline its physical basis [1,2] and consider its consequences to reconcile various experimental puzzles. (1) Peacock-Lopez, E.; Suhl, H. Phys. Rev. B 1982, 26, 3774. (2) Yelon, A.; Movaghar, B. Phys. Rev. Lett. 1990, 65, 618.

#### 3:45 PM B2.6

EVIDENCE OF THE MEYER-NELDEL RULE IN InGaAsN ALLOYS: CONSEQUENCES FOR PHOTOVOLTAIC MATERIALS. Steven W. Johnston and Richard S. Crandall, National Renewable Energy Laboratory, Golden, CO.

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 varying 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-Neldel rule, which states that all traps have the same emission rate at the isokinetic temperature. A fit of our trap data gives an isokinetic temperature of 327 K, which means that both deep and shallow traps emit slowly at the operating temperature of solar cellsthus, the traps are recombination centers.

#### 4:00 PM B2.7

WAFER-BONDED INTERNAL REFLECTORS FOR MONOLITHICALLY INTERCONNECTED GaInAsSb THERMOPHOTVOLTAIC DEVICES. C.A. Wang, D.A. Shiau, P.W. O'Brien, P.G. Murphy, R.K. Huang, M.K. Connors, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA; D.M. Depoy and G. Nichols, Lockheed Martin Corporation, Schenectady, NY; M.N. Palmisano, Betchel Bettis, Incorporated, West Mifflin, PA.

A new approach for high-efficiency thermophotovoltaic (TPV) systems using GaSb-based TPV cells bonded to a semi-insulating GaAs handle wafer with an internal reflector is being investigated. The resulting structure consists of a broad-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 (1) increases the effective optical thickness for above bandgap photons, and thus thinner active layers can be used to lower dark currents; (2) enhances photon recycling; (3) provides partial spectral control of below bandgap photons which are reflected back to the thermal radiator; and (4) can be designed to provide electrical isolation from the n-GaSb substrate, and thus allows monolithic series interconnection of TPV cells for voltage building. GaInAsSb/GaSb TPV epilayer structures were bonded to semi-insulating GaAs handle substrates using a dielectric/metal reflector consisting of  $\text{SiO}_x/\text{Ti}/\text{Au}$ , which serves as both the bonding layer and the reflector. The reflector is designed to provide high reflectivity while minimizing internal stress in the final structure. Wafers were bonded under 250 psi mechanical pressure at a temperature of 250°C. This low temperature is compatible with subsequent device processing. Finally, the GaSb substrate is chemically thinned and etch stop layers removed to expose the GaInAsSb/GaSb epilayers. This paper will discuss recent progress in fabrication, materials characterization, and device performance of these TPV structures with wafer-bonded internal reflectors.

#### 4:15 PM **B2.8**

##### ASSESSMENT OF OPTICAL AND STRUCTURAL PROPERTIES OF III-V SEMICONDUCTORS GROWN ON InP/Si AND Ge/Si WAFER BONDED EPITAXIAL TEMPLATES WITH APPLICATION TO A FOUR-JUNCTION SOLAR CELL.

A. Fontcuberta i Morral, J.M. Zahler, C.-G. Ahn, and H.A. Atwater, Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA; M. Wanlass, National Renewable Energy Laboratory, Golden, CO.

A four-junction solar cell consisting of GaInP/GaAs/InGaAsP/InGaAs fabricated on a Si support substrate has a predicted theoretical efficiency of 41.6% under 15 suns AM0 illumination. However the large lattice mismatch between the GaInP/GaAs and InGaAsP/InGaAs subcell structures and between the InGaAsP/InGaAs subcell structure and the Si substrate prohibits the use of heteroepitaxy for fabrication of this cell design. Wafer bonding and layer transfer by hydrogen induced exfoliation can potentially overcome this challenge by integration of two two-junction tandem subcells, while isolating the associated misfit dislocations at the bonded interfaces. We have developed processes to transfer thin layers of GaAs or Ge to InP and InP to Si that serve as epitaxial templates for GaInP/GaAs and InGaAsP/InGaAs subcells. In this paper we present current results on growth and characterization of the InGaAsP/InGaAs subcell structure on InP/Si substrates and also for InGaP/GaAs on Ge/Si. InP/Si and Ge/Si heterostructures were fabricated from vicinally cut (100) InP and (100) Ge wafers implanted with either  $\text{H}^+$  at 80keV or co-implanted with  $\text{H}^+/\text{He}^+$  at 80keV/115keV to a total dose of  $2 \times 10^{17} \text{cm}^{-2}$ . Prior to bonding Ge, InP, and Si substrates were cleaved into  $\sim 1 \text{cm}^2$  samples. The surfaces of these samples were cleaned to remove particulates and hydrocarbon contamination and were rendered hydrophobic by an HF dip. Once bonded, the structure was annealed under a uniaxial pressure of  $\sim 0.5 \text{MPa}$  at 225°C to induce layer splitting. InP and Ge layers approximately 700nm thick with an rms roughness of 9-10nm and 10-15nm respectively, as determined by AFM, were transferred to Si substrates. InGaAsP/InGaAs double heterostructures grown on InP/Si templates by metallorganic chemical vapor deposition show room temperature photoluminescence intensities comparable to those grown on bulk InP substrates, but exhibit low photoluminescence decay lifetimes. Additionally, triple-junction GaInP/GaAs structures grown on Ge/Si templates have been studied to determine the optical quality of the GaAs cap material and the GaInP top cell structure. These studies indicate comparable photoluminescence to control InGaP/GaAs structures grown on a bulk Ge substrates. Work in progress to be discussed at the meeting includes the growth and characterization of double heterostructures to distinguish the InGaAs film minority carrier lifetime and surface recombination velocity InGaAsP/InGaAs interfaces. Additionally, GaInP/GaAs/GaInP double heterostructures grown on Ge/Si epitaxial templates to characterize of the minority carrier lifetime of the GaAs and the surface recombination velocity of the GaAs/GaInP interface will be discussed.

#### 4:30 PM **B2.9**

##### FORMATION OF SUBMICRON GALLIUM ARSENIDE ISLANDS ON N-TYPE SILICON BY ANNEALING OF ELECTRO-DEPOSITED GALLIUM IN ARSINE. J.D. Beach, R.T. Collins, N. Hamm, and M. Treaster, Colorado School of Mines, Physics Department, Golden, CO; H.-J. Kleebe, Colorado School of Mines,

Metallurgical and Materials Engineering Department, Golden, CO; A.A. Khandekar and T. F. Kuech, University of Wisconsin-Madison, Department of Chemical Engineering, Madison, WI; D. Senft, Air Force Research Laboratory, Advanced Space Power Generation, Kirtland AFB, NM.

Large-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, spontaneous nucleation across the substrate surface. This results in 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 0.1 M  $\text{GaCl}_3$ . Prior to the deposition, the silicon was patterned with photoresist 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 a standard calomel electrode. The duration of the pulses ranged from 10 to 100 ms, and the number of pulses ranged from 1 to 100. Both longer and more pulses produced more gallium islands. After electrodeposition, the photoresist was removed and the samples were annealed in hydrogen (78 Torr, 6 slm) at 700°C for 10 minutes, after which arsine,  $\text{AsH}_3$ , 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  $\mu\text{m}$  to 1  $\mu\text{m}$  in diameter, with the large dots showing evidence of grain boundaries. SEM images showed similarly sized features, and EDS 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. Jäger 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 dopant-induced dots in GaAs by cross-sectional 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-n multilayers. We find significant changes in the current-voltage 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 charge carriers. The similarity of the dots' configuration with n-p-n 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 B3: CdTe INTERFACE CHARACTERIZATION

Chairs: Victor Kaydanov and Vello Valdna  
Wednesday Morning, April 23, 2003  
Salon 10/11 (Marriott)

#### 8:30 AM **\*B3.1**

##### THE DYNAMICS OF CADMIUM TELLURIDE ETCHING.

K.D. Dobson, P.D. Paulson, B.E. McCandless, R.W. Birkmire, Institute of Energy Conversion, University of Delaware, Newark DE.

The inability to prepare stable ohmic contacts to p-CdTe has hindered the development of CdTe/CdS solar cells. Pseudo-ohmic back contacts to CdTe/CdS cells can be prepared by doping Te-rich CdTe surfaces with metals. Oxidizing wet chemical etches are generally employed 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 investigations to determine mechanistic details of CdTe etching will be presented. The use of variable angle spectroscopic ellipsometry, coupled with glancing 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  $\text{HNO}_3/\text{H}_3\text{PO}_4$  (NP) for 45-60s produces a  $\sim 100 \text{nm}$  crystalline-Te surface film, which is stable to

atmospheric oxidation for a number of hours. NP etches of 15-35s form thinner films with a significant amorphous-Te component, which spontaneously crystallizes following removal from the etch solution. NP 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 Br<sub>2</sub>/methanol produces 1-2 nm amorphous-Te surface films, which begin to oxidize in air immediately following treatment. Br<sub>2</sub> is less aggressive towards CdTe surfaces and GBs, however, GB diffusion of Br has been previously observed in CdTe/CdS structures. The presence of Br 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 CdHgTe THIN LAYERS ON CdTe AFTER NP-ETCHING AND HgTe-GRAPHITE PASTING. Yanfa Yan, 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 (HNO<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub>) 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 films and followed with HgTe-graphite pasting. We found that after NP-etching, HgTe-graphite pasting and thermal annealing, a thin-layer (about 20 nm thick) of CdHgTe was formed between CdTe and Te-rich layers, giving the structure like CdTe/CdHgTe/Te. High-resolution electron microscopy images show clearly that the CdHgTe 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 pastes and annealed at different temperatures. However, no CdHgTe layer has been observed.

#### 9:15 AM B3.3

CHEMICAL AND ELECTRONIC PROPERTIES OF CdTe/Sb<sub>2</sub>Te<sub>3</sub> CONTACTS FOR CdTe THIN FILM SOLAR CELLS STUDIED BY PHOTOEMISSION. D. Kraft, A. Thissen, A. Klein, W. Jaegermann, 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 properties, which limits the use of Cu containing back contact materials. Stable CdTe solar cells with reasonable back contacts have been prepared using Sb<sub>2</sub>Te<sub>3</sub>/metal layer systems. We have investigated the chemical and electronic properties of such layer system using *in-situ* photoelectron spectroscopy. Sb<sub>2</sub>Te<sub>3</sub> layers deposited onto CdTe do not react with the substrate and form no good back contact. By subsequent deposition of metals 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 Gessert 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 contacting 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 the vacuum processes used for this contact can enable systematic variation of critical aspects of the contact design. For example, changing only the thickness of the ZnTe:Cu layer affects Cu concentration within the CdTe and CdS layers but does not significantly affect current transport at the ZnTe:Cu/Ti tunneling 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  $\sim 1.57$  eV and  $\sim 1.4$  eV, and that these vary considerably in intensity as different regions of the CdTe device are probed. 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 contacting process. The broad group of peaks centered at  $\sim 1.4$  eV have been ascribed to a deep donor-to-acceptor pair (DDAP) in which the acceptor is believed to have an activation energy of  $\sim 150$  meV. Analysis of CdTe bi-crystals indicates that this peak is not observed prior to typical CdCl<sub>2</sub> treatments. Because CdCl<sub>2</sub> treatments 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 effect of impurity diffusion from the contact region into the CdTe device.

#### 10:30 AM B3.5

Cu K-EDGE EXAFS IN CdTe BEFORE AND AFTER TREATMENT WITH CdCl<sub>2</sub>. Xiangxin Liu and Alvin D. Compaan, Department of Physics and Astronomy, University of Toledo, OH; Nadia Leyarovska, 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 diffuser 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 CdCl<sub>2</sub> vapor treatment in an oxygen ambient—a critical step needed to improve the performance of CdTe thin-film cells—changes the local environment of the Cu in CdTe. Samples were prepared through the same process as completed cells except without the SnO<sub>2</sub> and CdS layers. The 2-3 micron CdTe layers were magnetron sputtered at  $\sim 250^\circ\text{C}$  onto either fused silica 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 13-element Ge detector. We find the Cu absorption spectra to be similar to that of Cu<sub>2</sub>Te in the as-deposited CdTe film but with substantial changes after the vapor CdCl<sub>2</sub> treatment. These differences are interpreted in terms of changes in the near-neighbor environment of the Cu following 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 Visoly-Fisher, Amit Sitt, David Cahen, 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 of the grain surface properties can significantly change the materials carrier concentration and mobility. We used chemical treatments, such as surface etching, oxidation and the adsorption of series of organic molecules with varying dipole moment, and different redox potentials, to study this. FTIR spectroscopy indicates adsorption of molecules with di-carboxylic acid and di-sulfide 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. I-V measurements confirmed this: adsorption of molecules in cells, before back contact formation, changed  $V_{OC}$  and  $J_{SC}$  compared to cells without molecules, indicating the molecules effect on the CdTe / back contact interface. Molecule adsorption after contact formation, via the porous CdTe, mainly changed  $V_{OC}$ , indicating the molecules effect on 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

MAGNETRON SPUTTERING FOR LOW-TEMPERATURE DEPOSITION OF CdTe-BASED PV. Alvin D. Compaan, 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 appears to work particularly well for the heterojunction CdS/CdTe thin-film solar cell in which both components are lightly doped with native defects. Recently we have used magnetron sputtering also to obtain 5 ohms/square ZnO:Al (TCO) films. Using this TCO we have fabricated cells with the structure: aluminosilicate glass/ZnO:Al/CdS/CdTe/metal which had an NREL-confirmed 14.0% efficiency at AM1.5. ( $V_{OC} = 814$  mV,  $J_{SC} = 23.6$  mA/cm<sup>2</sup>, FF = 73%.) We believe that keys to using the ZnO as the TCO in these superstrate cells is to use dry processing and hold all processing steps well below 400 C. First results also will be given for this cell structure on polymer super/substrates. 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 CdS/CdTe SOLAR CELLS. T. Toyama, H. Oda, K. Nakamura, T. Fujihara, K. Shimizu, H. Okamoto, Osaka Univ, Dept of Physical Science, Graduate School of Engineering Science, Toyonaka, JAPAN.

Energy conversion efficiency of 16.5% has been realized in R&D level with the use of CdS/CdTe 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  $\mu$ m, must be reduced. We have proposed low "environmental-load" CdS/CdTe thin-film solar cells with a photovoltaic layer thickness of < 3  $\mu$ m, and already achieved a high conversion efficiency over 13% [2]. For the further improvement of the photovoltaic performances, control of CdS nanostructures including crystallinity of the CdS layer and interdiffusion at CdS/CdTe interface is one of the key issues because it has a large influence on growth of CdTe as well as interdiffusion at CdS/CdTe 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 CdS layers. Also shown here are the electrical properties and photovoltaic performances of the CdS/CdTe solar cells made with the CdS layers with different deposition temperatures. Fabrication methods of the CdS/CdTe solar cells including MOCVD 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/CdTe solar cells with the CdS layer. The solar cells based on the CdS layer with a well preferential-orientation tend to obtain large  $V_{oc}$ , which would be related to change in the ionized charge distribution evaluated by C-V measurements. Finally, we have achieved a conversion efficiency of 14.1% mainly due to an enhancement of  $V_{oc}$ . [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., Sol. Energy. Mat. & Sol. Cells 75 (2003) 185.

#### 11:45 AM B3.9

14% CdS/CdTe THIN FILM CELL WITH ZnO:Al TCO. Akhlesh Gupta and Alvin D. Compaan, 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/CdTe thin-film solar cells. An Al-doped ZnO front contact was deposited on aluminosilicate glass by RF sputtering from a ZnO:Al<sub>2</sub>O<sub>3</sub> target. The ZnO:Al film has ~95% average transmission in the visible spectrum with ~3 ohm/square sheet resistance. The CdS and CdTe thin films were also deposited by RF sputtering and devices were completed with vapor CdCl<sub>2</sub> 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 CdCl<sub>2</sub> treatment. The devices were tested at NREL, and an efficiency of 14% was confirmed, which is a record for an all-sputtered CdS/CdTe solar cell. The ZnO-based cell had JSC of 23.6 mA/cm<sup>2</sup> compared to 20.7 mA/cm<sup>2</sup> for our recent NREL tested 12.6% cell on a commercial soda-lime/SnO<sub>2</sub>:F substrate. Other parameters of the 14% ZnO based cell are: FF = 73.25% and VOC = 814 mV. The improved performance is almost entirely in the higher current due to the better transmission of the glass and the TCO. The devices on both kinds of TCO are being stressed to determine their stability under simulated 1 sun illumination. Comparative stability data will be presented. This work was supported by NREL.

#### SESSION B4: CIGS INTERFACE CHARACTERIZATION

Chair: Uwe Rau

Wednesday Afternoon, April 23, 2003

Salon 10/11 (Marriott)

#### 1:30 PM \*B4.1

SOFT X-RAY SPECTROSCOPY OF BURIED INTERFACES IN Cu(In,Ga)(S,Se)<sub>2</sub>-BASED THIN FILM SOLAR CELLS: BAND ALIGNMENT, INTERMIXING, AND HUMIDITY EFFECTS. C. Heske, L. Weinhardt, U. Groh, M. Morkel, E. Umbach, Experimentelle Physik II, Universität Würzburg, Würzburg, GERMANY.

The main goal of this presentation is to demonstrate the unique capabilities of UV and soft X-ray spectroscopies for the characterization of interfaces in Cu(In,Ga)(S,Se)<sub>2</sub> (CIGSSe) thin film solar cells. We will present recent data compiled with photoelectron spectroscopy (PES), inverse photoemission (IPES), and X-ray emission spectroscopy (XES) to elucidate the electronic and chemical structure of several interfaces in CIGSSe-based devices. Particular focus will be put on CdS/CIGSSe, ZnO/CIGSSe, and ZnO/CdS(/CIGSSe) heterojunctions, especially in view of surface band gaps, the electronic alignment of valence and conduction bands, and the impact of chemical pre-treatment steps and 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 Cu(In,Ga)Se<sub>2</sub>/CDS HETEROJUNCTIONS. Chun-Ming Li, I. Robertson, A. Rockett, Univ. of Illinois, Dept. of Materials Science and Engineering, Urbana, IL.

The microstructure and microchemistry of Cu(In,Ga)Se<sub>2</sub> (CIGS) alloys and CIGS/CdS interfaces 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/CdS heterojunctions. In addition, point defect superstructure ordering as in Cu-Au compounds, dislocations, stacking faults, and twins were examined and the results were correlated with the optical properties and in particular the photoluminescence lifetimes of the materials. In addition, correlations were drawn with device performances. Preliminary results suggest that minority carrier properties are directly correlated with dislocation densities. Both Na and O have been found in grain boundaries along with changes in the cation to anion ratios 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 properties of the materials.

#### 2:15 PM B4.3

CHEMICAL APPROACH TO MANEUVER THE DEFECT DENSITY IN CIGS FILMS. S. Menezes, Y. Li, S.J. Menezes, InterPhases Research, Thousand Oaks, CA.

CIS-alloys are more sensitive to the deposition process and their environment than the CIS film. The higher sensitivity to the ambience is related to their Ga content. Thus a CdS buffer layer is indispensable to the stability of the CIGS device performance. This paper investigates chemical methods to manipulate the defects in CIGS films. The CIGS films were characterized with photoelectrochemical and spectral measurement techniques. The effects of environment, specific chemical solutions and time, were monitored with photocurrent spectral response of the CIGS films in an electrolytic medium. Based on the photocurrent output, specific surface treatment steps were devised for processing the CIGS films. The surface modified films were fabricated into solid-state devices, and device performance was assessed with reference to untreated CIGS films. The results reveal that the CIGS films respond easily to a number of external stimuli with either positive or negative changes in the electro-optic properties. Strong time dependence of the photocurrent suggests a dynamic equilibrium of the point defects in the CIGS film. The results may be interpreted in terms of deep defects from excess Ga and/or creation of Cu vacancies. The results provide new insights into the effects of stoichiometry, deposition method and oxide formation on the defect chemistry of the CIGS film. They provide directions for tailoring surface treatments to engineer the defects in inexpensively deposited CIGS films, without the need for the toxic etchants or buffer layers and the environmental hazards associated with these steps.

#### 2:30 PM B4.4

XAFS INVESTIGATIONS OF THE LOCAL STRUCTURE OF CADMIUM IN CuInSe<sub>2</sub>-BASED MATERIALS. C.-H. Chang, Giang Ma, Oregon State University, Corvallis, OR; S. Yoon and T.J. Anderson, University of Florida, Gainesville, FL; R. Noufi, National Renewable Energy Laboratory, Golden, CO.

High efficiency thin film CuInSe<sub>2</sub> (CIS)-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 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 about the metallurgical junction to chemically modify the near surface region and shift the electrical junction into the CIS. In this model, Cd diffuses into CIS lattice 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 in CIS, a compound forms (e.g., CdSe, or CdIn<sub>x</sub>Se<sub>y</sub>), which produces a graded interface structure [1]. The interdiffusion/chemical reaction proposed in this hypothesis appears to play a crucial role in the determining the device performance. Furthermore, the interplay between the In-rich compounds (e.g. CuIn<sub>3</sub>Se<sub>5</sub>) and the chemical bath solution is suggested to be important to producing high efficiency cells by burying the junction between the CuIn<sub>3</sub>Se<sub>5</sub> and CuInSe<sub>2</sub> layers. In support of this hypothesis, a recent study has demonstrated high efficiency CuInSe<sub>2</sub> cells using only a Cd electrolyte 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 CIS lattice. In this work Cd-K edge XAFS, including XANES and EXAFS, was used to study the Cd atomic local structure on bulk CuInSe<sub>2</sub>, CuIn<sub>3</sub>Se<sub>5</sub>, and thin film Cu(In,Ga)Se<sub>2</sub> samples treated with an aqueous electrolyte solution containing Cd ions. The compounds CdSe and CdIn<sub>2</sub>Se<sub>4</sub> were used as structure references in the data analysis. The EXAFS results have shown that the nearest Cd atom neighbors in bulk CdSe and CdIn<sub>2</sub>Se<sub>4</sub> are almost identical. The Cd partial electrolyte treated CuInSe<sub>2</sub> and CuIn<sub>3</sub>Se<sub>5</sub> samples, however, have very different local arrangement. A simple 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 near surface region with a Cd partial electrolyte treatment. 1. K. Ramanathan, H. Wiesner, S. Asher, D. Niles, R.N. Bhattacharya, J. Keane, M.A. Contreras, and R. Noufi, Proc. 2nd WCPEC, Vienna, pp. 477-481 (1998). 2. J. Kessler, K.O. Velthaus, M. Ruckh, R. Laichinger, H.W. Schock, Proc. 6th Int. PVSEC, New Delhi, p. 1005 (1994).

#### 2:45 PM B4.5

ANALYSIS OF ZINC COMPOUND BUFFER LAYERS IN Cu(In,Ga)(S,Se)<sub>2</sub> THIN FILM SOLAR CELLS BY SYNCHROTRON-BASED SOFT X-RAY SPECTROSCOPY. I. Lauer mann, M. Bär, A. Ennaoui, U. Fiedeler, Ch-H. Fischer, A. Grimm, I. Kötschau, M. Ch. Lux-Steiner, J. Reichardt, B.R. Sankapal, S. Siebentritt, S. Sokoll Hahn-Meitner-Institut, Berlin, GERMANY; L. Weinhardt, O. Fuchs, C. Heske, Experimentelle Physik II, Universität Würzburg, GERMANY; C. Jung and W. Gudat, BESSY, Berlin, GERMANY; F. Karg and T.P. Niesen, Shell Solar, München, GERMANY.

Objective Zinc-based buffer layers on Cu(In,Ga)(S,Se)<sub>2</sub> absorber materials (CIGSSE) have yielded thin film solar cell efficiencies comparable to or even higher than standard CdS/CIGSSE cells. However, little is known about surface and interface properties of these novel buffer layers. In this contribution we characterize the specific chemical environment at the interface using X-ray Emission (XES) and Photoelectron Spectroscopy (PES) in a complementary way. Method The use of X-ray emission spectroscopy (XES) with synchrotron radiation for the analysis of buried interfaces in CIGSSE solar cells has previously been demonstrated [1]. In order to examine Zn-containing buffer layers deposited on CIGSSE absorbers, we use an experimental station which was recently commissioned at the BESSY synchrotron radiation source in Berlin. It consists of several custom designed UHV-chambers which allow a direct vacuum and/or inert-gas transfer of layers freshly deposited with wet-chemical methods or magnetron sputtering. Results The deposition of ZnSe-buffer layers on CIGSSE by MOCVD leads to an attenuation of the L<sub>2,3</sub>-peak in XES spectra of sulfur compared to the absorber surface before buffer layer deposition (as expected). However, the spectra also show additional features, which we assign to the formation of Zn-S bonds at the buffer/absorber interface. In addition, we compare samples with different buffer-layer thickness. Similar spectral features are also found in S-XES spectra of ZnS buffer-layers deposited on CIGSSE absorbers by chemical bath deposition. Samples prepared using different buffer layer deposition conditions and times are compared. In studying the ZnO/CIGSSE interface, we find pronounced changes between ZnO deposited by an ion layer gas reaction (ILGAR) and sputtered i-ZnO. Only in the S-XES spectra of the former we observe spectral features which can be ascribed to the formation of sulfur-oxygen bonds, most likely in a sulfate species. 1. Heske, C., et al., phys. stat. sol., 2001. 187(1): p. 13-24, and references therein.

#### 3:30 PM DISCUSSION I

CONTACTS TO POLYCRYSTALLINE SOLAR CELLS: ARE THEY REALLY A PROBLEM? Moderated by [David Cahen](#), Weizmann Institute of Science.

#### SESSION B5: POSTER SESSION MATERIAL AND DEVICE CHARACTERIZATION

Chair: Rommel Noufi  
Wednesday Evening, April 23, 2003  
8:00 PM  
Salon 1-7 (Marriott)

#### B5.1

MICROSTRUCTURE AND OTHER PROPERTIES OF CVD-GROWN CuGaSe<sub>2</sub> THIN FILMS AND THIN FILM SOLAR CELLS. D. Fuertes Marron, A. Meeder, Th. Glatzel, U. Bloeck, P. Schubert-Bischoff, R. Wuerz, S.M. Babu, Th. Schedel-Niedrig, M. Ch. Lux-Steiner, Hahn-Meitner-Institut, GERMANY; L. Weinhardt, C. Heske, E. Umbach, Experimentelle Physik II, University of Würzburg, GERMANY.

The microstructure and electronic structure of interfaces involved in CVD-grown CuGaSe<sub>2</sub>(CGSe) based thin film solar cells as well as the surface and bulk related properties of CGSe thin absorber films have been investigated. The absorber films were grown in two stages by means of an open-tube chemical vapor deposition (CVD) process [1]. High-resolution transmission electron microscopy (HRTEM) combined with scanning energy dispersive X-ray (EDX) analysis have shown microstructural aspects related to the CVD-deposition technique of the absorber films, like the presence of an interfacial MoSe<sub>2</sub> layer between back contact and absorber, and directly linked to the poor PV performance of devices based on Cu-rich compositions [2]. Complementary information on the electronic structure has been imaged of the complete solar cell cross section by using Kelvin probe force microscopy (KPFM) [3]. Device grade CVD-CGSe thin films reveal a nearly stoichiometric chemical bulk composition while, on the other hand, the surface/near-surface chemical composition is Cu-poor, pointing towards a highly non-stoichiometric surface layer. Furthermore, an increase of the bulk band energy gap has been found for the surface/near-surface region by means of UV- and inverse photoelectron spectroscopy (UPS and IPES, resp.), suggesting the presence of a defect-rich surface/near-surface phase and a defect-poor bulk phase [4]. In this paper, examples of novel lift-off CVD-thin film absorber solar cells [5] will also be presented. [1] German Patent DE 198 55 021 C1. [2] D. Fuertes Marrón et al., Thin Solid Films (in press) [3] Th. Glatzel et al., Appl. Phys. Lett., 81 (2002) 2017. [4] A. Meeder et al., Proc. 13th ICTMC 2002 [5] German Patent pending.

#### B5.2

DEFECT SPECTRA OF EPITAXIAL Cu(In,Ga)Se<sub>2</sub> GROWN BY MOVPE. N. Rega, J. Albert, I. Beckers, J. Beckmann, S. Siebentritt, M. Lux-Steiner, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

The chalcopyrite Cu(In,Ga)Se<sub>2</sub> is a promising material for photovoltaics. It is a semiconducting compound, which is doped by intrinsic defects such as vacancies, interstitials or antisites. Therefore growth parameters (composition, temperature, etc.) influence the doping and thus the conduction type and density of carriers. To study the intrinsic defect structure, detailed photoluminescence (PL) measurements of epitaxial Cu(In,Ga)Se<sub>2</sub> grown by metalorganic vapor phase epitaxy (MOVPE) are performed. There are two distinct emissions with an energy difference about 50-60meV just below the band gap. The influence of the Cu content and the Ga/(In+Ga) ratio is investigated. Temperature and excitation power dependent measurements are performed to explore the origin of the PL emissions. As shown in our former work the defect spectra of the extreme compositions, CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>, contain each two acceptors, with the deeper one dominating for higher Cu-excess, and one shallow donor. The results are also compared to studies on polycrystalline, epitaxial and single crystal Cu(In,Ga)Se<sub>2</sub> grown by different methods. For our investigation epitaxial Cu(In,Ga)Se<sub>2</sub> are grown on GaAs (001) wafers using MOVPE. The growth temperature is varied between 500°C and 570°C, depending on the Ga/(Ga+In) ratio, aimed at. The growth rate is rather slow, about 50-100 nm/h. The composition of the films is given by the flux ratios of the different precursors and measured by energy dispersive X-Ray analysis (EDX), X-Ray Fluorescence Analysis (XRF) and XRD. Cu(In,Ga)Se<sub>2</sub> thin films with a special attention to a Ga/(Ga+In) ratio around 30% as used in best and commercially available solar cells are investigated. The epitaxial growth is verified by X-Ray diffraction (XRD), electron channeling (ECP) and transmission electron microscopy (TEM).

### B5.3

HIGH RESOLUTION CHARACTERIZATION OF A SINGLE GRAIN BOUNDARY AND THE VARIOUS LAYERS IN CdTe/CdS SOLAR CELLS. Iris Visoly-Fisher, Sidney R. Cohen, David Cahen, 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 polycrystalline electronic materials, notwithstanding their strong topographical variations. SCM shows a barrier for hole transport across CdTe grain boundaries, with some variation in barrier height between different 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. CdTe films that did *not* receive CdCl<sub>2</sub> treatment (commonly used in CdS/CdTe solar cell manufacture) showed no difference in SCM signal between grain surface 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)-SnO<sub>2</sub> layer were found to be similar electronically. This explains the role of the HR-SnO<sub>2</sub> 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, Veeco-Europe 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 Cai, Jingquan Zhang, Lili Wu, Wei Li, Wei Cai, Jiagui Zheng, Bing Li, Zhi Lei, Qiang Yan, Dept of Materials Science, Sichuan University, Chengdu, CHINA.

Recently, A.Luque et al and M.Green have proposed and discussed the concept of multi-band photovoltaic cells (MBPVC). They have shown efficiency advantages if a third band is included into the inversion 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 MBPVC, considering the direct band gap with different wideness of the semiconductors. For the impurity band MBPVC, the minimal optical losses of some elected compound semiconductors of wide band gap, such as ZnTe, CdS, ZnSe, CdO, TiO<sub>2</sub>, ZnO and In<sub>2</sub>O<sub>3</sub>, are calculated in the conditions of AM0 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 In<sub>2</sub>O<sub>3</sub>, which are much lower than 52% for standard crystal Si solar cells. The heat balance process of electrons transition through the impurity band and carriers transportation in the third band have been investigated, and the minimal state density in impurity band and concentrations of doping atoms have been estimated. In experiments, un-doped and doped ZnTe and ZnSe polycrystalline films have been deposited by co-evaporation. For multiples quantum well MBPVC, CdTe/ZnTe, ZnSe/CdSe and ZnS/CdS multiple quantum wells are interesting due to their small valence band or conductance band offsets which are 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 MBPVC, the results have been discussed.

### B5.5

PHOTOLUMINESCENCE EXCITATION STUDIES OF CuGaSe<sub>2</sub>. I.E. Beckers, S. Siebentritt, and M. Ch. Lux-Steiner, Hahn-Meitner-Institut, Berlin, GERMANY; Mt. Wagner, Dept. of Physics and Measurement Technology, Linköping University, Linköping, SWEDEN; R. Heitz and A. Hoffmann, Technische Universität Berlin, GERMANY.

Photoluminescence excitation (PLE) spectroscopy at liquid-helium temperature is used to study CuGaSe<sub>2</sub> epitaxial films grown by metal organic chemical vapor deposition (MOCVD). The growth conditions are varied to obtain compositions with [Cu]/[Ga] = 0.8 - 1.2. The PL excitation spectra for the two donor-acceptor transitions and their phonon replica show a peak at 1.71 eV for Cu rich films, which can be correlated to the excitonic absorption. This peak vanishes for films grown by Ga excess. For increasing Ga excess an increasing overlap can be observed between the onset of the PLE signal 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 Ga-rich material by potential fluctuations [1]. It has been shown that net charge carrier 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 Ga rich CuGaSe<sub>2</sub>, that disappear for material with a lower degree of compensation (Cu rich CuGaSe<sub>2</sub>) and high laser excitation power. [1] A. Bauknecht, S. Siebentritt, J. Albert, and M. Ch. Lux-Steiner, J. Appl. Phys., 89 (2001) 4391. [2] S. Siebentritt, A. Bauknecht, A. Gerhard, U. Fiedeler, T. Kampschulte, S. Schuler, W. Harneit, S. Brehme, J. Albert, and M. Ch. Lux-Steiner, Solar Energy Mater. Sol. Cells, 67 (2001) 129.

### B5.6

INFILTRATION OF NANOPOROUS TiO<sub>2</sub> WITH CuInS<sub>2</sub> USING ATOMIC LAYER DEPOSITION: TOWARDS A 3D SOLAR CELL. Marian Nanu, Laboratory for Inorganic Chemistry, Faculty of Applied Sciences, Delft University of Technology, Delft, THE NETHERLANDS; Catelijne Grasso, Electronics and Information Systems, Ghent University, Ghent, BELGIUM; Frank Lenzmann, ECN Solar Energy, Energy Research Center of The Netherlands, Petten, THE NETHERLANDS; Albert Goossens and Joop Schoonman, Laboratory for Inorganic Chemistry, Faculty of Applied Sciences, Delft University of Technology, Delft, THE NETHERLANDS.

This paper deals with the infiltration of nanoporous TiO<sub>2</sub> with CuInS<sub>2</sub> using Atomic Layer Deposition (ALD). This type of nanocomposite, in which a wide bandgap n-type semiconducting oxide and a p-type visible light sensitive semiconductor are mixed on a nanometer scale, is 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 TiO<sub>2</sub> (~100 nm) is applied onto TCO-glass (SnO<sub>2</sub>:F). On top of this, a 2 μm thick nanoporous TiO<sub>2</sub> film is applied with primary particles between 10 and 50 nm in diameter. Next these substrates are infiltrated with CuInS<sub>2</sub> using ALD. The process conditions are: 2 mbar reactor pressure, temperature between 350 and 500°C, and CuCl, InCl<sub>3</sub>, and H<sub>2</sub>S as precursors. The influence of process conditions on the structure and the electrical properties of CuInS<sub>2</sub> 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 H<sub>2</sub>S (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 TiO<sub>2</sub> and CuInS<sub>2</sub> is necessary. There are several reasons for this improvement. The alignment between the conduction bands of TiO<sub>2</sub> and CuInS<sub>2</sub> leads to significant energy loss. Also the back flow of current leads to a poor quantum efficiency. Copper diffusion out of CuInS<sub>2</sub> into the TiO<sub>2</sub> is also a problem as the deposition temperature must be above 350°C. A well-chosen buffer film can deal with these issues. Present investigations focus on application of In<sub>2</sub>S<sub>3</sub> and CdS, which are both deposited by ALD. A tunnel barrier can also improve the performance of the device. When a 1-2 nm thin Al<sub>2</sub>O<sub>3</sub> films is applied as buffer the Voc and the fill factor improve significantly. Future investigations will focus on modeling of ETA-type solar cells with CuInS<sub>2</sub> as absorber in order to allow stepwise improvement of the energy conversion efficiency.

### B5.7

PHOTOLUMINESCENCE FATIGUE IN CdTe PHOTOVOLTAICS. Diana Shvydka, C. Verzella 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 chalcogenide glasses. In our work it was studied as a function of time at different laser beam intensities and temperatures. Both contact-free and metallized 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 percent in two 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 fatigue saturates. We have worked out a simple analytical model that fits 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. Compaan, University of Toledo, Department of Physics and Astronomy, Toledo, OH.

We have performed electro-modulated photoluminescence (EMPL)[1] on polycrystalline thin-film CdS/CdTe solar cells, excited with HeNe and Ar lasers. The cells were fabricated from small-grain films produced by magnetron sputtering (CdS thickness = 0.13  $\mu\text{m}$ , CdTe thickness = 2.3  $\mu\text{m}$ ) and larger-grain films from vapor-transport deposition with somewhat thicker layers. The effects of light soak on the EMPL from these cells has also been studied. A typical peak-to-peak modulation voltage was 150 mV. EMPL peaks as a function of d.c. offset bias were similar in shape to that of the first derivative of PL intensities as a function of offset bias, as expected. The 1.95 eV light excites EMPL from the CdTe bandgap, while argon laser-excited EMPL 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 EMPL spectra 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-excited PL which does not respond to the modulation. This work has been supported by NREL. [1] K. Nakamura, M. Gotoh, T. Fujihara, T. Toyama, and H. Okamoto, Materials Research Society Symposium Proceedings Vol 668 (2001) [2] Diana Shvydka, A.D. Compaan, V. G. Karpov, presented at IEEE PVSC 2002, New Orleans, Louisiana.

**B5.9**  
TEMPERATURE-DEPENDENT ELECTROLUMINESCENCE FROM CdTe/CdS SOLAR CELLS. K.J. Price<sup>†</sup>, L. Gorrell, A. Vasko, A.D. Compaan, University of Toledo, Department of Physics and Astronomy, Toledo, OH. <sup>†</sup>Summer Faculty Scholar from Morehead State University, Morehead, KY.

Electroluminescence (EL) from polycrystalline CdTe/CdS solar cells was studied over the temperature range  $\approx 50\text{ C}$  to  $50\text{ C}$ . We are able to observe above-background EL at forward current densities as low as  $3\text{ mA/cm}^2$ , allowing us to explore the EL behavior at 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,  $EL \sim I^b$ , where  $I$  is the forward current density and  $b$  is near 2. The exact value of  $b$  varies with temperature and from sample to sample. The relationship of EL to cell performance before and after stressing will be presented. This work supported in part by a Faculty Summer Research Grant from Morehead State University, the NSF REU program, and NREL.

**B5.10**  
DEVELOPMENT OF ELECTROLUMINESCENCE IMAGING CHARACTERIZATION FOR CdS/CdTe SOLAR CELLS. S.D. Feldman, T.R. Ohno, V. Kaydanov, and R.T. Collins, Colorado School of Mines, Dept of Physics, Golden, CO.

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 carrier recombination is collected with a CCD camera. Because EL intensity depends upon radiative vs. non-radiative recombination lifetimes, it provides insight into material quality. Spatial resolution is a key benefit of EL as it provides insight into the non-uniformities of polycrystalline CdTe. At high magnification the resolution is diffraction 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 data 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 means that EL can be a non-destructive probe. 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 in many cases. Changes in EL become 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**  
CHARACTERISATION OF DEEP DEFECTS IN CdS/CdTe THIN FILM SOLAR CELLS USING DEEP LEVEL TRANSIENT SPECTROSCOPY. Jorg Versluys, Paul Clauws, Ghent University, Department of Solid State Sciences, Gent, BELGIUM.

The presence of deep defect levels in thin film solar cells can highly affect the characteristics of the photovoltaic 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 320K revealed semi-shallow and mid-gap majority traps. These mid-gap 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 mid-gap traps can be characterised completely. Optical DLTS has revealed the presence of minority carrier traps. Laserdiodes 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), where 635nm only excites the CdS/CdTe interface because of the high absorption. A complete characterisation 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.

**B5.12**  
CHEMICAL AND ELECTRONIC PROPERTIES OF WELL DEFINED Cu(In,Ga)Se<sub>2</sub>/CdS INTERFACES. B. Canava, J. Vignerot, A. Etcheberry, Institut Lavoisier (IREM), Université de Versailles, Versailles, FRANCE; D. Guimard, J.F. Guillemoles, D. Lincot, Laboratoire de Electrochimie et de Chimie Analytique, ENSCP, Paris, FRANCE; S. Ould Saad, Z. Djebbour, D. Mencaraglia, Laboratoire de Genie Electrique de Paris, Gif-sur-Yvette, FRANCE.

Oxidative etches, and specially those based on bromine water mixtures, enable preparation of planar, smooth, specular Cu(In,Ga)Se<sub>2</sub> 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<sup>-</sup>) or of oxides (HCl, NH<sub>3</sub>), or both. First, we will present an overview the Cu(In,Ga)Se<sub>2</sub> surface composition after such etches, and where it was possible (e.g. with Br), we will present a model of the etch mechanisms and kinetics. We will also compare those surface composition to the bulk ones and to those observed in vacuum just after film growth of coevaporated samples. These well defined surfaces 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 CIGS/CdS interface will be presented and discussed.

**B5.13**  
Transferred to B9.3

**B5.14**  
THE LINEAR COMBINATORIAL STUDY ON CdO-SnO<sub>2</sub> TERNARY COMPOUNDS. Xiaonan Li, Tim Gessert, 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 cadmium oxide (CdO)-tin oxide (SnO<sub>2</sub>) 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 spectrum. As reaction gas further flowed down 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 Cd<sub>2</sub>SnO<sub>4</sub>. When Cd to Sn ratio close to 2/1, the films were dominated by cubic spinel Cd<sub>2</sub>SnO<sub>4</sub> structure. As Sn concentrations continue to increase, the films became amorphous and stayed as amorphous structure for a very wide composition range. Finally, the tetragonal SnO<sub>2</sub> 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 compositional range, the Hall mobility was low. The carrier concentration of the films varied from the high  $10^{17}\text{ cm}^{-3}$  to the middle of  $10^{20}\text{ cm}^{-3}$ . The optical band gap varied from 2.75 eV to 3.65 eV due to the changes of composition and carrier concentration.

#### **B5.15**

**ALTERNATE CONFIGURATION AND METHOD FOR FABRICATING A FLEXIBLE CIS PV CELL.** S. Menezes, Y. Li, S.J. Menezes, InterPhases Research, Thousand Oaks, CA; D. Albin and B. To, 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 CIGS 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*-copper 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 photoelectrochemical 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 of CIS films. They lead to a simple four-step method for roll-to-roll PV cell fabrication.

#### **B5.16**

**TRANSPARENT CONDUCTING ZINC OXIDE FILMS PREPARED BY BIPOLAR PULSED BIASING TECHNIQUE.** H.W. 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 temperature as low as 80°C. An off-plane double bend filter is used to remove macroparticles produced in the arc process; the obtained films are uniform over large area. The growth rate can reach 80nm/min. The influence of growth parameters on film properties, such as transmittance, stress and conductivity is studied systematically. The films were characterized by XRD, Raman, AFM and TEM. The ZnO films are highly (002) preferred oriented. Substrate bias was found to play a key role for deposition of highly conductive films at low temperature. The resistivity of the films prepared with and without bias is  $5 \times 10^{-4}\Omega\text{ cm}$  and  $6 \times 10^{-3}\Omega\text{ cm}$  respectively. To overcome the charging problem of insulating substrate, bipolar bias with different frequencies is used. At substrate temperature of 100°C, films were deposited with bipolar bias of 200V and the ratio of positive pulse duration to negative pulse duration at 90 percent, and these films exhibit transmittance above 80 percent and resistivity as low as  $5 \times 10^{-4}\Omega\text{ cm}$  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.

#### **B5.17**

**DEFECT ESTIMATION OF  $\text{CuGaSe}_2$  ON PHOTOLUMINESCENCE SPECTRUM TRANSFORMATION CAUSED BY GAS ANNEALING.** A. Yamada, A. Nishio, P. Fons, H. Shibata, S. Niki, National Institutes of Advanced Industrial Science and Technology, Tsukuba, JAPAN; H. Nakanishi, Science University of Tokyo, Noda, JAPAN.

$\text{CuGaSe}_2$  as the end material of  $\text{Cu}(\text{InGa})\text{Se}_2$  alloy system is worthy to be investigated for advancement of the high-voltage solar cell performance. Many studies have been done on  $\text{CuGaSe}_2$  defect characterization 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 then photoluminescence (PL) spectrum analysis was adopted for characterization 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 gaseous atmospheres. Epitaxial  $\text{CuGaSe}_2$  films  $\sim 0.6\ \mu\text{m}$  thick were grown on (001)-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 (EPMA) using 7 kV accelerating voltage were from 1.1 to 1.4 due to existence of a Cu-Se 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  $\text{CuGaSe}_2$ ; [Cu]/[Ga] ratio was close to unity as 0.98-1.00. KCN-etched samples were annealed at a temperature range from 300°C to 450°C in various atmospheres as argon, selenium and oxygen with the intension of driving defects. Annealing of the samples changed greatly the PL spectra indicating that it had caused the defects not only to move but also to create and/or to extinguish. Coordinated 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.

#### **B5.18**

**PREPARATION AND CHARACTERIZATION OF Cu-Ga-Se FILMS OF ORDERED VACANCY COMPOUND.** Shiro Nishiwaki, Susanne Siebentritt, Martha Ch. Lux-Steiner, Hahn-Meitner-Institute Berlin, Berlin, GERMANY.

Cu-poor surface layer plays important role in  $\text{Cu}(\text{In,Ga})\text{Se}_2$  solar cells. In general, it is believed that the surface layer has an ordered vacancy structure and wider band gap than the bulk part. However, the surface layer with the different structure from the bulk has not been observed so far. In this contribution, Cu-Ga-Se films with compositions in the pseudo-binary system of  $\text{Cu}_2\text{Se-Ga}_2\text{Se}_3$  were prepared under various conditions by thermal co-deposition and characterized. The phases in the films obtained were identified by x-ray diffraction. It was found that, depending not only on the composition but also on the substrate and preparation conditions, phases with different atomic orderings were formed. The film with the compositions of  $\text{CuGa}_3\text{Se}_5$  prepared on the Na free glass showed vague super lattice peaks that belong to the stannite structure. On the other hand, the film prepared on soda-lime glass in the same run clearly showed the stannite structure. This probably suggests that Na diffuses from the soda-lime glass to the Cu-Ga-Se film and assists the ordering of atoms and vacancies. Na might preferably occupy one of the 4-coordination sites instead of Cu in the crystal structure. Furthermore, it was shown that, with the deposition of Cu and Se onto the  $\text{Ga}_2\text{Se}_3$  film prepared on Na free glass, a vertically inhomogeneous film was prepared: a bottom layer with a sphalerite like structure with vacancies, i.e. the stannite structure, and the top layer with an all sites occupied structure, i.e. chalcopyrite. The films were characterized by x-ray photoelectron spectroscopy and the results were discussed based on the composition and crystal structure in the films. Information on dominant phase transitions taking place during the formation of the chalcopyrite structure was gained.

#### **B5.19**

**CHARACTERIZATION OF TRANSPARENT AND CONDUCTIVE ZnO:Ga THIN FILMS PRODUCED BY RF SPUTTERING AT ROOM TEMPERATURE.** E. Fortunato, V. Assuncio, A. Marques, H. Iguas, 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  $10^{-3}\ \Omega\text{-cm}$  have been widely used as electrodes for optoelectronic devices. Most of the previous research on TCOs has been focused on ITO and FTO. However, TCO films based on zinc oxide are taking a great impact 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 covalent bond lengths of Ga-O and Zn-O are estimated to be 1.92 and 1.97 Å, respectively. The slightly smaller bond length of Ga-O than that of Zn-O is an advantage since it allows to minimize the deformation 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 ( $1.9 \times 10^{-4}\ \Omega\text{-cm}$ ) was obtained for an rf power density of 9 W/cm<sup>2</sup> at RT. The films are polycrystalline with a hexagonal structure and a strong crystallographic c-axis orientation (002). The films present an overall transmittance in the visible spectra of about 85%. The low resistivity, accomplished with a high growth rate deposited at RT, enables the deposition of these films onto polymeric substrates for flexible applications.

#### **B5.20**

**EXPLANATION OF LIGHT/DARK SUPERPOSITION FAILURE IN CIGS SOLAR CELLS.** Markus Gloeckler, 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) curves, which generally becomes more pronounced at lower temperatures. J-V measurements under red light may also show an additional distortion, known historically as the "red kink". The proposed explanation is that a secondary barrier can result from the conduction band offset between CIGS and the commonly employed CdS window layer. This barrier acts similarly like a second diode with the same polarity and in series with the primary photodiode. The barrier is shown to be modified by photoinduced modification of trap occupancy in the CdS layer, hence creating a voltage shift between dark and light conditions. 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 sub-band-gap illumination. The latter point argues strongly that the CdS trap occupancy is integral to superposition failure. Previous explanations of non-superposition have also included barrier modification. They have generally, however, postulated a dense charge layer at the CdS/CIGS interface, and have not addressed the transition in J-V behavior with photons above and below the CdS gap. This research was supported by the U.S. National Renewable Energy Laboratory.

#### **B5.21**

**HIGH FLUX CHARACTERIZATION OF CI(G)S SOLAR CELLS.**  
J.S. Ward, F.S. Hasoon, D.L. Young, T.J. Coutts, R. Noufi, A. Duda, B. Keyes, S. Johnson, and J. Kiehl, National Renewable Energy Laboratory, Golden, CO.

Cu(In,Ga)Se<sub>2</sub> is one of the more 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 reporting conditions. Recently, these devices have been investigated for their use in solar concentrator systems. Under 14 suns CI(G)S 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 CI(G)S devices are fabricated on soda lime glass substrates. Unfortunately, the poor thermal conductivity of glass makes this an impractical approach for the fabrication of concentrator cells where thermal management is an important issue. Therefore we have begun fabricating these devices on stainless steel substrates. These devices have lower one-sun conversion efficiencies, 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 life-time 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.

#### **B5.22**

**VAPOR TRANSPORT DEPOSITION AND CHARACTERIZATION OF POLYCRYSTALLINE CDTE SOLAR ADSORBERS.**  
James M. Kestner, Sarah McElvain, and Colin A. Wolden, Department of Chemical Engineering; Stephen Kelly and Tim R. Ohno, Physics Department, Colorado School of Mines, Golden, CO; Lawrence M. Woods and Rosine Ribelin, 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 for the high rate synthesis of polycrystalline cadmium telluride. The VTD system employs a choked flow 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 CdTe 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 variables investigated include source pressure, substrate pressure, source temperature, substrate 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),

capacitance-voltage (CV), and quantum efficiency (QE) analyses. The effect of various substrate modifications was also examined. Window layer (CdS) thickness was varied from 500 nm to less than 200 nm. The influence of high resistance buffer layers was investigated as a function of thickness and resistivity. In this paper we describe the process-property-performance relationships for this system.

#### **B5.23**

**ELECTRONIC AND CHEMICAL PHENOMENA AT Cu(In,Ga)Se<sub>2</sub>/CdS HETEROJUNCTIONS AND THEIR IMPLICATIONS FOR PHOTOVOLTAIC DEVICES.** Angus Rockett, Univ of Illinois, Dept of Materials Science and Engineering, Urbana, IL.

The chemical composition and electronic properties of Cu(In,Ga)Se<sub>2</sub> (CIGS) alloys and CIGS/CdS interfaces are becoming increasingly well known. Experimental data has now reached the point at which relatively reliable device models can be obtained. This paper reviews recent results on single crystal and polycrystalline materials and devices and argues for specific values or ranges of values for key parameters needed for device modeling. The paper then applies these parameters using the AMPS computer code developed by S. Fonash et al. It is argued from the simulation results that devices based on high Ga content alloys are limited primarily by failure to dope the surface of CuGaSe<sub>2</sub> sufficiently n-type, resulting in pronounced minority carrier recombination at the heterojunction. The effect of observed defect states in the energy gap is considered, in particular with respect to pinning of the Fermi level near the heterojunction. By contrast, devices based on high In-content alloys show strong surface inversion in CIGS/CdS heterojunctions, which passivate intrinsic defects at the junction and unpin the surface. It is further argued that the primary reason for failure of devices based on single crystal epitaxial layers is due to relatively poor electron lifetime properties, and on minority carrier lifetimes in general. Microstructural and microchemical analyses of device layers will be incorporated into the above arguments in support of the model results.

#### **B5.24**

**TRAP FILLING PROBLEMS IN PHOTOVOLTAIC MATERIALS: CONSEQUENCES FOR DEFECT MEASUREMENTS.**  
David L. Young and Richard S. Crandall, National Renewable Energy Laboratory, Golden, CO.

We find that an inability to saturate the capacitance signal in Cu(In,Ga)Se<sub>2</sub> (CIGS) thin-film solar cells with a short-time, trap-filling, voltage pulse precludes measuring capture cross-sections and defect densities by conventional deep level transient spectroscopy. We subject CIGS solar cells to voltage filling pulses of variable length (10  $\mu$ s - 1,000 s) and record the capacitance transient signal over several decades of time (10  $\mu$ s - 10,000 s). The amplitude, A, of the initial capacitance transient, after the voltage pulse, increases logarithmically with pulse time. A similar trend was seen in a-Si [1]. We fit the pulse time dependence of A to a trap-filling theory [1] based on a model of charging mesoscopic regions that further reduce charge trapping. We can determine the size of these mesoscopic regions by combining the fit to the data with an independent measure of the total defect density using drive-level capacitance profiling. The size of these regions correlates with scanning electron microscopy-determined film grain size. [1] R.S. Crandall, Journal of Electronic Materials 9, 713-726 (1980).

#### **B5.25**

**EVOLUTION OF ELECTRONIC PROPERTIES OF Cu(In,Ga)Se<sub>2</sub> (CIGS)-BASED SOLAR CELLS DURING A 3-STAGE GROWTH PROCESS.** Jehad A. AbuShama, S. Johnston, R. Ahrenkiel, R.S. Crandall, D.L. Young, and R. Noufi, National Renewable Energy Laboratory, Golden, CO.

We investigated the electronic properties of ZnO/CdS/CIGS /Mo/SLG polycrystalline thin-film solar cells with compositions ranging from Cu-rich to In-rich by deep-level transient spectroscopy (DLTS) and capacitance-voltage (C-V) measurements. This compositional change represents the evolution of the film during growth by the three-stage process. Two sets (four samples each) of CIGS thin films were prepared with Ga/(In+Ga) ratios of  $\sim$ 0.3 (low Ga) and  $\sim$ 0.6 (high Ga). The Cu/(In+Ga) ratio ranges from 1.24 (Cu-rich) to 0.88 (In(Ga)-rich). The films were treated with NaCN to remove the Cu<sub>2-x</sub>Se phase where needed. We collected DLTS data with a Sula DLTS Spectrometer using a 1 MHz frequency and an 80-300 K temperature range. All C-V measurements were collected with an HP 4274A multi-frequency LCR meter at room temperature using a frequency of 100 kHz. Key results include: (1) For low-Ga devices, DLTS data show that acceptor-like traps dominate in samples where CIGS grains do not go through the Cu-rich to In(Ga)-rich transition, whereas donor-like traps dominate in In(Ga)-rich samples. Therefore, we see a clear transformation of defects from acceptor-like to donor-like traps. The activation energies of these traps range from

0.12 to 0.63 eV. We also observed that NaCN treatment eliminates a deep minority trap in the In(Ga)-rich devices; (2) For high-Ga devices, only majority-carrier traps were detected. These traps again range from shallow to deep; (3) The carrier concentration (from C-V) decreases as the CIGS becomes more In(Ga)-rich; (4) All our data for low- and high-Ga devices show that the charge-carrier emission rate obeys the Meyer-Neldel 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.

#### **B5.26**

INTEGRATION OF CHEMICALLY DEPOSITED SnS THIN FILMS INTO PHOTOVOLTAIC STRUCTURES. M.T.S. Nair, P.K. Nair, J. Campos, O. Gomezdaza, A. Sanchez, Universidad Nacional Autónoma de México, Centro de Investigación en Energía, Temixco, Morelos, MEXICO.

SnS thin films of thickness up to 1000 nm is deposited from chemical baths containing tin(II) chloride and thioacetamide. These films are slightly p-type and photoconductive. By heating in air for 10-60 min at 400°C to 500°C, the films are converted to SnO<sub>2-x</sub>, with x decreasing from the substrate towards the film surface, thereby making a graded conductivity film. By depositing again an SnS thin film on such an SnO<sub>2-x</sub> thin film, heterostructures of the type, (n)SnO<sub>2-x</sub>-(i)SnO<sub>2</sub>-(p)SnS are formed. With the addition of a chemically deposited top layer of Cu<sub>x</sub>S thin film on the SnS thin film, photovoltaic structures are produced. Optimization of the film thickness and process condition to improve the open-circuit voltage above 400 mV is currently underway.

#### **B5.27**

OPTIMIZATION AND CHARACTERIZATION OF A PHOTOVOLTAIC DEVICE STRUCTURE UTILIZING PHOTOINDUCED BALLISTIC ELECTRON CAPTURE.

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; Galen Stucky, Univ California Santa Barbara, Dept of Chemistry and 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 (10nm) layer of Au deposited on anodically formed TiO<sub>2</sub> to form a Schottky barrier. Separation of the primary photosensitive subsystem and the system for charge/energy storage in the device separates the tasks allowing flexibility in optimization and fabrication. Electron-hole recombination in the thin semiconductor is eliminated, by restricting charges to the majority carriers, and band gap per se is no longer a constraint. Barrier height (photovoltage) and photosensitization for the solar spectrum are independently controllable. Methods for optimization of the Au and TiO<sub>2</sub> interfaces and dye sensitization of the surface have been developed. Under simulated AM1.5 illumination (100 mW/cm<sup>2</sup>), devices presently show open-circuit voltages of 0.34 V and short-circuit current densities of 0.12 mA/cm<sup>2</sup>, with fill factor of 0.58. Complete I-V, C-V, and electro-optic characterizations of fully fabricated solar cell devices of varying metal layer thickness, surface sensitization, and semiconductor preparation have been performed.

#### **B5.28**

IN-SITU CONTROL OF NANOSCALE TEXTURE FORMATION DURING DEPOSITION OF ZnO LAYERS FOR LIGHT TRAPPING IN THIN FILM SOLAR CELLS. Renato P. Camata, 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 used extensively, there 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 in part due to the generation of a broad range of particulates during PLD. Although these particulates 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 particulates 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 direct in-situ measurements on gas-suspended nano- and submicron particles during materials 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 KrF pulsed laser deposition of Zinc oxide (ZnO) films with sub-micron texture. ZnO targets were ablated in

inert gas atmosphere with background pressures in the 70-400 Torr range and laser fluences of 1-5 J/cm<sup>2</sup>. In-situ measurements reveal that during ZnO deposition the gas-suspended nanoparticle 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/cm<sup>2</sup>), the population is dominated by 5-10 nm nanoparticles. For fluences above 3 J/cm<sup>2</sup> 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

Chairs: Yanfa Yan and Tokio Nakada  
Thursday Morning, 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, Keiichiro Sakurai, Akimasa Yamada, Paul Fons, Kakuya Iwata, Koji Matsubara, and Hitoshi Tampo, Energy Electronics Research Institute, AIST, JAPAN; Ralf Hunger, University of Darmstat, GERMANY; Roland Scheer, Hahn-Meitner Institute, 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  $\eta > 18\%$  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 techniques for 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 first stage of the three stage process, and was found to correspond to changes in film thickness, making possible accurate thickness control of CIGS films. Spectroscopic light scattering techniques have been also 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 techniques has been explored. First, pulsed laser deposition technique has been investigated. High-quality ZnO transparent conducting oxide films with a resistivity as low as  $\rho \sim 2 \times 10^{-4} \Omega\text{-cm}$  and a rms roughness below 1 nm have been demonstrated. A novel ion plating technique in the attributes of soft deposition technique providing both superb controllability of the high density plasma as well as ion beam shape has been developed for large-area deposition of transparent conducting oxides. ZnO films have been deposited on glass substrate at 200°C at a growth rate of 0.6  $\mu\text{m}$  using a Ga-doped ZnO target. Resistivities of  $\rho \sim 2 \times 10^{-4} \Omega\text{-cm}$  with carrier concentrations of  $n \sim 1 \times 10^{21} \text{cm}^{-3}$  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)(S,Se)<sub>2</sub> BY GRAZING INCIDENCE X-RAY DIFFRACTION. I.M. Kötschau, Hahn-Meitner-Institut, Berlin, GERMANY; H.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)(S,Se)<sub>2</sub> (CIGSSe) 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 nonintentionally 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 Cu<sub>x</sub>(S,Se) 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 recrystallisation 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 recrystallisation of the film. By using GIXRD measurements it is therefore possible to refine 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 $\text{Cu}(\text{In,Ga})\text{S}_2$ THIN FILMS.

Axel Neisser, Reiner Klenk, Marta Ch. Lux-Steiner  
Hahn-Meitner-Institut, Berlin, GERMANY.

As reported earlier the growth of  $\text{Cu}(\text{In,Ga})\text{S}_2$  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  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$  phases, i.e. the final Ga-depth profile, 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  $\text{CuGaS}_2/\text{CuInS}_2$  diffusion couples have been investigated by thermal annealing. Annealing experiments have been performed in the temperature range from 500°C to 600°C. Annealed samples have been examined by XRD and SNMS depth profiling. From 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, and - the interdiffusion process is much more effective if copper-sulfide is present in the sample. To quantitatively describe the interdiffusion process and the associated Ga-depth profile a numerical simulation of the XRD spectra was combined with modelled Ga-depth profiles based on a diffusion model. In contrast to earlier studies about Ga-diffusion in  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin films the observed experimental data could only be described when applying a 2-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 phases indicates the role of the secondary phase as a high mobility path for cations.

#### 9:30 AM **B6.4**

INVESTIGATION OF  $\text{CuInSe}_2$  GROWTH KINETICS USING TIME-RESOLVED HIGH TEMPERATURE X-RAY DIFFRACTION ANALYSIS. Suku Kim, Woo Kyoung Kim, Timothy J. Anderson, Oscar D. Crisalle, Department of Chemical Engineering, University of Florida, Gainesville, FL; E. Andrew Payzant, 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  $\text{CuInSe}_2$  from precursor films consisting of stacked binary M-Se 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 structure. For example, the isothermal phase evolution of the  $\text{InSe/CuSe}$  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  $\text{InSe/CuSe} \rightarrow \text{InSe/CuInSe}_2/\text{CuSe}$ . The shape of the fractional reaction ( $\alpha$ ) vs. time curve exhibits a deceleratory behavior, consistent with a diffusion-controlled reaction mechanism. The rate constant and apparent activation energy for  $\text{CuInSe}_2$  formation were estimated.

#### 9:45 AM **B6.5**

$\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$  GROWTH STUDIES BY IN SITU SPECTROSCOPIC LIGHT SCATTERING. R. Scheer and A. Neisser, Hahn-Meitner Institut, Division Solar Energy, Berlin, GERMANY; K. Sakurai, P. Fons, S. Niki, Thin Film Solar Cells Group, Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

The growth of polycrystalline  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$  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 process, which is interesting for industrial solar cell production, is comprised of the stages In-Ga-Se deposition, Cu-Se deposition, and In-Ga-Se deposition. The development of surface roughness is monitored by the intensity of the diffusively 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 formation. It is shown that on-line monitoring of the spectroscopic light scattering can be used for process control and for adjustment of the final film roughness.

#### 10:30 AM **\*B6.6**

$\text{Cu}(\text{In,Ga})\text{Se}_2$ -BASED DEVICES: FROM MATERIALS TO PRODUCTS. John Kessler, Angstrom Solar Center, Uppsala University, Uppsala, SWEDEN.

The goal of thin film  $\text{Cu}(\text{In,Ga})\text{Se}_2$ -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 synergies between some of the technical aspects of a potential  $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based product. A first synergy, concerning synthesis, is found in the triangular relationship between materials, processes and deposition equipment. Desired materials are only accessible if processes can be established that permit their synthesis, and are only realistic if product size equipment can be defined to perform this synthesis. For example, the debate behind aspects such as co-evaporation versus selenization for the  $\text{Cu}(\text{In,Ga})\text{Se}_2$  growth results from different optimizations of this triangulation. This situation is not limited to the  $\text{Cu}(\text{In,Ga})\text{Se}_2$  layer, but is applicable to all of the other involved materials. As the understanding of the material systems and structures improve, and as the know-how concerning their growth progresses, 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 redefinition of the device and module structures, as well as of the involved materials. Less technical issues, such as market acceptance, can impose modifications, as for example Cd-free devices. These in turn require a better functional understanding of the interfacial issues and of the junction itself. Taking examples from the recent progress made in throughput (rapid and thinner growth), process ease (simplicity and tolerance), and process control, as well as the product 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  $\text{CuInS}_2$  FILMS ON Si. W. Calvet, H. Lewerenz, C. Pettenkofer, Hahn-Meitner-Institut SE5, Berlin, GERMANY.

$\text{CuInS}_2$  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 Cu/In ratio and the film thickness was limited to 150 nm. In-situ photoelectron spectroscopy (PES) was used to determine the surface stoichiometry whereas the volume composition was investigated by Rutherford backscattering (RBS). Structural analysis by x-ray diffraction (XRD) yielded besides the chalcopyrite lattice a CuAu ordering of the cation sublattice on non (111) orientated substrates independent from the Cu/In-ratio. On the contrary the epitaxial relations showed a strong dependency on the Cu/In-ratio. For Cu-rich films a growth direction parallel to [112] independent from the substrate orientation was found whereas for In-rich films the growth direction is given by the substrate orientation with [112] microfacets detected by low energy electron diffraction (LEED). The surface composition of the epitaxial films differed from the volume: instead of the expected variation along the  $\text{Cu}_2\text{S-In}_2\text{S}_3$  binary, the surface composition varied along the  $\text{Cu}_2\text{S-InS}$  cut through the Gibb's phase triangle yielding a S-deficiency. The role of electronic effects on growth mode and phase formation is discussed.

#### 11:15 AM **B6.8**

$\text{Cu}(\text{In,Ga})(\text{Se,S})_2$  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, Shell Solar, T-CIS, Munich, GERMANY.

Large area  $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$  (CIGSSe) thin films for solar modules are processed by rapid thermal processing of stacked elemental layers. A pilot line for 60×90 cm<sup>2</sup> absorbers and 30×30 cm<sup>2</sup> modules is now running. We will present the current status of our pilot line. Modules with efficiencies at 12% 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 (XRFA), secondary ion mass spectroscopy (SIMS), photo luminescence (PL) decay and spectral response (SR). Sequentially processed CIGSSe films show typical depth distribution profiles of gallium and sulfur. Based upon 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 chalcopyrite formation proceeds from top to bottom, resulting in the typical morphology and a segregation of Ga towards the bottom. The sulfur incorporation is investigated by comparing XRFA data and

SIMS profiles of samples from different sulfurization recipes. Two different mechanisms for sulfur incorporation are proposed: If S is available before CIS formation is completed, S diffuses fast into the Cu-Se binary phases 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 CIS 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 molybdenum sulfo-selenide 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 CIS SOLAR CELLS PREPARED BY ELECTRODEPOSITION WITHOUT VACUUM POST DEPOSITION STEP.** Denis Guimard, Nicolas Bodereau, Jamal Kurdi, Jean-Francois Guillemoles, Daniel Lincot LECA, CNRS, Paris, FRANCE; Pierre-Philippe Grand, Moez Ben-Farah, Stephane Tannier, Olivier Kerrec, EDF-R&D, FRANCE; Paul Mogensen, Saint-Gobain Recherche, Aubervilliers, FRANCE.

CuInSe<sub>2</sub> and Cu(In,Ga)Se<sub>2</sub> 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. Annealed 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 CIS. Ga has been inserted within our CIS films during the electrodeposition step. We have been able to insert up to 25% of gallium (vs. all elements). Films with gallium have very good morphology which is suitable, after recrystallisation and 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 cm<sup>2</sup> CIS substrates have been obtained with very homogeneous composition and morphology. Material characterisation has been performed on all the different elaborated absorbers (XRD, SEM, EDX), as well as current-voltage, capacitance-voltage and spectral response analysis, which will be presented for losses mechanisms discussion. 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 CuInS<sub>2</sub> FILMS ON SAPPHIRE BY RF REACTIVE SPUTTERING.** Yunbin He, I. Physikalisches Institut, Justus-Liebig-University Giessen, GERMANY; Alois Krost, Institut für Experimentelle Physik, Otto-von-Guericke University Magdeburg, GERMANY; Thorsten Kraemer, Angelika Polity, Bruno Meyer, I. Physikalisches Institut, Justus-Liebig-University Giessen, GERMANY.

We demonstrate the first deposition of CuInS<sub>2</sub> thin films on sapphire by radio frequency reactive sputtering with a Cu-In alloy target and H<sub>2</sub>S gas. The RF power was kept constant at 200 W (2.47 W/cm<sup>2</sup>) and the substrates were heated up to 500°C, while the H<sub>2</sub>S flow was varied from 28 to 35 sccm during the sputter process. X-ray diffraction revealed that the as-sputtered films are of mainly (112)-oriented CuInS<sub>2</sub> phase incorporating with a minor CuIn<sub>2</sub> phase, which is only visible by using logarithm scale and may be attributed to the In-rich composition of the target used. The X-ray diffraction rocking curve measurements on (112) showed a typical full width at half maximum of 0.1°, indicating an epitaxial-like growth of (112)-CuInS<sub>2</sub> films on (001)-sapphire. There are mainly six peaks shown in the phi-chi 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 CuInS<sub>2</sub> layer. The two main reflection groups rotate by 180° with respect to each other, and lead to twins in the CuInS<sub>2</sub> layers. Transmission electron microscopy was carried out to investigate further the microstructure and orientation of the nearly epitaxially sputtered CuInS<sub>2</sub> 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 Afternoon, April 24, 2003  
Salon 10/11 (Marriott)

#### 1:30 PM \*B7.1

**THE ROLE OF TRANSPARENT CONDUCTING OXIDES IN**

**SOLAR CELLS.** Timothy J. Coutts, Timothy A. Gessert, David L. Young, J. Scott Ward, and Rommel Noufi, 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 if not carefully controlled. The high free-carrier concentration of TCOs 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 higher bandgap, single-junction 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's High Performance Photovoltaics program, it is even more likely that the TCO properties will influence cell performance, unless very high mobilities are maintained. However, mobilities as high as 75 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, together with carrier concentrations of 7x10<sup>20</sup> cm<sup>-3</sup>, have been achieved for Cd<sub>2</sub>SnO<sub>4</sub> and other TCOs, which would be sufficiently high quality to avoid free-carrier losses. Although films of this quality have been made in the research laboratory, they require post-deposition annealing at high temperature (680°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 shall 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

**BANDGAP ENGINEERING OF ZnO TRANSPARENT CONDUCTING FILMS.** K. Matsubara, H. Tampo, A. Yamada, P. Fons, K. Iwata, K. Sakurai, and S. Niki, National Institutes of Advanced Industrial Science and Technology, Ibaraki, JAPAN.

As the band lineup of Cu[InGa]Se<sub>2</sub> (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 a 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 Al<sub>2</sub>O<sub>3</sub> powder was pressed into a pellet and sintered in air. The sintered target was ablated in an oxygen ambient by a KrF<sup>+</sup> 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 10<sup>-3</sup> Ω cm or less. A minimum resistivity of 7.8 x 10<sup>-4</sup> 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

**CORRELATING STRUCTURE/PROPERTY RELATIONSHIPS FOR PULSED LASER DEPOSITED Zn-Sn-O FILMS.** C. Warmstrong, J. Perkins, P. Parilla, J.L. Alleman, M. Van Hest, H. Kleebe, D. Readey, and D. Ginley.

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 Zn-Sn-O transparent conducting oxides (TCOs) are quite low compared with well known simple TCOs such as In<sub>2</sub>O<sub>3</sub>:Sn and ZnO:Al. Nevertheless, our interest in Zn-Sn-O TCOs is two fold: First, Zn<sub>2</sub>SnO<sub>4</sub> is an important interface layer in the CdS/CdTe world record polycrystalline solar cells (16.5% total-area efficiency); Second, ZnSnO<sub>3</sub> has 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 Cd<sub>2</sub>SnO<sub>4</sub>/Zn<sub>2</sub>SnO<sub>4</sub> bilayer from the CdS/CdTe device if the conductivity of ZnSnO<sub>3</sub> can be improved to be comparable to Cd<sub>2</sub>SnO<sub>4</sub>. We have deposited ZnSnO<sub>3</sub> and Zn<sub>2</sub>SnO<sub>4</sub> films were grown by Pulsed Laser Deposition (PLD). We explored various deposition conditions to optimize 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, ZnSnO<sub>3</sub> showed substantially better electrical properties than Zn<sub>2</sub>SnO<sub>4</sub>. All of the ZnSnO<sub>3</sub> films deposited at 400°C and lower are amorphous. HRTEM on highly conductive films indicated uniform composition and amorphous structure. Films

that were ex-situ annealed in the 4% H<sub>2</sub> in argon at 400°C showed improved electrical properties. In most cases, the electrical properties of ZnSnO<sub>3</sub> converged to a conductivity of approximately 360 ohm<sup>-1</sup>cm<sup>-1</sup>. However the ZnSnO<sub>3</sub> films decomposed after high temperature annealing (>650°C). Result on how crystal structure affects electrical properties will be discussed.

#### 2:30 PM B7.4

**HIGH-QUALITY TRANSPARENT CONDUCTING OXIDE FILMS DEPOSITED BY A NOVEL ION PLATING TECHNIQUE.** Kakuya Iwata, Koji Matsubara, Hitoshi Tambo and Shigeru Niki, Energy Electronics Institute, AIST, Ibaraki, JAPAN; Toshiyuki Sakemi, Sumitomo Heavy Industries, Ehime, JAPAN; Kiyoshi Awai, Sumiju Technical Center Co., Ltd., Ehime, JAPAN; Tetsuya Yamamoto, Kochi University of Technology, Kochi, JAPAN.

A novel ion plating technique that has the attributes 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 RT-200°C. Resistivities of  $\rho \sim 1.2 \times 10^{-4} \Omega\text{-cm}$  and RA surface roughness of below 0.2 nm with excellent uniformity over an 800 mm wide substrate have been demonstrated. The low ion energy and the uniform dispersion of tin atoms were considered to contribute to low resistivity in ITO films. ZnO films have been deposited on glass substrate at 200°C at a growth rate of 0.6mm using Ga-doped ZnO target. Resistivities of  $\rho \sim 2 \times 10^{-4} \Omega\text{-cm}$  with carrier concentrations of  $n \sim 1 \times 10^{21} \text{cm}^{-3}$  have been demonstrated. Advantages of this technique include reduced ion damage, scale-up capability, in-plane uniformity, use of low growth temperatures and fast deposition speed suggesting that the technique is very promising for solar cell applications.

#### 2:45 PM B7.5

**THE INFLUENCE OF SUBSTRATE AND CONCENTRATION ON CVD-GROWN p-TYPE Cu-Al-O TRANSPARENT OXIDE SEMICONDUCTING FILMS.** Jianling Cai and Hao Gong, National University of Singapore, Department of Materials Science, SINGAPORE.

Copper aluminum oxide films were grown by the use of metalorganic plasma enhance chemical vapor deposition (MO-PECVD). It is observed that 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 substrates but be semiconductors when growing on single crystal quartz. Different techniques, such as XRD, Seebeck, AFM, SEM, uv-visible spectroscopy, Hall effect measurement, were employed to study the structural, electrical and optical properties of the films. Models and mechanisms of carrier transfer are 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 PM DISCUSSION II

**POLYCRYSTALLINE THIN FILM TANDEM CELLS: ARE THEY A VIABLE OPTION FOR HIGH EFFICIENCY?** Moderated by Tim Coutts, National Renewable Energy Laboratory.

SESSION B8: POSTER SESSION  
GROWTH AND JUNCTION FORMATION

Chair: Lars Stolt  
Thursday Evening, April 24, 2003  
8:00 PM  
Salon 1-7 (Marriott)

#### B8.1

**THE EFFECTS OF SUBSTRATE ROUGHNESS ON CIGS DEVICES DEPOSITED ON STAINLESS STEEL FOIL.** Wendi K. Batchelor 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 surface 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 steels, and device results are compared with those on glass. It is possible to closely mimic the properties of glass for a more accurate comparison of devices if the substrate properties are thoughtfully chosen. For example, the use of stainless steel foil of various thicknesses 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 correlation to substrate surface roughness, substrate preparation, and substrate characteristics are discussed in this paper.

#### B8.2

**CHEMICAL AND ELECTRONIC STRUCTURE OF THE ZnO/CdS INTERFACE IN Cu(In,Ga)(S,Se)<sub>2</sub> THIN FILM SOLAR CELLS.** L. Weinhardt, O. Fuchs, C. Heske, and E. Umbach, Experimentelle Physik II, Universität Würzburg, GERMANY; T.P. Niesen, S. Visbeck, and F. Karg, Shell Solar, Munich, GERMANY.

In solar cells based on Cu(In,Ga)(S,Se)<sub>2</sub> (CIGSSE), one potential target for further optimization of cell performance is the commonly used ZnO window layer. Today, a n-ZnO/i-ZnO structure is generally used, separated from the CIGSSE 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 CIGSSE thin film solar cell device, taking into account the previously found electronic and chemical structure of the CdS/CIG(S)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 EPSEC Munich 2001. [2] M. Morkel et al., Appl. Phys. Lett. 79 (2001) 4482.

#### B8.3

**MEASUREMENT OF THE ELECTRICAL POTENTIAL IN EPITAXIAL III-V AND THIN-FILM Cu(In,Ga)Se<sub>2</sub> SOLAR CELLS BY SCANNING KELVIN PROBE MICROSCOPY.** Chun-Sheng Jiang, H.R. Moutinho, D.J. Friedman, J.F. Geisz, F.S. Hasoon, and M.M. Al-Jassim, National Renewable Energy Laboratory, Golden, CO.

The built-in electric potential plays a major role in photovoltaic devices, because it collects photo-excited carriers and is a key factor in determining the open-circuit voltage of the device. However, characterization of the built-in potentials has been limited to indirect ways such as current-voltage and capacitance-voltage measurements. We have recently employed scanning Kelvin probe microscopy technique and measured distributions of the electrical potential on cross sections of the solar cells, quantitatively and with sub-micrometer 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 III-V and thin-film Cu(In,Ga)Se<sub>2</sub> solar cells.

On a GaInP<sub>2</sub> 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 GaInP<sub>2</sub> base layer and the GaAs substrate. The potential on the p-n junction was photoactive and that on the GaInP<sub>2</sub>/GaAs interface was photo-inactive. On a GaInP<sub>2</sub>/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 by light with photon energies greater than the band gap of the top junction, dramatic changes in the potential profile were measured due to charge accumulations on the bottom junction in the condition of unbalanced photocurrent between the top and bottom cells.

On a Cu(In,Ga)Se<sub>2</sub> thin-film cell, profiles of the electrical potential demonstrate that the p-n junction is a buried homo-junction. The built-in electric field terminates at the Cu(In,Ga)Se<sub>2</sub>/CdS interface, indicating that the CdS and ZnO layers of the device structure are inactive for the collection of photo-excited carriers.

#### B8.4

**GaInAsSb MATERIALS FOR THERMOPHOTOVOLTAIC DEVICES.** C.A. Wang, C.J. Vineis, D.A. Shiao, R.K. Huang, M.K. Connors, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA; D. Donetsky, S. Anikeev, G. Belenky, State University of New York, Stony Brook, NY; L.R. Danielson, G. Nichols, Lockheed Martin Corporation, Schenectady, NY.

The quaternary GaInAsSb alloys are attractive materials for thermophotovoltaic (TPV) devices because the energy gap can be varied from 0.3 to 0.7 eV while maintaining an epitaxial layer that is lattice 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 2.7  $\mu\text{m}$  were reported. To achieve further improvements in TPV device performance, detailed materials studies of the GaInAsSb 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 GaInAsSb. Minority carrier lifetime measurements were performed by time-resolved photoluminescence to study bulk recombination and surface recombination velocity at various heterostructure interfaces. This paper reports the material characteristics of the superlattice and heterostructure interface designs, and their implications on TPV device performance.

**B8.5**  
ELECTRODEPOSITION OF CIGS ON METAL SUBSTRATES. Andreas Kampmann, Juan Rechid, Rudolf Thyen, Sonja Wulff, Andreas Raitzig, Maria Mihailova and Klaus Kalberlah, CIS Solartechnik Ltd, Hamburg, GERMANY.

The development of a low cost roll to roll production process for CIGS remains an attractive goal. In the present approach, the absorber is prepared by an electrodeposition technique, while copper or stainless steel have been chosen as flexible substrates. During the actual R&D phase a feasibility investigation is performed which should prove that electrodeposition on these metals yields at least 8% in efficiency. This approach poses two major challenges. The first one is related to the metal substrate. Here, good adhesion of the CIGS absorber layer has to be reached and at the same time the metallic 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 absorber. Adhesion problems occur mainly for the copper substrate. They could be overcome by an electrodeposited 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 analysed by EDX and SIMS measurements. Up to now best results are obtained with a Ta barrier layer. For R&D electrodeposition is carried out on a rotating disc electrode with a surface area of about 60  $\text{cm}^2$ . Two electrodeposition routes are evaluated. Sequential plating of Cu, In, Ga and Se is compared to simultaneous electrodeposition. For molybdenum substrates, which have been used for comparison reasons, the actual best efficiency of the sequential process is 7.1%, while 5.9% have been obtained with the simultaneous plating process on 0.25  $\text{cm}^2$  aperture area.

**B8.6**  
INTERFACE FORMATION BETWEEN POLYCRYSTALLINE Cu(In,Ga)Se<sub>2</sub> AND II-VI COMPOUNDS. T. Schulmeyer, Frank Saeuberlich, A. Klein, R. Hunger, W. Jaegermann, Darmstadt University of Technology, Institute of Materials Science, Darmstadt, GERMANY; R. Kniese, M. Powalla, Zentrum für Sonnenenergie und Wasserstoff-Forschung, Stuttgart, GERMANY.

The interface between Cu(In,Ga)Se<sub>2</sub> (absorber) and CdS (buffer) is crucial for the performance of CIGS thin film solar cells. Although the presence 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 with 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)Se<sub>2</sub> and II-VI semiconductors CdX and ZnX (X= S, Se,Te) using *in-situ* photoelectron spectroscopy. Contamination-free Cu(In,Ga)Se<sub>2</sub> surfaces were prepared by heating-off of Se layers, which were deposited onto the absorber layers in the deposition chamber directly after absorber deposition. Interfaces with II-VI compounds were prepared by stepwise evaporation. The determined band alignments are compared to theoretical calculations.

**B8.7**  
NUCLEATION AND GROWTH OF Cu(In,Ga)Se<sub>2</sub> ON MOLYBDENUM SURFACES. T. Schlenker, K. Orgassa, H.W. Schock, J.H. Werner, Institute of Physical Electronics, University of Stuttgart, GERMANY.

Our research on thin film Cu(In,Ga)Se<sub>2</sub> 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)Se<sub>2</sub> on Mo films on glass, as the typical back contact for

Cu(In,Ga)Se<sub>2</sub> solar cells. Mo films are either fabricated by a sputter process or by electron beam evaporation. Each technique results in a different morphology of the Mo surface. We deposit Cu(In,Ga)Se<sub>2</sub> films of nominal 2.9 nm to 29 nm thickness using a thermal evaporation process with varying rates at constant substrate temperature of 550°C. An ultra high resolution scanning electron microscope serves to analyse the growth process. For polycrystalline Mo substrates, that were fabricated by a sputter process, the theory of homogeneous nucleation (i.e. no special sites or point defects) explains Cu(In,Ga)Se<sub>2</sub> cluster formation and island density. According to this theory, a power law relationship between the island density and the evaporation rate is found. The "critical nuclei size" (cluster size that is more likely to grow than decay) is 4 to 10 atoms (depending on formation and stoichiometry of the nuclides). For the island 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 homogeneous case. Most probably, on these substrates, in addition heterogeneous nucleation takes place. In this case, diffusing adatoms get captured by randomly distributed mesoscopic defect sites with high trapping energy. At later growth stages the transition from isolated islands to closed films takes place in the coalescence regime.

**B8.8**  
ROLE OF SURFACE BAND-GAP WIDENING IN Cu(In,Ga)(Se,S)<sub>2</sub> THIN-FILMS FOR THE PHOTOVOLTAIC PERFORMANCE OF ZnO/CdS/Cu(In,Ga)(Se,S)<sub>2</sub> HETEROJUNCTION SOLAR CELLS. Uwe Rau and Mircea Turcu, Institute of Physical Electronics, University of Stuttgart, GERMANY.

The CdS/Cu(In,Ga)(Se,S)<sub>2</sub> interface and the surface region of the Cu(In,Ga)(Se,S)<sub>2</sub> absorber film are the most important part of the ZnO/CdS/Cu(In,Ga)(Se,S)<sub>2</sub> heterojunction solar cell. Despite the importance of this part of the solar cell, 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 work uses numerical simulations as well as analytical modeling of the device properties. The outcome of the theoretical work is compared to experimental results on a wide variety of Cu(In,Ga)(Se,S)<sub>2</sub> heterojunction solar cells. Our main conclusion from experiment and theory is that the most important feature of Cu-poor prepared Cu(In,Ga)(Se,S)<sub>2</sub> absorber layers 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.

**B8.9**  
OXYGENATED CdS WINDOW LAYER FOR SPUTTERED CdS/CdTe SOLAR CELLS. Akhlesh Gupta, Karthikeya Allada, Sung Hyun Lee, and Alvin D. Compaan, Department of Physics and Astronomy, University of Toledo, Toledo, OH.

The conventional polycrystalline CdS heterojunction partner/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 density (J<sub>sc</sub>) in the devices. The J<sub>sc</sub> 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/O<sub>2</sub> at various substrate temperatures, and the use of these films in sputtered cells. At a substrate temperature of 250°C the addition of O<sub>2</sub> 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 that observed for room temperature deposition which gives a blue shift (2.35 eV to 3.27 eV). Raman spectra of the room-temperature-deposited films show a considerable broadening of LO phonon peaks indicating nanocrystallinity as the O<sub>2</sub> fraction increases. XRD measurements of these films showed the formation of an amorphous structure at high O<sub>2</sub> fractions. We shall report on the electrical and compositional properties of the films. Preliminary CdS/CdTe device results have demonstrated an improvement in J<sub>sc</sub> 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 (a-CdS:O) window layer" presented in 29th IEEE photovoltaic specialist conference, 20-24 May 2002, New Orleans.

**B8.10**  
FORMATION AND IONIZATION ENERGIES OF POINT DEFECTS IN COPPER INDIUM GALLIUM DISELENIDE USING AB INITIO METHODS. C. Domain, S. Laribi, J.M. Raulot, S. Taunier, EDF R&D, Departement MMC, Les Renardieres, Moret sur

Loing; J.F. Guillemoles, Ecole Nationale Supérieure de Chimie Paris, LECA, Paris, FRANCE.

The opto-electronic properties of Cu(In,Ga)Se<sub>2</sub> 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 new 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 CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> 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 method used is based on the density functional theory within the framework of pseudo-potentials and plane waves basis. The results will be discussed in view of the existing data, models and calculations.

#### **B8.11**

##### **SPUTTERED ZnTe:N AND ZnO:Al FOR SOLAR CELL ELECTRODES AND RECOMBINATION JUNCTION.**

Jennifer Drayton, V. Parikh, G. Rich, A. Gupta, C. Taylor, Y. Yu, R.G. Bohn, A.D. Compaan, 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 CdTe based solar cells. ZnTe:N is reactively sputtered with 3% N<sub>2</sub> in the sputter gas. The ZnTe:N films typically have transmission near 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<sub>2</sub>O<sub>3</sub> (2%) target. The ZnO:Al films have resistivity as low as 4 x 10<sup>-4</sup> ohm-cm with 80-95% transmission over the visible spectrum. To test the stability of the films, ZnTe:N films were annealed in argon, dry air, and nitrogen at a range of temperatures from 200°C to 500°C. Resistivity decreased with annealing temperatures less than 325°C and increased with annealing temperatures above 325°C. ZnO:Al films were annealed in dry air and nitrogen at temperatures from 300°C to 550°C. Though the resistivity increased at higher temperatures, there was no change in the transmission. 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 CdS/CdTe 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 rf sputtered ZnTe:N and ZnO:Al films were characterized by AFM, STM, XRD, transmission, 4-point probe, and Hall measurements. This work is supported by the NREL High Performance Photovoltaic Project.

#### **B8.12**

##### **REAL-TIME FAULT DIAGNOSIS OF SENSORS FOR FAULT-TOLERANT CONTROL OF THIN-FILM (CIGS) PHOTOVOLTAICS PROCESS.**

Bharat S. Joshi, Nick Gomez, Michael Chaffin, ITN Energy Systems, Inc., Littleton, CO; Scott Weideman, Markus Beck, John Muha, 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 process 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 process 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.

#### **B8.13**

**EFFECTS OF ZnTe/ZnTe:Cu COMPLEX BACK-CONTACT ON DEVICE CHARACTERISTICS OF CdTe SOLAR CELLS.** Lili Wu, Daolin Cai, Lianghuan Feng, Yaping Cai, Wei Cai, Jiagui Zheng, Qiangu Yan, Sichuan Univ, Dept of Materials Science, Chengdu, CHINA.

Zinc telluride is an ideal back-contact material for CdTe solar cells due to the small valence-band offset with CdTe 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 work function can make a stable and low ohmic contact. In order to prevent the diffusion of Cu atoms into CdTe layer and decrease the interface state densities between p-CdTe and Cu-doped ZnTe layers, we have proposed to introduce an un-doped ZnTe film as a buffer between both the layers. In this paper, ZnTe:Cu layers have been deposited by vacuum co-evaporation, and the CdTe solar cells with three kinds of back contact, i.e. complex ZnTe/ZnTe:Cu layer, single ZnTe:Cu layer and no buffer layer, have been fabricated. The influences of Cu concentration in the doped ZnTe layer as well as the thickness of un-doped and Cu-doped layers on I-V characteristics of these cells have been studied. Considering the abnormal temperature dependence of dark conductivity in ZnTe:Cu films, we have investigated the effects of annealing temperatures on the performance of the cells. The results show that the "roll over" and "cross over" phenomena of dark and photo I-V 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 than that without back contact layer. It has been demonstrated that the diode quality factor has decreased to 1.8 and the fill factor has increased to 73% for CdS/CdTe/ZnTe/ZnTe:Cu cells, in which there is no high resistance transparent layer. The relative reasons have been discussed.

#### **B8.14**

**OPTIMISED GROWTH CONDITIONS FOR Cu(In,Ga)Se<sub>2</sub> 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 the Cu(In,Ga)Se<sub>2</sub> (CIGS) layer, while maintaining high material quality, is desired for low cost fabrication of CIGS based solar cells. In this study, solar cell devices from over 40 different CIGS runs are analysed, where the evaporation time of the CIGS is varied from 60 minutes down to under 4 minutes. Some of these devices have been discussed earlier [1], but here all of the devices are analysed and with a focus on the optimal growth conditions at the different evaporation times. It is found that devices with CIGS layers grown at shorter evaporation 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 does that of devices with CIGS layers grown at longer evaporation times. Thus, at higher growth rates the compositional 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 at an evaporation time of 3.75 minutes a 12.8% efficient device, without antireflective coating, has been fabricated. [1] O. Lundberg, M. Bodegard and L. Stolt, Rapid Growth of Thin Cu(In,Ga)Se<sub>2</sub> Layers for Solar Cells, EMRS 2002, Strassbourg.

#### **B8.15**

**HIGH-PERFORMANCE BARRIER LAYERS FOR FLEXIBLE CIGS THIN-FILM SOLAR CELLS ON METAL FOILS.** Dirk Herrmann, Friedrich Kessler, Konrad Herz, Axel Eicke, Michael Powalla, Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden Württemberg (ZSW), Stuttgart, GERMANY; Andreas Schulz, Joachim Schneider, Uwe Schumacher, Institut für Plasmaforschung (IPF), Universität Stuttgart, GERMANY.

Commonly CIGS (Cu(In,Ga)Se<sub>2</sub>) based thin-film solar cells are deposited on sodium 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. Most promising alternative materials with regard to 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 module and metal substrate. These issues have been addressed in this paper. Preferred foils with regard to costs and physical properties were ferritic steel, titanium and Fe/Ni/Co-alloys (e.g. Kovar). SiO<sub>x</sub>- and Al<sub>2</sub>O<sub>3</sub>-based barriers were fabricated by different deposition means (sol-gel, PECVD, sputtering). Sodium was added in-situ or via an additional layer. SIMS and SNMS depth profiles revealed the various suitability of the diffusion barriers and the effectiveness of Na-doping. For example, the SiO<sub>x</sub> barrier deposited by the sol-gel method proved to be a suitable candidate for diffusion barrier. On ferritic steel a decrease in iron and chromium 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 isolation with these layers is a big challenge. With the help of a newly implemented measurement technique, based on electrolysis combined with SEM images, pinholes in the barrier layers could be localized and correlated with growth failures. Best suitabilities for high efficiency CIGS solar cells were provided by the combination of two layers with distinct properties (e.g. isolation/diffusion barrier plus sodium-containing smoothing layer). For CIGS solar cells on metal substrate foils including Na-containing diffusion barriers efficiencies of 12.9 % (AM1.5, 1000 W/m<sup>2</sup>) could be achieved. In this paper we will present results on various barrier layers as well as on CIGS mini-modules (5x5 cm<sup>2</sup>) on flexible metal foils.

#### **B8.16**

**CURRENT STATUS AND FUTURE PROSPECTS OF CISCuT BASED SOLAR CELLS AND MODULES.** Olaf Tober, Michael Winkler, Jeannette Wienke<sup>a</sup>, Jürgen Penndorf, Joachim Griesche, IST - Institut für Solartechnologien, Frankfurt (Oder), GERMANY. <sup>a</sup>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/S 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 stripes of this cell tape in a roof tile manner in an automated assembly line. J-V characteristics and spectral responses that show efficiencies of 9% so far and that have been certified by the Fraunhofer Institut Solare Energiesysteme are presented. Stability tests over more than 3000 h show promising results. Best results obtained from cells and from 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 module. Latest results including the unique mechanical properties of CISCuT-based solar cells and modules are highlighted. An outlook on the future prospects of this exciting technology is given.

#### **B8.17**

**MODIFICATION OF Cu(In,Ga)Se<sub>2</sub> SURFACE BY TREATMENT IN CADMIUM SOLUTIONS.** Q. Nguyen Hong and H.W. Schöck, Institute of Physical Electronics, University of Stuttgart, GERMANY.

We introduce Cd into Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber by wet chemical treatment in Cd<sup>2+</sup> solution with varying NH<sub>3</sub> 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 NH<sub>3</sub> concentration: a slight reduction in the case of solution without NH<sub>3</sub> and much stronger with a solution containing 1 molar NH<sub>3</sub>. X-ray photoelectron spectroscopy (XPS) reveals the presence of Se atoms, Metal (Cu, In, Cd) oxides and hydroxides on the CIGS surface after treatments. The oxidation products on CIGS surface are decreased with increase of the NH<sub>3</sub> concentration and disappear in the case of 1.5 molar NH<sub>3</sub> solution due to the decrease of the redox potential. Secondary Ion Mass Spectroscopy (SIMS) shows that treatment of the CIGS layer in Cd-solution with NH<sub>3</sub> introduces more Cd into the CIGS absorber than non-NH<sub>3</sub> solution. Thus, the diffusion of Cd into the CIGS absorber is intimately tied to the CIGS surface reduction-oxidation process which is controlled by the NH<sub>3</sub> concentration. We conclude that Cd-diffusion and the creation 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.

#### **B8.18**

**IN-SITU XRD STUDIES OF SEQUENTIAL CuIn(S,Se)<sub>2</sub> FORMATION.** Jovana Djordjevic, Eveline Rudigier, Roland Scheer, Hahn-Meitner Institut, Berlin, GERMANY.

The formation of CuInS<sub>2</sub>-CuInSe<sub>2</sub> alloy films from chalcogenisation 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 = 1.8) were sputtered on molybdenum coated soda-lime glass and selenium was introduced as a layer of elemental selenium or as a In<sub>2</sub>Se<sub>3</sub> layer. Such prepared precursor films were then sulfurized in elemental sulfur vapor. The effects of the selenium precursors and the influence of sulfurization conditions on the resulting absorber films composition and properties were investigated. It is shown that the ternary phases in the final film were CuInS<sub>2</sub>, CuIn(Se,S)<sub>2</sub>, and CuInSe<sub>2</sub> in the case of elemental Se precursor deposition and CuInS<sub>2</sub>, CuIn(Se,S)<sub>2</sub> in the case of In<sub>2</sub>Se<sub>3</sub> precursors. The difference in the formation path ways are investigated in detail.

#### **B8.19**

**DEVELOPMENT OF PLASMA-ASSISTED CO-EVAPORATION FOR SYNTHESIS OF SOLAR ABSORBERS.** Sreenivas Kosaraju, Nathan Torres, and Colin Wolden, Department of Chemical Engineering, Colorado School of Mines, Golden, CO; Ingrid Repins, ITN Energy Systems, Littleton, CO.

One factor hindering the commercialization of copper-indium-gallium-selenide (CIGS) solar cells has been hindered by the low reactivity of the chalcogen precursor. Consequently issues related to long processing times and poor material utilization must be overcome. We are developing a novel plasma-assisted co-evaporation (PACE) processing technique to address these deficiencies. In the PACE process chalcogen (S and/or Se) vapors are activated using an inductively coupled plasma (ICP) and mixed with metal vapors produced by conventional evaporation. In this presentation we will describe the PACE reactor that has been designed and built for this purpose. Initial studies are focused on the synthesis of In<sub>2</sub>Se<sub>3</sub>, In<sub>2</sub>S<sub>3</sub>, and In<sub>2</sub>Se<sub>x</sub>S<sub>3-x</sub> alloys. The ability to substitute sulfur for selenium in CIGS films would allow one to engineer the absorber bandgap for optimal efficiency and creating multijunction cells. In thermal systems this has proven difficult, and we are investigating the ability of PACE to overcome equilibrium limitations. The high vacuum deposition system includes thermal evaporation of indium and ICP sources for chalcogen generation. The sources are directed at a temperature-controlled substrate under near collisionless conditions. The plasma chemistry in the ICP devices was studied using optical emission spectroscopy (OES) measurements. A parametric study of the effects of RF power, pressure and, composition in the ICP device on sulfur and selenium plasmas will be presented. Preliminary data on film deposition and characterization will be included as well.

#### **B8.20**

**T-x PHASE DIAGRAM OF THE Cu<sub>2</sub>Te - CuAlTe<sub>2</sub> QUASIBINARY SYSTEM.** B.V. Korzun, A.A. Fadzeyeva, Institute of Physics of Solids and Semiconductors, Minsk, BELARUS; K. Bente, W. Schmitz, Th. Doering, G. Kommichau, Leipzig University, Institut fuer Mineralogie, Kristallographie und Materialwissenschaft, Leipzig, GERMANY.

In recent years growing interest has been shown to complex semiconducting compounds I-III-VI<sub>2</sub> (where I-Cu, Ag; III-Al, Ga, In; VI-S, Se, Te). These chalcopyrite semiconductors are considered to be possible candidates for application in photovoltaics and optoelectronics. The CuAlTe<sub>2</sub> semiconductor is one of these compounds but up to now there is not the information about its region of homogeneity in the literature. This compound is crystallized in the Cu<sub>2</sub>Te - Al<sub>2</sub>Te<sub>3</sub> quasibinary system that may be divided into two equal parts (the Cu<sub>2</sub>Te - CuAlTe<sub>2</sub> and CuAlTe<sub>2</sub> - Al<sub>2</sub>Te<sub>3</sub> quasibinary systems). The aims of this paper are (i) the preparation of alloys of the Cu<sub>2</sub>Te - CuAlTe<sub>2</sub> system and (ii) the construction of T-x phase diagram using the differential thermal analysis (DTA), X-Ray powder diffraction (XRD) and wave-length dispersive electron microprobe analysis (EMPA). To obtain the CuAlTe<sub>2</sub> and Al<sub>2</sub>Te<sub>3</sub> compounds and their alloys the method of melting of the constituent elements of copper (99.9998%), aluminum (99.9997%) and tellurium (99.999%) was used. The charges were sealed in evacuated quartz ampoules into the crucible from BN and then heated to the temperature higher above 20-30 K that the melting point of corresponding alloys. It was discovered only the formation of two compounds Cu<sub>2</sub>Te (chemical composition of the binary compound is Cu<sub>1.88</sub>Te) and CuAlTe<sub>2</sub> in this system. CuAlTe<sub>2</sub> has the peritectic character of melting with the temperature 1241K. The melting point for Cu<sub>2</sub>Te is 1388K. The region of homogeneity of CuAlTe<sub>2</sub> is shifted towards to Cu<sub>2</sub>Te and is limited by composition with 0.96 molar part of CuAlTe<sub>2</sub>. The binary composition Cu<sub>2</sub>Te is crystallized in the orthorhombic system with the lattice parameters being (10.188±0.008) Å, (10.310±0.008) Å, and (4.238±0.003) Å for a, b, and c constants, respectively. CuAlTe<sub>2</sub> is crystallized in the tetragonal structure with lattice constants (5.964±0.003) Å for a and (11.78±0.01) Å for c.

#### **B8.21**

**FEASIBILITY STUDY OF NON-VACUUM TECHNIQUES FOR FABRICATING CuInS<sub>2</sub> THIN FILMS SOLAR CELLS.**

Yoshio Onuma, Kenji Takeuchi, Sumihiro Ichikawa, Kenji Nakamura, Ryo Fukasawa, Masao Nakazawa, Koji Takei, Core Technology Research Laboratory, Shinko Electric Industries Co., Ltd., Nagano, JAPAN.

CuInS<sub>2</sub> based thin films are one of the most promising optical absorbers for high efficiency solar cells. There is a need to prepare low-cost thin films to reduce the cost of device fabrication and produce higher efficiency cells in the near future. In this paper, we proposed a novel solar cell fabrication process using non-vacuum techniques for precursor and buffer and transparent conducting oxide which are advantageous for the low-cost production and large-sized cells. A MOCVD method in atmospheric pressure was examined for the use of the buffer and the transparent electrode layers deposition.

Deposition processes of the Cd-free buffer layer (ZnS, InS) and the transparent conducting oxide layer (ZnO:Al) were studied by the MOCVD and then applied for the solar cell fabrication. Furthermore, an electroplating method was applied to the deposition of Cu/In precursor for the CuInS<sub>2</sub> absorption layer. The sulfate based high purity solution are used for the plating bath. Finally, we found out the suitable solution and the plating conditions necessary for preparation of homogeneous layers. The precursor was formed from indium top layer and copper under layer at just after deposition, however, it was found that indium diffused into copper layer at room temperature from Cu/In ratio depth profiles. The Cu/In precursor showed the entire alloying at 4 days after deposition. The CuInS<sub>2</sub> films were prepared by sulfurization of the precursor. The CuInS<sub>2</sub> films showed the uniform morphology (low roughness) by optimization of sulfurization conditions. As a result, the leak current due to the pin holes on the CuInS<sub>2</sub> films was remarkably decreased. Seeking better film quality and cell efficiency the deposition conditions of the MOCVD and the electroplating were investigated. These results showed the possibility of low-cost cell production by means of non-vacuum technique.

#### **B8.22**

**MODELING OF FLUX COMPOSITION FOR THERMAL CdCl<sub>2</sub>:02 ANNEALING OF POLYCRYSTALLINE CdTe.** Jaan Hiie and Vello Valdna, Tallinn Technical University, Department of Materials Science, Tallinn, ESTONIA.

Presence of residuals and precipitates in grain boundaries, on interfaces and in the grains is a frequent bar on the way to high performance chalcogenide solar cell. The inclusions are responsible for surface contamination and over-optimal lattice concentrations of dopants. We present investigation results of thermal stability of model flux compositions of CdTe - CdCl<sub>2</sub> with CdTeO<sub>3</sub>, the last recognized as a main oxidation product of CdTe. The composition of the flux was chosen to obtain larger quantity of residual phases for analyses by retaining 10 volume per cent of solid CdTe phase at the fusion temperature between 350C and 500C in a vacuum-closed isothermal quartz ampoule. Quantity of CdTeO<sub>3</sub> constituted 10 at per cent of the whole CdTe mass. The batches of water slurry from high-dispersed components were fused to attain columnar growth perpendicular to the substrate with a minimum grain boundaries and volume of intergranular residual phases, and a maximum separation of flux and grown CdTe crystalline phase. The fused batches were vacuum annealed between 350C and 500C in a long narrow quartz tube with deposition of volatile components CdTe, TeO<sub>2</sub>, CdCl<sub>2</sub> and Te. The condensates were separated and gravimetrically analysed. The residual phases were characterised by x-ray diffraction, electrical and optical methods and microscopically. Differential thermal analysis was performed for flux before and after fusion. Considerable lowering of melting and solidification temperatures with increasing CdTeO<sub>3</sub> concentration was observed. CdCl<sub>2</sub> is a source of chlorine for p-type doping of CdTe and in the composition of the flux, CdCl<sub>2</sub> has a role of catalytic agent forming low melting point eutectics with native oxides and CdTe. After processing, CdCl<sub>2</sub> can be separated in high purity condition. We believe that the results are useful for development of new flux compositions and processings for better performance of CdTe solar cells.

#### **B8.23**

**THE EFFECT OF FILM COMPOSITION ON THE TEXTURE AND GRAIN SIZE OF CuInS<sub>2</sub> PREPARED BY CHEMICAL SPRAY PYROLYSIS.** Michael H.-C. Jin and Kulbinder K. Banger, Ohio Aerospace Institute, Brookpark, OH; Jerry D. Harris, Cleveland State University, Dept of Chemistry, Cleveland, OH; Aloysius F. Hepp, NASA Glenn Research Center, Cleveland, OH.

The objective of this work is the development of thin film solar cell materials that can be deposited on large-area, flexible, lightweight substrates for future space applications by enhancing the mass-specific power. We previously developed new ternary single-source precursors (SSPs) for chalcopyrite materials and demonstrated CuInS<sub>2</sub> thin film deposition using chemical spray pyrolysis [1,2]. It is well understood that precise control of composition during film growth is critical for chalcopyrite materials. In this study, we investigated the composition of CuInS<sub>2</sub> films deposited using SSPs, and its effect on texture, secondary phase formation, and grain size. Films with either (112) or (204/220) preferred orientation always showed Cu-rich and In-rich composition, respectively. Interestingly, Cu-rich (112)-oriented films with dense columnar grains can only be prepared without a secondary phase. The In-rich (204/220)-oriented films always contained a secondary phase evaluated as an In-rich compound based on composition analysis and Raman spectroscopy. The preferred orientation of the film is likely related to the molecular structure of the precursors and its subsequent effect on their decomposition kinetics and the nucleation at the surface. The equivalent symmetry between the {102} plane of CuInS<sub>2</sub> and the {100} plane of the In compound with a hexagonal structure is

also thought to be associated with the observed correlation between (204/220) texture and the In compound. The largest grain size obtained was about 0.5 μm, and further improvement is expected by implementing 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 layer for large grain growth. [1] K.K. Banger, J. Cowen and A.F. Hepp, Chem. Mater. 13, 3827 (2001). [2] M.H.-C. Jin, K.K. Banger, J.D. Harris, J.E. Cowen, and A.F. Hepp, 29th IEEE Photovoltaic Specialists Conference, 2P2.5 (2002).

#### **B8.24**

**QUANTUM DOT SENSITIZED SCHOTTKY BARRIER SOLAR CELLS.** Jing Tang, Univ. of California-Santa Barbara, Materials Dept, Santa Barbara, CA; Ajay K. Kochhar and Eric W. McFarland, Univ. of California at Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Galen 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 photo-excitation of CdSe/CdS semiconductor quantum dots (QD) (5 nm) for photon-to-electron conversion and subsequent injection and transport of ballistic electrons through a ultrathin Au film on a Au/TiO<sub>2</sub>/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 bands, hot electron transport in the noble metal film and over the Schottky barrier, and 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 across the barrier. We have improved the electronic coupling between the quantum dots and Au layer by surface 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 charge transport. A typical device shows an open circuit voltage of 340 mV and a short circuit current density of 0.05 mA/cm<sup>2</sup>, with a fill factor of 0.46 under AM1.5 broadband illumination (100 mW/cm<sup>2</sup>). This work demonstrates an alternative approach for the fabrication of low cost and durable solar cells.

#### **B8.25**

**FABRICATION AND PROPERTIES OF CdZnTe THIN FILMS FOR TANDEM SOLAR CELL APPLICATION.** Ramesh Dhere, Tim Gessert, Sally Asher, and Helio Moutinho, 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 1.6-1.8 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 powders of CdTe and ZnTe as the source for film deposition by CSS. Even for the ZnTe/CdTe (95:5 ratio) source material, the deposited films were entirely CdTe due to higher vapor pressure of CdTe. In the second approach, we used prealloyed CdZnTe powders (obtained from CERAC, Inc.) as the source. Due to the lower sticking coefficient of 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/substance 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 effect of different post-deposition anneals on the interdiffusion and alloy formation, as well as the results from the first two approaches.

#### **B8.26**

**EFFECT OF THE THERMINAL TREATMENT WITH CdCl<sub>2</sub> ON THE ELECTRICAL PROPERTIES OF SOLAR CELLS OF CdS/CdTe THIN FILMS GROWN BY SPUTTERING LARGE AREA AND CSVT.** H. Hernandez-Contreras, G. Contreras-Puente, J. Vidal-Larramendi, J. Aguilar-Hernandez, O. Vigil-Galan, Escuela Superior de Fisica y Matematicas del IPN, DF, MEXICO.

Several structural and electrical properties have been studied in semiconductor bilayers and specially 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 hereojunction has not carried out to our knowledge. By sputtering in large area grown CdS and by CSVT grown CdTe. We present in this paper a study on the influence of the grain size mismatch on the diode

characteristics. Particularly the efficiency of the solar cells, Voc, Jsc, ideal diode factor and saturation current are reported and the results are presented and discussed.

#### **B8.27**

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

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

One of the most promising strategies for lowering the cost of photovoltaic (PV) solar energy is the use of thin-film technologies, 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 materials 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 nanoparticulate materials. Homogeneous CIGS layers are formed by incorporating the desired materials (e.g. Cu, In, Ga, etc.) into phase-stabilized, sub-micron particulate metal/oxide precursor materials. Layers of particles are deposited using spraying and printing methods, and particulate layers are converted into solid CIGS films by reactive sintering at atmospheric pressure. Sprayed precursor 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 typical spray-derived CIGS films reduces the average sheet conductance of overlying coatings; thin coatings of transparent conductors deposited on rough CIGS films exhibit sheet resistances up to two orders of magnitude higher than equivalent coatings on planar surfaces. Slurry 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.

#### **B8.28**

##### **REDUCTION OF MICRO-CRACKS IN LARGE DIAMETER**

**In<sub>x</sub>Ga<sub>1-x</sub>Sb BULK CRYSTALS.** K. Juliet Vogel, Dept of Engineering Science; Partha Dutta, Electrical, Computer and Systems Engineering Dept, Rensselaer Polytechnic Institute, Troy, NY.

The ternary alloy, In<sub>x</sub>Ga<sub>1-x</sub>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 infra-red regime. Bulk crystal growth followed by impurity diffusion to form p-n junctions is a well-established process for low cost, large volume devices using diffused Ge or binary III-V and II-VI compounds. However, similar research and development on bulk ternary and quaternary compounds has not been as successful, primarily due to experimental difficulties in growing spatially-homogeneous, 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 crystal 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 III-V mixtures. Utilizing a unique system based upon vertical Bridgman technique, large diameter (50 millimeter) In<sub>0.25</sub>Ga<sub>0.75</sub>Sb polycrystals of high compositional uniformity and remarkable quality have been grown. Novel methods of mixing 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, initial experiments will be reviewed, detailing the system and crystal growth parameters. Electron probe microscopy (EPMA) data of vertical and horizontal cross-sections will be presented to examine the compositional variations throughout grown crystals. Further microscopic evidence of the reduction in cracking resulting from specific melt mixing schemes will be also be presented.

#### **SESSION B9: DEVICE CHARACTERIZATION AND FORMATION**

Chairs: John M. Merrill and William N. Shafarman  
Friday Morning, April 25, 2003  
Salon 10/11 (Marriott)

#### **8:30 AM \*B9.1**

**NEW JUNCTION CAPACITANCE METHODS FOR THE STUDY OF DEFECT DISTRIBUTIONS AND CARRIER PROPERTIES IN THE COPPER INDIUM DISELENIDE ALLOYS.** J. David Cohen, Jennifer T. Heath, Department of Physics and Materials Science Institute, University of Oregon, Eugene, OR; William N. Shafarman, Institute for Energy Conversion, University of Delaware, Newark, DE.

Junction capacitance methods are routinely applied to the study of new semiconducting materials to learn about deep defect states within the energy gap. In studies of copper indium diselenide (CIS) and its related alloys, methods such as admittance spectroscopy and DLTS have been used quite successfully over the past decade for this purpose. However, these methods can suffer from a number of 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 micron thick semiconducting films from defect states at or near the barrier 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/or 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 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 DISELENIDE FILMS AND THEIR IMPACT ON PHOTOVOLTAIC DEVICE PERFORMANCE.** Jennifer T. Heath, Department of Physics, Linfield College, McMinnville, OR; J. David Cohen, Department of Physics, University of Oregon, Eugene, OR; William N. Shafarman, Institute of Energy Conversion, University of Delaware, Newark, DE.

We have characterized the thermal and optical transitions associated with electronically active defects in CuIn<sub>1-x</sub>Al<sub>x</sub>Se<sub>2</sub> (CIAS) films. The films studied were incorporated as the absorber layer in high efficiency photovoltaic devices, which have the structure Mo/CIAS/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 > 0.35 the open circuit voltage is pinned 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 film. 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 CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (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<sup>17</sup> cm<sup>-3</sup>), which effectively pins the bulk Fermi level. This may also account for the pinning of the open circuit voltage when 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)Se<sub>2</sub> THIN FILMS.** Manuel J. Romero, Jehad AbuShama, Chun-Sheng Jiang, Mowafak M. Al-Jassim, Rommel Noufi, National Renewable Energy Laboratory, Golden, CO.

Thin-film solar cells are promising for future, cost-effective, terrestrial photovoltaics. So far, the record efficiency for these solar cells has been demonstrated by thin films of Cu(In,Ga)Se<sub>2</sub> (CIGS) deposited by the three-stage process. However, the full potential of CIGS in

single and multi-junction solar cells has yet to be realized. An initial stage in the development of tandem solar cells involves the production of individual cells with Ga/(In+Ga) compositional ratios (between 0.25 and 1) to match the solar spectra irradiance. Understanding the evolution of these films during the three stages of physical vapor deposition becomes critical because of the complexity of thermodynamic and kinetic aspects derived from the multinary polycrystalline CIGS and the three-stage process itself. In this contribution, we employ cathodoluminescence spectroscopy and imaging to investigate how CIGS thin films progress towards the final stage of deposition. In our measurements, spectra are acquired with multi-channel detectors and wavelength-dispersive images are subsequently reconstructed from the spectra. Acquisition times by pixel of 10-20 ms avoid e-beam damage. We have observed similar and dissimilar aspects in the evolution of the microscopic luminescence for different compositional ratios. Among the similarities, at the beginning of the third stage, upon transformation of the excess copper selenide into the primary phase, the spatial distribution of the emission becomes highly uniform in terms of photon energy. Further addition of In and Ga increases spatial variations in the luminescence, probably by differences in the diffusion of In and Ga into the absorber. On the other hand, we show that the electronic configuration of grain boundaries and its evolution during the three stage process are very dissimilar for different compositions. We hope to learn from these studies the extent of recombination in the surface layers of CIGS thin films and its impact on the cell performance.

#### 9:30 AM B9.4

REVERSIBLE AND IRREVERSIBLE EFFECTS OF HIGH-ENERGY ELECTRON AND PROTON IRRADIATION ON Cu(In,Ga)Se<sub>2</sub>. Uwe Rau and Kristin Weinert, Institute of Physical Electronics, University of Stuttgart, GERMANY.

The radiation hardness of Cu(In,Ga)Se<sub>2</sub> 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 after 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.

#### 10:15 AM B9.5

PHOTOCONDUCTIVE CdS IN CdTe/CdS SOLAR CELLS. Steven S. Hegedus, Kevin D. Dobson, Brian E. McCandless, Darhini Desai, Dan Ryan, Institute of Energy Conversion, University of Delaware, Newark, DE.

The impact of photoconductive CdS (PC-CdS) in CdTe/CdS solar cells manufactured by several different methods has been investigated using spectral response (SR) with spectrally filtered bias light; i.e. dual beam photoresponse measurements, along with photocapacitance and current-voltage (J-V) measurements. Cu-compensated CdS is a well known photoconductor. One manifestation of PC-CdS 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 CdS dark conductivity. Another signature of PC-CdS in this work is a significant increase in the blue SR when the device is illuminated with red 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 4 different deposition processes containing Cu. The PC-CdS signature is not present in the absence of the CdS layer. The PC spectrum was extracted from the increased SR at a probe wavelength of 450 nm by varying the bias light spectrum with bandpass filters. This spectrum is similar to the PC-CdS response data of Shiozawa (1968) for Cu-compensated CdS, peaking around 700 nm. We conclude that Cu-compensated CdS is responsible for the increased dark resistance of the CdS in stressed CdTe/CdS solar cells suggesting that Cu in CdS has changed the doping hence field profile in the devices. This has implications for stability.

#### 10:30 AM B9.6

ADMITTANCE SPECTROSCOPY AND MODIFICATIONS INCLUDING DLCP APPLIED TO CdS/CdTe SOLAR CELLS. A.S. Gilmore, V. Kaydanov, T.R. Ohno, Colorado School of Mines, Dept of Physics, Golden, CO.

Electrical characterization of defects in CdS/CdTe thin film solar cells is important to provide an understanding of how to produce better cells in the future, as well as how degradation operates in today's cells. Admittance spectroscopy provides tools to detect and characterize defect states. Defect properties such as emission rates, energy position in the band gap, and estimates of defect concentrations for a specific defect level or band can be obtained using admittance spectroscopy. Modifications to admittance spectroscopy such as drive level capacitance profiling (DLCP) allow further analysis of the defect levels/bands in these cells, including defect state densities as a function of depth through the absorber layer in a cell. CdS/CdTe thin film solar cells provided from several institutions using various deposition methods including vapor transport, closed space sublimation, and sputtering were characterized with these techniques. In all cells studied, high defect state densities (even greater than the doping level obtained from common CV profiling) were observed. In each cell, at least two defect levels were observed with energies of approximately 0.4 and 0.6 eV above the valence band. The levels were attributed to Cu ions on Cd sites and to Cd vacancies, respectively. Identification of the levels/bands included recognizing expected dominant defects in these cells, matching energy levels with previously reported literature values, and observing variations in defect state densities due to changes in cell processing. Various processing steps were investigated including the standard cadmium chloride treatment, the surface etch prior to application of the back contact, and the intentional doping of the cell with copper. The influence of degradation under various conditions on defect state densities was also observed. In all the cells studied, the expected inverse correlation between efficiency and defect state density was not observed. Surprisingly, cells with higher efficiency often had the highest defect state densities.

#### 10:45 AM \*B9.7

NANOCOMPOSITES BETWEEN TiO<sub>2</sub> AND CuInS<sub>2</sub>: TOWARDS SOLID STATE 3D SOLAR CELLS. Albert Goossens, Faculty of Applied Sciences, Delft University of Technology, Delft, THE NETHERLANDS.

With the advent of dye-sensitized (Grätzel-type) solar cells and C60/polymer bulk heterojunctions a perspective towards the construction of all-solid three dimensional (3D) solar cells has emerged. In this design, an n-type and a p-type semiconductor are mixed on a nanometer scale to form an interpenetrating network. In this network, the photo-active interface is enhanced tremendously. Henceforth, the minority carrier diffusion length can be reduced down to a few tens of nanometers, which provides a high tolerance for contamination. In the present investigations, nanoporous anatase TiO<sub>2</sub> films (n-type) are infiltrated with CuInS<sub>2</sub> (p-type) being the optical absorber. The direct bandgap of CuInS<sub>2</sub> is 1.5 eV and matches the solar spectrum very well. Atomic Layer Deposition (ALD) is used to deposit CuInS<sub>2</sub> inside the pores of nanoporous TiO<sub>2</sub>. With ALD it is possible to infiltrate nanoporous TiO<sub>2</sub> films with a pore size of 15 nm over more than a micrometer, as has been confirmed by Rutherford Back Scattering (RBS). Nanoporous TiO<sub>2</sub> with 25 nm or larger particles can be filled completely. X-ray diffraction, Raman spectroscopy, photoluminescence spectroscopy, along with (photo-) current and (photo-) capacitance analysis are used to elucidate the defect structure of CuInS<sub>2</sub> deposited inside nanoporous TiO<sub>2</sub>. Prototypes of 3D solar cells, based on nanocomposites of TiO<sub>2</sub> and CuInS<sub>2</sub>, indeed show a remarkable photovoltaic activity. To improve the defect chemistry of CuInS<sub>2</sub> post-annealing in sulfur and oxygen is required. Both the concentration of sulfur vacancies and the fraction of Cu-Au order are reduced considerably by the anneal treatment. Also the introduction of a film between TiO<sub>2</sub> and CuInS<sub>2</sub> appears to be advantageous to the cell performance. While there are still barriers that limit the device performance, already it is clear that the construction of solid state 3D solar cells is possible and may open a new horizon for future photovoltaic devices.

#### 11:15 AM B9.8

NANOSTRUCTURAL AND DIFFUSION PROPERTIES AT THE Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub>/TRANSPARENT CONDUCTING OXIDE BACK CONTACT FOR TANDEM SOLAR CELLS. Tokio Nakada, Takehito Tokado and Yutaka Hirabayashi, Department of Electrical Engineering and Electronics, Aoyama Gakuin University, Setagaya-ku, Tokyo, JAPAN.

Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (CIGS, x=1 or 0.3)-based thin film solar cells have been fabricated using a transparent conducting oxide (TCO) back contacts including ITO, SnO<sub>2</sub>:F, ZnO:Al and ZnO:Ga.

Nano-structural 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).  $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$  (CIGS) thin films were deposited by the modified three-stage process onto the TCO-coated glass substrates at deposition temperatures of 400-580°C.  $\text{CuGaSe}_2$  (CGS) 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  $\text{ZnO:Al}/\text{ZnO}/\text{CBD-CdS}/\text{CIGS}/\text{TCO}/\text{glass}$  structure. Almost no intermixing at the CIGS/ITO, CGS/ITO, CIGS/ $\text{SnO}_2:\text{F}$ , and CGS/ $\text{SnO}_2:\text{F}$  interface boundaries fabricated at a deposition temperature of 530°C was found by SIMS and EDX analyses. The lattice image revealed that the CIGS and CGS grains grew epitaxially (grain by grain) onto  $\text{SnO}_2:\text{F}$  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/ $\text{ZnO}$  and CGS/ $\text{ZnO}$  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 CGS 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 DRY Cd-FREE CIGS SOLAR CELLS USING ATOMIC LAYER DEPOSITED INDIUM SULFIDE BUFFER LAYERS.

Negar Naghavi, Jean-Francois Guillemoles, Daniel Lincot, Laboratoire Dielectrochimie et de Chimie Analytique, UMR 7575 CNRS, ENSCP, Paris, FRANCE; Bruno Canava and Arnaud Etcheberry, Institut Lavoisier (IREM), Université de Versailles-Saint-Quentin, Versailles, FRANCE; Stefanie Spiering and Mickeal Powalla, Zentrum fuer Sonnenenergie-und Wasserstoff-Forschung, Stuttgart, GERMANY.

Thin film solar cells based on  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) are entering the industrial period. At present high efficiency devices and modules use thin CdS interfacial buffer prepared by chemical bath deposition. Alternative 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 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 characterisation of these devices open important new vistas 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.

F. Säuberlich, G. Liu, F. Rüggeberg, W. Jaegermann, A. Klein, Darmstadt Univ of Technology, Inst of Materials Science, Darmstadt, GERMANY.

Oxidic conductors as  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$  or  $\text{TiO}_2$  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  $\text{Cu}_2\text{S}$  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/ $\text{ZnO}$  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).