SYMPOSIUM F

Thin-Film Compound Semiconductor Photovoltaics

March 28 - April 1, 2005

Chairs

William Shafarman
Institute of Energy Conversion
University of Delaware
Newark, DE 19716
302-831-6215

Tim Gessert
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401
303-384-6451

Shigeru Niki
NAIST
1-1-1 Umezono, Tsukuba
Ibaraki, 305-8568 Japan
81-298-61-5610

Susanne Siebentritt
Hahn-Meitner-Institut
Glienicker Str. 100
Berlin, 14109 Germany
49-30-8062-2442

Symposium Support

DuPont Central Research and Development
National Renewable Energy Laboratory (NREL)

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 865
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

TUTORIAL

Young Scientist Tutorial on Characterization Techniques for Thin-Film Solar Cells
Monday March 28, 2005
1:30 PM - 5:00 PM
Room 2005 (Moscone West)

This tutorial is intended for young researchers (including students and post-graduates within three years of degree completion) that are new in the field of thin-film solar cells and want to learn the fundamentals of characterization methods that are being utilized in the research and development of these materials and devices. The tutorial will begin with an introduction to thin-film solar cells based on copper indium diselenide, cadmium telluride, and silicon thin-films and critical materials and device issues. This will be followed by more detailed presentations focusing on four specific characterization techniques being used to address these issues:

(1) **Transmission Electron Microscopy (TEM)**

(2) **X-ray Fine Structure Studies at Synchrotron Sources**

(3) **Admittance Measurements**

(4) **Hall-Effect Measurements**

The presentations on characterization techniques will be given by young researchers who are active in the characterization of thin-film solar cells. Because the presentations will focus on the characterization techniques rather than the specific materials, the tutorial should be of broad interest to participants of other symposia.

A unique aspect of this tutorial is that it will primarily be presented by students and young researchers for students and young researchers. It is believed that a more open atmosphere for discussion of ideas will be facilitated by the absence of senior scientists in the session. Scientific exchange and discussion between students will be encouraged by the lecture-style presentations and by having sufficient time allotted for discussions.

Instructors:
William Shafarman, University of Delaware
Daniel Abou-Ras, ETH Zurich
Xiangxin Liu, University of Toledo
Jennifer Heath, Linfield College
Thorsten Rissom, Hahn-Meitner-Institut Berlin

SESSION F1: Optical Characterization
Chairs: Rommel Noufi and Ingrid Repins
Tuesday Morning, March 29, 2005
Room 2005 (Moscone West)

8:30 AM F1.1
Multichannel Mueller Matrix Analysis of the Evolution of Surface Roughness on Different In-Plane Scales during Polycrystalline Film Processing. Chi Chen[1], Christoph Ross[3], Christopher R. Wronski[2] and Robert W. Collins[1]; [1]Department of Physics and Astronomy, The University of Toledo, Toledo, Ohio; [2]Dept. of Electrical Engineering, The Pennsylvania State University, University, University Park, Pennsylvania; [3]Inst. of Photovoltaics, Julich, Germany.

Polycrystalline semiconductors used in photovoltaics, including CdTe, Cu(In,Ga)(S,Se)$_2$, and transparent conducting oxides often develop extensive roughness during preparation and processing, making it difficult to interpret quantitatively real time optical measurements based on specular reflection. The recently-developed techniques of real time spectroscopic ellipsometry based on Stokes vector[1] and Mueller matrix[2] measurement show considerable promise for extracting surface roughness thicknesses on a wide range of in-plane scales, and thus for solving the full optical problem. The *microscopic* roughness (in-plane scale $L < 50$ nm) and bulk layer optical properties can be determined by fitting the ellipsometric (Ψ, Δ) spectra. These spectra can be overdetermined from the Mueller matrix using methods that reject non-specular scattered light. The fitting in this case applies a conventional approach based on specular reflection from a multilayer structure that includes effective medium layers. The *macroscopic* surface roughness (in-plane scale $0.05 < L < 5$ mm) can be determined using a scalar scattering theory by fitting the measured unpolarized reflectance R, deduced from the (1,1) Mueller matrix element. In this latter fitting procedure, the sample structure is also required as deduced from the (Ψ, Δ) spectra. Roughness on the *geometric* optical scale ($L > 5$ mm) can be extracted in an analysis of the weak deviations from unity in a consistency parameter p that employs all Mueller matrix elements to describe depolarization. As a demonstration, this overall methodology is applied to extract the optical properties (ϵ_1, ϵ_2) of a ZnO film along with the evolution of its microscopic, macroscopic, and geometric scale surface roughness amplitudes from spectra collected in real time during etching by HCl/H$_2$O in a liquid cell. The resulting best fits to the spectra in $\{(\Psi, \Delta), R, p\}$ are excellent, and the deduced parameters are internally consistent with roughness profiles showing fractal behavior. Correlations with atomic force microscopy will be presented. 1. J. Lee, P.I. Rovira, I. An, and R.W. Collins, "Rotating-compensator multichannel ellipsometry: applications for real time Stokes vector spectroscopy of thin film growth", *Rev.Sci.Instrum.* **69**, 1800-1810 (1998). 2. R.W. Collins and J. Koh, "Dual rotating-compensator multichannel ellipsometer: an instrument design for real time Mueller matrix spectroscopy of surfaces and films", *J.Opt.Soc.Am.* A **16**, 1997-2006 (1999).

8:45 AM F1.2
Real Time Analysis of Magnetron-Sputtered Thin-Film CdTe by Multichannel Spectroscopic Ellipsometry. Jian Li[1], Jie Chen[1], J. A. Zapien[2], N. J. Podraza[1], Chi Chen[1], J. Drayton[1], A. Vasko[1], A. Gupta[1], S. L. Wang[1], R. W. Collins[1] and A. D. Compaan[1]; [1]Department of Physics and Astronomy, The University of Toledo, Toledo, Ohio; [2]The City University of Hong Kong, Hong Kong SAR, Hong Kong.

Real time spectroscopic ellipsometry (RTSE) based on the rotating-compensator principle[1] is currently being implemented for analysis of CdTe and related ternary alloy deposition by magnetron sputtering. The spectral range of the instrument used in these studies is 0.75 to 6.5 eV, and complete spectra in the ellipsometric angles (ψ, Δ) can be collected in a time as short as $(30.7\ \text{Hz})^{-1} = 32$ ms, where 30.7 Hz is the rotation frequency of the compensator. The CdTe films studied here were sputtered onto crystalline Si wafers or on Mo-coated glass, held at nominal temperatures of 200°C, and probed at angles of incidence of 65.6-65.7°. The Si wafer was used as an ideal substrate due to its smoothness; as a result, complications of substrate-induced roughness are completely avoided. The Mo was used due to its relevance as a back contact in the substrate solar cell configuration; however, its surface exhibited significant roughness that led to complications in the data interpretation due to the filling of this roughness layer simultaneously with the nucleation process. In general, this research demonstrates the ability to extract the time evolution of (i) bulk layer thickness, (ii) surface roughness thickness, (iii) instantaneous deposition rate, (iv) near-surface void volume fraction, (v) electronic transition characteristics, and (vi) substrate temperature, the latter two from the E_0 (fundamental gap) and E_1 critical points of CdTe, respectively. Among the observations made here include: (i) monolayer thickness ($\sim$3$\AA$) surface roughness at the onset of bulk layer growth and during the first $\sim$50$\AA$ of bulk growth on c-Si; (ii) a higher E_0 critical point in the initial stages of growth apparently due to a quantum confinement effect in the ultrasmooth film, (iii) gradual development of a lower density bulk film after 1000$\AA$ thickness; and (iv) much broader critical points in the dielectric function for the thin film compared to the single crystal, that provide information on the grain structure. CdTe depositions performed on glass/ZnO/CdS to simulate the structure used for 14% efficient solar cells will also be discussed. 1. R.W. Collins, I. An, J. Lee, and J.A. Zapien, "Multichannel ellipsometry", in: *Handbook of Ellipsometry*, edited by H.G. Tompkins and E.A. Irene, (Noyes, Norwich, NY, 2004) p. 479-564.

9:00 AM F1.3
Effect of Cu Deficiency on the Optical Properties and Electronic Structure of CuIn$_{1-x}$Ga$_x$Se$_2$ Determined by Spectroscopic Ellipsometry. Sung-Ho Han[1,2], Falah S. Hasoon[1], Joel W. Pankow[1], Allen M. Hermann[2] and Dean H. Levi[1]; [1]National Renewable Energy Laboratory, Golden, Colorado; [2]Department of Physics, University of Colorado, Boulder, Colorado.

Spectroscopic ellipsometry provides a sensitive measure of the optical properties of a material. The optical properties can be expressed in terms of the dielectric function, which in turn is closely related to the electronic structure of the material. Through the analysis of the dielectric function we gain information about the band structure through both the joint density of states and the energies of the critical points. In this paper we report the results of our studies of the optical and electronic structure of a wide range of polycrystalline thin-film CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) alloys. The composition range includes nearly stoichiometric (slightly Cu-poor) (24.5 at.% Cu) CIGS, moderately Cu-poor (21.0 at.% Cu) CIGS, and very Cu-poor (15 at.% Cu) CIGS with $x \equiv$ Ga/(In+Ga) = 0, 0.25, 0.35, 0.5, 0.75, and 1.0. In previous publications we have used spectroscopic ellipsometry to establish an increase in band gap and a reduced density of states in the upper valence band caused by the moderate copper deficiency in CuInSe$_2$ (CIS) and CuIn$_{0.8}$Ga$_{0.2}$Se$_2$. [S. Han, A. M. Hermann, F. S. Hasoon,

H. A. Al-Thani, and D. H. Levi, Appl. Phys. Lett. **85**, 576 (2004)] Relative to nearly stoichiometric CIS and CIGS, we find a reduction in the absorption strength in the spectral range 1-3 eV. The absorption is reduced by approximately 10% in that spectral region. This reduction can be explained in terms of the predominance of Cu 3d and Se 4p states at the valence band maximum. In addition, Cu-poor CIS and CIGS materials show an increase in bandgap since the p-d repulsive interaction in Cu-poor CIGS is less than that in nearly stoichiometric CIGS. High-efficiency CIGS photovoltaics (PV) use slightly Cu-poor (23.5-24.5 at.% Cu) CIGS absorber layers. Although there is not a consensus of why slightly Cu-poor CIGS is necessary for high efficiency solar cells, recent work has implied an important role of Cu deficiency at surfaces and grain boundaries. [C. Persson and A. Zunger, Phys. Rev. Lett. **91**, 266401 (2003)] Thus it is important to understand the effects of Cu-deficiency on the electronic properties of CIGS. In addition, the differences in the effects of Cu deficiency between $x = 0.25$ and $x = 0.35$ are particularly relevant to PV because device efficiency declines once $x > 0.30$. Understanding how the role of Cu deficiency changes with the gallium concentration is important to a fundamental understanding of the material properties determining PV device efficiency. Finally, as researchers press towards higher gallium concentration and higher band gaps for the top cell in high efficiency tandem devices, it will become more important to understand the properties of CuGaSe$_2$ and high-Ga CIGS.

9:15 AM F1.4
Analysis of Cu(InGa)Se$_2$ Alloy Films Optical Properties and the Effect of Cu Off-Stoichiometry. Paulson D. Puthur[2] and W. N. Shafarman[1]; [1]Institute of Energy Conversion, University of Delaware, Newark, Delaware; [2]Miasole, Inc., San Jose, California.

Variable angle spectroscopic ellipsometry (SE) has been used to characterize Cu(InGa)Se$_2$ thin films as a function of relative Ga content and to study of the effects of Cu off-stoichiometry. Uniform Cu(InGa)Se$_2$ films were deposited on Mo-coated soda lime glass substrates by elemental evaporation with a wide range of relative Cu and Ga concentrations. X-ray diffraction measurements were carried out to obtain phase information about the material. Due to their high surface roughness, the films were generally not suitable for quantitative analysis by SE. A method was developed whereby the SE measurements were carried out on the reverse side of the Cu(InGa)Se$_2$ films immediately after peeling them from Mo-coated soda lime glass substrates. Optical constants of Cu(InGa)Se$_2$ were determined over the energy range of 0.75-4.6 eV for films with 0=Ga/(In+Ga)=1 and used to determine electronic transition energies. Further, the changes in the optical constants and electronic transitions as a function of Cu off-stoichiometry were determined by the characterization of CuInSe$_2$ and Cu(InGa)Se$_2$ [with Ga/(In+Ga)=0.3] films with 0.3=Cu/(In+Ga)=1. Films with Cu/(In+Ga) less than $\sim$ 0.8 contain 2 phases so a model for optical behavior of a heterogeneous system is needed to describe the optical constants. Different optical models will be compared. Analysis of the optical constants and related electronic transitions will be presented and discussed in context of the CuInSe$_2$ band structure and phase diagram. Two distinctive features are observed in the optical spectra as the Cu concentration decreases. First, the fundamental bandgaps are shifted to higher energies, which can be related to the decreasing coupling between the Cu d- and Se p-orbitals resulting in lowering of the valance band maxima. Second, the critical point features at higher energies become broader suggesting degradation of the crystalline quality of the material. References 1. P.D. Paulson, R.W. Birkmire, W.N. Shafarman, J. Appl. Phys. 94, 879 (2003). 2. M.I. Alonso, M. Garriga, C.A. Durante Rincon, E. Hernandez and M. Leon, Appl. Phys. A 74, 659, (2002).

9:30 AM F1.5
Sub-micron Optoelectronic Properties of Polycrystalline Solar Cell Materials. S. Smith, T. Gessert, R. Dhere, P. Stradins, T. Wang and A. Mascarenhas; NREL, Golden, Colorado.

Generation, transport and collection of carriers in polycrystalline (PX) solar cells and their constituent materials are likely significantly different than in their single-crystal counterparts. Recent theoretical and experimental results have put forth the expectation that grain boundaries in PX-solar cell materials such as CdTe and CuInGaSe$_2$, either as-grown or after appropriate post-growth treatment, may have electronic properties which are advantageous to charge separation and solar cell operation[1-3]. However, a microscopic picture of the spatial variations in the optoelectronic properties of these materials is, for the most part, still lacking. The goal of the work reported here is to explore the optoelectronic and spectroscopic properties of grain-boundaries in these materials at the nanometer length-scale, via novel, high-resolution optical techniques. Towards this end, a significant enhancement in photo-response near grain boundaries in CdTe solar cells, consistent with models put forth in reference 2, was observed via near-field Optical Beam Induced Current (n-OBIC) [4]. A systematic μ-PL study of the effect of CdCl$_2$-treatment on recombination in CdTe/CdS solar cell structures of varying thickness directly examined the variation in optoelectronic properties at grain-boundaries in this material, revealing the grain-boundary and surface passivation effects of this important post-growth processing step. For comparison, we also studied the effects of SiN$_x$ post-growth treatment and annealing on the photo-response of PX-silicon solar cells using n-OBIC. These results and our most-recent n-OBIC measurements in CdTe and CuInGaSe$_2$ solar cells will be discussed. [1] C.-S. Jiang, R. Noufi, K. Ramanathan, J.A. AbuShama, H.R. Moutinho, and M.M. Al-Jassim, *AppliedPhysicsLetters*, **85** 2625 (2004). [2] I. Visoly-Fischer, S.R. Cohen, A. Ruzin, and D. Cahen, *AdvancedMaterials(Weinheim, Ger.)* **16**, 879 (2004). [3]Clas Persson and Alex Zunger, *PhysicalReviewLetters* **91** 266401 (2003). [4]S. Smith, P. Zhang, T. Gessert, and A. Mascarenhas, *AppliedPhysicsLetters* **85** 3854 (2004).

9:45 AM F1.6
Electron Radiation Damage in Copper-Indium-Gallium-Diselenide Observed in-situ by Cathodoluminescence in a Transmission Electron Microscope. Hanne Scheel, Niels Ott and Horst P. Strunk; Institute of Microcharacterisation, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Erlangen, Bavaria, Germany.

Analytical transmission electron microscopes in general lack possibilities to analyze the optical answer of a specimen in addition to the normally evaluated characteristic x-ray emissions and electron energy losses. We have equipped our transmission electron microscope (accelerating voltage up to 300 kV) with a cathodoluminescence (CL) system that covers a wavelength range of 1800 - 180 nm and temperatures from 10 K upwards. This contribution is part of an extended effort to relate the defect and chemical structures to the electronic properties of Cu(In,Ga)Se2 thin solar films and studies the radiation damage properties of such films. Cathodoluminescence in the TEM is advantageous as it is sensitive to the initial damage processes. These processes occur on an atomic level and are thus inaccessible otherwise in the microscope. The in-situ character of the investigation permits to analyze also the defect formation kinetics directly. We discuss the development of the CL spectra in dependence of electron dose, specimen temperature and accelerating voltage for the whole Ga composition range of 0 - 100%. The results indicate that increasing Ga content makes the films less radiation sensitive. The voltage dependence of the damage rate indicates that the damage arises essentially due to displacement by electron knock-on (in the voltage range 150 kV- 300 kV).

SESSION F2: Electronic Structure
Chairs: Rommel Noufi and Ingrid Repins
Tuesday Morning, March 29, 2005
Room 2005 (Moscone West)

10:30 AM *F2.1
Synchrotron-Based Spectroscopy for the Characterisation of Surfaces and Interfaces in Chalcopyrite Solar Cells. Iver Lauermann[1], Immo Koetschau[1], Marcus Baer[1], Paul Pistor[1], Alexander Grimm[1], Stefan Sokoll[1], Martha Ch. Lux-Steiner[1,2] and Christian-Herbert Fischer[1,2]; [1]SE 2, Hahn-Meitner-Institut, Berlin, Germany; [2]Fachbereich Physik, Freie Universitaet Berlin, Berlin, Germany.

Spectroscopic methods based on synchrotron radiation yield valuable information on surface, interface and bulk composition as well as on the local chemical environment of chalcopyrite solar cells and their components. This knowledge is necessary to understand these photovoltaic devices, which consist of stacks of at least five different materials, and improve them in a systematic way. In this presentation we show some synchrotron based state-of-the-art methods for the analysis of polycrystalline materials and entire photovoltaic devices and their limitations. Using results obtained with the "CISSY" end station at the BESSY synchrotron in Berlin, Germany, we show how surface sensitive synchrotron excited photoelectron spectroscopy (PES) and soft X-ray emission spectroscopy (XES), which yields compositional and chemical information well beyond the depth sensitivity of PES up to a micrometer scale, have increased our knowledge of the chemistry of surfaces and "hidden" interfaces of these systems. The CISSY end station allows in-system sputter deposition of buffer and window materials as well as wet-chemical surface modification and material deposition in an attached glove-box with a subsequent contamination-free transfer into the ultra-high vacuum analysis chamber. Examples of recent results are the non-destructive detection of chemical reactions and interdiffusion at the buffer/absorber interface by XES, the quantitative elemental analysis by XES, the locally resolved analysis of surfaces of absorbers and structured solar modules by scanning PES/XES and the depth-resolved composition analysis of chalcopyrite surfaces using PES with different excitation energies. Furthermore the possibility of an in-situ analysis of wet-chemical reactions at semiconductor surfaces in a special UHV-compatible liquid cell is explored.

11:00 AM *F2.2

On the Electronic Band Structure of CuInSe2 Investigated by Angle-Resolved Photoelectron Spectroscopy.

Ralf Hunger[1], Wolfram Jaegermann[1], Wolfram Calvet[2], Carsten Lehmann[2], Christian Pettenkofer[2], Keiichiro Sakurai[3] and Shigeru Niki[3]; [1]Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany; [2]SE 6, Hahn-Meitner-Institute, Berlin, Germany; [3]Research Center for Photovoltaics, AIST, Tsukuba, Ibaraki, Japan.

We have investigated the valence band structure of CuInSe2 by angle-resolved photoelectron spectroscopy (ARPES). Even though CuInSe2 finds widespread application in thin film solar cells, a fundamental property of this material like the valence band structure was hitherto scarcely investigated by electron spectroscopic methods due to the difficulty of preparing clean and ordered crystal surfaces. We have chosen the approach of preparing heteroepitaxial CuInSe2(001)/GaAs films by molecular beam epitaxy which were covered by a protective selenium cap. In the UHV analysis system, clean and ordered CuInSe2(001) surfaces were prepared by thermal desorption of the Se cap layer. The ARPES experiments were performed at the synchrotron Bessy II. The band structure in the Gamma-T direction of the tetragonal chalcopyrite lattice, i.e. the [001] direction, was investigated by measuring electron distribution curves in normal emission, using excitation energies hn from 10 eV to 40 eV. The resulting experimental band structure will be presented and compared to calculations by Jaffe&Zunger (PRB 28 (1983) p. 5822).

11:30 AM F2.3

Se Vacancy as the Origin of Light-Induced Metastability in Cu(In,Ga)Se$_2$.

Stephan Lany and Alex Zunger; National Renewable Energy Laboratory, Golden, Colorado.

Cu(In,Ga)Se$_2$ (CIGS) photovoltaic devices often exhibit pronounced light-induced metastability. Thus, illumination experiments on CIGS cells have proven to cause open circuit voltage relaxation, and metastable changes in the junction capacitance. Also, light-soaking was shown to re-establish the initial state, when the conductivity deteriorated after thermal treatment. The underlying metastability can be viewed as persistent photoconductivity (PPC), and it has been shown that it is an intrinsic property of the absorber material, rather than a junction effect. Despite significant research on this long-standing problem, the physical mechanism causing the persistent photoconductivity in CIGS still is unknown. Using first-principles electronic structure calculations, we recently found [1] that the anion vacancies in II-VI and chalcopyrite semiconductors are deep double donors that introduce electronic states which are strongly coupled to charge state dependent large lattice relaxations. We identified the anion vacancies in these materials as a class of intrinsic defects that can produce metastable behavior and PPC, arising from the coupling between electronic and structural degrees of freedom. While II-VI and chalcopyrite I-III-VI$_2$ compounds are closely related material classes, the anion vacancies behave differently: In n-ZnO, the optical excitation of the neutral oxygen vacancy $V_O{}^0$ into the metastable $V_O{}^{2+}$ state releases two electrons to the conduction band. This causes persistent *electron* conductivity. On the other hand, the ionized Se vacancy $V_{Se}{}^{2+}$ in p-type CIS or CGS absorbers can capture electrons from the conduction band when such carriers are created by illumination or by electron injection. During this capture, $V_{Se}{}^{2+}$ transforms into the metastable $V_{Se}{}^0$ state. Since the defect level of $V_{Se}{}^0$ is located well below the valence band maximum, two free holes are released during the light-induced transition. Thus, the Se vacancy gives rise to persistent *hole* conductivity, constituting the unusual case where a donor-like defect causes p-type PPC. In CIS, the V_{Se} donor can form complexes with the abundant acceptor V_{Cu}. In fact, based on the calculated formation and binding energies, we expect that almost all Se vacancies are complexed as (V_{Se}-V_{Cu}). This complex shows a similar metastability like the isolated anion vacancy, with the distinction that an deep single acceptor state is created in the metastable configuration. Capacitance measurements after illumination or electron injection have shown that the occurrence of PPC is accompanied by the creation of deep hole traps. Since the (V_{Se}-V_{Cu}) complex transforms into the metastable state by capturing 2 electrons (releasing 2 holes), our model explains the exact 2:1 ratio of increased net acceptor concentration to the concentration of the deep hole trap. [1] Stephan Lany and Alex Zunger, Phys. Rev. Lett. 93, 156404 (2004).

SESSION F3: Defects and Impurities

Chairs: Al Campaan and Thomas Unold
Tuesday Afternoon, March 29, 2005
Room 2005 (Moscone West)

1:30 PM F3.1

In Situ Observation of Na-Induced Structure Changes in CuIn$_x$Se$_y$ Thin Films.

Gerd Lippold[1], Hans Neumann[1], Carsten Bundesmann[2] and Mathias Schubert[2]; [1]Solarion GmbH, Leipzig, Germany; [2]Institute of Experimental Physics II, University of Leipzig, Leipzig, Germany; [3]Institute of Experimental Physics, University of Leipzig, Leipzig, Germany.

An experimental setup allowing thermal co-evaporation of Cu, In, Se, and elemental Na is used to prepare CuIn$_x$Se$_y$ (CIS) thin films with the aim to get more detailed insight into the processes underlying the beneficial influence of Na on the efficiency of CIS-based solar cells. A Mo-coated polyimide film held at 400 °C was used as substrate. In the roll-to-roll deposition system, the film was continuously moved through the deposition zone. The as-grown CIS film was studied by in situ analytics: elemental composition and thickness by x-ray fluorescence and structure by Raman scattering. First, the evaporation rates of Cu and In were chosen to produce an In-rich film having the structure of the β-phase with some admixture of the α-phase. Subsequently, the In/Cu concentration ratio in the layer was held unchanged and the Na source switched on. The continuous increase of the Na supply leads to an also continuous decrease of the β-phase CIS content in the layer, and at some critical Na supply the layer is completely transformed into the α-phase. This structure change is reversible in the sense that during subsequent decrease of the Na supply the original structure of the CIS layer is recovered. Furthermore, the critical Na supply, required to completely transform the layer into the α-phase, is found to increase with increasing In/Cu concentration ratio and thus an increasing amount of β-phase CIS in the layer. The experimental results obtained are considered as a direct evidence for the incorporation of Na into the CIS crystal lattice. They confirm the theoretical predictions of Wei et al. (J. Appl. Phys. 85, 7214 (1999)) made on the basis of first-principles calculations. Accordingly, incorporation of Na into CIS reduces the stability of the neutral defect complex ($2V_{Cu}$+In_{Cu}) and thus suppresses the formation of the β-phase. From our results it follows that for the range of In/Cu concentration ratios covered in the experiments the number of the neutral defect complexes can be reduced by incorporation of Na to such an extent that the remaining concentration of these defects can be adapted in the α-phase structure. Under specific growth conditions, such in situ observations afford the experimental determination and control of the optimum amount of Na required to produce the desired structural and electronic property changes for an improved solar cell device performance.

1:45 PM F3.2

n-type doping of CuInSe$_2$ and CuGaSe$_2$: Is it possible?

Alex Zunger, Clas Persson, Stephan Lany and YuJun Zhao; National Renewable Energy Laboratory, Golden, Colorado.

While CuInSe$_2$ (CIS) can be obtained both p-type and n-type by controlling the growth conditions, improving the efficiency of CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) solar cells is severely hampered by the difficulty to obtain type inversion for Ga contents exceeding $x \approx 0.3$. In pure CuGaSe$_2$ (CGS), it is even questionable if n-type doping can be obtained at all under equilibrium doping conditions. Since the defect physics that limits the success of n-type doping is not very well understood, we develop n-type doping principles for chalcopyrite photovoltaic materials, based on theoretical investigations. Here, we regard donor doping in CIS by halogen (X = Cl, Br, I), and divalent (M = Zn, Cd) atoms. Under equilibrium growth and/or doping conditions at a given temperature, the defect concentrations, i.e. the concentration of dopants and that of intrinsic defects, are determined by the defect formation energies, which, in turn are functions of the chemical potentials of the host and dopant atoms. The doping principles are discussed in terms of five factors which determine the success of n-type doping in CIS: (i) Dopant solubility, (ii) Constraints of the chemical potentials imposed by formation of competing phases, (iii) Formation of the electron-killer defect V_{Cu}, (iv) Assisting n-type doping by the intrinsic donor In_{Cu}, (v) Wrong-site substitution of divalent atoms as acceptors, e.g. Cd_{In}, instead of donor incorporation, e.g. Cd_{Cu}. In order to obtain quantitative predictions of dopant and intrinsic defect concentrations under different growth/doping conditions we use first-principles supercell calculations to deduce the defect formation energies. Using these formation energies, the equilibrium defect concentrations are obtained by a subsequent thermodynamic calculation. In case of donor doping with halogens, we remarkably find that the conditions that maximize the incorporation of the halogen atoms according to (i) above do not yield n-type conductivity, because of overcompensation by V_{Cu} [factor (iii)]. In contrast, maximally In-rich conditions, that favor the formation of intrinsic In_{Cu} double donors according to (iv), lead to n-type doping. In this case, apart from the halogen donors, the In_{Cu} donors provide a dominant contribution to the n-type doping. In case of the divalent dopants, Cu-poor conditions do not lead to n-type doping, because of wrong-site substitution [factor (v)] at the In site. However, n-type doping from M_{Cu} donors can be obtained under maximally In-rich conditions, which correspond at the same time to Se-poor conditions as present in the classic experiments of Zn and Cd doping in CIS single crystals [B. Tell et al., Appl. Phys. Lett. 28, 454 (1976)].

2:00 PM *F3.3

A Study of Phenomena Related to the Interaction of Cu with the CdTe(111)-B Surface. Glenn Teeter, Timothy Gessert and Sally Asher; National Renewable Energy Laboratory, Golden, Colorado.

Post-deposition processing of CdTe-based thin-film photovoltaic (PV) devices often includes an annealing step in which Cu is diffused into the back-contact region. It is known that Cu acts as a p-type dopant in CdTe, and that Cu incorporation aids in the formation of a pseudo-ohmic back contact, thereby improving device performance. At the same time, the diffusion of Cu to the CdS/CdTe junction has been implicated as a possible mechanism for cell degradation. While it is clear that Cu plays an important role in CdTe thin-film devices, the full effects of Cu on CdTe device performance are the subject of ongoing research and discussion. Fundamental studies of the interaction of Cu with CdTe single-crystal surfaces provide a means for identifying and understanding phenomena related to Cu/CdTe interactions at surfaces, interfaces, grain boundaries and in the bulk, within the confines of a simple, well-defined system. Lessons learned in this context may be readily extended and applied to 'real-world' PV thin-film structures and devices. In the present study, a combination of *insitu* and *exsitu* techniques, including Temperature-Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS) and Scanning Auger Microscopy (SAM), are used to probe interactions between Cu thin films and the CdTe(111)-B surface. Zero-order kinetics are observed for the reaction of elemental Cu with CdTe(111)-B substrates, and the kinetic parameters for the reaction are extracted from TPD measurements. SAM measurements reveal that a metastable Cu$_x$Te phase forms upon reaction of Cu with CdTe. Temperature-programmed XPS data sets demonstrate the existence of a temperature-reversible, surface-segregated Cu phase on Cu-doped CdTe(111)-B substrates. UPS measurements indicate that the surface-segregated Cu alters the near-surface valence-electronic structure of the CdTe(111)-B substrate.

2:30 PM F3.4

A Comparison of As Doping with ex situ Cadmium Chloride Treatment of CdTe Solar Cells. Stuart James Irvine[1], Vincent Barrioz[1], Rachel L. Rowlands[1], Eurig W. Jones[1], Ken Durose[2] and Guillaume Zoppi[2]; [1]Chemistry, University of Wales Bangor, Bangor, Gwynedd, United Kingdom; [2]Physics, University of Durham, Durham, United Kingdom.

Thin film structures of CdTe and CdS have been grown onto ITO coated glass substrates using metal organic chemical vapour deposition (MOCVD). This method of deposition allows for a high degree of control over the material properties and very low background impurity concentrations. In this study there were two sets of layers grown. The first was undoped with the CdS grown at 300o C and the CdTe grown at 350o C. These layers were subsequently coated with CdCl2 and annealed under a variety of different conditions. The second set were grown with arsenic doping of the CdTe layer using tris-dimethylaminoarsenic (TDMAAs) and processed into test devices without CdCl2 treatment. In both cases a considerable increase in Jsc was observed over the undoped cells but the IV characteristics were different with a higher shunt current for the CdCl2 annealed layers. These results will be presented along with characterisation of the structure and morphology of these films using X-ray diffraction, SEM and AFM. The CdCl2 layer undergoes considerable change in structure and morphology whereas the in situ arsenic doped layers do not show large changes compared with the undoped layers. In order to elucidate the effect of the annealing temperature, which was up to 500o C, some annealing was carried out on the in situ arsenic doped layers, at the same temperature. This was found to depend critically on the atmosphere used during annealing where under hydrogen the photo-response was considerably reduced. These experiments show that the changes observed in the CdCl2 annealed samples cannot be simply explained by solid state diffusion and grain growth mechanisms. This comparative study shows new insights into the annealing treatment of CdTe/CdS solar cells and a possible method for avoiding this ex situ processing step.

2:45 PM F3.5

Influence Of Bi Doping On CdTe Based Solar Cells. Carmen Maria Ruiz[1], Osvaldo Vigil-Galan[1,2], Edgardo Saucedo[1], Gerardo Contreras-Puente[2] and Veronica Bermudez[1]; [1]Fisica de Materiales, Universidad Autonoma de Madrid, Madrid, Spain; [2]Escuela Superior de Fisica y Matematicas, Instituto Politecnico Nacional, Mexico D.F, Mexico.

CdTe based solar cells are one of the most efficient systems on photovoltaics. However physical properties of CdTe such as high resistivity on p-type and elevated superficial work function limit the behaviour of these systems and avoid obtaining high efficiency cells. In order to improve these limitations, on initial stages of cell development, Cu was used as back contact for two reasons: i) It presents an ohmic behaviour ii) Exhibits a high diffusion coefficient, so CdTe was doped with Cu, decreasing the resistivity value. The main problem was that diffusion coefficient was so big that Cu atoms migrated up to the junction degradating the system properties. The next step in improving CdS/CdTe system has been concentrated in contact characteristics leaving CdTe properties unchanged. In this way, contacts with bigger atoms such as Sb or Mo were used and chemical etchings such as bromine-methanol or PN (phosphoric acid-nitric acid) were performed to create a p+ region on the CdTe surface and to decrease the work function. Finally alloys such as Sb$_2$Te$_3$ are being used with good results. All these efforts have improved solar cell efficiency, but modifications on CdTe properties have not yet being optimised for these systems. Recent investigations on bulk CdTe Bi doped crystals grown by Bridgman technique, demonstrates that resistivity on single crystals can be reduced up to four orders of magnitude with Bi concentration. Coupled with decreasing in resistivity, an important increase of photoconductivity with Bi concentration has been reported. Finally Bi is a good candidate for doping CdTe films because of it is mainly located on Te lattice sites, so diffusion processes are very limitated and atom migration is minimized. In this work we present the results of doping with Bi CdTe thin films, and its effect on CdS/CdTe:Bi solar cells To do this, CdTe films were deposited with CSVT from different CdTe:Bi targets (from non doped up to 1000ppm) previously sintered by Bridgman method. X-Ray Diffraction and Secondary Ion Mass Spectroscopy measurements demonstrate that CdTe films are formed and Bi is incorporated. Electrical and optical characterizations show that thin films reproduce bulk material behaviour with a decrease of resistivity and an increase of photoconductivity. Finally, following the same procedure, CdS/CdTe solar cells were prepared and their properties studied as a function of Bi concentration.

SESSION F4: Structural Characterization
Chairs: Al Campaan and Thomas Unold
Tuesday Afternoon, March 29, 2005
Room 2005 (Moscone West)

3:30 PM *F4.1

Glancing Incidence X-Ray Diffraction of Thin Films. Brian E. McCandless, Institute of Energy Conversion, University of Delaware, Newark, Delaware.

Glancing incidence x-ray diffraction (GIXRD) is presented as a powerful tool for non-destructive analysis of thin film materials and structures. This paper contains three sections, relating to GIXRD theory, measurement and analysis, and application. The theory of the GIXRD measurement technique is reviewed with respect to planar polycrystalline thin-film materials having coherent scattering domain size from $\sim$10 nm to many microns. The critical incident beam angle for diffraction and detection sensitivity are calculated for selected elemental and compound, II-VI, III-V, I-III-VI, materials systems. Measurement techniques and optimal instrumental configuration and alignment are reviewed. Quantitative GIXRD analysis with Cu-kα radiation is applied to formation rate and activation energy of native oxides on CdTe films, recrystallization of ultra-thin Cd$_{1-x}$Zn$_x$S films, compositional grading in CuIn$_{1-x}$Ga$_x$Se$_2$ films deposited on flexible substrates, and correlation of in-plane residual stress with deposition conditions for sputtered Mo films.

4:00 PM F4.2

Cu K-edge EXAFS Studies of CdCl2 Effect on CdTe Solar Cell. Xiangxin Liu[1], Alvin D. Compaan[1] and Jeff Terry[2,3]; [1]Department of Physics and Astronom, The University of Toledo, Toledo, Ohio; [2]Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago, Illinois; [3]Department of Physics, University of Notre Dame, Notre Dame, Indiana.

The highest performance CdS/CdTe thin film solar cells are generally completed with a Cu-containing back contact. The copper appears to be critical for achieving heavy p-type doping of the CdTe at the contact to permit the formation of a low resistance contact. However, experimental data have shown most of the copper in regular CdTe cells is electrically inactive. In the extended x-ray absorption fine structure (EXAFS) work we have determined that most of the Cu in CdTe films resides at the grain boundaries of CdTe either as Cu2Te or Cu2O, depending on whether the film has received a chloride treatment in the presence of oxygen . This has suggested how grain boundaries may be passivated in thin-film CdTe solar cells. In particular, we found that the typical CdCl2 vapor treatment in an oxygen ambient-a critical step needed to improve the performance of all CdTe thin-film cells-changes the final local environment of the Cu from Cu2Te to Cu2O. We also find evidence that the grain-boundary Cu2O in CdCl2 treated CdTe films is unstable and tends to transform to CuO under some stress conditions. We are studying this instability of Cu2O under stressing as a mechanism for CdTe cell degradation. This work was supported by NREL and the DOE.

4:15 PM *F4.3

Application of Advanced Microstructural and Microchemical Microscopy Techniques to Chalcopyrite Solar Cells.

Ian M. Robertson, Changhui Lei, Chun-Ming Li and Angus Rockett; Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois.

Advances in instrumentation and techniques available in state-of-the-art transmission electron microscopes provide unparalleled opportunities to explore the microstructure and microchemistry of chalcopyrite solar cells. This talk will highlight application of these advanced capabilities by comparing and contrasting the microstructure and microchemistry of Cu(In,Ga)Se_2 solar cells prepared using different processing strategies. The emphasis will be on the structure and chemistry of the film, the grain boundaries and the CIGS/CdS interface and correlating these with device performance. We will also explore how the next generation of aberration-corrected microscopes will impact our ability to resolve chemical and structural differences in these materials.

4:45 PM F4.4

The Structure and Passivation Effects of Double-Positioning Twin Boundaries in CdTe.

Yanfa Yan, Kim Jones and Mowafak Al-Jassim; NREL, Golden, Colorado.

The atomic structure and passivation effects of double-positioning (DP) twin boundaries in CdTe are studied using high-resolution electron microscopy, image simulation, and density-functional total-energy calculations. The DP twin boundaries are found to contain more Te dangling bonds than Cd dangling bonds, resulting in energy states in the bandgap, which are detrimental to the electronic properties of CdTe. We find that Br, Cl, S, and O atoms present passivation effects on the DP twin boundaries with different degrees, whereas H and Na do not passivate the boundaries. Of all these impurities, Cl atoms present the best passivation effects on the double-positioning twin boundaries. The superior passivation effects are realized by either terminating the Cd atoms with dangling bonds, or substituting the Te atoms with dangling bonds in the DP twin boundaries in CdTe by Cl atoms.

SESSION F5: Poster Session: Posters I

Chair: Bill Shafarman
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

F5.1

Photovoltaic Effect in the Anysotype GaSe–InSe Heterojunctions Under Pressure.

Stepan Drapak, Maxym Vorobets and Zakhar Kovalyuk; Chernivtsi Department, Frantsevich Institute of Material Sciences Problems, the National Academy of Sciences of Ukraine, Chernivtsi, Chernivetska, Ukraine.

Photodiodes based on InSe–GaSe heterojunctions (HJ) are analogues of Si–structures for operating in high radiation conditions. The photoconversion efficiency of such devices lies in the range 0.5–3.2 % depending on the parameters of starting substrates of indium and gallium monoselenides as well as from design peculiarities of the structures [1]. As it is shown in [2], a InSe/GaSe heterocontact is a semiconductor–insulator–semiconductor structure where a layer of oxygen atoms adsorbed form atmosphere acts as a dielectric layer. This layer is in non-equilibrium state with a very long time of relaxation. At long-term keeping the HJ because of diffusive penetration of oxygen into bulk of indium and gallium selenides or due to removing oxygen from the interface the semiconductor plates become more closely contacted. However, the area of such close contact is of about 10 % of the geometrical area of the structure. In [2] it is also supposed that photoconversion efficiency can be essentially improved making more close the contact over all the geometric surface of the HJ. In this report we present investigations of the influence of static pressure, normal to the barrier plane, on the photoconversion parameters of a n–InSe–p–GaSe HJ. They indicate on a possibility to increase essentially the photoconversion efficiency in such structures. For instance, for structures subjected to a pressure of about 35 to 40 kPa an increase of the open circuit voltage nearly twice and the short circuit current by a factor not less than five was observed in comparison to the initial samples. The following increase of pressure up to P≥65–70 kPa leads to both sharp decreasing of open circuit voltage (more than in three times) and increasing of short circuit current (even up to 8–10 times in comparison with initial samples). The changes of the photoconversion parameters of the InSe/GaSe heterojunction are discussed from the point of view both reconstruction of the interface layer and change of gallium and indium selenides electrical and optical properties because the increasing of resistivity of these semiconductors and changes in absorption spectra of GaSe are observed under pressure. References 1. Drapak S.I., Katerinchuk V.N., Kovalyuk Z.D., Manassom V.A., Phys. Electronics, 1988, No 41, P.92-94. (in Russian). 2. Drapak S.I., Orletskii V.B., Kovalyuk Z.D., Semiconductors, 2004, V.38, No 5, P.566-599.

F5.2

Cu_3BiS_3, Cu_3BiS_4, Ga_3BiS_3 and $Cu_5Ga_2BiS_8$ as Potential Solar Absorbers for Thin Film Photovoltaics.

Nathan Gerein and Joel Haber; Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

We are interested in developing new photovoltaic device architectures that incorporate only materials which are cost effective, abundant, and non-toxic. Our approach is based on the identification of suitable absorber layers, followed by device development using thin film combinatorial methods. We have identified four compounds, three of which have been previously unreported, that we expect to be promising candidates for photovoltaic applications. Cu_3BiS_3 (E_g=1.2 eV) has been previously reported to be a suitable solar absorber.[1] Three additional compounds: Cu_3BiS_4, Ga_3BiS_3, and $Cu_5Ga_2BiS_8$, have been targeted for exploratory synthesis due to the expectation that they will adopt diamond-like configurations, and the fact that other bismuth sulfides have suitable properties for use as solar absorbers (Bi_2S_3, E_g=1.28 eV; $AgBiS_2$, E_g=0.95 eV). Current efforts are focused on the development of thin film synthetic methods for Cu_3BiS_3 using physical vapor deposition, and the study of phase stability over a narrow composition range using continuous composition gradient combinatorial methods. Subsequent device development incorporating the novel absorber will be carried out using fractal masking combinatorial methods, in an effort to produce a device exhibiting sufficient efficiency to capture the interest of the photovoltaics community. Efforts are also being made to develop bulk synthetic methods for Cu_3BiS_4, Ga_3BiS_3, and $Cu_5Ga_2BiS_8$. If samples are synthesized successfully their optical and electronic properties (band gap (E_g), conductivity type (p or n), carrier mobility (μ), and free carrier lifetime (τ)) will be measured to assess their suitability for use in photovoltaic devices. If any of these previously unreported compounds are found to be suitable for use as solar absorbers, thin film synthetic methods will be developed and the compound(s) incorporated into combinatorial device development strategies. In this presentation we will report results on the development of thin film synthetic methods for Cu_3BiS_3, and the analysis of phase stability as a function of composition. We will also report results on the exploratory synthesis and characterization of Cu_3BiS_4, Ga_3BiS_3, and $Cu_5Ga_2BiS_8$, and outline our methods and strategy for the combinatorial development of promising device architectures. (1) Estrella, V.; Nair, M.T.S.; Nair, P.K. *Semiconductor Science and Technology* **2003**, *18*, 190-194.

F5.3

Spray Deposition of Solid-State Nanocomposite CuInS2/TiO2 Solar Cells.

Marian Nanu, Joop Schoonman and Albert Goossens; Laboratory for Inorganic Chemistry, Delft University of Technology, Delft, Netherlands.

To date, polycrystalline silicon photovoltaic (PV) devices dominate the solar cell market. Despite of the abundance of silicon, the complex technological processes necessary to obtain silicon cells are expensive. The high production costs of conventional solar cells inhibit their large-scale production. The search for low-cost PV alternatives, with adequate conversion efficiency and an improved energy payback time, calls for innovative combinations of materials and a novel solar cell configuration. Sulfur- and selenium, based semiconductors have a great potential for PV application. CuInS2 (CIS) is considered a promising candidate because of its high absorption coefficient and optimum direct bandgap energy, i.e., Eg=1.55 eV, which is well matched to the solar spectrum. A film less than 1μm thick can absorb more than 90% of the sunlight if internal light scattering is optimized. However, these materials are usually deposited using vacuum techniques, which lifts the price benefit to a large extent. This paper is focused on the production process of thin film CuInS2/TiO2 nanostructured heterojunction solar cells, or what we refer to as the 3D solar cell concept. In previous investigations on the 3D CIS solar cells, Atomic-Layer Deposition has been used to deposit the CIS into the nanostructured matrix. These investigations demonstrate the high potential offered by the 3D solar cell concept [1,2]. However, it is questionable whether ALD can be employed in a fast and effective industrial process. By introducing spray deposition we now show that indeed 3D solar cells can be produced in a remarkably simple way. Spray pyrolysis offers a cheap alternative to deposit semiconductor thin-films, which is the topic of the present study. Careful selection of the deposition parameters results in a homogeneous deposition. The thin films obtained have the desired properties, which make them suitable for use in solar cells. The nanopores of a 2μm thick nanoporous anatase TiO2 thin film (particle size of 100 nm) have been filled with CuInS2 deposited by spray pyrolysis. Besides the large area offered by these nanostructured TiO2 films, also the scattering of light enhances the energy-conversion. Deposition of the absorber film takes place in ambient atmosphere and at a temperature between 300 and 350 0C.With the aid of a very simple spray deposition method we have been able to obtain nanocomposit thin films that show a remarkable energy conversion efficiency of 5%. The new 3D solar cell concept has, therefore, demonstrated its high potential for replacement of the present generation of solar cells in the coming years. This 3D solar cell, based on the nanocomposite TiO2—CuInS2, opens up a new direction towards cheap and efficient PV devices. References: [1] M. Nanu, J. Schoonman, A. Goossens, Adv. Mat. 2004, 16, 5, 453. [2] M. Nanu, J. Schoonman, A. Goossens, Adv. Func. Mat. in press.

F5.4

Some Novel Photovoltaic Structures Using Chemically Deposited Absorber Films. P. Karunakaran Nair, M. T. S. Nair, Sarah R. Messina, Bindu Krishnan, Yolanda Pena, Oscar GomezDaza, Jose Campos and Aaron Sanchez; Centro de Investigacion en Energia, Universidad Nacional Autonoma de Mexico, Temixco, Morelos, Mexico.

Semiconductor thin films of thickness 200 to 500 nm are obtained by chemical bath deposition, where the thin film yield is $> 50\%$. Photovoltaic hetero-junctions formed with chemically deposited and subsequently modified thin films of Sb2S3, AgSbSe2, AgSbS2, CuSbS2 as absorber components will be presented. The Voc in these structures is 300-500 mV, and the Isc is in the range of 0.1 to 5 mA/cm2. We expect that the overall characteristics in some of these structures may be improved through optimization of individual film thickness and heat treatment. Initial results indicate that all-chemically deposited CdS-Sb2S3-Cu2-xSe and CdS-Sb2S3-Cu3SbS4-Cu2-xSe solar cells are feasible.

F5.5

Direct Water Splitting Using Multiple Bandgap Tandem of Thin Film Photovoltaic Cell and a Photocatalyst. Anant H. Jahagirdar, Upendra S. Avachat and Neelkanth G. Dhere; Florida Solar Energy Center, University of Central Florida, Cocoa, Florida.

The general enthusiasm for the use of hydrogen as an environmentally friendly fuel has been encouraged by the fact that the combustion of hydrogen results in the generation of water, which neither results in air pollution nor leads to the emission of greenhouse gases. This consideration is correct assuming that hydrogen is generated using a source of renewable energy, such as solar, wind, hydroelectric, or hydrothermal energy. To date, the technologies for hydrogen generation using sources of renewable energy are in the incubation stage. The growing interest in hydrogen has resulted from the increasing need to develop hydrogen technologies that are based on the utilization of renewable sources of energy. The photoelectrochemical (PEC) splitting of water into hydrogen and oxygen using solar energy is a potentially clean and renewable source for hydrogen fuel. FSEC photovoltaic (PV) Materials Lab has developed a PEC setup consisting of two-illuminated PV cells, a RuS_2 anode for oxygen evolution and a platinum foil cathode for hydrogen evolution. With this setup, a PEC efficiency of 5.25% has already been achieved. The oxygen overpotential was reduced by using RuS2 photoanode which can be illuminated by the infrared photons transmitted through the PV cell. A p-type transparent conducting back layer of ZnTe:Cu was deposited at the back of superstrate type CdS/CdTe thin film PV cells for this purpose. ZnTe by itself is p-type. Additionally, small amounts of copper (2 atomic %) was incorporated so as to enhance the p-type conductivity. Hot-wall evaporation technique was used for the preparation of ZnTe:Cu. The hot-wall evaporation technique provided i) better stoichiometry, ii) economy of the material and iii) better film thickness uniformity. Effort presented here is different and distinct from development of two-junction thin-film PV tandem cell typically with individual absorber bandgaps of 1.1 eV and 1.68 eV that have to be grown one on top of the other. The PEC cells used here have the potential of being as efficient as III-V tandem cells while being significantly cheaper. Also the unique design of the PEC setup avoids the immersion of PV cells in the solution thus solving the potential problem of corrosion. This paper presents the preparation and characterization of PV cells, ZnTe:Cu p-type transparent conducting back layer, and photoanodes and efficient PEC cell for generation of hydrogen by water splitting.

F5.6

Abstract Withdrawn

F5.7

Highly Mismatched Alloys for Intermediate Band Solar Cells. Wladek Walukiewicz[1], Kin Man Yu[1], J. Wu[2], J. W. Ager[1], Wei Shan[1], M. A. Scarpulla[3,1] and O. D. Dubon[3,1]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; [3]Department of Materials Science and Engineering, University of California, Berkeley, California.

It has long been recognized that the introduction of a narrow band of states in a semiconductor band gap could be used to achieve improved power conversion efficiency in semiconductor-based solar cells. The intermediate band would serve as a "stepping stone" for photons of different energy to excite electrons from the valence to the conduction band. An important advantage of this design is that it requires formation of only a single p/n junction, which is a crucial simplification in comparison to multijunction solar cells. A detailed balance analysis predicts a limiting efficiency of more than 50% for an optimized, single intermediate band solar cell. This is higher than the efficiency of an optimized two junction solar cell. Using ion beam implantation and pulsed laser melting we have synthesized $Zn_{1-y}Mn_yO_xTe_{1-x}$ alloys with $x<0.03$. These highly mismatched alloys have a unique electronic structure with a narrow oxygen-derived intermediate band. The width and the location of the band is described by the Band Anticrossing (BAC) model and can be varied by controlling the oxygen content. This provides a unique opportunity to optimize the absorption of solar photons for best solar cell performance. We have carried out systematic studies of the effects of the intermediate band on the optical and electrical properties of $Zn_{1-y}Mn_yO_xTe_{1-x}$ alloys. We observe an extension of the photovoltaic response towards lower photon energies, which is a clear indication of optical transitions from the valence to the intermediate band. K. M. Yu et al Phys. Rev. Lett., 9, 246 403 (2003).

F5.8

TEM Studies of High-Efficiency CdTe Solar Cells on Commercial SnO2/Soda-Lime Glass. Yanfa Yan, Xuanzhi Wu, Jie Zhou and Mowafak Al-Jassim; NREL, Golden, Colorado.

The microstructure of high-efficiency CdTe solar cells on commercial SnO2/Soda-lime glass is investigated by a scanning transmission electron microscope. The CdTe solar cells have a structure of SL-glass/SnO2/ZTO/CdS:O/CdTe. We find that there is no interdiffusion between the SnO2 layer and the ZTO layer. Weak diffusion of Zn from the ZTO layer into the CdS:O layer is observed. However, the diffusion is not uniform. Interdiffusion also occurs at the CdTe/CdS:O interface. The enhancement of S diffusion along grain boundaries in CdTe is also observed. In the back-side of CdTe, a thin layer of Te is found, which was formed during NP-etching. In addition, a very thin layer of CdHgTe is observed at the CdTe/Te interface.

F5.9

Defects and Interfaces in $Cu(In,Ga)Se_2$-Based Thin-Film Solar Cells With and Without Na Diffusion Barrier. Helge Heinrich[1,2], Sephalika Senapati[1], Shripad Kulkarni[2], Ankush Halbe[1], Dominik Rudmann[3] and Tiwari N. Ayodhya[4,3]; [1]AMPAC, University of Central Florida, Orlando, Florida; [2]Physics Department, University of Central Florida, Orlando, Florida; [3]Laboratory of Solid State Physics, ETH Zurich, Zurich, Switzerland; [4]Department of Electronic and Electrical Engineering, Loughborough University, Loughborough, Leicestershire, United Kingdom.

Thin-film solar cells based on $Cu(In,Ga)Se_2$ (CIGS) absorber layers have the potential for low production costs and reasonable conversion efficiency for the generation of solar electricity. High-efficiency CIGS thin film solar cells have been obtained by using soda-lime glass as substrate material. To characterize the influence of sodium diffusion on the CIGS layer (deposited with the 3-stage process at 643 K, 773 K or 853 K), samples with and without an Al_2O_3 diffusion barrier were investigated by transmission electron microscopy (TEM) with a FEI-Tecnai F30 operating at 300 kV. Special regions of the solar cells containing surface defects and regions near the Al-front contact were selected for these investigations. Cross sectional TEM samples were obtained using the Focused Ion Beam technique. Special emphasis was put on the identification of defects, grain boundaries and chemical gradients in the CIGS layer. Additionally, the continuity of coverage of the chemical bath deposited thin CdS layer was evaluated. The three-stage growth process was used for CIGS deposition resulting in slightly columnar CIGS grains around 100 nm in diameter near the Mo back contact and larger grains up to 1000 nm in diameter near the top surface. The comparison of samples with and without a diffusion barrier yields no significant difference in grain size for the CIGS layer indicating that grain growth is not enhanced by sodium diffusion. The smoothness of the surface of the CIGS layer and therefore the continuity of the following layers is improved by Na incorporation. However, extended defects are formed on the surface of the ZnO layer. These surface defects in the ZnO window layer can alter reflectivity and absorption properties of these solar cells. Additionally, the electronic properties of the interfaces below these defects might be negatively affected. The roughness of the CIGS surface causes bending of the 50 nm thick CdS layer and of the ZnO layer. Elemental distribution maps show the influence of the rough surface of the CIGS layer on the following layers on top of it. Despite the high surface roughness and an average thickness of only 50 nm, the CdS layer appears continuous. The Cd distribution map indicates diffusion of Cd along the grain boundaries in CIGS, in other cases, extended diffusion of sulfur along grain boundaries in the CIGS layer may alter charge carrier recombination.

F5.10

CIGSS Thin Film Solar Cells on Mo Coated Glass Substrates - Materials Aspects. Anant H. Jahagirdar, Ankur A. Kadam and Neelkanth G. Dhere; Florida Solar Energy Center, University of Central Florida, Cocoa, Florida.

Copper indium diselenide, CuInSe$_2$, is an excellent material for the development of high-efficiency and low-cost thin film solar cell devices due to its high absorption coefficient and near optimal bandgap value. Addition of gallium and sulfur has been used to produce graded bandgap structures. This will enhance the internal electric field and obtaining a higher charge carrier collection. A critical problem related to the selenization growth process is the formation of a graded film structure with most of the gallium residing at the back of the film, because of the diffusion of gallium towards back contact. Thus, the gallium does not increase the band gap of the material in the active region of the solar cell. Attempts have been made to obtain high efficiency by composition grading in co-evaporated CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) solar cells. The present best efficiency in CIGS solar cells is 19.5%. Once a graded CIGS film is formed, converting the film to a homogeneous single-phase material becomes extremely difficult. In an effort to increase the band gap in the near surface region, films are reacted with H$_2$S. This results in an increased open circuit voltage of the solar cell and hence the efficiency due to increased bandgap near the junction and also possibly due to grain-boundary passivation. Present industrial processes may include a post-sulfurization step in which a certain fraction of the selenium species at the surface of the absorber films is replaced with sulfur. So far CuIn$_{1-x}$Ga$_x$Se$_{2-y}$S$_y$ (CIGSS) has the highest module efficiency of 13.1%. Excellent facilities developed over last few years at FSEC PV Materials Lab and state-of-the-art characterization techniques are being used to prepare and characterize CIGSS thin film solar cells. CIGSS thin films are grown on molybdenum coated glass substrates by the two-stage method. Stage one involves the deposition of CuGa-In metallic precursors using DC magnetron sputtering and stage two involves selenization/sulfurization of metallic precursors in diluted diethylselenide (DESe) and N$_2$:H$_2$S (4% H$_2$S) atmosphere respectively. Thin film solar cells are completed by the deposition of n-type CdS layer by chemical bath deposition, ZnO/ZnO:Al transparent conducting window bilayer by RF magnetron sputtering and Ni-Al front contact fingers by e-beam evaporation technique. Aim of this study is to prepare and characterize the CIGSS thin film, improve the understanding of material properties and further enhance the solar cell performance. Structural properties and various phases of the CIGSS material were studied by using X-ray diffraction, morphology of the layers was examined by scanning electron microscopy, and elemental analysis for stoichiometry was carried out using electron probe microanalysis and Auger electron spectroscopy (AES). CIGSS/CdS layers were analyzed by secondary ion mass spectrometry and AES while the cells were characterized by current-voltage and quantum efficiency measurements.

F5.11

Chemical Fluctuation-Induced Nano-Domains in CIGS Films. Yanfa Yan, Kim Jones, Jehad A. AbuShama, Kannan Ramanathan, Rommel Noufi and Mowafak Al-Jassim; NREL, Golden, Colorado.

The microstructure and chemistry of Cu(In,Ga)Se2 thin films from high efficiency devices were investigated at the nano-scale by high-resolution scanning transmission electron microscopy imaging and X-ray energy dispersive spectroscopy. We found strong chemical fluctuations at the nanoscale, which result in relatively Cu-poor and Cu-rich nanodomains. These nanodomains are interconnected forming three-dimensional intermixed Cu-poor and Cu-rich networks. If we assume that the Cu-poor domains exhibit an n-type conductivity and the Cu-rich domains exhibit a p-type conductivity, the entire CIGS films are composed of nano p-n junction networks. The n-type networks can act as electron-free ways and the p-type networks can act as hole-free ways. Because the domains are crystallographically coherent, dislocations and other lattice defects do not have to form at the interface between the domains, rather, the interface will be smeared as a result of gradual interdiffusion, carriers generated by photons can be separated and collected rapidly and efficiently into the electron and hole free ways. We propose that this novel mechanism may explain the superior high performance of CIGS devices. Our goal is to link the nano-scale structure in the CIGS absorber to the current transport in the device.

F5.12

Structural Properties of AG-Based Chalcopyrite Compound Thin Films for Solar Cells. Hiroki Ishizaki, Keichiro Yamada, Ryota Arai, Yasuhito Kuromiya, Yukari Masatsugu, Naoomi Yamada and Tokio Nakada; Department of Electrical Engineering and Electronics College of Science and Engineering, Aoyama Gakuin University, Sagamihara, Kanagawa, Japan.

Ag(In1-xGax)Se2(AIGS) takes several advantages over CuIn1-xGaxSe2 such as wide band gap energy, melting point. The band gap energy of Ag(In1-xGax)Se2 film can control by Ga/(In+Ga) atomic ratio into Ag(In1-xGax)Se2. Thus, the AIGS has a potential of efficient top cell for the tandem solar cell. High efficiency AIGS solar cell with a ZnO:Al/ZnO/CBD-CdS/Ag(In1-xGax)Se2/Mo structure has demonstrated by our previous works. In this work, we investigated the influence of the structural properties of Ag(In1-xGax)Se2 thin films on the Ga/(Ga+In) and Ag/(Ga+In) atomic ratios. The Ag(In1-x,Gax)Se2 thin films were deposited with different Ag/(Ga+In) atomic ratios ranging from 0.32 to 1.5 and Ga/(Ga+In) atomic ratios ranging from 0.0 to 1.0. Ag(In1-xGax)Se2 thin film has been deposited on Mo-coated soda-lime glass substrates and 7059 glass substrates by three-stage process using a molecular beam epitaxy system. The film composition, the crystallographic structure and electrical properties were investigated using inductively coupled plasma spectroscopy (ICP), X-ray diffraction and scanning electron microscope (SEM), respectively. The structural parameters of Ag(In,Ga)5Se8 were refined by Rietveld analysis using RIETAN-2000(1). The diffraction lines observed at 27.7, and 43.8 and 49.5 degrees were due to a tetragonal Ag(In1-x Gax)5Se8 structure. These 2-theta values related to tetragonal Ag(In1-x Gax)5Se8 structure linearly increased with increasing Ga/(In+Ga) atomic ratio. This result indicates that the tetragonal Ag(In1-x Gax)5Se8 structure stably existed, regardless of Ga content. The other diffraction lines were identified to those of Ag(In1-x,Gax)Se2 with chalcopyrite structure. The tetragonal Ag(In,Ga)5Se8 phase became more dominant as the Ag/(Ga+In) atomic ratio decreased. As the Ga content decreased, the crystal grains of surface region became smaller and tetragonal Ag(In,Ga)5Se8 phase became dominant. The influence of cell performance on the crystallographic structure will also be presented. Reference 1)F. Izumi and T. Ikeda, Mater. Sci. Forum, 321-324 (2000) 198

F5.13

Photostimulated Changes of Electrical Characteristics of Ag/CdTe Thin Film Structures. Tayyar Dzhafarov[1,2] and Murat Caliskan[2]; [1]Department of Solar Cells, Institute of Physics, Baku, Azerbaijan; [2]Department of Physics, Yildiz Technical University, Istanbul, Esenler, Turkey.

Elements of the group I (Cu, Ag, Au) are used as contact material for fabrication of CdTe/CdS solar cells. These materials are known as substitutional acceptor impurities in CdTe. In addition, they are reported to be incorporated also as interstitial donors and the diffusion coefficient of interstitial ions is known to be very high. The role of Cu, Ag and Au in CdTe/CdS cells is dual. On the one hand, it is generally accepted that these metals aid the formation of a better ohmic contact. On the other hand, these impurities are considered to be principal component responsible for the degradation of CdTe/CdS cells due to their ability to diffuse through the CdTe film to the cell junction. The present work reports data on thermal and photostimulated diffusion of Ag in CdTe thin films and the influence of the Ag diffusion on change of electrical and photovoltaic characteristics of Ag/CdTe junstions. CdTe thin films were deposited on glass substrates by close-spaced sublimation (CSS) technique. The prepared CdTe films were high resistivity (r=104-107 Ohm.cm) n-type conductivity. The following thermal annealing of n-type CdTe at 400oC for 1 hour in the air resulted in the conversion of conductivity type from n-type to p-type. Ag/CdTe structures were fabricated by electron-beam evaporation of Ag films on CdTe surface at the room temperature. CdTe films and Ag/CdTe structures were characterized by structural (X-ray diffraction), electrical, optical absorption and photovoltaic measurings. Resistivity studies of Ag/CdTe structures exposed to sequental cycles of thermal (in dark) or photoannealing (under white light illumination) at fixed temperatures (50-140oC) showed that the rate of change of resistivity for photoannealing is higher than that for thermal annealing. Estimated effective diffusion coefficient for photostimulated diffusion of Ag in CdTe is significantly higher than that for thermal diffusion. The possible mechanisms of acceleration of Ag diffusion under illumination are discussed. It is found that the annealing of Ag/CdTe at 400oC for 1h resulted in formation of Ag2Te phase and decreases the energy band gap up to 0.07eV. Electrical and photovoltaic characteristics of Ag2Te/CdTe junctions are presented.

F5.14

Excitonic Resonances and Lattice Vibrations in CuInSe2 Crystals. Nicolae Syrbu, Radioelectronics, Technical University of Moldova, Chisinau, Moldova.

The lines n = 1 of A, B and C excitonic series have been found in the region of minimum interband interval of CuInSe2. A structure of maximums due to exciton states in found in the reflectivity spectra of CuInSe2 crystals in the region 1.0-1.1 eV. The 1.037 eV and 1.043 eV maxima are due to S-state of the A and B exciton series. Features related to n = 2 and n = 3 exited states of the A and B excitons series are found in the short-wavelength region of spectrum in wavelength modulated spectra. Both exciton binding energy and the minimum energy intervals responsible for excitonic states are determined according to the energy position of n = 1, n = 2 and n = 3 lines. For A and B excitons the Rydberg constants are equal to 39.1 and 36.3 meV and band gaps are respectively equal to 1.0760 and 1.0794 eV. In the high-energy region of spectrum two bands at 1.2864 and 1.3092 eV, which are due to C exciton series, can be found. Assuming that the bands 1.2864 and 1.3092 eV are due to lines n = 1 and n = 2 of the C excitons, we obtain that the energy difference n1(B) - n1(A) is equal to 6.2 meV and n1(C) - n1(B) is equal to 0.243 eV (n1(A), n1(B) and n1(C) are the S-state energy position of the A, B and C excitons). The Rydberg constant and band gap for the C series is equal to 0.0304 and 1.3168 eV, respectively. In the I-III-VI2 compounds provided that the crystal-field $\Delta cf < Eg$, intervals between $\Gamma7(V1)$ - $\Gamma6(V2)$ and $\Gamma6(V2)$ - $\Gamma7(V3)$ energy levels are marked as E1 and E2, respectively. These values are assessed from the Hamiltonian matrix [1]. At present, the splitting of upper valence bands $\Gamma7(V1)$ - $\Gamma6(V2)$ and $\Gamma6(V2)$ - $\Gamma7(V3)$ is determined from n = 1 line energy levels for A, B and C excitons. Taking into account that E1 is equal to 0.0034 eV and E2 is equal to 0,2374 eV, we have calculated the "de facto" values of $\Delta cf = 0.0051$ eV and $\Delta so = 0{,}2367$ eV. Thus, the given values Δcf and Δso result in the splitting of bands $\Gamma7(V1)$ - $\Gamma6(V2)$ equal to 0.0034 eV and $\Gamma6(V2)$ - $\Gamma7(V3)$ equal to 0.2374 eV. Infrared reflectivity spectra of CuInSe2 crystals have been investigated for the polarizations $E||c$ and $E\perp c$. The contours of the reflectivity spectra were calculated and phonon parameters and dielectric constants were determined. The effective ionic charges of Cu, In and S ions in these materials were determined accordingly to the previously proposed model [2]. The effective ionic charges of CuInSe2 and CuGaSe2 are rather different for $E||c$ and $E\perp c$ polarizations. To described the results obtained for different crystals we introduced a parameter of effective ionic charges anisotropy ΔZ. This parameter represents the difference of the effective ionic charges measured in $E||c$ and $E\perp c$ polarizations. ΔZ characterizes the electronic cloud of ions and it deviation from the spherical form. [1] J. E. Jaffe and A. Zunger, Phys. Rev. B 28, p. 5822, 1983 [2] K. Wakamura and T. Ogawa, Japan J. Appl. Phys. 19, p. 249, 1980

F5.15

In-situ Photoelectron Spectroscopy Study on the Oxidation of CuGaSe2. Thomas Johann Schedel-Niedrig[1], Roland Wuerz[1], Marin Rusu[1], Martha Lux-Steiner[1], Hendrik Bluhm[2], Michael Haevecker[2], Evgueni Kleimenov[2], Axel Knop-Gericke[2] and Robert Schloegl[2]; [1]SE2, Hahn-Meitner-Institute Berlin, Berlin, Germany; [2]Fritz-Haber-Institut MPG, Berlin, Germany.

The thermal and native oxidation of CuGaSe2 thin films was studied by in-situ X-ray photoelectron spectroscopy (XPS). The special design of the XPS chamber allowed to measure XP-spectra under oxidizing gas atmospheres at pressures of up to 5 mbar (in-situ) or in ultra high vacuum (UHV). During thermal oxidation, the formation of predominantly Ga2O3 and some amount of SeO2 were observed, but no copper oxides could be detected in the near-surface region of the thin films. The same oxides were found after native oxidation in air under ambient conditions. Only after long term native oxidation for longer than four months Cu(OH)2 was detected. An additional sodium oxide compound are formed at the thin film surface, NaxO and Na2CO3 after thermal and native oxidation, respectively. The amount of these sodium oxide compounds depends on the Na content on the as prepared surface. The formation of SeO2 under humid conditions at 100 degree C was found to depend on the surface composition of the thin film.

F5.16

Band Alignment at CdS/Wide-Band-Gap $Cu(In,Ga)Se_2$ Hetero-Junction by using PES/IPES. S. H. Kong[1], H. Kashiwabara[2], K. Ohki[2], K. Itoh[2], T. Okuda[2], N. Terada[2], S. Niki[3], K. Sakurai[3], A. Yamada[3] and S. Ishizuka[3]; [1]Venture Business Laboratory, Kagoshima University, Kagoshima, Japan; [2]Nano-Structure and Advanced Materials, Kagoshima University, Kagoshima, Japan; [3]National Institutes of Advanced Industial Science and Technology, Tsukuba, Japan.

Several theoretical calculations have indicated a potential of a high conversion efficiency as high as 25 % in the solar cells based on $Cu(In,Ga)Se_2$ [CIGS] with a band gap of 1.3~1.4 eV. In previous reports, the efficiency of the CIGS based cells takes a maximum of 19.2 % at a condition of the band gap around 1.2 eV. One of the origins of this discrepancy between the theory and the experiments is a saturation of open circuit voltage (V_{oc}), which is correlated with band alignment at p-n junction in the cell structure. Therefore, characterization of the band alignment in the wide band gap CIGS based solar cell is desired. Recent studies of electron microscopy about the CdS/CIGS interface indicate their compositional transition regions gets thinner with an increase of the Ga substitution ratio. It means that a sophisticated etching technique, where atomic mixing is well suppressed, is necessary for the evaluation of the interface over the CIGS with the high Ga content. In the present study, we have carried out a development of etching technique and an investigation of electronic structure at interfaces between CdS and the wide gap CIGS. It was found that an Ar ion beam etching at the condition of the ion kinetic energy (E_k) above 500 eV for long time caused a development of metallic feature in a valence band of the CIGS layer. This means that the ion beam etching of E_k above 500 eV is not proper for the characterization of CIGS with the high Ga content. In the etching condition of Ar ion beam with E_k of 350 eV, the semiconducting feature was conserved even after a long etching time over 2000 s. It is noteworthy that, in the $Cu(In_{0.25}Ga_{0.75})Se_2$ films, an employment of this low energy etching yields a removal of its surface region with a band-edge gradient and successful exposure of its interior region with its intrinsic band gap of 1.4~1.45 eV. These results mean that the low energy etching is useful for evaluation of buried region at arbitrary depth in wide gap CIGS. The measurements of interfaces between CdS and the wide gap CIGS reveals a variety of electronic structure; Ga deficiency and reduced band gap of the CIGS at the interface regions, serious sample-dependence of band gradients in the CIGS layer near the interface. In spite of the higher Ga concentration in the CIGS layer, an energy spacing between conduction band minimum of CdS and valence band maximum of $Cu(In_{0.25}Ga_{0.75})Se_2$ was not expanded, in comparison with that of the interfaces over the CIGS with the Ga substitution ratio below 40 %. These results may explain the reason of that CIGS based solar cell with high Ga content exhibited saturation of V_{oc}, which should also induce the decrease of conversion efficiency.

F5.17

Analysis of Proton Induced Defects in Cu(In,Ga)Se2 Thin-Film Solar Cells. Shirou Kawakita[1,3], Mitsuru Imaizumi[1], Koichi Kibe[1], Takeshi Ohshima[2], Hisayoshi Itoh[2] and Shinichi Yoda[1,3]; [1]Spacecraft Electrical Engineering Group, Japan Aerospace Exploration Agency, Tsukuba, Japan; [2]Japan Atomic Energy Research Institute, Takasaki, Japan; [3]Tokyo Institute of Technology, Tokyo, Japan.

CIGS solar cells have higher radiation tolerant than that of Si, GaAs and tandem solar cells. Therefore, CIGS solar cells have great candidate for space solar cells in near future. However the mechanism of radiation induced-defect in CIGS solar cells has not revealed yet. Spectral response characteristic is useful for analysis of radiation response of solar cells. From comparison of spectral response cells before and after irradiation test, the information of defects in the solar cells can be acquired. We have analyzed radiation response of Cu(In,Ga)Se2 thin-film solar cells by spectral response measurement. We analyzed the radiation defect in CIGS solar cells by the solar cell simulator (PC1D). Using the simulator, we can see the damage coefficient of minority carrier diffusion length or lifetime. CIGS solar cells were irradiated 1MeV protons. The analyzed results of spectral response of CIGS solar cells irradiated proton show good agreement with the measurement. Diffusion length of proton irradiated CIGS solar cells can be estimated by fitting of spectral response. From these result, KL was estimated to be 4.7E-5. This value is smaller than that of Si solar cells. This implies that CIGS solar cells have higher radiation tolerant than Si. In addition, we estimated the proton induced-defect introduction rate of CIGS solar cells using the same method. Then, we examined defect introduction rate of proton irradiated CIGS solar cells using the same method and compared with the frenkel-pair defect model. From this result, the radiation defect may be point defects. The radiation damage coefficients of CIGS solar cells were revealed by spectral response measurement with the solar device simulator. This data is necessary to analyze the radiation response of CIGS solar cells and the forecast cell performance in space.

F5.18

N2 in CuGaInSe2 is a Complex of Se on III-site, Cu on III-site, and Cu Vacancy. James A. Van Vechten, Electrical Engineering, Oregon State University, Corvallis, Oregon.

Theory is presented to identify the N2 defects that limits open circuit voltage in CGIS solar cells and that appear when and where the Fermi Level rises 0.8 V above the VBM as Cu diffuses out the crystal. Argument is made that the loss of Cu after crystal growth cannot be accommodated solely by formation of ordered defect crystals because this would not conserve Group III atoms and that this loss is too large to be treated as an independent reaction with a quasi-heat of reaction. Group III and Se atoms must also react in order to preserve the crystal structure. This also explains the formation of N1 defects, which have previously been firmly identified as Se vacancies. Comparison of this theory is made with available experiments. It implies that Cu out diffusion must be stopped if the open circuit voltage is to be increased. Amorphous metal diffusion barriers at the back contact and SiON between grains might do this.

F5.19

The Relation between V_{OC} and Conduction-Band Offset of Cu(InGa)Se$_2$ Solar Cells. Akimasa Yamada[1], Koji Matsubara[1], Keiichiro Sakurai[1], Shogo Ishizuka[1], Paul Fons[1], Hitoshi Tampo[1], Kakuya Iwata[1], Tomoyuki Baba[2], Satoshi Nakamura[2], Yasuyuki Kimura[2], Hisayuki Nakanishi[2] and Shigeru Niki[1]; [1]National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; [2]Tokyo University of Science, Noda, Japan.

CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) is a promising absorber layer material for thin film solar cells because, in cooperation with its large absorption coefficient, its energy gap, E_g can be tuned by increasing the value of x to the optimum, which is believed to be 1.4-1.5 eV for single junction solar cells of terrestrial work. Conversion efficiency of CIGS cells has increased with x from zero up to around 0.4 and it turns rather to decrease for larger x. Open circuit voltage, V_{OC} also has reasonably increased with x until ~0.4, the efficiency turnover point, then the rate of increase has become weak for larger x. The V_{OC} shortage can be regarded as the primary origin of the efficiency fall. The reasons why the theoretically-estimated V_{OC} with large x values has not been realized are discussed. Typically, the reduction in V_{OC} is estimated only on the basis of conventional models for the p-n diode and the conduction-band offset between the absorber and the window materials, CdS and i-ZnO. Positive offset of the window to the absorber expands the depletion region resulting in higher potential but the offset itself works as a barrier for photoelectrons to cancel just the increased potential, and consequently, the effective built-in potential is unchanged. On the other hand, negative offset reduces the depletion region and the potential then directly reduces the effective built-in potential. This theoretical estimation interprets straight the trend of V_{OC} data in literature. Based upon the discussion on the band offset of the window to the absorber also on the contact of the transparent electrode to the window, a material selection guideline is reported for the window and the transparent electrode layers suitable for high-x CIGS absorbers-based solar cells.

F5.20

Thin CuInS$_2$ Films Prepared by MOMBE: Interface and Surface Properties. Christian Pettenkofer[1], Carsten Lehmann[1] and Wolfram Calvet[2,1]; [1]SE6, HMI, Berlin, Germany; [2]Specs GmbH, Berlin, Germany.

CuInS$_2$ (CIS) films were prepared by MOMBE on Si(111) with TBDS as an organic sulfur source. Film properties were investigated in situ by LEED, XPS and UPS with respect to morphology, chemical composition and electronic structure. film growth starts with a In-S bufferlayer on H-terminated Si(111) substrates. No carbon contaminations from the sulfur precursor are incorporated in the samples. Depending on the deposition conditions metallic In precipitations or Cu$_2$In phases were detected for In rich film. A Cu$_2$S surface phase is found for Cu rich films. Cu to In ratio and growth temperature were varied and optimised to obtain near stoichiometric CIS films. A bandalignment for the interface with respect to the bufferlayer and Si will be discussed.

F5.21

Band Offsets at the ZnSe/CuInS2 Interface. Olga Papathanasiou[1], Susanne Siebentritt[1], Iver Lauermann[1], Thomas Hahn[2], Heiner Metzner[2] and Martha Lux-Steiner[1]; [1]Hahn-Meitner-Institut, Berlin, Germany; [2]Friedrich-Schiller-Universitaet, Jena, Germany.

Conventional CuInS2 solar cells are equipped with a CdS buffer layer. In an effort to replace CdS, ZnSe has been shown a promising alternative. CuInS2 solar cells with ZnSe buffer layers prepared by metal organic chemical vapor deposition (MOCVD) achieved efficiencies above 7%, which is in range of the CdS references at that time. However, to understand and model solar cells, the band structure in the pn-junction has to be known. It has been shown before that CdS forms a "cliff" with CuInS2, i.e. the conduction band of the buffer is below the conduction band of the absorber. This configuration favors interface recombination. Due to the higher band gap of ZnSe a "spike" structure is expected, with the conduction band of the buffer above the conduction band of the absorber, the favorable configuration for solar cells. For a well defined interface structure epitaxial CuInS2 films grown be MBE on Si(100) are used as substrates. ZnSe layers of varying thickness are prepared by MOCVD. The samples are then transferred to the measurement system under inert atmosphere. The valence band structure of the ZnSe/CuInS2 interface is investigated by means of ultra violet photoelectron spectroscopy (UPS). To correlate the energies the energy positions of the In 4d and Zn 3d core levels are measured by X-ray photoelectron spectroscopy (XPS) for a series of ZnSe layers of increasing thickness. Additionally XPS using synchrotron light at 170eV is measured, to improve resolution and reliability. First results show a spike structure in the conduction band at the ZnSe/CIS interface, with a conduction band offset of +0.4eV. The implications for solar cells will be discussed.

F5.22

The Optical Properties of the Interface Layers in CdS-CdTe Heterojunctions. Mihail I. Caraman, Petru A. Gasin and Sergiu A. Vatavu; Physics, Moldova State University, Chisinau, Moldova.

The generation of nonequlibrum charge carriers in CdS-CdTe heterojunction based solar cells take place in CdTe layer at the interface of the junction. The optical properties of the interface layer are determined by the CdS layer's presence, the evaporation thermal characteristics and the heat treatment regime of the whole structure in the presence of CdCl$_2$. The analysis of CdTe thin film, grown on the CdS polycrystalline film by close spaced sublimation was performed. The thickness of CdTe layers determined from interference in the IR spectral region is 1.1-3.0 μm. The reflection spectra in the fundamental absorption edge wavelength region and the photoluminescence excited by He-Ne laser (λ=0.63 μm) before and after heat treatment in the presence of CdCl$_2$ of CdS-CdTe cells have been measured. The absorption coefficient in the fundamental band edge region of CdTe films ($h\nu$=1.54 eV) is (7-9)$\cdot 10^4$ cm^{-1}. The annealing leads to absorption decrease to (5-6)$\cdot 10^4$ cm^{-1}. At the same time, the shape of the edge of absorption band at the lateral surface and at the interface modifies. The light absorption mechanisms at the surface of CdTe layer have been studied by reflection spectra using the Kramers-Kronig transformations. The energetic spectra of the localized states in CdTe film and the dynamics of its modification as a result of annealing have been determined from the analysis of photoluminescence spectra at 78K. The relaxation time for the components of the impurity luminescence band and the energies of states having high values of lifetime have been determined from the analysis of photoconductivity kinetics.

F5.23

Nonequilibrum Charge Carrier Generation - Recombination Mechanisms in CdMnTe Thin Films. Iuliana M. Caraman[1], Valentina Z. Nicorici[2], Liudmila S. Gagara[2] and Petru A. Gasin[2]; [1]Physics, "Al.I.Cuza" University, Iasi, Romania; [2]Physics, Moldova State University, Chisinau, Moldova.

The optical and photoelectrical properties of thin films are determined by energetic and kinetic characteristics of the recombination levels, which are influenced by the synthesis's technological factors. Taking into consideration, the great interest of opto- and photoelectronics for CdTe-MnTe solid solutions, the luminescent and photoelectrical properties of thin film ternary compounds Cd$_{1-x}$Mn$_x$Te (x=0.5) have been studied. The samples being studied have been prepared on mica substrates from vapor phase deposition and flash evaporation. The Cd$_{0.5}$Mn$_{0.5}$Te single crystals, grown by Bridgeman method, were used as source material. The 2-5 μm thick films have been studied. The edge of absorption band of the thin films synthesized by vapor phase deposition is determined by impurity absorption at 1.45 eV and 1.55 eV at 293K and 78K respectively. An absorption edge at 2.2 eV (T=293K) in the $\alpha(h\nu)$ dependencies is observed. The absorption coefficient in the middle of fundamental band increases from ~10^5 cm^{-1} in 2.25-2.8 eV range. The deposited CdMnTe layers have high conductivity in a wide energy range, its edge is situated at ~1.46 eV. The sharp photoconductivity increase near the band edge is followed by a weak increase for energies up to 3 eV. Temperature decrease from 293K down to 78K leads to the photocurrent decrease by about two orders of magnitude in the 1.5-3 eV energy interval. The luminescence spectrum of Cd$_{1-x}$Mn$_x$Te (x=0.5) consists of four bands with peaks at 1.73 eV, 1.66 eV, 1.51 eV and 1.44 eV. The first three one's intensity is low and together they amount less than 10% of total radiative intensity. The edge of absorption band, studied by means of absorption and photoconductivity of Cd$_{0.5}$Mn$_{0.5}$Te layers prepared by discrete evaporation, is also determined by impurity states localized at ~30 meV from valence band. The bandgap for this layers is 2.1 eV at 293K and increases to 2.18 eV at 78K. The luminescence spectra of thin films and single crystals used as source material have been investigated. The photoconductivity and photoluminescence kinetics is analyzed for each radiative band. The lifetime, for the recombination levels causing high photosensitivity in Cd$_{0.5}$Mn$_{0.5}$Te layers grown by vapor phase deposition, has been determined.

F5.24

CdTe Solar-cell Materials with Different Growth Processes: Comparison of Defects with Treated Crystalline Samples. Caroline Corwine[1], Tim A. Gessert[2], James R. Sites[1], Wyatt K. Metzger[2], Pat Dippo[2] and Anna Duda[2]; [1]Physics Department, Colorado State University, Fort Collins, Colorado; [2]National Renewable Energy Laboratory, Golden, Colorado.

Polycrystalline thin-film CdTe is one of the leading materials used in photovoltaic (PV) solar cells. One way to improve device performance and stability is through understanding how various process steps alter defect states in the CdTe layer. Recent low-temperature photoluminescence (PL) studies have shown a 1.456-eV PL peak in single-crystal CdTe that is likely due to a Cu_i - O_{Te} defect complex. A similar peak, observed in two as-deposited glass/$\mathrm{SnO_2}$:F/CdS/CdTe thin-film structures, strongly suggests a common origin. This study uses low-temperature PL to examine thin-film CdTe solar cell materials produced by various institutions, under different processing conditions and intentional variations in sample growth. The 1.456-eV peak in the crystalline CdTe was also studied with selective-pair luminescence (SPL), which probes the defect states with sub-bandgap excitation, to narrow the possible energy range for this defect level.

F5.25

Photoluminescence from Ion Implanted CdTe Crystals. Xiangxin Liu and Alvin D. Compaan; Department of Physics and Astronomy, The University of Toledo, Toledo, Ohio.

Photoluminescence is a convenient and powerful method to probe the material properties of an operating solar cell and to investigate the defect states in the active semiconductor material. Doping with ion implantation is a convenient way to introduce specific dopants and to introduce a uniform doping level in a thin surface layer. We have done this by using a standard Monte Carlo simulation program-SRIM to plan an implant dosage at three different energies. The lattice damage has been annealed by thermal annealing in an inert atmosphere using a proximity cap to avoid surface deterioration. The implants were done on high-quality, single-crystal CdTe, from Nikko Materials Co., Ltd. Uniform implants of chlorine, copper and phosphorus were done at the Toledo Heavy Ion Accelerator Lab in the Department. The PL spectra at 10K were obtained at 488 nm to match the absorption depth with the implant profile. Using implant densities typically of 101̂6, 101̂7, and 101̂8 /cm3̂, and laser excitation power densities ranging over several orders of magnitude, we are able to identify band-to-band transitions, free-to-bound transitions, bound-exciton lines, and donor-acceptor pair transitions related to these species. This work was supported by NREL Thin Film Partnership program.

F5.26

Electroluminescence as a Characterization Technique in CdTe/CdS Solar Cells. Kent Price, Tim Taylor and Chris Lacy; Physical Science, Morehead State University, Morehead, Kentucky.

We have constructed a system to detect very low-intensity electroluminescence (EL) emission from CdTe/CdS solar cells. The cells are placed immediately adjacent to a photomultiplier tube, allowing detection of EL intensities less than 50 photons. Consequently, EL can be detected from the cells at voltages at or below open circuit voltage and at current densities less than 2 $\mathrm{mA/cm^2}$, significantly below short circuit current in most cells. EL can thus be used as a non-destructive characterization technique. We have measured EL intensity vs. current density for a number of cells, and find that many cells have super-quadratic dependence of EL intensity on current density. We propose that this dependence is related to the progressive saturation of non-radiative recombination pathways at higher current densities. We will also show that light-soaking of cells decreases EL intensity. This work supported by Kentucky NSF EPSCOR.

F5.27

Effects of Extrinsic Doping on the Photoluminescence of $\mathbf{CuGaSe_2}$ Thin Films. S. Doka[1], M. Rusu[1], A. Meeder[1], E. Arushanov[3], N. Fabre[4], S. Fiechter[2], Th. Schedel-Niedrig[1] and M. Ch. Lux-Steiner[1]; [1]Hahn-Meitner Institut, SE2, Berlin, Germany; [2]Hahn-Meitner Institut, SE5, Berlin, Germany; [3]Institute of Applied Physics, Academy of Sciences, Chisinau, Moldova; [4]LAAS- CNRS, Toulouse, France.

Photoluminescence (PL) spectra of as grown Ga-rich, and Ga-rich plus Ge-doped and annealed CCSVT (Chemical Close-Spaced Vapor Transport)-$\mathrm{CuGaSe_2}$ thin films have been investigated. Visible (514.5 nm) and Ultra- Violet (351.1nm) excitation energies of the laser have been used in order to determine intrinsic and extrinsic defects created due to the implantation as well as separating near surface from bulk recombination. Both visible and UV-PL spectra of the undoped films show the well known luminescence of Ga-rich $\mathrm{CuGaSe_2}$, which can be described by the widely accepted model of fluctuating potentials. Unlike the visible- and UV-PL emissions of Ge- implanted and annealed films differ strongly. Obviously, Ge-implantation in combination with the thermal treatment results in an extrinsic doping of the material producing so far unknown states in the $\mathrm{CuGaSe_2}$ band gap. Comparing the visible- and the UV-PL spectra we found an accumulation of these extrinsic doping levels in the near-surface-region of the films. A first approach to an extended recombination model of Ge-implanted Ga-rich $\mathrm{CuGaSe_2}$-thin films is given.

F5.28

Photoluminescence Studies of $\mathbf{GuGaTe_2}$ Crystals. Andri Jagomagi[1], Juri Krustok[1], Maarja Grossberg[1], Mati Danilson[1], Jaan Raudoja[1] and Mike Yakushev[2]; [1]Department of Materials Science, Tallinn University of Technology, Tallinn, Estonia; [2]Department of Physics and Applied Physics, Strathclyde University, Glasgow, United Kingdom.

Due to their high optical absorption coefficient and optimal bandgap energy, I-III-$\mathrm{VI_2}$ chalcopyrite compounds have captured lot of attention as an alternative to silicon based photovoltaic devices. $\mathrm{CuGaTe_2}$ has a direct optical bandgap with the room temperature energy about 1.22 - 1.24 eV. Natively, $\mathrm{CuGaTe_2}$ has the p-type conductivity. The complex nature of its pseudo-binary phase diagram leads to the formation of high concentration of intrinsic defects that originate from the deviation from the stoichiometry. Therefore, wide range of bandgap energies and other parameters are reported in the literature. At the same time it is believed that in this compound a very shallow acceptor level with the activation energy about 1 meV is present that leads to the degeneration of the samples. Therefore, by using optical absorption, higher bandgap energies are often measured due to Burstein-Moss shift. Another interesting fact is the presence of the photoluminescence (PL) bands at higher energies than the lowest bandgap energy of $\mathrm{CuGaTe_2}$. It has been proposed that lower valence bands can be responsible for these PL bands. The p-like highest valence band in $\mathrm{CuGaTe_2}$ is characterized by three split bands. This splitting is due to the combined effect of crystal field and spin-orbit splitting. However, the valence band structure of $\mathrm{CuGaTe_2}$ is not completely understood. This paper investigates the low temperature PL properties of various monocrystalline and polycrystalline $\mathrm{CuGaTe_2}$ samples. The $\mathrm{CuGaTe_2}$ monocrystals showed high concentration of native defects. The PL spectra of "heavily doped" semiconductors are usually characterized by the broadening of the PL bands that is caused by the fluctuations of the forbidden band edges. On the PL spectra of compensated $\mathrm{CuGaTe_2}$ monocrystals, one broad asymmetric emission band was dominating. The thermal annealing with the presence of Cu increased slightly the compensation ratio of the samples. This was detected by the decreased conductivity of the annealed samples. Also, the depth of the potential fluctuations in the annealed samples was changed. This implies to the enhanced screening of the defects in compensated samples. Surprisingly, the $\mathrm{CuGaTe_2}$ as-grown samples showed the lower depth of potential fluctuations by giving rich PL spectra with well resolved peaks. The spectra were divided into two regions. The deep region (0.6 - 1.2 eV) of the spectra comprises two deep PL bands including totally new band at 1.14 eV with the thermal activation energy of 63 meV. The edge emission region (1.25 - 1.45 eV) comprises over 10 different PL bands. The possible origins of all these bands are discussed.

F5.29

Ellipsometry Studies of CdCl2 Treated CdTe and Related Ternary Alloy Films for Solar Cell Applications. Shanli Wang, Jie Chen, Jian Li, Akhlesh Gupta, Robert W. Collins and Alvin D. Compaan; Department of Physics & Astronomy, University of Toledo, Toledo, Ohio.

CdTe-based polycrystalline thin-film and tandem solar cells are well known for their low cost and high conversion efficiencies. The former have achieved 16.5% efficiency [1], and the latter tandem cells are expected to reach much higher (25%) efficiencies [2]. CdTe-based ternary alloys, such as Cd1-xZnxTe, Cd1-yMnyTe, and Hg1 zCdzTe, are considered as candidates in such tandem cell structures, not only due to their continuously variable band gaps, but also due to their small lattice mismatch in this alloy system. We have successfully deposited these alloys by RF sputtering, demonstrated their p-type characterizations and fabricated single junctions combined with a CdS layer [3, 4]. The conversion efficiency of single junction of Cd1-xZnxTe/CdS can reach 7.2 % with Voc = 737 mV and Jsc = 19 mA/cm2 [3]. A prototype tandem cell based on Hg1 zCdzTe (Eg = 1.15 eV)/ CdTe contributes Voc = 992 mV and Jsc = 2.1 mA/cm2 [5]. Although this is far from our goal of 25% conversion efficiency, the primary results indicate that there is much improvement possible in cell performance with further process optimization. An important step in fabricating high performance CdTe-based solar cells is the CdCl2 activation treatment. Various explanations of the CdCl2 treatment invoke the formation of shallow acceptor complexes, improvements of the microstructure, and interdiffusion. It is expected that chloride treatments may improve the performance of cells fabricated from the ternary alloys, as well. In order to understand such treatments, a multichannel spectroscopic ellipsometer with a 0.75 - 6.5 eV photon energy range is used under ex situ and in situ modes on CdTe and its ternary alloy films. An atomic force microscope was used to complement optical studies of the surface structural characteristics. The E1, E1+Δ1, and E2 critical-point structures were clearly observed in the spectra for as-deposited samples. The variation of the pseudodielectric function of CdCl2 treated samples was observed by in situ ellipsometry. These investigations are expected to be useful for optimizing the CdCl2 treatment process. This work is being supported by the NREL High Performance PV project. References [1] X. Wu et al., Proc. of 17th European PVSEC, (2001) pp. 995. [2] T. J. Coutts, K. A. Emery, and S. Ward, Prog. Photovolt: Res. Appl. 10 (2002) 195 [3] S.H.Lee, A.Gupta, S.L.Wang, A.D.Compaan and B.E.McCandless, Solar Energy Materials & Solar Cells, (in press) [4] S.L. Wang, S.H.Lee, A.Gupta, and A.D.Compaan, phys. stat. sol. (c) 1 (2004) 1046. [5] S. L.Wang, J.Drayton, V.Parikh, A. Vasko, A. Gupta, and A.D.Compaan, MRS Fall Meeting (12/2004)

F5.30

CELLO Measurements of CIGS and μcSi Solar Cells. Stefan Mathijssen[1], Juergen Carstensen[1], Helmut Foell[1], Georg Voorwinden[2] and Helmut Stiebig[3]; [1]Chair for General Materials Science, Faculty of Engineering, Christian-Albrechts-University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany; [2]ZSW Stuttgart, Stuttgart, Germany; [3]FZ Juelich, Juelich, Germany.

The CELLO (solar CELl LOcal characterization) technique allows to measure all parameters of the equivalent circuit of a solar cell *locally*. The technique uses the local current and voltage modulations induced by local illumination with a modulated LASER beam. These (small signal) modulations are superimposed on the current or voltage of a globally illuminated solar cell held at a fixed working point by either impressing a fixed current or voltage. Several sets of data obtained by measuring current or voltage responses at various working points allow extracting any local parameter of a suitable equivalent circuit numerically. By performing measurements at different points of the IV-characteristic of the solar cell, CELLO allows the detection of various types of localized defects on a solar cell with high lateral resolution ($\sim$200 μm) that do not show up in standard LBIC measurements, as well as non-uniformities on a larger scale, e.g. gradients in the series resistance, which are difficult to assess with other methods. In particular, by numerical combinations of suitable measurements, high-resolution maps (e.g. 500.000 pixels for a (100 x 100) mm^2 cell) of, e.g., shunt and serial resistance, lifetime of minorities, emitter quality, or even back surface field efficiency, can be obtained. Based on this data set it is then possible to assess quantitatively the possible improvement of a given solar cell (technology) if defects or deficiencies detected by CELLO would be avoided. While the principle is relatively simple, the application to thin film compound cells is not. Here we report the first results obtained with thin film compound cells, in particular from Cu(In,Ga)Se$_2$ based cells (CIGS-cells) and microcrystalline/amorphous Si cells (μcSi-cells) fabricated as tandem cells. Small CIGS cells (size: 17 mm x 70 mm) from the ZSW Stuttgart have been investigated with CELLO. The results show different aspects of the cell: inhomogeneities in the CIGS layer, the influence of the structuring into individual cells, and the influence of the metal back contact on the serial resistance of the cell. The impact of those different characteristics of the cell on the efficiency is calculated, showing possible relative efficiency gains of larger than 10 %. The results on μcSi-cells were obtained from a μc-Si:H module consisting of 16 series connected cells (80 mm x 5mm each) made at the research center Juelich. The Cello maps were found to correlate well with available thermo camera images. Various systematic patterns are observed: A degeneration of the whole module in the upper part due to a treatment after the structuring, and recurring structures related to the thin film quality leading to an increased serial resistance and considerable losses at the working point of the module. An approximation to the influence of these different effects on the efficiency of the cells will be presented, demonstrating possible relative efficiency gains > 10 %.

F5.31

Study of Meyer-Neldel Rule Behavior Detected with Slow Capacitance Transients in CdTe Solar Cells. Fred H. Seymour, Victor Kaydanov and Tim R. Ohno; Physics, Colorado School of Mines, Golden, Colorado.

Numerous deep electronic state (DES) signatures have been detected with capacitance transient (CTr) measurements from batches of CdTe solar cells obtained from multiple sources. The signatures, characterized by their activation energy Ea and apparent cross section σ, exhibit a wide distribution of values for Ea and σ. They have been classified into several groups where for each group Ea and σ obey Meyer-Neldel Rule (MNR) behavior and fit a linear plot of the form, log $\sigma = \alpha + \beta$Ea. Each group or MNR family has unique values for α and β. Within each MNR family, Ea can vary by several tenths of an eV and σ can vary by several orders of magnitude. There are grounds to suggest that the signatures in a particular MNR family belong to the same DES. This helps bring order to the detected signatures and helps simplify attributing them to specific defects and impurities. Possible mechanisms of variation of Ea and σ within the MNR families are discussed. CTr are triggered with either a voltage bias or light pulse that lasts from seconds to hours to charge the DES and this is followed by a recovery period of zero bias and dark. CTr data is collected both during and following the pulse. The characteristic time, τ, is determined by analyzing the DLTS function, dC/dlnt. For the exponential time dependence ΔC(t) $-$ ΔC0 exp(-t/τ), the peak of this DLTS function is located on the time scale at tpeak $= \tau$. The origin of the time scale, t=0, corresponds to when the bias pulse is switched on or off. The signature characteristic Ea, and σ are estimated from the Arrhenius plot ln(τ T$\hat{2}$) vs. 1000/T regression slope and Y-intercept. The detected CTr signatures have estimated τ ranging from tens to hundreds of seconds and have been detected at temperatures ranging from 240K to 360K. Because irreversible changes begin to occur in CdTe solar cells at temperatures as low as 370K, only modest heating was applied to lower τ. At room temperature, non-exponential capacitance decay has been observed that lasts for several days. Slow transients have been frequently observed in thin film solar cells and they are of interest to manufacturers because they can delay cell performance stabilization and hinder real time quality control functions. To the best of the authors' knowledge, these slow CTr have not been thoroughly studied in CdTe solar cells. The concentrations of these DES sometimes exceeds the doping level and they are suspected to contribute to cell performance degradation through Shockley-Read-Hall recombination. Preliminary correlations between DES concentration and cell efficiency have been established. Also, the combination of the slow transient decay and the high concentration relative to doping can alter C-V profiles and provide incorrect doping level estimates.

F5.32

General Explanation of J-V Distortion by the Conduction-Band Offset in CdS/CI(G)S Solar Cells. Ana Kanevce, Markus Gloeckler, Alexei Pudov and James R. Sites; Physics, Colorado State University, Fort Collins, Colorado.

A type-I ('spike') conduction-band offset (CBO) greater than few tenths of an eV at the n/p interface of a solar cell can lead to significant distortion of the current-voltage (J-V) curve under illumination. Such distortion has been observed in CdS/CIS cells, low-gallium CdS/CIGS cells, and CIGS cells with alternative windows that increase the CBO. Its basic feature is a reduced current collection in forward bias. The distortion is mitigated by photoconductivity in the CdS or other window layer, and it is therefore more severe if the illumination does not contain photons with energies greater than the window band gap. Hence, the distortion is commonly referred to as the 'red kink'. The purpose of this presentation is to explain the device physics that determines whether there is a major J-V distortion, a small J-V distortion, or none at all. The approach is to use numerical simulation incorporating a straightforward three-layer [TCO/CdS/CI(G)S] approximation for the solar cell. There are a number of parameters that influence the band structure, and hence the existence and the magnitude of the distortion. These include the magnitude of the CBO, the doping of the p- and n- layers, the defect density of the CdS, and the thicknesses of the CdS and TCO layers. The key value, however, is the maximum energy difference between the quasi-Fermi level for electrons and the conduction band. Thermionic emission across the interface will limit the current collection, if the difference exceeds 0.48 eV under standard conditions of 300 K and one-sun illumination. Comparison with cell data shows that this constraint is consistent with experiment, and strategies to satisfy the 0.48 eV limit when designing solar cells will be enumerated in the presentation.

F5.33

Open-Circuit Voltage Decay in CdTe/CdS Solar Cells. Kent Price[1] and Kevin Cooper[2]; [1]Physical Science, Morehead State University, Morehead, Kentucky; [2]Lewis County High School, Vanceburg, Kentucky.

Open-Circuit Voltage Decay (OCVD) is a common technique used to characterize numerous semiconductor devices. However, to the knowledge of the authors, the technique has not previously been applied to CdTe-based solar cells. We use a simple setup consisting of a function generator, rectifying diode, and digital oscilloscope to measure the dark open circuit voltage decay as a function of time across a CdTe solar cell. We find the decay to be described by the equation $v(t) = v_0 + A \exp(-t/T_1) + B \exp(-t/T_2)$ where v is the voltage, t is time, T_1 and T_2 are characteristic decay times, and A, B and v_0 are constants. The two characteristic decay times are approximately 10 μs and 500 μs, and depend on the magnitude of the initial applied voltage pulse. We will describe the correlation between the OCVD and solar cell performance, including the effects of light-soaking on OCVD behavior. This work supported by the Kentucky Science and Engineering Foundation (KSEF).

F5.34

Strong Leakage Current Influence on Deep Level Transient Spectroscopy Signals of Copper Indium Gallium Diselenide Thin Film Solar Cells? Verena Mertens[1], Juergen Parisi[1], Marc Koentges[2] and Rolf Reineke-Koch[2]; [1]Institute of Physics, Energy and Semiconductor Research Laboratory, University of Oldenburg, Oldenburg, Germany; [2]Thin Film Technology, Institute for Solar Energy Research Hameln-Emmerthal (ISFH), Emmerthal, Germany.

We investigated copper indium gallium diselenide solar cells with different gallium content using capacitance and current-voltage measurement techniques. We used two techniques to scan the depletion layer of the solar cell with deep level transient spectroscopy (DLTS) in the constant voltage mode. During the measurements, the samples were never biased in forward direction, so that injection currents can be excluded. By varying the height of the applied voltage pulse, we observe at temperatures well below 200 K a minority carrier and/or majority carrier signal, depending on the pulse applied (The DLTS-signal-temperature spectra of both measurement series were obtained from the transients using the double boxcar as weighting function.). Strangely enough the corresponding capacitance transients show exclusively a positive or a negative amplitude concerning these relatively fast decaying signals and do never consist of a combination of two fast transients with opposite sign, which would be typical of traps with similar activation energies and attempt to escape frequencies. Scanning the space charge region by DLTS measurements with different levels of reverse bias, the spectra consist, in contrast to the aforementioned variation of the voltage pulse height, always only of a minority carrier signal. In general the signal amplitudes in the DLTS temperature spectra become very rapidely smaller with increasing rate windows, which is not expected to happen that fast even for a distribution of traps. Comparing the arrhenius data from DLTS investigations with respective results from admittance measurements indicates that the signals observed seem to be identical but occur in two different temperature ranges. We believe that our experimental findings can be explained by the influence of the non-negligible leakage current in our devices. Similar observations were made by Chen et al. on Au/Cr/SiN$_x$/GaAs metal-insulator-semiconductor structures. Moreover we believe that the DLTS low temperature minority and majority carrier signals observed might not stem from two different traps but show possibly the emission from and the capture into one single trap or distribution of traps, which might also be a consequence of the solar cell's dark current.

F5.35

Investigating Minority-Carrier Traps in p-type Cu(InGa)Se$_2$ Using Deep Level Transient Spectroscopy. Steven W. Johnston and Jehad AbuShama; National Renewable Energy Laboratory, Golden, Colorado.

Measurements of p-type Cu(InGa)Se$_2$ (CIGS) using deep-level transient spectroscopy (DLTS) have showed peaks associated with minority-carrier traps, even though data were collected using reverse bias conditions not favorable to injecting minority-carrier electrons. These DLTS peaks occur in the temperature range of 50 to 150 K for the rate windows used and correspond to electron traps having activation energies usually in the range of 0.1 to 0.2 eV for alloys of CIS, CGS, and CIGS. The peak values also depend on the number of traps filled. For short filling times of 10 to 100 μs, a small peak appears. As the DLTS filling pulse width increases, the peak increases in response to more traps being filled, but it also broadens and shifts to lower temperature suggesting that a possible series of trap levels, perhaps forming a defect band, are present. The peaks usually saturate in a timeframe of seconds. Band modeling is used to calculate the relative amounts of filled electron traps for various reverse bias conditions and is compared to DLTS data. The filling times are sufficient for electrons to fill traps at or near the interface from the n-type side of the device due to a thermionic emission current. Admittance spectroscopy data show similar activation energies and trap concentrations and may be detecting the same defect level.

F5.36

Native Oxidation of CuGaSe$_2$ Crystals and Thin Films Studied by Electron Paramagnetic Resonance (EPR). Klaus Lips[1], Roland Wuerz[2], Alexander Meeder[2], David Fuertes Marron[2] and Thomas Schedel-Niedrig[2]; [1]Silizium-Photovoltaik, Hahn-Meitner-Institut, Berlin, Germany; [2]Heterogene Materialsysteme, Hahn-Meitner-Institut, Berlin, Germany.

The knowledge of intrinsic defects like stoichiometry deviations and extrinsic defects like unintentional doping are important prerequisites to understand the electronic properties of a material such as CuGaSe$_2$ and to identify strategies for device optimization. Electron paramagnetic resonance (EPR) is a power-ful tool for this purpose but only a few EPR investigations of CuGaSe$_2$ crystals and powders have been performed. In this paper the native oxidation of CuGaSe$_2$ crystals and polycrystalline thin films are investigated. We observe an EPR signal assigned to Cu^{2+} that evolves when the samples were stored under ambient conditions for a few months, independent of the morphology of the specimens. When the oxide phase was reduced by annealing in vacuum at 200°C or removed by etching in KCN also the Cu^{2+} EPR signal disappeared. By comparison with photoelectron spectroscopy (PES) data it is shown that the Cu^{2+} EPR signal originates from a Cu(OH)$_2$ phase and the activation energy for the thermal reduction of Cu^{2+} to non-paramagnetic Cu$^+$ is $E_a = 0.29$eV. A model for the native oxidation of CuGaSe$_2$ will be presented and implications for solar cell device performance discussed.

F5.37

Doping by Deposition: Compensating CdS by Tuning rf Sputtering. Jennifer Drayton, Diana Shvydka and A. D. Compaan; Physics and Astronomy, The University of Toledo, Toledo, Ohio.

In the recently developed MIS model of a CdTe/CdS solar cell [1] the role of the CdS layer had changed from a traditional n-type hetero-junction partner of CdTe to that of an insulator between the front contact (TCO) and the semiconductor (CdTe). This model stresses the importance of the proper front contact preparation in fabrication of an efficient device. In particular, depending on the TCO/CdS interfacial properties and the CdS doping (compensation) level, significant changes in the front contact quality and device efficiency are expected. It has been a long standing folklore that these properties are sensitive to the CdS deposition technique. In this work we deposit CdS by rf sputtering, varying the deposition parameters such as gas pressure. Some films are also exposed to post-deposition CdCl$_2$ treatment, standard in complete PV device preparation. We monitor the effect of the film fabrication on its electrical properties. As a comparison, we also prepare samples in which CdS compensation is achieved through Cu doping, leading, in some respects, to the effects similar of the deposition parameter variation. Measuring the resistivity of CdS film deposited on highly conductive TCO layer is a challenging problem. In the present work, we solve it mainly by virtue of two techniques allowing for separating out the CdS resistivity contribution, which are (1) the current-sensing AFM and (2) photo-voltage spatial decay measurements, conducted on TCO/CdS/TCO structures. Our results show how tuning rf sputtering parameters can lead to a highly compensated CdS layer. This layer, created without Cu doping, can be used as a step in manufacturing Cu-free CdTe solar cells. We discuss how our findings can be incorporated in a recipe of high-efficiency Cu-free CdTe/CdS photovoltaics. This work is partially supported by the NREL Thin Film Partnership Program. 1. Y. Roussillon, D. M. Giolando, V. G. Karpov, Diana Shvydka, and A. D. Compaan, Applied Physics Letters 85, 2004, pp 3617-3619.

SESSION F6: Interfaces

Chairs: Iver Lauermann and Uwe Rau
Wednesday Morning, March 30, 2005
Room 2005 (Moscone West)

8:30 AM *F6.1

Interfaces in CdTe Solar Cells: From Idealized Concepts to Technology. Wolfram Jaegermann, Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany.

Most thin film semiconductor devices as e. g. the CdTe solar cells are layer sequences of dissimilar materials. High conversion efficiencies can only be obtained, if certain preparation and processing steps are followed as e. g. the CdCl2 activation step which is still not completely clarified in its effects. As a consequence the electronic device properties as the band energy diagrams are still a matter of debate as no general accepted experimental data set exists nor clear theoretical reasonings for the observed properties. We will start our presentation with the theoretical concepts developped for atomically abrupt semiconductor heterojunctions and examples for their validity. It will be shown that a high number of interfacial defects are formed whenever lattice mismatched semiconductors are deposited on each other at low sample temperature (room temperature). In relation to the CdTe thin film solar cells the CdS/CdTe as well as at the TCO interfaces will be presented. Next surface science results indicating interdiffusion processes at all heterointerfaces of interest will be presented. At the TCO/CdS and CdS/CdTe interface the interdiffusion is a consequence of the activation step. But also reasonable ohmic back contact properties can only be obtained if indiffusion of defect states are taken into account. Also the morphology of the absorber film seems to be strongly affected by the interdiffusion process at the heterointerfaces. The evident deviations in the theoretical descriptions of interdiffused heterointerfaces will be deduced. It will be suggested that interdiffusion and extended phase boundaries will be a precondition for efficient thin film solar cells whenever dissimilar and lattice mismatched heterointerfaces are combined.

9:00 AM F6.2

Chemical and Electronic Properties of the Deeply Buried Cu(In,Ga)(S,Se)$_2$/Mo Interface in Thin Film Solar Cells.

Lothar Weinhardt[1], Oliver Fuchs[1], Eberhard Umbach[1], Clemens Heske[2], Joerg Reichardt[3], Marcus Baer[3], Iver Lauermann[3], Immo Koetschau[3], Alexander Grimm[3], Stefan Sokoll[3], Christian-Herbert Fischer[3], Martha Ch Lux-Steiner[3], Thomas P Niesen[4], Franz Karg[4], Christian Jung[5] and Wolfgang Gudat[5]; [1]Experimentelle Physik II, Universitaet Wuerzburg, Wuerzburg, Germany; [2]Department of Chemistry, University of Nevada, Las Vegas, Nevada; [3]Hahn-Meitner-Institut, Berlin, Germany; [4]Shell Solar GmbH, Munich, Germany; [5]BESSY GmbH, Berlin, Germany.

For a further optimization of ZnO/buffer/Cu(In,Ga)(S,Se)$_2$/Mo thin film solar cells a detailed understanding of the chemical and electronic properties at the various interfaces is needed. In contrast to the interface between the absorber and the buffer layer, the understanding of the absorber/Mo back contact is still poor because it is buried underneath the 2μm-thick absorber. To get access to this interface, we used suitable lift-off techniques to remove the absorber from its back contact. Then we investigated both the CIGSSe absorber back side as well as the Mo surface with X-ray emission spectroscopy and photoelectron spectroscopy. Both techniques give detailed information about electronic and chemical properties, albeit in a different way and with a different information depth ($\sim$10-200 nm and $\sim$1 nm, respectively). We found the formation of MoS$_2$ and MoSe$_2$, but no Mo on the absorber back side. Furthermore, we observed pronounced composition differences between the external CIGSSe surface and the absorber back side. Based on these findings, an electronic and compositional picture of the CIGSSe/Mo interface will be discussed.

9:15 AM F6.3

A Study of the Diffusion and pn-Junction Formation in CIGS Solar Cells Using EDX and EBIC Measurements.

Shogo Ishizuka[1], Keiichiro Sakurai[1], Koji Matsubara[1], Akimasa Yamada[1], Minoru Yonemura[2], Shimpei Kuwamori[2], Satoshi Nakamura[2], Yasuyuki Kimura[2], Hisayuki Nakanishi[2] and Shigeru Niki[1]; [1]Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Tokyo University of Science, Noda, Chiba, Japan.

Cu(In1-xGax)Se2 (CIGS) is a promising material for the fabrication of highly efficient and cost effective thin film solar cells. To achieve higher efficiencies and attain optimized cell performance for practical applications, detailed device characterization is indispensable. As for CIGS solar cells, an understanding of the basic science with respect to junction formation and inter-diffusion mechanisms has not jelled despite the relatively extensive CIGS research efforts reported in the literature and the high efficiencies already reported. In this study, cross sectional measurements of CIGS solar cells, prepared under several different conditions, were carried out using an energy dispersive x-ray spectrometer (EDX) and an electron-beam induced current (EBIC) equipped high-resolution field-emission scanning electron microscope (FE-SEM). The correlation of the extent of the space charge region and the observed shift in the pn-junction location with the diffusion in CIGS was investigated. CIGS layers were prepared by the three-stage process on Mo-coated soda-lime glass substrates. CdS buffer layers were then deposited by chemical bath deposition (CBD). i- and n-ZnO layers were successively deposited by radio-frequency (RF) magnetron sputtering. Al grids were formed by evaporation. Samples for cross sectional EDX and EBIC measurements were prepared by cleaving CIGS solar cells to an appropriate size. EBIC measurements revealed that the pn-junction location of CIGS solar cells, which were fabricated using a 773K vacuum annealing process after CdS deposition, shifted into the CIGS layer compared with that of CIGS solar cells fabricated without use of the annealing process. In this case, the inter-diffusion of Cd into the CIGS layer was observed while that of Zn from ZnO layers was not observed by EDX measurements. These results suggest that only Cd plays an important role in forming a buried pn-junction in the CIGS layer via diffusion, and deemphasize the possibility of the formation of a hetero pn-junction based at the CdS/CIGS heterointerface. Furthermore, EBIC images indicated a reduction in the extent of the space charge region in small CIGS grain regions. Although it has been commonly accepted that grain boundaries are passivated and the carrier recombination process at grain boundaries is negligible for CIGS layers, this result suggests that these grain boundaries may have an influence on cell performance as defects, which cause degradation. It is, therefore, suggested that technical developments to eliminate such defects are required to achieve higher cell performance.

9:30 AM *F6.4

Study of Change of Electronic Structure of CdS/Cu(In, Ga)Se$_2$ Interfaces with Ga Concentration of Cu(In, Ga)Se$_2$ by Photoemission and Inverse Photoemission Spectroscopy.

N. Terada[1,2], S. H. Kong[3], H. Kashiwabara[1], R. T. Widodo[1], K. Ohki[1], T. Okuda[1], S. Niki[2], K. Sakurai[2], A. Yamada[2] and S. Ishizuka[2]; [1]Nano Structure and Advanced Materials, Kagoshima University, Kagoshima, Japan; [2]National Institutes of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; [3]Venture Business Laboratory, Kagoshima University, Kagoshima, Japan.

Control of nature of interfaces between buffer layer and Cu(In$_{1-x}$Ga$_x$)Se$_2$ [CIGS] is one of the keys for further improvement of performances of CIGS based solar cells. Characterization of a dependence of electronic structure of the interfaces on band gap energy of the CIGS should give useful information for modeling of the electronic properties of the cells and pursuing their potentials of higher efficiency. By using photoemission and inverse photoemission spectroscopy, we have been attempting the characterization of Ga substitution ratio x dependence of alignments of valence band and conduction band at the interfaces between CdS buffer layer grown by chemical bath deposition (CBD) and CIGS by three-stage co-evaporation. Experimental results up to now are represented as follows: In a low region of x, the CIGS region adjacent to the interface had a band gap around 1.3 $\sim$ 1.4 eV, which was much wider than that of bulk-specimen with corresponding composition. Valence band offset (VBO) and conduction band offset (CBO) at these interfaces were finite, where the conduction band minimum of CdS located above that of CIGS (positive CBO). For the CdS/Cu(In$_{0.80}$Ga$_{0.20}$)Se$_2$, VBO and CBO were 0.7 and 0.25 eV, respectively. In the region of x up to 0.4, an increase of VBO and a reduction of CBO with a rise of x were observed. An almost flat conduction band alignment was observed at the CdS/Cu(In$_{0.60}$Ga$_{0.40}$)Se$_2$ structure. This result is consistent with that the conversion efficiency of our cells takes a maximum around $x = 0.3$. In the interfaces over the CIGS with the higher x, it was observed variety of their electronic structure, involving reduced band gap of the CIGS in comparison with that of bulk with the corresponding nominal Ga-substitution ratio of the films and serious sample-dependence of band-edge gradients in the CIGS layer adjacent to the interface. Some results also indicated a change of the sign of CBO. These results would be consistent with the saturation tendency of open circuit voltage and a deterioration of the conversion efficiency in of the wide gap CIGS based cells. The present study indicates the usefulness of the direct characterization of the CdS/CIGS interfaces for clarification of the correlation between the electronic structure and macroscopic properties of the CIGS based cells over the wide range of the Ga substitution ratio.

SESSION F7: TCOs and Window Layers

Chairs: Iver Lauermann and Uwe Rau
Wednesday Morning, March 30, 2005
Room 2005 (Moscone West)

10:30 AM F7.1

Transparent Conducting Oxide Sculptured Thin Films for Photovoltaics Applications.

Robert W. Collins[1], Chi Chen[1], Nicolas J. Podraza[1], Deepak Sainju[1], Obi Ezekoye[2], Mark W. Horn[2] and Christopher R. Wronski[3]; [1]Dept.of Physics and Astronomy, The University of Toledo, Toledo, Ohio; [2]Dept. of Engineering Sciences and Mechanics, The Pennsylvania State University, University Park, Pennsylvania; [3]Dept. of Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Optical losses in thin film solar cells arise due to reflections at the top interface between the transparent conducting oxide (TCO) and the semiconductor structure where the dielectric discontinuity is usually the largest. In some cell structures that exploit thin or wider gap semiconductor layers, absorption in the metal back-contact can reduce the photon flux available for collection in a second pass after back-reflection. Advanced optical engineering approaches are needed to minimize all such losses. One possible approach is to incorporate multilayered or graded index TCO films that can act as broad-band anti-reflectors at the top of the devices or narrower-band enhanced reflectors at the back. Thus, it is important to be able to modulate the long-wavelength index of refraction of the TCO over a relatively wide range (e.g., $1.4 < n < 2.0$) without increasing its extinction coefficient k or significantly degrading its electrical conductance. Here we report an investigation of SnO$_2$ and ZnO sculptured thin films (STFs) under development for this purpose.[1,2] Sculptured thin films are deposited under low surface mobility conditions using stepwise or continuous variations in the polar and/or azimuthal angles of the deposition flux impinging on the surface. Through self-shadowing, deposition at a glancing polar angle leads to columnar growth, optical anisotropy, and low ordinary indices of refraction, whereas normal incidence deposition under the same conditions leads to dense isotropic films and high indices. In this study, we explore the dependence of the optical properties of ZnO and SnO_2, including index and birefringence spectra, on the polar deposition angle. Results will be presented for films deposited continuously with a modulated polar angle, as well. Optical modeling will explore the ability of the STF concept to provide tailored TCOs for advanced optical engineering of selected solar cell structures. 1. R. Messier, V.C. Venugopal, and P.D. Sunal, "Origin and evolution of sculptured thin films", *J.Vac.Sci.Technol.* A **18**, 1538-1545 (2000). 2. N.J. Podraza, C. Chen, I. An, G.M. Ferreira, P.I. Rovira, R. Messier, and R.W. Collins, "Analysis of the optical properties and structure of sculptured thin films from spectroscopic Mueller matrix ellipsometry", *ThinSolidFilms* **455 – 456**, 571-575 (2004).

10:45 AM F7.2

Transition Metal Doped Indium Oxide – Next Generation Transparent Conductors. M. F. A. M. van Hest, M. S. Dabney, J. D. Pekins and D. S. Ginley; National Renewable Energy Laboratory, Golden, Colorado.

Recently, transition metal doped In_2O_3 has shown improved properties in terms of both transparency and mobility. In this study, we use combinatorial/high throughput research tools to study Mo and Ti doped indium oxide materials. Combinatorial co-sputtering from two different targets was used to produce compositionally graded transparent conducting oxides (TCO) films on 2" x 2" glass substrates. This approach allows for a large or small composition gradient across the deposited film. Material ratios in a range from 1:0 to 0:1 can be mapped in as little as five depositions. The doped indium oxide materials are grown using one indium oxide target and a doped indium oxide target or a pure metal oxide target. The targets have been sputtered using RF power in an argon gas atmosphere. Deposition temperatures range from room temperature to 550 °C. For the Ti and Mo metal dopants studied films with very good conductivity ($<2.0 \times 10^{-4}$ Ω cm) and high mobility (>80 cm^2/Vs) were obtained. Typically the best conductivity is obtained when the doping is in the range from 1 to 4% for films deposited at high temperature (550 °C). The metal doping content has been determined by means of electron probe micro analysis. Ti doping results in the generation of one carrier per Ti doping atom, while Mo genertates less than a carrier per Mo. Films were analyzed by XRD and optical transmission and reflection spectroscopy. The best films are highly crystalline and high optical transmission across the visible portion of the spectrum (>85%). Comparison of the data obtained for Ti doping and Mo doping will provide insight into the mechanism of dopant incorporation.

11:00 AM F7.3

Electronic and Optical Properties of Spinel Transparent Conducting Oxides. David Segev and Su-Huai Wei; National Renewable Energy Laboratory, Golden, Colorado.

SnZn2O4, SnCd2O4, and CdIn2O4 are ternary compounds that can exist in the spinel structure. They have emerged as promising transparent conducting oxides (TCOs), which are transparent and at the same time conductive, thus are suitable for optoelectronic applications such as solar cell. However, despite many recent studies of these compounds, many of their physical properties are still unknown. Their band structure and optical properties are not well established, nor are the reasons for their combined transparency and conductivity. Using the band-structure method, we have studied the structural, electronic and optical properties of the transparent conducting oxides SnZn2O4, SnCd2O4, and CdIn2O4. We analyzed the atomic and orbital characters of the band edge states and explained the general trends observed in the fundamental band gap, the optical band gap, the energy difference between the first and the second conduction bands, and the electron effective mass. General rules for designing more efficient transparent conducting oxides are proposed.

11:15 AM F7.4

Buffer Layers of Zn-Sn-O and Their Influence on the Characteristics of Thin Film CdTe Solar Cells. Chris Ferekides[1], Gayam Sudhakar[1], Srilatha Banapalti[1], Robert Mamazza[2], Hehong Zhao[1], Lingeswari Nemani[1] and Don Morel[1]; [1]University of South Florida, Tampa, Florida; [2]Solar Power Technologies, Tampa, Florida.

Thin film CdTe solar cells are typically of the superstrate configuration where the junction is fabricated on a glass substrate coated with a transparent (front) contact. The role of the transparent contact extends beyond providing a low sheet resistance for lateral current transport. High resistivity ('buffer') layers are used by both CIGS and CdTe thin film solar cells to enhance the overall device performance. In the case of CdTe the use of zinc stannate (Zn_2SnO_4) has resulted in the highest efficiency cells fabricated to-date as demonstrated by the National Renewable Energy Laboratory. The properties of transparent Zn-Sn-O layers and their impact on solar cell performance are the focus of this work. Thin films of Zn-Sn-O have been deposited by rf co-sputtering of ZnO and SnO_2 targets (in an Ar/O_2 ambient). In order to study the effect of film stoichiometry and composition on solar cell characteristics, the Zn/Sn ratio was varied during the deposition by varying the deposition rates of the oxides. The films were typically deposited at room temperature and were subsequently heat treated (ambient varied); their structural properties were studied using x-ray diffraction. As-deposited films were amorphous and begun to crystallize for annealing temperatures of approx. 575°C. The Zn_2SnO_4 phase was identified in films deposited at a Zn/Sn ratio of 2.0. No additional phases were identified for small (on the order of 5%) variations in the Zn/Sn ratio (1.9-2.1). Larger variations lead to the formation of mixtures of the ternary compound with Zn and Sn binary oxides. Solar cells were fabricated using bi-layers of Zn-Sn-O as the 'buffer' with CVD-deposited SnO_2:F as the conductive layer. The devices were characterized using standard solar cell techniques. Using as-deposited Zn-Sn-O as a buffer layer lead to poor solar cell characteristics regardless of the Zn/Sn ratio; this was primarily due to excessive dark currents associated with a highly defective interface. For annealing temperatures over 575°C (films begin to crystallize at these temperatures) solar cell performance improved dramatically, indicating that the crystallinity of the buffer can greatly influence device performance. Spectral response measurements suggested that the stoichiometry of the Zn-Sn-O films can influence the consumption of CdS during the cell fabrication process, providing a means of controlling and enhancing the blue response, and therefore the short-circuit current density of the cells. The consumption of CdS is believed to be a result of the presence of zinc oxides in the buffer layer. Results from the work described above, as well as from on-going work on the properties of Zn-Sn-O films deposited directly on glass will be discussed at the meeting.

11:30 AM F7.5

Design of a Window Layer for Flexible Cu(In,Ga)Se_2 Thin Film Solar Cell Devices. Christian A. Kaufmann, Axel Neisser, Hans-Juergen Muffler, Reiner Klenk, Roland Scheer and Hans-Werner Schock; Hahn-Meitner-Institut Berlin, Berlin, Germany.

Using titanium foil instead of glass as a substrate for Cu(In,Ga)Se_2 (CIGSe) thin film solar cells produces lightweight, robust and highly efficient flexible devices. Such flexible devices are an attractive option for use as power generators, in particular for mobile applications. One example is the use as power source for communication satellites. Due to their excellent radiation hardness and a favorable power to weight ratio, chalcopyrite solar cells on flexible substrates are one of the main future alternatives to existing space photovoltaic technologies. Thin film solar cell devices consisting of the layer sequence Mo/CIGSe/CdS/ZnO/ZnO:Al have been prepared on a 25μm thick titanium foil substrate. The CIGSe absorber layer is deposited by means of a co-evaporation process with laser light scattering (LLS) used as an in-situ process control. So far, for large area devices with a total area of 27.1 cm^2, a maximum total area efficiency of 13.8% is demonstrated. The initial transfer of the thin film technology from glass to the flexible substrate involved the elimination of shunts, attributed with the roughness of the flexible substrate, plus the optimization of the sodium content of the CIGSe layers on titanium. For small area devices (0.5cm^2), this technology transfer is considered achieved, with the maximum total area efficiencies on glass and titanium foil substrates being at 16.9% and 16.2% respectively. It is known form the in-situ LLS process control that the optical behavior of the flexible titanium foil substrate, in terms of scattering, differs due to its roughness from the much smoother glass substrate. Hence the optical light loss for a device on titanium foil may also be different to an otherwise identical device deposited onto glass. This contribution investigates device optimization aspects that are concerned with the transparent window layers. The thickness of the transparent conductive oxide for flexible devices is optimized accordingly and the effect of an anti reflective coating is compared for devices on glass and on titanium foil. Further more a novel light-trapping layer is deposited onto completed flexible devices and its effect is assessed in comparison to the above. Device characterization carried out for this work includes performance measurements under AM1.5 illumination, the measurement of quantum efficiency and the optical reflectance of completed devices.

SESSION F8: Back Contacts

Chairs: John Merrill and Wyatt Metzger
Wednesday Afternoon, March 30, 2005
Room 2005 (Moscone West)

1:30 PM F8.1

Dependence of the MoSe2 Formation on the Mo Orientation and the Na Concentration in Cu(In,Ga)Se2 Thin-film Solar Cells. Daniel Abou-Ras[1,2], Debashis Mukherji[1], Gernot Kostorz[1], David Bremaud[2], Marc Kaelin[2], Dominik Rudmann[2] and Ayodhya N. Tiwari[2,3]; [1]Institute of Applied Physics, ETH Zurich, Zurich, Switzerland; [2]Thin Film Physics Group, Laboratory for Solid State

Physics, ETH Zurich, Zurich, Switzerland; [3]Centre for Renewable Energy Systems and Technology, Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire, LE11 3TU, United Kingdom.

The formation of MoSe2 has been studied on poly- and single crystalline Mo substrates in dependence of the Mo orientation, the Na concentration and the substrate temperature. The Mo substrates were selenized by physical vapor deposition of Se powder. The samples were analyzed by means of X-ray diffraction, Rutherford backscattering spectrometry, conventional and high-resolution transmission electron microscopy (including electron diffraction), and energy-dispersive X-ray spectrometry. It was found that the crystal structure and orientation of the MoSe2 layer change with increasing substrate temperature. The Na concentration was regulated by the deposition of NaF layers with different thicknesses on the Mo substrate. MoSe2 growth was found to depend sensitively on the Na concentration at substrate temperatures of 450°C and 580°C. In addition, it was found that the texture of MoSe2 does not depend on the orientation of the Mo substrate. The results of this study help to improve the performance of MoSe2 as buffer layer in Cu(In,Ga)Se2 solar cells between the absorber and different back contact materials, such as transparent conducting oxides.

1:45 PM F8.2

Understanding Aniline Surface Treatment of CdTe.
Kevin D. Dobson, Stephanie A. Einstein, Dan D. Sadowsky, Brian E. McCandless and Robert W. Birkmire; Institute of Energy Conversion, University of Delaware, Newark, Delaware.

Surface treatments of polycrystalline CdTe are critical for the successful processing of back contacts to CdTe/CdS devices. Such treatments are generally used to remove metal oxides and other contaminants, and to generate a Te-rich surface which will assist the formation of metal telluride back contacts. Due to their ease of use and fast treatment times, wet chemical oxidizing etchants are often employed. Recently, a new surface treatment, based on aqueous aniline solutions, was reported to produce good quality devices [1]. These treatments, carried out by illumination of an immersed CdTe film, were proposed to block electrical micro-nonuniformities and pinholes in the CdTe film by selective etching or deposition of an interfacial layer from the treatment bath. In this paper we report an investigation of the chemistry of the aniline-based bath. A successful treatment of CdTe was found to result in the formation of a light-gray crystalline-Te surface layer, confirmed by glancing incidence x-ray diffraction and variable angle spectroscopic ellipsometry. Control of bath conditions, including aniline concentration, pH, the presence of Cl^- ions and dissolved O_2, and consistent illumination are critical for the surface reaction to proceed. A chemical mechanism for the formation of Te-rich surfaces by aniline-based baths will be presented. The proposed process involves the oxidation of aniline by photo-generated holes, complemented by the reduction of O_2 by conduction band electrons to form H_2O_2, which etches the CdTe to Te. The surface reaction is self-limiting, allowing generation of reproducible surfaces and prevents over-etching of the sample. Devices processed with the aniline treatments were promising, with >11.5% conversion efficiencies being achieved with Cu-based back contacts. [1] Y. Roussillon et al., Appl. Phys. Lett., 84 (2004) 616.

2:00 PM F8.3

P-ZnTe for Back Contacts to CdTe Thin Film Solar Cells.
Bettina Spaeth, Jochen Fritsche, Andreas Klein and Wolfram Jaegermann; Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany.

CdTe thin film solar cells promise a high potential to reach good conversion efficiencies with a low cost production process. A good ohmic contact to the absorber layer is needed most for efficient solar cells without electrical losses. In previous studies CdTe/metal contacts have shown significant limitations. A promising option for the realization of ohmic back contacts is the use of highly p-doped ZnTe interlayers on top of the CdTe absorber, in particular since ZnTe/metal contacts have shown very good electrical properties. In this work we studied the electronic und chemical surface and interface properties of differently prepared nitrogen doped p-ZnTe films. p-ZnTe:N films were prepared either using reactive RF magnetron sputtering with N_2/Ar gas mixtures or by thermal evaporation with an additional nitrogen plasma source. Samples have been prepared in DAISY-SOL (DArmstadt Integrated SYstem for SOLar cell research) which combines a full vacuum production with an in-situ photoelectron spectroscopy (XPS/UPS) analysis. ZnTe/metal contacts have also been prepared in the vacuum system. The results of XPS/UPS investigations and electrical measurements will be discussed in comparison to previous results on CdTe/metal contacts. As ZnTe forms an interlayer in the CdTe thin film solar cell the CdTe/ZnTe interface properties must be also taken into consideration. Our experiments have shown in agreement to previous studies that the valance band offset is nearly ideal for hole transport across the interface. Also electrical measurements have been carried out to investigate the CdTe/ZnTe/metal layer sequences in their contact properties.

2:15 PM F8.4

Back Contact Effect on CdS/CdTe Thin-Film Solar Cells: Reach-Though Diode. Yann Roussillon[1], Victor G. Karpov[2], Diana Shvydka[2], Jennifer Drayton[2] and Al D. Compaan[2]; [1]Chemistry, University of Toledo, Toledo, Ohio; [2]Physics and Astronomy, University of Toledo, Toledo, Ohio.

Back barriers are detrimental in PV devices where they act as diodes in the opposite direction to the main-junction (e.g. the CdS/CdTe junction) diode, thus blocking the flow of photo-generated carriers. The corresponding physics is usually modeled as a "leaky" diode in series with the main-junction photo-diode, but of the opposite polarity. One obvious related result is that, since the back-diode does not generate any photocurrent, it should not affect the device open-circuit voltage (Voc). Contrary to this understanding, it was observed in many experiments that the back contact recipe strongly affects Voc. Here we show that when the height of the back barrier grows above a certain value ($\sim$0.5 eV), then the device turns into a qualitatively new system, which in the physics of semiconductors is known as a reach-through (RT) diode. The underlying physics is that the standard back diode regime dominates when the barrier is low enough to let a charge carrier leave the device before another is generated nearby. If the back barrier grows above a certain value, the carriers are blocked even under short-circuit conditions. Applying a forward bias above a threshold value V > VRT, turns the device into a reach-though diode, where VRT is function of the main junction and back barrier heights. In applying this philosophy, it is also important to remember that the back barrier transparency is laterally nonuniform, typical of barriers in many systems. In particular, while transparent enough on average, it can have rare microscopically "bad" spots of low hole transparency. Those are connected in parallel with the "standard" micro-diodes whose effective Voc are independent of the back barrier height. This parallel connection leads to a J-V characteristic with short-circuit current Jsc close to that of the standard micro-diodes, but with a low Voc, which, in fact, is equal to VRT, corresponding to the local reach-though diodes. To verify the above model, Au, Cu/Au and ZnTe:N/Ni back contacts were deposited on weak junction devices (with surface photovoltage, SPV $\sim$ 550 mV) and strong junction devices (SPV$\sim$ 800 mV); the back contacts were not given any thermal treatments. Consistent with our understanding, it was found that only Au led to devices which Voc was identical to the SPV for the case of strong junction devices. Using Au back contact, combined with the presence of a buffer layer (needed to have a strong junction device without any Cu doping) led to a 13% efficient CdS/CdTe solar cell. Furthermore, such a structure might have the potential for better long-term stability than the standard Cu doped ones.

SESSION F9: Discussion Session I
Back Contacts: Are they the Key to Improved CIGS and CdTe Solar Cells?

Discussion Leaders:
Chris Ferekides, University of South Florida
Ayodya Tiwari, ETH Zurich

Wednesday March 30, 2005
3:00 PM - 5:00 PM
Room 2005 (Moscone West)

SESSION F10: Grain Boundaries and Inhomogeneities

Chairs: Kevin Dobson and Michael Powalla
Thursday Morning, March 31, 2005
Room 2005 (Moscone West)

8:30 AM *F10.1

Physics of CdTe Photovoltaics: From Front to Back.
Victor G. Karpov, Diana Shvydka and Yann Roussillon; Physics and Astronomy, University of Toledo, Toledo, Ohio.

While the device physics has been a key factor in established semiconductor technologies, the acquired knowledge does not explain some features of thin-film PV. This work is aimed at clarifying the physical concepts specific to thin-film devices. In particular, we discuss a model of CdTe-based thin-film PV including such phenomena as lateral nonuniformity, reach-through band bending, and shunting. The effects of lateral nonuniformity are described in the model of Random Diode Arrays (RDA), where weak (low Voc) diodes are most detrimental: a) Under forward bias generated by their more robust neighbors, they run currents in the wrong direction, and short the device. b) They localize stresses and promote nonuniform degradation. Based on the above physics, we have developed a self-healing electrolyte treatment. Our data suggest that, contrary to the common believe, CdS/CdTe PV operates not as a p-n junction, but rather as a MIS structure. The originally conductive CdS gets strongly compensated as imbedded in the device structure, where it behaves as an insulator. This suppresses the Schottky barriers between CdS and its tangent layers, and couples the transparent conducting oxide (TCO) part of the device with the CdTe; this results in a strong bending of the CdTe bands which leads to a high Voc. The CdS compensation can be achieved through Cu doping or, alternatively, through creating surface states as a result of interaction with a buffer layer (placed between the TCO and CdS layer). In other words, doping and surface modification have the same effect. We also have resolved a longstanding mystery of (optically inactive) back surface having a profound impact on the device Voc. Our understanding assumes local spots of high back barriers operating in the reach-through regime. When connected in parallel with the standard (low) back barrier regions, they shunt the device and thus lower its Voc. Our findings sum up to a recipe of Cu-free CdTe 13% efficient PV device (with CdS thickness of 100 nm) whose degradation rate under light soak is significantly lower than that of the Cu doped standard devices. Last, we have developed a quantitative model of shunting-like phenomena, according to which a conductive path through a thin film device has a precursor in the form of chain of defects that facilitate the electron tunneling. Small film thickness exponentially increases the shunting probability and our understanding predicts a way of suppressing it.

9:00 AM *F10.2

Exploring Electron Transport and Recombination on Grain Boundaries and Grain Interiors in Cu(In,Ga)Se$_2$: The Effects of Ga Addition and Cu Removal. Manuel J. Romero, Chun-Sheng Jiang, Rommel Noufi and Mowafak M. Al-Jassim; National Renewable Energy Laboratory, Golden, Colorado.

Solar cells based on Cu(In,Ga)Se$_2$ (CIGS) have demonstrated record photoconversion efficiencies encouraging exploratory research toward multiple junctions based entirely on these compounds. However, this early effort revealed that CuInSe2 (CIS) and CuGaSe2 (CGS) are electronically very different. Electron transport and recombination in these compounds are very much affected by grain boundaries and nanoscale domains in grain interiors. How does composition influence all of this? In this contribution, we address this question from our most recent investigation of CIGS thin films by cathodoluminescence (CL), scanning tunneling luminescence (STL), and other methods based on scanning tunneling microscopy (STM). Additional results from scanning Kelvin probe microscopy (SKPM) and nanoprobe will be presented. We observe a local built-in potential on grain boundaries in CIS but not in CGS. In CIS, the emission spectrum on grain boundaries is not affected by the external excitation. In CGS, recombination is dominant instead. In CIS, higher photocurrents in STM are observed at grain boundaries, which is the reverse for CGS. On the other hand, within grain interiors, nanoscale domains are observed in CIS but they are absent in CGS. Nanoscale domains can be explained from the stability of $2V_{Cu}{}^{-}+Cu_{In}{}^{2+}$ complexes but the impact on the electron transport is more difficult to predict. The reverse stands for grain boundaries, where it becomes clear that the absence of a built-in potential is detrimental to cell performance, but a complete model for grain boundaries is still elusive.

9:30 AM F10.3

Electronic and Chemical Structure at Micro-Interfaces of CuIn$_{1-x}$Ga$_x$Se$_2$ Grain Boundaries. M. Hetzer[1], Y. M. Strzhemechny[2], M. Gao[3], L. J. Brillson[1,2,3], M. A. Contreras[4] and A. Zunger[4]; [1]Department of Physics, The Ohio State University, Columbus, Ohio; [2]Center for Materials Research, The Ohio State University, Columbus, Ohio; [3]Department of Electrical Engineering, The Ohio State University, Columbus, Ohio; [4]National Renewable Energy Laboratory, Golden, Colorado.

We have used micro-Auger electron spectroscopy, cathodoluminescence spectroscopy, and secondary electron threshold measurements in CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) to investigate the physical and chemical properties of micro-interfaces between polycrystalline grains. In recent years, CIGS/CdS-based solar cells have achieved record efficiencies, rendering them potential candidates for extensive commercial application. It has become apparent that the polycrystalline nature of the CIGS absorber layer is key to the high performance of the cell, yet a consistent explanation for this is still lacking. A recently suggested theory[1,2] predicts that at interfaces between grains the surface of the grain is stabilized through significant (~50%) reduction in Cu surface content and the formation of Cu-deficient defect pairs. A consequence of this restructuring is the formation of a potential barrier for the majority carriers at the grain boundaries (GBs). Notwithstanding this band bending, the grain boundary region is predicted to be charge neutral, with no additional charged deep levels promoting recombination at the micro-surface. This model also suggests that the minority carriers are unaffected by any barrier at the GBs. In an effort to elucidate the properties of CIGS grains and their boundaries, we have studied CIGS polycrystalline solar cell films cleaved in ultrahigh vacuum. The measurements were performed with high lateral (5-10 nm) and energy (50 meV) resolution. The work function values were extracted from secondary electron threshold measurements of individual CIGS grains. We have established that copper composition at CIGS GBs decreases, sometimes by almost a factor of two, work function decreases by several hundred millivolts, and that no radiative recombination centers appear at the GBs. These results confirm the Cu deficiency, potential barrier and absence of new deep level recombination centers at the GBs predicted in the recent theoretical work. Interestingly, comparison of polycrystalline CIGS grown by different techniques shows significant variance in GB morphological, chemical, and electrical behavior. The absence of new states at the grain boundaries also differs from those observed at free surfaces of single crystal CIGS.[3] Thus, the phenomenon of majority carrier barriers and reduced GB electron-hole recombination could explain the high performance of polycrystalline CIGS-based devices. The reduction of recombination rates by such changes opens new possibilities for polycrystalline films in transport devices. These studies also highlight the importance of measuring electronic and chemical properties at micro-scale interfaces in order to analyze optoelectronic properties of macro-scale semiconductor layers. 1. J. E. Jaffe and A. Zunger, Phys. Rev. B 64, 241304(R) (2001) 2. C. Persson and A. Zunger, Phys. Rev. Lett., 91, 266401, (2003) 3. Y. M. Strzhemechny, et al. J. Vac. Sci. Technol. B 20, 2441, (2002)

9:45 AM F10.4

Two-Dimensional and Multi-Experimental Modeling of Polycrystalline Cu(In,Ga)Se$_2$ Solar Cells. Wyatt K. Metzger[1], Markus Gloeckler[2] and Richard K. Ahrenkiel[1]; [1]National Renewable Energy Laboratory, Golden, Colorado; [2]Physics, Colorado State University, Fort Collins, Colorado.

Cu(In,Ga)Se$_2$ solar cell models generally have been limited to one dimension and have focused primarily on current-voltage (JV) curves and quantum-efficiency (QE) spectra. One difficulty of this approach is that many physical models can generate acceptable JV curves and QE spectra, and the multi-dimensional nature of polycrystalline solar cells cannot be fully incorporated. Here, we present simulations of JV curves, QE spectra, time-resolved photoluminescence (TRPL), cathodoluminescence (CL), electron-beam induced current (EBIC), and near-field scanning optical microscopy (NSOM) on two-dimensional Cu(In,Ga)Se$_2$ solar cell models with grain boundaries. Attempting to reconcile all of these simulations with experimental observations significantly narrows the range of workable solar cell and grain-boundary models. At the same time, it elucidates how grain boundaries affect all of these measurements. For example, strong (hundreds of mV) electrostatic potentials along grain boundaries significantly shorten TRPL decay times and alter their injection dependence. Consequently, TRPL measurements can place an upper limit of the electrostatic potential along grain boundaries in the *interior* of the absorber layer. The simulations show that these potentials can separate charge and create current collection channels, thereby increasing the QE spectral response and the diffusion lengths measured in EBIC experiments. The degree of grain-boundary current collection and passivation can be quantified by NSOM. But even when potentials on grain boundaries enhance photocurrent, they can still decrease the overall solar cell efficiency.

SESSION F11: Performance of Solar Cells
Chairs: Kevin Dobson and Michael Powalla
Thursday Morning, March 31, 2005
Room 2005 (Moscone West)

10:30 AM *F11.1

Novel Wide-Band-Gap Ag(In$_{1-x}$Ga$_x$)Se$_2$ Thin Film Solar Cells. Tokio Nakada, Keiichiro Yamada, Ryota Arai, Hiroki Ishizaki and Naoomi Yamada; Electrical Engineering and Electronics, Aoyama Gakuin University, Sagamihara, Kanagawa, Japan.

Wide band gap chalcopyrite materials are required for a top cell of tandem solar cells. Although Ag(In$_{1-x}$Ga$_x$)Se$_2$ (here after AIGS) has several advantages such as higher band-gap energy and a lower melting point than CIGS. However, a few papers have been reported on this material and an efficient solar cell has not been achieved so far. We thus have investigated the growth and properties of AIGS thin films and devices in order to check the possibility of this material as a top cell for tandem devices using XRD, TEM, EDX, SEM, ICP and SIMS. The junction formation mechanism of AIGS devices was discussed based on the data of scanning capacitance microscopy (SCM) and electron beam induced current (EBIC). Ag(In$_{1-x}$Ga$_x$)Se$_2$ thin films have been deposited on Mo-coated soda-lime glass substrates by three-stage process using a molecular beam epitaxy (MBE) system. We found for the first time a remarkable decrease in the substrate temperature at the 2nd step in which the film becomes Ag excess composition. This phenomenon was used for the decision of the end point for obtaining AIGS thin films with a slightly Ag poor composition. Large grain AIGS thin films with chalcopyrite structure were grown if they passed through the Ag excess step. XRD analysis revealed that a tetragonal Ag(In,Ga)Se$_2$ phase became predominant as the Ga/(In+Ga) and/or Ag/(In+Ga) atomic ratios increased. The solar cells with a ZnO:Al/ZnO/CBD-CdS/AIGS/Mo structure were fabricated with a similar process to CIGS devices. We achieved a high efficiency wide-gap (Eg=1.7eV) Ag(In$_{0.2}$,Ga$_{0.8}$)Se$_2$ thin film solar cell with total-area efficiency of 9.3% (10.2% active area efficiency), V$_{oc}$ = 949mV, J$_{sc}$ = 17.0 mA/cm^2, FF = 0.577, and total area = 0.42cm^2. Very strong EBIC signal was observed from the surface to the half of the AIGS absorber layer (approximately 800 nm) for this solar cell. The depletion layer was wider than the other wide-gap devices such as CuGaSe$_2$ which shows a very narrow depletion layer near the CdS/CGS interface. Scanning capacitance microscopy (SCM) analysis revealed that a Ag(In$_{0.2}$,Ga$_{0.8}$)Se$_2$ device had an n+-n or n-n$^-$junction which could be used for a top cell for tandem devices with a conventional CIGS bottom cell even if the conduction of AIGS thin film was n-type. In order to investigate the cause for the junction formation mechanism, SIMS analysis was carried out. As a result, the diffusion of Cd and S into the AIGS matrix was clearly observed at the CdS/AIGS interface. This result suggests an increase in electron at the surface region of AIGS, resulting in the formation of n+-n or n-n$^-$junction due to the substitution of Cd^{2+} for Ag^{+1}.

11:00 AM F11.2

Surface-modified CuGaSe$_2$ (CGS) Solar Cells with Improved Performance. Jehad A. AbuShama[1,2], Steve Johnston[1], David Young[1] and Rommel Noufi[1]; [1]NREL, Golden, Colorado; [2]Department of Physics, Colorado School of Mines, Golden, Colorado.

We report the growth and characterization of record-efficiency surface-modified CuGaSe$_2$ (CGS) solar cells. The NREL-confirmed device operating parameters for this cell are: V$_{oc}$= 0.823 volts, J$_{sc}$ = 18.61 mA/cm^2, fill factor = 66.8%, and total-area efficiency = 10.23%. The recent understanding of the differences in structural and electronic properties between CuInGaSe$_2$ (CIGS) and CGS thin films and devices has led to varying the growth process in a way that is likely to make the CGS surface region similar to that of CI(G)S in composition and to minimize defects in the material. This change had led to a gain in the current density of about 3.7 mA/cm^2 versus the previous best cell. We examined the new cell using deep level transient spectroscopy (DLTS) and drive level capacitance profiling (DLCP). The DLTS data exhibit minority traps with activation energies ranging from E$_C$-0.3 to E$_C$-0.6 eV (where E$_C$ is the energy of electrons at the conduction band minimum). While varying the filling pulse duration, we observed the gradual increase in the amplitude of the DLTS signal for these states until it apparently saturates at a pulse duration of ~1s. Increasing the duration of the filling pulse also results in broadening of the DLTS signals and shifting of the maximum of these signals towards lower temperature, whereas the high-temperature sides coincide. Using a model that allows us to distinguish between bandlike states and localized ones based on the dependence of the shape of their DLTS-signal on the filling-pulse duration, we relate the electron trap to bandlike states. We also examined our cell using DLCP and found that the new cell has a lower carrier concentration, a more uniform defect density profile, a larger depletion width, and a higher drift collection length for photo-generated carriers as compared to our previous 9.53% CGS cell. We also recorded the transient capacitance versus time and found that the new cell has faster transient capacitance decay rates at lower temperatures as compared to the previous one, whereas at higher temperatures, the rates are comparable. In the presentation, we will discuss our data in more details.

11:15 AM F11.3

Effect of Zn and Mg Doping on CuInS$_2$ Thin Films and Solar Cells. Tobias Enzenhofer[1], Thomas Unold[2], Roland Scheer[1] and Hans-Werner Schock[1]; [1]SE3, Technology, Hahn-Meitner-Institut, Berlin, Germany; [2]SE5, Solar Energy, Hahn-Meitner-Institut, Berlin, Germany.

Solar cells based on CuInS$_2$ still suffer from V$_{oc}$ limitation compared to their theoretically achievable value. Although there has been evidence that the open circuit voltage can be enhanced via controlled doping of small amounts of Zinc or Magnesium (<1 at.%), the underlying physical reason for this improvement is not understood so far. In order to investigate this phenomenon we have systematically studied the effect of diffusion of Zn (Mg) into the absorber layers with photoluminescence and quantum efficiency measurements. ZnO (MgO) has been deposited onto the absorber layers and photoluminescence (PL) spectra at room temperature were recorded as a function of the annealing temperature. We find that rising the annealing temperature strongly changes the defect spectrum resulting in a single broad emission at about 1.38 eV for the highest annealing temperature (500°C). For Zn or Mg doped absorber layers the luminescence intensity does not change after buffer and window deposition whereas the luminescence signal of the near band edge emission of pristine CuInS$_2$ increases strongly after cell completion. At the same time the open-circuit voltage of the Zn (Mg) doped CuInS$_2$ cells are around 800 mV which is nearly 100 mV higher than the values found for the undoped cells from the same device process. We interpret this result with reduced defect state density at the surface induced by the incorporation with Zn (Mg). Comparison of quantum efficiency (QE) and I/U measurements with the PL results support observed changes of interface properties.

11:30 AM F11.4

High-Efficiency CdTe Polycrystalline Thin-Film Solar Cells with an Infrared Transmission of ~50%. Xuanzhi Wu, Jie Zhou, Anna Duda, James Keane, Tim Gessert, Yanfa Yan and Rommel Noufi; NREL, Golden, Colorado.

In the polycrystalline thin-film tandem cell project, the most critical work is to make high-efficiency top cell with high bandgap (Eg=1.5-1.8 eV) and high transmission (T>70%) in the near infrared (NIR) wavelength region. Several high-bandgap alloys based on I-III-VI2 and II-VI compounds, such as CuGaSe2 (CGS), Cu(InGa)(SeS)2 (CIGSS), and Cd1-xZnxTe (CZT), are being investigated. The 10.2%-efficient CGS cell (1.64 eV) and the 10.9%-efficient CIGSS cell (1.50 eV) have been reported. Both CGS and CIGSS cells have an opaque back contact (Mo). The CdTe cell is also a candidate for the top cell, because its state-of-the-art single junction device with efficiency of 16.5% is available, even its bandgap (1.48 eV) is slightly lower as a top cell in a dual-junction device. To make the CdTe cell as a qualified top cell, one of the challenges is to substitute the opaque back contact with a transparent one. In the past, almost all R&D activities in this area focused on developing a transparent back contact with high Eg, such as ZnTe:Cu or N with Eg of ~2.26 eV, or BaCu2S2 with Eg of ~2.3 eV. In this paper, we present a different approach: using a thinner low-Eg back contact material, CuxTe with Eg of ~1.08 eV, to achieve high transmission in the NIR wavelength region. We also introduce three novel materials: cadmium stannate (Cd2SnO4) transparent conductive oxide, ZTO (ZnSnOx) buffer layer, and nanocrystalline CdS:O window layer, as well high-quality CdTe film used in this work, which can enhance device performance and reduce T losses due to absorption of the front contact and of the sub-bandgap in the NIR region. The preliminary device results have demonstrated that high-efficiency poly-CdTe thin-film solar cell with higher NIR transparency can be prepared by exploiting a thinner CuxTe back contact. We have fabricated a number of CdTe cells with efficiencies of more than 13% by this technique. The best cell has an NREL-confirmed, total-area efficiency of 13.9% (Voc=806.1 mV, Jsc=24.97 mA/cm2, FF=69.22%, and area=0.41 cm2) with ~60%-40% transmission in the wavelength range of 860-1280 nm. We believe that the efficiency of the mechanical tandem cell, which combines the transparent CdTe top cell and NREL's world-record 15.0%-efficient CuInSe2 (CIS) cell with Eg of ~0.96 eV as a bottom cell, could be over 15%.

SESSION F12: Electrical Characterization

Chairs: Susanne Siebentritt and Takahiro Wada
Thursday Afternoon, March 31, 2005
Room 2005 (Moscone West)

1:30 PM F12.1

Current Transients in CdS/CdTe Solar Cells. Alan L. Fahrenbruch, Physics, Colorado State University, Fort Collins, Colorado.

Current transient response to voltage and illumination steps are investigated to elucidate the mechanisms involved in current transport in CdS/CdTe cells. For some cells, the response to a dark, forward-bias step after a long dark soak at zero bias is a complex current growth curve For example, for one such cell, the magnitude of the transient is 10 to 20% of the starting value with half of the growth occurring within about 10 sec, and the other half requiring 1000's of seconds. The effect is completely reversible and a current decay curve versus time at zero bias after dark bias-on equilibration can be measured; half of this decay also occurs in about 10 sec. Similarly, a complex of growth and decay curves are observed on application of illumination steps while bias is held constant. Voc and ff decays are similar but generally smaller in magnitude. Similar transients have been observed by McMahon [1] and del Cueto et al. [2] For other cells, fabricated by different labs, the step response is reversed (i.e., dark, forward-bias current decays with time after a dark soak). In these cells Voc increases with time. Beside the important implications these transients have for accurate measurements of cell efficiency and stability, they provide clues about the current transport mechanisms. The CdTe absorber layer is highly compensated material with densities of Cu and Cl much larger than the net ionized impurity densities given by C-V measurements [e.g., 3]. In addition, a large portion of the absorber layer is usually depleted. Several hypotheses for the origin of the transients are advanced and discussed, with the aid of modeling using AMPS [4] and other simulation programs. One such hypothesis involves the occupation of deep donor traps with small hole cross sections, changing their recombination kinetics. The second hypothesis involves the modulation of the junction barrier profile by changing the charge on deep acceptors and donors, leading to a change in the effective junction barrier height. A third involves defect mutation such as that of [Cui] donors into [VCd - Cui] acceptor complexes, depending on the position of the quasi-Fermi levels. [1] T.J. McMahon, Proc. 29th IEEE PV Specialists Conf., May. 20-24, 2002, New Orleans, LA, pp. 768-771. [2] J.A. del Cueto, J. Pruett, and D. Cunningham, NCPV and Solar Program Review Meeting 2003 NREL, p. 183, and J.A. del Cueto and C. Osterwald, DOE Solar Program Review 2004. [3] S. Gilmore, V. Kaydanov, and T.R. Ohno, Mat. Res. Soc. Symp. Proc. Vol. 763 (2003). [4] AMPS-1D, written by S. Fonash, Pennsylvania State Univ., supported by EPRI.

1:45 PM F12.2

Spatial and Temporal Variations in Electronic Transport Through a CdTe-Based Schottky Barrier. Diana Shvydka, V. Parikh, V. G. Karpov and A. D. Compaan; Physics and Astronomy, University of Toledo, Toledo, Ohio.

We study the electric current flow through symmetric metal-semiconductor-metal structures. More specifically, a thin-film rf-sputtered CdTe layer was sandwiched between two contacts of the same metal. The CdTe thickness varied from approximately 0.5 to 1.5 microns. Current-sensing contact mode AFM was employed to measure the current-voltage characteristics and current variations under fixed voltage. We found that (i) in a polycrystalline semiconductor - metal junction the electric current flow across a thin film is laterally nonuniform on a microscopic scale, showing strong spot-to-spot variations. (ii) Most unexpectedly, the current dramatically varies over time, exhibiting a chaotic behavior, when measured at the same position under a constant voltage. (iii) In many cases, depending on the applied voltage and observation time, the structures showed transitions from highly conductive to highly resistive states and vice-versa. (iv) This behavior did not correlate with the sample surface topography. We interpret the above observations in terms of defect assisted tunneling. This mechanism is based on the concept of rare yet most efficient N-defect pathways through the barrier. Electrons penetrate the barrier along these pathways in N successive tunneling steps of length $\sim L/N$ where L is the barrier width. Each step has exponentially large tunneling probability exp (-L/Na) compared to that without defects, exp (-L/a) where a is the electron wave function decay length. Statistical fluctuations in local defect concentration have exponentially strong effect on tunneling. In particular, the above pathways will disappear and reappear when the defects are mobile. This explains the spatial and temporal fluctuations observed in our experiments, their independence of the surface topography, and transitions between the conductive and insulating states. The latter is attributed to the conductive pathway suppression resulting from the defect sedimentation in strong electric fields. Related important questions addressed in our work include that of how the temporal chaotic behavior averages out into macroscopically observed relatively stable currents, what is the relationship between the time and space averages, how does correlation function decay over time, etc. One immediate application for our study is the transport properties of a back contact formed in a superstrate solar cell. This work is supported by NREL grants.

2:00 PM F12.3

The Influence of Traps on Carrier Concentration Profiles Measured by Capacitance-Voltage and Drive Level Profiling in CIGSe-Based Heterojunctions. Pawel Lech Zabierowski[1], Michael Cwil[1], Magorzata Igalson[1] and Marika Edoff[2]; [1]Faculty of Physics, Warsaw University of Technology, Warszawa, Poland; [2]Angstrom Solar Center, Uppsala University, Uppsala, Sweden.

It is well known that at temperatures above 200 K it is relatively easy to create large metastable changes in the shape of capacitance-voltage (C-V) characteristics, and one of the factors inducing these changes is a voltage sweep itself. Thus the interpretation of results in terms of the carrier concentration profile is reasonable only for low temperature measurements. However Mott-Schottky plots of the ZnO/CdS/CIGSe heterojunctions, especially at low temperatures, are usually highly nonlinear, which is reflected in characteristic U-shaped carrier concentration profiles. Very often these profiles are quite steep, indicating that the doping density in the bulk of the absorber changes by more than an order of magnitude on a distance smaller than 200 nm. Technologically, however, such gradients are rather not expected, which suggests that the profiles obtained from low temperature C-V curves may be artifacts as well. The aim of this work is to discuss possible factors affecting these profiles and to clarify whether they correspond to true charge distribution. We systematically compare the profiles deduced from C-V characteristics with that obtained by use of drive level capacitance profiling (DLCP). We perform the experiments for several samples in different matastable states. We find that in the low temperature range C-V profiling basically gives the same information as DLCP. On the other hand we observe that C-V characteristics dramatically depend on the direction of the bias scan if only a voltage sweep rate is fast enough comparing to the emission rate from the N1 level. Since time dependence and magnitude of this hysteresis are directly correlated with the time constant and the height of the N1 peak, these results confirm that the N1 peak originates from the minority carrier traps located in the vicinity of the absorber interface. This is corroborated by the experiments performed on samples without CdS buffer layer, which give very similar results. However, since DLCP is thought to be insensitive to interface states, this could be somewhat surprising. In the second part of the work we explain this discrepancy and discuss possible origin of the U-shaped profiles.

2:15 PM F12.4

Detailed Study of Metastable Effects in the Cu(InGa)Se_2 Alloys: Test of Defect Creation Models. JinWoo Lee[1], Jennifer T. Heath[2], David Cohen[1] and William N. Shafarman[3]; [1]Physics, University of Oregon, Eugene, Oregon; [2]Physics, Linfield College, McMinnville, Oregon; [3]Institute of Energy Conversion, University of Delaware, Newark, Delaware.

It has been well established that metastable changes in Cu(In,Ga)Se_2 solar cells occur in response to optical exposure or carrier injection. While some metastable effects, such as those caused by exposure to blue light, are believed to originate in the CdS layer and affect only the interface properties of the solar cell, others have definitely been shown to originate from changes in the bulk Cu(In,Ga)Se_2 material itself[1]. Recent work has also suggested a link between the metastable changes in the concentration of free hole carriers and those of the deep acceptors[1,2]. Based on these observations, Lany and Zunger have proposed a specific microscopic model, involving chalcogen vacancy/copper vacancy pairs, that might account for these experimental results[3]. In support of this, and related models, we have now more firmly established the 1:1 relationship between increases in carrier concentration and increases in deep acceptors. This was accomplished by exposing samples to monochromatic light at different wavelengths so that, by employing the drive-level capacitance profiling (DLCP) method, their spatial profiles could be correlated. The DLCP method also enables us to clearly distinguish barrier interface from bulk metastable effects. In addition, we have been carrying out measurements to examine the creation and annihilation kinetics of these metastable effects, to see if they agree with the energy barriers predicted by the model. This includes comparing the effects of carrier injection to those of optical exposure. Finally, transient photocapacitance (TPC) spectroscopy has been employed in conjunction with transient photocurrent (TPI) spectroscopy for the first time to correlate metastable changes in defects in the upper half of the gap with those observed for defects in the lower half of the gap, and shallow donors. [1]J. Heath, J.D. Cohen, and W.N. Shafarman, J. Appl. Phys. 95, 1000 (2004). [2]M. Igalson and H.W. Schock, J. Appl. Phys. 80, 5765 (1996). [3]S. Lany and A. Zunger, Phys. Rev. Lett. 90, 156404 (2004).

SESSION F13: Discussion Session II
Critical Issues for Thin Film Polycrystalline PV: What Do We Have and Where are We Going?

Discussion Leaders:
Al Compaan, University of Toldeo
Uwe Rau, University of Stuttgart

Thursday March 31, 2005
3:00 PM - 5:00 PM
Room 2005 (Moscone West)

SESSION F14: Poster Session: Posters II
Chair: Tim Gessert
Thursday Evening, March 31, 2005
8:00 PM
Salons 8-15 (Marriott)

F14.1

Simulation of Polycrystalline Cu(In,Ga)Se_2 Solar Cells in Two Dimensions. Markus Gloeckler[1], Wyatt K. Metzger[2] and James R. Sites[1]; [1]Colorado State University, Fort Collins, Colorado; [2]National Renewable Energy Laboratory, Golden, Colorado.

The extent to which grain boundaries in polycrystalline materials could be detrimental, benign, or even beneficial is explored with numerical simulations in two dimensions. We focus on the effects of grain-boundary (GB) recombination in CIGS solar cells and its effects on solar-cell performance. The simulations predict that (1) GB recombination by itself is not generally distinguishable from bulk recombination, (2) for record efficiency devices, the effective GB recombination velocity must be the order of 10^3 cm/s or less, (3) grain boundaries within the space charge region lower the open-circuit voltage, whereas the short-circuit current is reduced by the density of grain boundaries in the CIGS bulk, and (4) horizontal GB's are relatively benign unless they are located in the space charge region. Modifications to the electronic structure near grain boundaries are discussed and show that charge-induced band bending at grain boundaries will most likely have a negative effect on device performance, whereas shifts in the valence-band energy at the grain surface can effectively passivate the grain boundaries. For none of the models considered does the efficiency exceed the efficiency of grain-boundary free devices, and hence, GB's alone cannot explain the apparent superiority of poly-crystalline over single-crystalline CIGS materials.

F14.2

Photo-Hall-Measurements of Epitaxial and Polycrystalline $CuGaSe_2$ Films. Thorsten Rissom, Siebentritt Susanne, Niklas Rega and Martha Ch. Lux-Steiner; SE2, Hahn-Meitner-Institut Berlin, Berlin, Germany.

In order to achieve high-efficiency wide-band-gap chalcopyrite solar-cells a better understanding of basic electric material properties is necessary. Especially the role of grain boundaries has to be further investigated. Two models have been put forward for the electronic structure of the grain boundaries. Both imply a barrier for majority carriers at the grain boundary: the "electronic" model ascribes the barrier to charged defect states at the grain boundary that lead to a space charge region on either side of the boundary, while the "structural" model attributes the barrier to a down shift of the valence band due to Cu deficiency at the grain boundary. Epitaxial MOCVD-grown $CuGaSe_2$-epilayers and polycrystalline $CuGaSe_2$ are measured by Hall-Effect and compared. Previous investigations have shown that a barrier to majority carrier transport is present at the grain boundaries. With photo Hall measurements properties of minority carriers are accessible as well. On the other hand the evaluation of the transport properties is complicated by the fact that transport takes place not only in the valence but also in the conduction band. First experiments show that the current transport at low temperatures under illumination is dominated by electrons while at high temperatures still hole transport dominates. The detailed analysis of these measurements will allow conclusions on the behaviour of the barrier under illumination and thus a separation between the two models, as in the structural model the barrier should be independent of illumination, while in the electronic model it should depend on illumination.

F14.3

2-D Simulation of the Effect of Grain Boundaries in CuInSe2 Solar Cells. Seokhyun Yoon[1], Sheng S. Li[2] and Timothy J. Anderson[1]; [1]Chemical Engineering, University of Florida, Gainesville, Florida; [2]Electrical and Computer Engineering, University of Florida, Gainesville, Florida.

Polycrystalline CuInSe2-based solar cells, in which the absorber layer typically has an average grain size of a few μm, surprisingly show efficiencies that are equal or better than those of single crystalline cells. Although different mechanisms have been suggested to explain the influence of grain boundaries on device performance (charge build-up at trap states, compositional gradients produce band offsets), their effect is positive. In this work, Poisson's equation and the minority carrier continuity equation are solved self-consistently to better understand the role of grain boundaries. Specifically, the effect of grain boundaries in the CuInSe2 absorber layer of a cell with the structure ZnO/CdS/CIS/Mo/glass was investigated by 2-D simulation. The grain boundary potential was calculated self-consistently by specifying the energy level and density of hole trap states at the grain boundary as a function of grain size. For AM 1.0 conditions, the efficiency was estimated to decrease from 14.4% without grain boundaries to 9.6% with a grain size of 0.2 μm. The fill factor and the open circuit voltage also decreased from 81.1% to 68.4% and from 0.584 V to 0.468 V, respectively. The short circuit current, however, remained almost the same, which may be attributed to the large injection level compared to the minority carrier density in the CIS absorber layer. The reverse saturation current was calculated to increase as grain size decreased and explains the increase of the recombination current with decreasing grain size. It was also predicted that the grain boundary potential decreased from 0.220 to 0.199 eV as a result of injection of carriers by photo generation for the 0.2 μm grain size case. The effect of other parameters such as a doping level, buffer layer properties, density and energy level of grain boundary traps, and the type of the grain boundary trap was also studied.

F14.4

Optimization of RF-Sputtered ITO Films for High IR Transparency at Low Deposition Temperature. Jie Zhou, Xuanzhi Wu and Tim Gessert; National Renewable Energy Lab, Golden, Colorado.

Thin films of Sn-doped indium oxide (ITO) have been used for many years in various types of photovoltaic (PV) solar cell devices. Recently, ITO has been used as an element for IR-transparent back contacts of CdS/CdTe devices intended for high-bandgap top cells in multiple-junction designs. In this application, high infrared (IR) transparency is essential for all elements, especially the transparent conducting oxide (TCO) layers. IR transparency for ITO is typically maximized by limiting free-carrier concentration via low Sn and high oxygen concentrations, and by maximizing electron mobility by using a high substrate temperature. Unfortunately, the particular CdS/CdTe cell design presently under development limits ITO deposition temperature to <=250C, and few studies exist to guide ITO optimization in this temperature range. In this study, RF-sputtered ITO films deposited at temperatures <=250C are optimized for high IR transparency. Results show that the deposition temperature required for significant carrier activation (due to Sn defects), previously reported to occur at between 200-300C, actually occurs at <=230C. Because this temperature is less than 250C, high oxygen partial pressures can be used during deposition to enhance both overall material quality and IR transparency. Resulting films have the desired properties in that carrier concentration is low enough to avoid free-carrier absorption, yet the optical and electrical properties remain stable following post-processing at 250C.

F14.5

Substatutional Doping of the Electrically Bipolar Transparent Conductor $CuInO_2$ Using Pulsed-Laser Deposition from $Cu_2In_2O_5$ Targets. Charles Teplin, John D. Perkins, Matthew Dabney, David Young, Tatiana Kaydanova and David S. Ginley; NREL, Golden, Colorado.

P-type transparent conductors could be used as contacts in organic photovoltaic (PV) cells, in tunnel junctions in tandem thin film solar cells, or as UV-junction layers in 3rd generation PV technologies. Among candidate transparent oxide p-type conductors, the reported bipolar doping of $CuInO_2$ makes it particularly interesting. Ca-doped $CuInO_2$ is p-type and Sn-doped material is reportedly n-type. This initial work was done using pulsed laser deposition (PLD) from phase-pure $CuInO_2$ targets, which are, however, difficult to fabricate. Recently, we have found that $CuInO_2$ thin films can be readily deposited by PLD from $Cu_2In_2O_5$ targets. The $Cu_2In_2O_5$ targets can be easily fabricated in air using standard solid state synthesis thereby making expanded doping studies feasible. At present, we are investigating Ca, Sn, Zn and Ti as possible dopants. We have found that optimized deposition conditions for 5% Ca-doped films yield p-type conductivities of 0.003 S/cm. We will report on the electrical, optical and structural properties of $CuInO_2$ films grown from $Cu_2In_2O_5$ targets with different dopants.

F14.6

Wide-Gap CIGS Solar Cells with $Zn_{1-x}Mg_xO$ Transparent Conducting Film as a Window Layer. Koji Matsubara[1], Akimasa Yamada[1], Shogo Ishizuka[1], Keiichiro Sakurai[1], Hitoshi Tampo[1], Yasuyuki Kimura[2], Satoshi Nakamura[2], Minoru Yonemura[2], Hisayuki Nakanishi[2] and Shigeru Niki[1]; [1]Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Tokyo University of Science, Noda, Chiba, Japan.

It is well known that the band alignment between the conduction band minimum of $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) absorber layer and that of ZnO window layer is important for the solar cell performance; the conduction band minimum of ZnO is lower than that of CIGS. As the conduction band minimum of $Zn_{1-x}Mg_xO$ is higher than that of ZnO, it is expected that the use of $Zn_{1-x}Mg_xO$ instead of ZnO improves cell performance. So far we have succeeded in fabricating

Al-doped $Zn_{1-x}Mg_xO$ transparent conducting films with bandgap of about 4 eV and the resistivity of less than 10^{-3} Ω cm. In this study, Al doped $Zn_{1-x}Mg_xO$ transparent conducting films were applied to CIGS solar cells with relatively high Ga content x: more than 0.5. CIGS absorber layers were prepared by the three-stage process on Mo coated soda-lime glass substrates. After a deposition of CdS buffer layer, undoped- and Al-doped $Zn_{1-x}Mg_xO$ layers were deposited by pulsed laser deposition system. Preliminary results showed that conversion efficiency of small area cell (0.465 cm^2) was 15.4 % without anti-reflection coating; this is comparable with our CIGS ($x \sim 0.5$) cells with i- and n-ZnO window layers. Further improvements in the $Zn_{1-x}Mg_xO$ deposition processes may lead to higher conversion efficiencies than the solar cells with a ZnO window layer.

F14.7

Structural, Optical and Electrical Properties of p-type Transparent Conducting CuAlO2 Thin Films prepared by RF Reactive Sputtering. Bruno Karl Meyer and Bin Yang; I. Physikalisches Institut, Giessen, Germany.

In recent years, p-type transparent conducting oxide compounds based on the delafossite structure have attracted much attention because of their potential in preparing novel transparent p-n junction for device applications. In this work, transparent conducting CuAlO2 thin films have been deposited by RF reactive sputtering technique on glass and quartz substrates using CuAl alloy target in a mole ratio of 1:1. A study of structural, optical, and electrical properties was performed on the films, varying deposition parameters such as the substrate temperature and the oxygen partial pressure. The crystalline phase in the films was identified to be the delafossite structure by x-ray diffraction. The optical properties, such as the wavelength dependence of the transmittance and the band gap, were determined. Hall effect measurements confirmed the p-type nature of semiconductors.

F14.8

Gallium Oxide Transparent Conducting Oxide Films by Deposited by Pulsed Electron Beam and Pulsed Laser Deposition Techniques. John Muth, Christian Mion, Jason Kekas and Ailing Cai; ECE Dept Box 7911, NC State University, Raleigh, North Carolina.

Gallium Oxide is a normally n-type semiconducting oxide with a bandgap of ~4.9 eV at room temperature and monoclinic crystal structure. The wide band gap suggests that Gallium Oxide may be used as a transparent conductor for wavelengths as short as 250 nm. This is substantially shorter wavelength cutoff than Indium Tin Oxide which typically absorbs wavelengths shorter than 400 nm. High resistivity single crystal Gallium Oxide films with RMS surface roughness of ~ 1nm were obtained on c-axis sapphire substrates by pulsed laser deposition. HTEM was used to observe the epitaxial relationship between the Gallium oxide and sapphire. Transmission was greater than 80 percent below the band gap. Films deposited by pulsed electron beam deposition had similar optical and electrical characteristics. By doping the Gallium oxide films with Sn, the electrical conductivity was found to increase and the band gap lowered. Lowering the deposition temperature to 400 degrees C resulted in amorphous, conductive, transparent films with an optical absorption edge at 300 nm.

F14.9

Development of Transparent ZnTe: Cu Contacts for Bifacial Characterization of CdTe Solar Cells. Darshini Desai, Steven Hegedus and Brian McCandless; Institute of Energy Conversion, University of Delaware, Newark, Delaware.

CdTe solar cells are usually fabricated in a superstrate configuration with an opaque ohmic contact to the p-type CdTe. This back contact is typically Cu doped to provide both Cu2Te, essential for low resistance contact, and bulk CdTe doping, essential for higher open circuit voltage. A transparent back contact would allow bifacial device characterization to determine junction and transport properties by applying conventional characterization techniques to backwall(through ZnTe:Cu back contact) illumination. Development of a transparent back contact is also critical to achieve a polycrystalline thin film tandem solar cell. We have succeeded in making cells with Cu doped ZnTe as a (semi) transparent back contact using galvanic deposition. Initially films had low transparency and devices with the ZnTe:Cu contacts had low fill-factors due to shunting, suggesting too much free Cu. Tri-ethylamine (TEA) was investigated as a complexing agent to control the chemical reactivity of the Cu in the solution. Variations in solution concentration and time were evaluated by measuring the optical absorption and conductivity of films, and by making contacts to solar cells. Based on those results, chemical constituent concentrations and optimum annealing conditions were selected. The ZnTe:Cu films with TEA had transmission greater than 85% and device efficiencies with ZnTe:Cu contacts were 9-10%, fill-factors were 68-69% and open circuit voltages were 800-820mV.These device parameters are comparable to conventional graphite and Cu/Au back contacts on same CdS/CdTe substrates. Devices with TEA had less JV hysteresis and shunting. JV curves indicated a blocking contact formation when illuminated from front (through glass) and in dark but not when illuminated from the back (through ZnTe) This indicates that the back contact is photoconductive. It is the first time that photoconductive behavior of back contact has been observed. Backwall QE has little response below 800nm, and is sharply peaked at 840nm indicating that most carriers are collected near the CdS/CdTe interface. Temperature dependence of the open circuit voltage was also studied with front and back illumination. CdTe cells fabricated by several companies and laboratories have shown saturation of Voc at temperature lower than 220K for front illumination. In contrast we observe that Voc continues to linearly increase below 220K for back-wall illumination (through ZnTe:Cu) indicating that mechanism causing Voc saturation for front-wall illumination is not a bulk effect. This behavior also correlates to the photoconductive behavior of back contact for front and back illumination. Transparent contacts provide a tool to study aspects of junction behavior and minority carrier transport previously unavailable with front illumination, and thus allowing a better understanding of the efficiency limiting mechanisms.

F14.10

P-Type Transparent Conducting Contacts for Thin-film Compound Semiconductor Solar Cells. S. Vakkalanka, P. Mahawala, C. S. Ferekides and Don Morel; Electrical Engineering, University of South Florida, Tampa, Florida.

Next generation tandem thin-film compound semiconductor solar cells can achieve efficiencies in the 25 - 30% range. To do so requires development of a top cell that is transparent to wavelengths beyond the absorption edge of its absorber. This cell also needs effective p and n contacts that can be the terminal contact or in the role of a tunnel junction in series connected tandems. P-type contacts are difficult in general to develop, and these additional requirements add further to the challenge. We have been developing such contacts for use with CdSe absorbers. ZnSe/Cu and ZnTe/Cu have worked best as the transparent p-contact for these devices, and we have reported V_{oc}s up to 575 mV. In these films a thin layer of Cu is deposited on the ZnSe and ZnTe layers, and there is an apparent reaction as the Cu diffuses into the host material. While it seems reasonable to assume that Cu is a substitutional dopant suggesting that the contact is ZnSe:Cu, when we use Au in place of Cu we find similar results for V_{oc}, but J_{sc}s are reduced significantly. In this case we speculate that free Au is contributing to the effective contact energy but also effecting increased interface recombination. AMPS simulations support this position. Recently we also found Cu_2Se to be an effective p contact as well. As with Au doped films devices with Cu_2Se contacts suffer losses in J_{sc}. Together these results suggest a more complex role for Cu in the doping process in ZnSe and ZnTe. Understanding of these mechanisms is necessary to bring about further increases in Voc and overall device performance.

F14.11

Does CdTe Deposition Affect the Impurity Profile in Sputtered CdS Window Layers? Mahieddine Emziane[1], Ken Durose[1], Douglas P. Halliday[1], Nicola Romeo[2] and Alessio Bosio[2]; [1]Physics, University of Durham, Durham, United Kingdom; [2]Physics, University of Parma, Parma, Italy.

Insufficient experimental data is available regarding impurities and their behaviour in polycrystalline CdS/CdTe photovoltaic cells, despite their potential effect on the performance, stability and lifetime of such devices. The lack of data is even more obvious concerning the CdS window layer. We report here a systematic multi-element study of impurities in CdS window layers by dynamic and quantitative SIMS. Two CdS/TCO/glass samples, grown separately using nominally the same conditions, were considered. Fluorine-doped indium oxide (In_2O_3:F) layer was used as transparent conducting oxide (TCO) and grown by sputtering on soda-lime glass substrate at 500°C. The 150 nm-thick CdS layer was then sputtered at 200°C from a 4N purity CdS target. One of the samples was subsequently used to further grow CdTe layer by close-space sublimation (CSS) using 7N purity CdTe source material at around 500°C. The samples did not receive any further treatment or polishing. The SIMS study was carried out on both samples, and O, Na, Si, Cl, Sb, In, Zn, Sn, Pb, Cu, Te, S and Cd were depth profiled. The purpose was to examine the influence of the subsequent CSS growth of the CdTe layer on the distribution and concentration of impurities in the structures. These impurity species were selected since they may be electrically active in the CdS window layer, and ultimately affect the characteristics of the CdTe/CdS device. The analysis proceeded from the TCO free surface to the CdTe absorbing layer in the CdTe/CdS/TCO/glass structure, with the glass substrate removed, and from the CdS free surface through to the TCO for the CdS/TCO/glass sample. For an accurate quantitative SIMS analysis, CdS relative sensitivity factors (RSFs) were derived from CdS single crystal implants. It was shown that before CdTe growth, the impurity elements O, Na, Cl, Sb, In, Zn and Te showed flat levels in CdS ranging from 2-3$\times10^{20}$ cm^{-3} for Zn and O to 2-3$\times10^{17}$ cm^{-3} for Na, Cl, Sb and Te. Si was found to segregate at the CdS/TCO interface with a maximum level of 10^{18} cm^{-3}. However, following CdTe growth, most of the impurities in the CdS layer showed higher concentrations and different profile shape compared to those before CdTe growth. Furthermore, while the concentrations of Sn, Pb and Cu before the CdTe growth were below the detection limit of the SIMS system used, Pb and Cu exhibited a maximum (10^{17} cm^{-3}) and a minimum (3$\times10^{17}$ cm^{-3}) respectively, after the subsequent CdTe growth. Some of the impurities also showed a diffusion profile following the CdTe growth as compared to before. Possible explanations of these changes are discussed in terms of the purity of CdS and CdTe starting materials as well as the growth environments, and the results compared with our previous SIMS measurements and with literature data.

F14.12

Properties of Cu(In,Ga)Se2:Fe Thin Films for Solar Cells. Keiichiro Sakurai[1], Satoshi Nakamura[2], Hajime Shibata[1], Shogo Ishizuka[1], Akimasa Yamada[1], Koji Matsubara[1], Minoru Yonemura[2], Shinpei Kuwamori[2], Yasuyuki Kimura[2], Hisayuki Nakanishi[2] and Shigeru Niki[1]; [1]Research Center for Photovoltaics, AIST Japan, Tsukuba, Ibaraki, Japan; [2]Elec. Eng., Tokyo Univ. of Sci., Noda, Chiba, Japan.

Cu(In,Ga)Se2 (CIGS), a member of the "chalcopyrites", is a promising material for absorber layers of future thin-film polycrystalline solar cells. Recently, due to the greatly increased market demand for ITO, there are some some fear for the future supply of indium, which may affect the cost performance of CIGS. Thus, it is meaningful to search for alternative materials that can reduce the use of indium. One possible candidate material for altering indium is iron, which is an component element of the original chalcopyrite. It have been reported that the bandgap of bulk CIGS decreases with increasing Fe content, suggesting that the use of iron would help reducing the use of indium. However, to the best of our knowledge, no reports on fabrication of thin film CIGS:Fe films, or the fabrication of actual solar cell devices, have been made. In this work, we have fabricated a series of polycrystalline CIGS:Fe films and actual solar cell devices, and investigated their properties and performances. We have fabricated CIGS:Fe polycrystalline thin films with various Ga / III and Cu / III ratios, using the same three-stage procedure that we usually use for our ~17% CIGS solar cells. 5N Fe was evaporated from a K-cell using an alumina crusible, and irradiated to the substrate during stage 1 and 3 (together with In, Ga). The Ga / III ratio was varied between 0.3 and 1.0 (= CGS). the Fe concentration was varied between 0.0 ~ 1.2 mol%. The film composition was roughly determined by EPMA. The films were evaluated by EPMA, SIMS, XRD, SEM, absorbance spectra and cell performance. No phase separation was observed by XRD. Increment of the grain size with higher Fe composition was observed by SEM. The Fe distribution was uniform at Fe = 0.1%, but slightly higher toward the back side at Fe = 1.1%. Redshift with higher Fe content was observed in the absorbance spectra. However, the redshift was much smaller (~0.1eV at Fe=1.1%) than the values previously reported for bulk crystals. The spectral responce of the fabricated solar cells deteriorated with higher Fe content, from the long wavelength side. Details would be presented at the conference site.

F14.13

Effect of Stressed Molybdenum Back Contact Film on Properties of CIGS2 Absorber Layer. Ankur Anant Kadam, Anant H. Jahagirdar and Neelkanth G. Dhere; Florida Solar Energy Center, University Of Central Florida, Cocoa, Florida.

Molybdenum is used as back contact layer in $\mathrm{CuIn_{1-x}Ga_xS_2}$ (CIGS2) absorber thin film solar cells. Mo is deposited using DC magnetron sputtering. Mo being refractory material develops stresses. It is essential to deposit stress-free and relatively inert Mo in order to achieve well adherent and highly efficient CIGS2 absorber thin film solar cells on stainless steel and glass substrates. Earlier studies have shown that films deposited at sputtering power of 300 W and working argon pressure of 0.3 mTorr develops compressive stress, while films deposited at 200 W and 5 mTorr pressure develops tensile stress. The work presented here demonstrates the variation in crystallinity and microstructure of CIGS2 absorber layer as a function of the deposition conditions and the nature of stress in the underlying Mo film. All the depositions were carried out on 10 x 10 cm^2 glass substrates. Mo film was deposited with four different combinations of deposition parameters. In first set of experiments molybdenum thickness of approximately 350 nm was deposited at power of 200 W and pressure of 5 mTorr. In the second set, molybdenum thickness of approximately 350 nm was deposited at 300 W power and 0.3 mTorr argon gas pressure. Two more experiments were carried out by using alternate layers to reduce the overall stress. In third experiment, two high power cycles were sandwiched between three low power cycles with total film thickness of 330 nm. In fourth experiment two low power cycles were sandwiched between three high power cycles resulting in effective thickness of 315 nm. Metallic precursors, copper-gallium and indium were deposited by DC magnetron sputtering with identical deposition parameters on all Mo films. Metallic precursors were sulfurized at 475°C for 20 minutes in a gas mixture of 4% $\mathrm{H_2S/N_2}$. The crystallinity, microstructure and elemental depth profiling were analyzed by X-ray diffraction, scanning electron microscopy and Auger electron spectroscopy. This paper describes the correlation between the microstructure, residual stress, and extent of sulfur diffusion in Mo back contact layer and the properties of CIGS2 thin films.

F14.14

An Alternative Junction Mechanism in CdS/CdTe Thin-Film Solar Cells. Yann Roussillon[1], Victor G. Karpov[2], Diana Shvydka[2] and Dean M. Giolando[1]; [1]Chemistry, University of Toledo, Toledo, Ohio; [2]Physics and Astronomy, University of Toledo, Toledo, Ohio.

The standard main junction mechanism in CdS/CdTe solar cells is that of a p-n junction between the n-type CdS layer and p-type CdTe layer. In such a structure, the doping density in the CdS layer is usually assumed to be several orders of magnitude higher than that in CdTe. This corresponds to a depletion width of a few micrometers in the CdTe layer as opposed to a few nanometers in the CdS layer. It follows then that any modification of the structure of the device, TCO/CdS/CdTe/metal before the CdS layer, such as the introduction of a buffer layer between the transparent conducting oxide (TCO) and CdS, should not have any impact on the device Voc. Contrary to the latter conclusion, recent experimental results obtained by our group and presented in this work show that adding a buffer layer between TCO and CdS has a dramatic effect on the device. Before any intentional Cu doping, samples containing a buffer layer show high Voc (~ 800 mV), similar to samples without buffer layer after Cu doping. Further characterization by EQE and C-V confirms this unexpected effect. To explain this phenomenon, an alternative mechanism of the main junction in CdTe based devices is proposed, similar to metal-insulator-semiconductor structures. The CdS is believed to be strongly compensated when imbedded in the structure. The compensation is achieved through either the presence of interfacial defects at the buffer-CdS interface or by Cu doping. This strongly increases the depletion lengths in CdS and thus suppresses the band bending between the CdS and its tangent layers. The net result of CdS turning into the insulating state is coupling between the buffer layer (or TCO) and the CdTe layer. Such a coupling causes a strong band bending in the CdTe component of the device, which, in turns, results in a high Voc when exposed to the absorbed light. Such a buffer layer based structure made a 13% efficient cell without any Cu doping, using Au as the back contact.

F14.15

Reconfiguring Defect Distribution in CIGS Films for Optimum Performance. S. Menezes, Y. Li and S. J. Menezes; InterPhases Research, Thousand Oaks, California.

The $\mathrm{CuInSe_2}$ semiconductor is undisputedly the perfect absorber material for solar cells. Engineering its bandgap with S and Ga invariably perturbs the optimum defect equilibrium, leading to many of the issues encountered in the manufacture of devices with $\mathrm{CuInGaSe_2}$ or $\mathrm{CuInGaSSe_2}$ alloys (CIGS). This work strives to develop a simple surface engineering step to reliably and reproducibly enhance the performance of CIGS PV modules made with low-cost large area coating methods. This strategy uses the chemical potential manipulation to regulate the deep defect density of CIGS films. Photocurrent and spectral response measurement monitor the effects of surface modification, specific metal ions and time, in an electrolytic medium. The CIGS films respond easily to a number of external stimuli with either positive or negative changes in their PV output. Strong time dependence of the photocurrent suggests a dynamic equilibrium of point defects in the CIGS film. The results provide compelling evidence that a simple chemical surface treatment alters CIGS electro-optic properties. They offer new insights into the effects of stoichiometry, deposition methods and the environment on the CIGS defect chemistry. These findings provide directions for reconfiguring the deep defects in CIGS to achieve uniform performance across large-area modules without the need for toxic etchants or buffer layers, and the environmental hazards associated with these steps. They promise substantial efficiency increase for PV modules made with inexpensive CIGS films.

F14.16

Pulsed Laser Annealing of CIGS Films and Devices. Valentin Craciun[1], Xuege Wang[2], Sheng Li[2], Andre Baran[3], Thimothy Anderson[3], Oscar Crisalle[3] and Julien Venturini[4]; [1]Materials Science and Engineering, University of Florida, Gainesville, Florida; [2]Electrical and Computer Engineering, University of Florida, Gainesville, Florida; [3]Chemical Engineering, University of Florida, Gainesville, Florida; [4]SOPRA, 92270 Bois-Colombes, France.

Investigations of the effects of Pulsed Laser Annealing (PLA) process on the surface morphology and defect properties of CdS/Cu(In,Ga)Se2 (CIGS) films and solar cells are reported in this presentation. CIGS films capped with a CdS layer were laser annealed in air using a specially built XeCl excimer laser (308 nm) that emits $\sim$200 ns long pulses. Based on previous experiments, the laser fluence used for the treatments was in the range from 30 to 110 mJ/cm2. Grazing incidence x-ray diffraction investigations showed that samples irradiated at fluences higher than 70 mJ/cm2 exhibited a significant improvement of the CdS layer crystallinity. Scanning electron microscopy investigations of the samples surface showed rounded features, an indication of melting. X-ray photoelectron spectroscopy investigations showed no increased oxidation of the capping CdS layer, although the PLA was performed in air. Deep-level transient spectroscopy (DLTS) and C-V results showed that the shallow defect density was reduced by half after low fluence PLA treatments.

F14.17

Growth Mechanisms of Electrodeposited CuInSe$_2$ and Cu(In,Ga)Se$_2$ Determined by Cyclic Voltammetry.
Estela Calixto, Kevin D. Dobson, Brian E. McCandless and Robert W. Birkmire; Institute of Energy Conversion, University of Delaware, Newark, Delaware.

CuInSe$_2$-based thin film solar cells have exhibited very promising performance, where the best photovoltaic quality films are deposited via high vacuum thermal evaporation. There is, however, interest in developing deposition techniques that avoid the use of high vacuum, especially when considering industrial scale-up. Electrodeposition (ED) is one of the best alternatives since deposition equipment is commercial availability and film growth is performed at low temperature and at high deposition rates over large areas. Single ED baths of CuInSe$_2$ and Cu(In,Ga)Se$_2$ have been evaluated and it was found that the ratio of bath [Se^{4+}]/[Cu^{2+}] has a significant effect on composition and morphology of deposited films. The films are generally of 1.5 - 2μm thickness and exhibit columnar growth. For ED of CuInSe$_2$, a [Se^{4+}]/[Cu^{2+}] $\geq$2 was found to allow growth of Cu-poor films of $\sim$23 at% Cu, $\sim$25 at% In and $\sim$52 at% Se. For ED of Cu(In,Ga)Se$_2$, a [Se^{4+}]/[Cu^{2+}] $\sim$ 1.75 was found to be required to maintain appropriate Se and Cu levels, where the In^{3+} concentration in the bath was varied to adjust Ga composition. Using these criteria and a substrate pretreatment prior to deposition, device quality films with composition of $\sim$25 at% Cu, 17-20 at% In, 6-8 at% Ga and $\sim$50 at% Se were obtained. All ED films have poor crystallinity and require annealing in selenium-containing atmospheres to recrystallize the films prior to device processing. After selenization treatment, solar cells with efficiency of $\sim$6.5% have been obtained. In order to understand the role of [Se^{4+}]/[Cu^{2+}] in the film growth, cyclic voltammetry measurements were performed to identify mechanisms leading to the formation of CuInSe$_2$ and Cu(In,Ga)Se$_2$. The study was made using Mo, Mo/ED-CuInSe$_2$ and Mo/ED-Cu(In,Ga)Se$_2$ substrates as the electrodes. Similar mechanisms were observed for deposition of Cu$_x$Se, CuInSe$_2$, Cu(In,Ga)Se$_2$ and CuGaSe$_2$. We gratefully acknowledge the financial support of Davis, Joseph & Negley.

F14.18

Growth and Properties of HF Magnetron-Sputtered CuInSe$_2$ Thin Films. Peter Gorley[1], Volodymyr Khomyak[1], Yuri Vorobiev[2], Jesus Gonzalez Hernandez[2], Sergiy Bilichuk[1], Vadim Grechko[1] and Paul Horley[1]; [1]Electronics and Energy Engineering, Chernivtsi National University, Chernivtsi, Chernivtsi, Ukraine; [2]Unidad Queretaro, CINVESTAV-IPN, Queretaro, QRO, Mexico.

Complex ternary diamond-like semiconductor compounds of A^{I}B^{III}C$_2$^{VI} type and solid solutions on their base are of great scientific interest for optoelectronic, non-linear optics and photovoltaic applications due to the peculiarities of their band structure, electrical and optical properties. Copper indium diselenide CuInSe$_2$ (CIS) is one of the most promising materials that could be used for fabrication of stable, high-efficient and cheap solar cells. To improve the efficiency of photovoltaic system one has to optimize existing technologies and be able to control the structural, electric, photoelectric and optical properties of the material. This paper presents investigation data on the influence of technological parameters, such as carrier gas pressure in the chamber, magnetron power, distance from the target to the substrate and temperature of the substrate on the film deposition rate and their electrical and optical properties. Thin films were obtained using vacuum equipment VUP-5M by HF magnetron sputtering in the atmosphere of high-purity argon using specially-manufactured HF generator. Crystalline disks of CIS cathodes (40mm in diameter) were made from either Bridgemann-grown crystals or grained and pressed CIS powder. The substrate were rotated around the vertical axis of the chamber during the growth process, resulting in low thickness inhomogeneity of the film (less than 5%) for the total area 48 by 60 mm^2. Depending on technological parameters it was possible to grow 180-600nm thick films over pre-cleaned glass and silicon substrates, heated to 330-673K during the film deposition. In all the cases studied film deposition rate was in the ranges of 1-1.5nm/min. Surface resistivity of the films obtained was measured by four-probe method, and their optical transmission was investigated with spectrometry equipment for the wavelengths of 340-2500nm at the room temperatures. The parameters of the films were characterized with high stability and reproducibility. It was shown that substrate temperature increase leads to steeper intrinsic absorption edge, shifted towards lower energies.

F14.19

Selective Laser-Micromachining of Flexible CuInSe2-Solar Cells-Layer using Different Pulse Durations and Wavelengths: A Comparison as well as a Machine Concept. Jens Haenel, Tino Petsch, Lars Pichler and Sven Albert; 3D-Micromac AG, Chemnitz, Saxony, Germany.

CuInSe2 solar cells consist of multilayer laminates. The reel-to-reel production process of flexible CIS solar cells on 20 um plastic film substrate requires concepts of geometrically flexible manufacturing. The industry as well as the scientists are focusing their attention on the development of selective and damage-free laser-structuring of this types of solar cells. The manufacturer can produce customized solar cell solutions with this laser technology and special machine concepts. This technical contribution shows the way from first tests up to the results of less-damage-laser-micromachining with CO2-, Excimer- and predominantly ultra short pulse laser. The test results are showing the aims of high-speed-laser-machining of CIS solar cells and the machine concept which was developed from the 3D-Micromac. Different main layer-composites of CuInSe2 solar cell like, molybdenum-polymer and CIS-molybdenum-polymer-molybdenum with diverse laser sources will be examined and compared. The results of the micro-structured layers demonstrate the important differences between laser types and laser parameters. Best results regarding smallest material-layer damages of CIS solar cells will be obtained by short or ultra short laser pulses. These realizations will be proved by SEM, Micro-Raman recordings and diagrams. The results are showing a new approach of Pico-second-laser-structuring of thermal sensitive layer systems, which will find numerous applications such as interconnecting of solar cells and production of polymer electronics. An application specific machine concept makes possible an efficient transformation of these small damages CIS-micromachining technologies.

F14.20

Characterization of CuInSe$_2$/In$_2$O$_3$ and CuIn$_3$Se$_5$/In$_2$O$_3$ Structures. P. Malar, Bhaskar Chandra Mohanty and Subbiah Kasiviswanathan; Department of Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India.

CuInSe$_2$/In$_2$O$_3$ and CuIn$_3$Se$_5$/In$_2$O$_3$structures were formed by depositing CuInSe$_2$/CuIn$_3$Se$_5$films by stepwise flash evaporation onto DC sputtered In$_2$O$_3$ films. Phase purity of the CuInSe$_2$ and CuIn$_3$Se$_5$ films was confirmed by Transmission Electron Microscopy. X-ray Diffraction results on CuInSe$_2$/In$_2$O$_3$/glass and CuIn$_3$Se$_5$/In$_2$O$_3$/glass structures showed sharp peaks corresponding to (112) plane of CuInSe$_2$/CuIn$_3$Se$_5$ and (222) plane of In$_2$O$_3$. Rutherford Backscattering Spectrometry investigations were carried out on CuInSe$_2$/In$_2$O$_3$/Si and CuIn$_3$Se$_5$/In$_2$O$_3$/Si structures in order to characterize the interface between CuInSe$_2$/In$_2$O$_3$ and CuIn$_3$Se$_5$/In$_2$O$_3$. The results show that the CuInSe$_2$ and CuIn$_3$Se$_5$ films were near stoichoimetric and In$_2$O$_3$ films were oxygen deficient. CuInSe$_2$/In$_2$O$_3$ interface was found to include a $\sim$ 20 to 25 nm thick region consisting of copper, indium and oxygen. However the interface between CuIn$_3$Se$_5$ and In$_2$O$_3$ was found to be sharp. The observed results are explained on the basis of diffusion of copper at the interface and in terms of the difference in copper concentration between CuInSe$_2$ and CuIn$_3$Se$_5$.

F14.21

Performance of CuGaSe$_2$ Solar Cells Grown by Co-Evaporation Process. Jae Ho Yun, R. B. V. Chalapathy, Seok Ki Kim, Jeong Chul Lee, Jinsoo Song and Kyung Hoon Yoon; Solar Cells Research Center, Korea Institute of Energy Research, Daejeon, South Korea.

CuGaSe$_2$ with band gap 1.68 eV is an attractive absorber material for solar sells to obtain high open circuit voltage and iedal partner for CuInSe$_2$/CuGaSe$_2$ based tandem solar cells. In this paper, we deposited CuGaSe$_2$ thin films by physical vapor deposition and fabricated solar cells based on slighly Ga rich absorber. CuGaSe$_2$ absorber layers were grown by evaporating elemental Cu, Ga and Se on to Molybdenum coated soda lime glass substrates using three-stage process. The substrate temperature during the first stage and second stage are at 350 ^{o}C and 550 ^{o}C, respectively. CuGaSe$_2$ films with different Cu/Ga ratios are grown by the Ga flux control during the deposition. Properties of the films are characterized by using XRD, SEM and EDX. Cells completed by deposition of CdS buffer layer by chemical bath deposition at 60^{o}C. The window layer consists of a radio-frequency sputtered intrinsic i-ZnO 50 nm and Al doped ZnO 500 nm. Electron beam evaporated Al grids were used as top contract. The cells are tested under AM 1.5 illumination of 100 mW/cm^2 irradiance. As grown films showed preferred (112) orientation. The grain size of the films decreased with the variation of Ga composition, but the morphology of the films improved. The optical band gap of the absorber is around 1.68 eV regardless of Ga concentration. Using these films the solar cells with a structure SLG/Mo/CuGaSe$_2$/CdS/ZnO/Al were fabricated. In optimal condition, we obtained Voc = 0.81 V, Jsc = 11.8 mA, ff = 0.635 and Eff. = 6.2 %. The absorber film is 1.9 μm thick and slightly Ga rich bulk composition [Cu]/[Ga] =0.83. The modification of interface by additional heat treatment and various buffer layer for improvement of fill factor and other junction properties are currently being conducted. And it will be presented at the meeting.

F14.22
Abstract Withdrawn

F14.23
Spray-ILGAR Thin Films For Chalcopyrite Solar Cells. Nicholas A. Allsop, Antje Schoenmann, Martha C. Lux-Steiner and Christian H. Fischer; Solar Energy SE2, Hahn-Meitner-Institut, Berlin, Germany.

A new deposition technique has been developed at the Hahn-Meitner-Institut Berlin called Spray-ILGAR (Ion Layer GAs Reaction). This method is based upon the proven dip-ILGAR method which has produced cells with a record efficiency [1]. The new process involves the sprayed deposition of an ionic salt layer 1-10nm in thickness followed by the conversion of the salt to a chalcogenide using a reactive gas. The process cycle is repeated to give the desired total layer thickness. As the precursor spray approaches the substrate it is vaporised and the final transport is via the gas phase, thus the microscopic process has much in common with Chemical Vapour Deposition and Atomic Layer Deposition (ALD). However, macroscopically the spray approach is well suited to in-line processing and the deposition times are substantially faster than ALD. Experiments using Spray-ILGAR indium sulfide buffers on Cu(In,Ga)(S,Se)2 absorbers from Shell Solar Munich have produced cells reaching an efficiency of 14.8%. Cells were completed using an i-ZnO, ZnO:Ga window and NiAl contacts from the HMI baseline. No wet-chemical treatment was performed and no antireflective coating was applied. The process is also very reproducible, 48 0.5cm2 total area cells were made with an average efficiency of 13.5% and an average excluding the lowest 25% (to remove the cells with scribing defects) of 14.3%. These highly efficient and cadmium free solar cells match and sometimes exceed the efficiencies of the CBD-CdS reference cells. Copper (I) sulfide and copper indium disulfide (CIS) have also been successfully produced and are of particular interest for nanostructured or ETA cells due to the ability of the gas to penetrate the porous structure. The theory behind the technique and the experimental influence of processing parameters will be discussed. While optimum parameters can be found, the technique is also very robust with wide processing windows. [1]. M. Baer, H.-J. Muffler, Ch.-H. Fischer, S. Zweigart, F. Karg and M.C. Lux-Steiner. Prog. Photovolt: Res. Appl. 10, 173, (2002).

F14.24
Surface Preparation Issues of CdSeTe/Si Material with Respect to Subsequent MBE Nucleation. Gregory Brill, Yuanping Chen, Priyalal Wijewarnasuriya and Nibir Dhar; U.S. Army Research Laboratory, Adelphi, Maryland.

At the Army Research Laboratory (ARL), a major research effort has been focused on transitioning the current state-of-the-art molecular beam epitaxial (MBE) HgCdTe material growth technology from bulk CdZnTe substrates to Si-based composite substrates. Through this effort, high quality CdTe grown on Si substrates has been achieved. Recently, this work has progressed at ARL toward achieving exact lattice matching with HgCdTe by incorporating approximately 4% Se into CdTe material. Although, the quality of CdSeTe/Si is extremely impressive, several issues related to the nucleation of HgCdTe on these layers need to be addressed. First and foremost is understanding the effect Se has on the surface chemistry with respect to appropriate surface preparation processes for subsequent MBE nucleation. In this work, the surface preparation process of CdTe, CdZnTe, and CdSeTe layers grown on Si(211) substrates were studied. Several different wet chemical etching processes were employed to prepare the layers for HgCdTe nucleation. The chemically cleaned surfaces were characterized using Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Reflection high-energy electron diffraction (RHEED) and by characterizing the properties of the MBE grown HgCdTe material. Initially, the standard Bromine-Methanol solution (0.5%) was used to etch CdSeTe. This etching process is used successfully to prepare both CdTe and CdZnTe layers. However, a vastly different surface is obtained on CdSeTe layers as observed by RHEED, with an extremely diffuse (211) RHEED pattern present at room temperature. This result is in stark contrast to Cd(Zn)Te layers prepared in the same manner. Surface chemistry studies using AES indicated that a highly Se-rich surface is produced using the Bromine-Methanol etching process, even for extremely dilute and brief etching durations. Additionally, it took much higher temperatures to recover a relatively sharp RHEED pattern than is typically needed for Cd(Zn)Te layers. Based on these observations, the overall surface quality was not adequate for high-quality HgCdTe nucleation. These studies indicate that the standard wet chemical and MBE thermal treatment process used for Cd(Zn)Te/Si is not entirely appropriate for nucleation on CdSeTe/Si. This fact is attributed to the difference between cation mixing and anion mixing within the CdTe matrix, even for only a small amount of material incorporated. These results will be discussed in further detail. In addition, a novel process was utilized to avoid any wet chemical cleaning of the as-grown CdSeTe layer. Instead, amorphous arsenic was deposited on the pristine surface immediately after the conclusion of growth. This layer was then thermally removed in the HgCdTe MBE growth chamber. A cleaner surface, as indicated by RHEED, was obtained and a reduction in the HgCdTe dislocation density was achieved. These results will also be discussed.

F14.25
High-Efficient ZnO/PVD-CdS/CuIn$_x$Ga$_{1-x}$Se$_2$ Thin Film Solar Cells: Formation of the Buffer-Absorber Interface and Transport Properties. M. Rusu, C. A. Kaufmann, A. Neisser, S. Siebentritt, Th. Glatzel and M. Ch. Lux-Steiner; SE2, Hahn-Meitner-Institut Berlin, Berlin, Germany.

High-efficiency thin-film solar cells based on CuIn$_x$Ga$_{1-x}$Se$_2$ absorber material have been developed using CdS buffer layers deposited by chemical bath deposition (CBD) [1]. However, for industrial production, an in-line vacuum deposition such as, e.g., physical vapour deposition (PVD) is preferred. This contribution reports on the preparation of highly-efficient ZnO/CdS/CuIn$_x$Ga$_{1-x}$Se$_2$ solar cells with PVD-deposited CdS buffer layers. The PVD-CdS preparation conditions were optimised for the deposition of the CdS layers suitable for highly-efficient ($>$ 14%, AM1.5, total area) solar cells. The solar cell devices with the PVD-CdS buffer layers show similar fill factors (FF $\sim$ 72%) and even higher short-circuit current densities (Isc $\sim$ 32 mA/cm2) as the reference cells with the CBD-deposited CdS. The open circuit voltage of devices with PVD-CdS is, however, lower which can be understood in terms of differences in the defect chemistry during the initial growth via CBD and PVD. In an effort to understand the peculiarities of the CdS deposition by the PVD technique, the microstructural properties and growth peculiarities of the PVD-CdS buffer layers on fresh CuIn$_x$Ga$_{1-x}$Se$_2$ surfaces were investigated by means of scanning electron microscopy (SEM). The top view and cross-sectional SEM images show that the PVD-grown CdS layers are closed and homogeneously deposited on the entire absorber surface. Additionally, Kelvin probe force microscopy (KPFM) measurements were carried out in-situ to monitor the initial growth of the absorber, as well as the CdS electronic properties, in particular its work function. It is observed by means of KPFM that the PVD-CdS growth is initially inhibited at the absorber grain boundaries. This allows us to suppose that during the initial growth stage a sulfur passivation of the grain boundaries occurs at the near-surface region of the absorber. The latter would explain the higher short-circuit currents of cells with the PVD-CdS. The investigation of the ZnO/PVD-CdS/CuIn$_x$Ga$_{1-x}$Se$_2$ transport properties shows that the main losses in the power conversion efficiency is due to the recombination processes which take place in the near-interface region of the absorber. Cells with CBD-CdS are dominated by recombination in the absorber bulk. [1] K. Ramanathan et al., Progr. Photovolt. 11 (4) (2003) 225.

F14.26
In-Depth Study of Morphological Defects of MBE-Grown CdTe on Si. Eva M. Campo[1], Thomas Hierl[1], James C. M. Hwang[1], Gregory Brill[2], Yuanping Chen[2] and Nibir K. Dhar[2]; [1]Center for Optical Technologies, Lehigh University, Bethlehem, Pennsylvania; [2]U.S. Army Research Laboratory, Adelphi, Maryland.

Morphological defects are known to nucleate during molecular beam epitaxial (MBE) growth of CdTe and related compounds [1]. Once present, any morphological defect present on the surface will remain during any subsequent overlayer MBE growth process and can appear similar to oval defects [2] that are typically found in III-V materials. These defects are known to degrade the performance and reliability of HgCdTe infrared detectors through the reduction of minority carrier lifetime and diffusion length. Therefore, it is critical to understand the formation of these defects during Cd(Se)Te composite substrate growth by MBE prior to HgCdTe nucleation. Recently, we investigated the origin and nature of morphological defects typically found in CdTe and CdSeTe layers deposited by molecular beam epitaxy on Si [3]. Focused ion beam (FIB) milling, secondary electron microscopy (SEM) and transmission electron microscopy (TEM) were used to analyze the morphology, structure and composition of the defects. The prior investigation showed that the subsurface morphology of these defects was comprised of polycrystalline material, and that the bottom of the morphological defects involved missing material. X-Ray energy dispersive spectroscopy (EDS) showed little composition variation inside or outside the defects. Additionally, no foreign elements were detected in the defect area. The defects appeared to originate near the CdSeTe/CdTe interface or in the middle of the CdTe layer where growth was interrupted and the substrate temperature was temporarily raised. These results suggested a correlation between defect nucleation and either shutter movement or growth interruption. In this work we further investigate the origin of these defects using FIB, SEM, and TEM. Several different growth experiments will be conducted to determine which precise processes within the growth sequence leads to surface morphological defect formation. The effect of shutter movement will be isolated from the growth interruption process during these experiments. Additionally, different combinations of material fluxes used during in-situ annealing cycles will be under investigation as well as the maximum temperature reached during the in-situ annealing cycle. Since preliminary results indicated the absence of material at the base of the defect, it is reasonable to expect a temperature and/or flux dependence on defect formation. Detailed results from these studies will be presented. REFERENCES [1] D.W. Snyder, S. Mahajan, E.I. Ko, P.J. Sides, Appl. Phys. Lett. 58 , 848 (1991) [2] J.C.M. Hwang, T.M. Brennan, A.Y. Cho, J. Electrochem. Soc. 130 ,493 (1983) [3] E.M. Campo, Thomas Hierl, James C. M. Hwang , Yuanping Chen, Gregory Brill, and Nibir K. Dhar, submitted to J. Elect. Mat.

F14.27

Formation and Characterization of CIS/Buffer Layer Interface in CIS Electrodeposited (CISEL) Solar Cells. Negar Naghavi[1,3], Cedric Hubert[4], Olivier Roussel[4], Melanie Lamirant[4], Bruno Canava[2], Jean-Francois Guillemoles[1,3], Arnaud Etcheberry[2], Daniel Lincot[3,1] and Olivier Kerrec[4]; [1]CNRS, CISEL, Chatou Cedex, France; [2]CNRS, Institut Lavoisier, Versailles, France; [3]CNRS, LECA, Paris Cedex 05, France; [4]EDF, CISEL, Chatou Cedex, France.

Our group have shown that electrodeposited CIS solar cells can actually achieve efficiencies over 11%. In CIS and CIGS solar cells high efficiencies are obtained in part due to the excellent optoelectronic properties of the active material (CIGS or CIS) and in part due to the ability to prepare an excellent interface between CIS and the buffer layer (usually CdS). Best buffer layers are prepared by chemical bath deposition. The chemical bath deposition (CBD) has been proven to be the most suitable method to produce buffer layer thin films for photovoltaic applications because it is an efficient, cost-effective, and large-scale method. We can note that the buffer layer (CdS), even if its thickness is very thin, is absolutely necessary to reach the highest efficiencies in solar cells. However a good quality of the buffer layer depends also on the quality of the surface of the CIS, that is why, currently one of the main challenge to progress in that technology is the control of interfacial properties, a task made difficult due to the chemical complexity of the interface in devices. The effects of the solution chemistry (nature of the precursors, complexing agents, pH) used for the preparation of the buffer layer, the kinetic of the growth, the nature of the substrate and its surface state, the lattice matching between the CIS and the buffer layer are all very important on the finale efficiency of the solar cells. The aim of this work is on one hand a better understanding of the interface between electrodeposited CIS precursor and the buffer layer and the influence of solution chemistry of CBD bath on the properties of the interface and on the other hand to see what are the possibilities to improve this interface. In this study we have modified the nature of the CBD bath, and specially the pH and complexation. The films are characterised by XPS, TEM, SEM and optoelctronic techniques.

F14.28

Tailoring the Composition of $CuInSe_2$ Monograin Powders in Growth Process. Marit Kauk, Mare Altosaar, Jaan Raudoja, Kristi Timmo, Maarja Grossberg and Enn Mellikov; Tallinn University of Technology, Tallinn, Estonia.

Monograin powders of $CuInSe_2$(CIS) have been found application as absorber material in monograin layer solar cells [1]. The monograin layer consists of one crystal thick layer of grains of monograin powder embedded into an organic resin. The advantages of the developed powder materials are single-crystalline structure of every grain, uniform distribution of doping impurities and narrow granulometric composition. Till now current-voltage (I-V) dependences of monograin layer solar cells with structure of graphite/CIS/CdS/ZnO have shown values of Voc up to 530mV and fill factors up to 60%. $CuInSe_2$ powders were synthesized proceeding from high-purity Cu-In alloys and elemental Se in liquid phase of alkaline halides as flux material in evacuated quartz ampoules. Modifying the preparation conditions, we studied the relationship between initial and final compositions and determined the preparation conditions for single-phase growth of $CuInSe_2$ monograin powders. As it is shown in [2], the formation of $CuInSe_2$ monograins takes place in the liquid phase of flux of a certain amount exceeding the limit for crystals sintering. We varied the Cu/In ratio in initial Cu-In alloys from 0,5 to 1,1. Powders were studied by photoluminescence (PL) measurements and characterized structurally by X-ray diffraction and Raman spectroscopy, compositionally by ICP-MS, polarographically and by energy-dispersive X-ray analysis, morphologically by scanning electron microscopy. As a result, single-phase powder crystals were synthesized from mixtures of initial components between 1> Cu/In>0,71. The powders with starting Cu/In<0,71 were found to consist of crystals with different compositions: Cu/In=0,92 and Cu/In=0,66. Cu-rich (Cu/In>1) mixtures of initial components have lost some amount of copper. This is suggest on arise of multiphase system. The samples with Cu/In ratio 0,9 exhibited PL spectrum with one dominant peak at 0,93eV, typical for In-rich $CuInSe_2$. The samples with lower Cu/In ratio exhibited two broad bands with peak position at 0,86eV and 0,93eV. [1] M.Altosaar, A.Jagomägi, M.Kauk, M.Krunks, J.Krustok, E.Mellikov, J. Raudoja, T.Varema. Monograin layer solar cells, Thin Solid Films 431-432 (2003) 460-469. [2] M.Altosaar, E.Mellikov $CuInSe_2$ Monograin Growth in CuSe-Se Liquid Phase, Jpn.J.Appl.Phys., 2000, 39, Suppl. 39-1, 65-66

F14.29

Abstract Withdrawn

F14.30

Liquid Phase Deposition of $CuInSe_2$ Films for Photovoltaic Applications. Jonathan Cowen[1], Frank Ernst[1], Pirouz Pirouz[1], Sheila Bailey[2] and Aloysius Hepp[2]; [1]Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio; [2]Photovoltaic Branch, NASA Glenn Research Center, Cleveland, Ohio.

Copper Indium Diselenide (α-CIS) has been extensively investigated and utilized for solar cell absorber layers over the past couple decades due to its unique optoelectronic properties. Due to the high absorption coefficient α-CIS possesses, films with thicknesses of 1 μm can achieve high power conversion efficiencies while maintaining high specific power (W/kg) values. Current deposition techniques, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and electrodeposition, all result in polycrystalline thin films possessing average grain sizes on the order of 1 μm or less. However, we have been investigating the possibility to grow α-CIS via liquid phase deposition. With the aid of the first complete ternary equilibrium phase diagram of the Cu-In-Se system, films are nucleated on suitable substrates directly from a growth solution. A major advantage of this technique lies in the fact that growth takes place under thermodynamic equilibrium conditions resulting with average grains sizes on the order of 10-30 μm or more depending on growth conditions. The study of such films can provide insight into some of the recently debated issues concerning the effects of grain boundaries in deposited CIS films. Therefore we will report on the importance of the newly established phase diagram, the construction of a liquid phase deposition reactor, and the characterization of the resulting microstructures of deposited films via TEM, XEDS, and SEM.

F14.31

Effects of Rapid Thermal Annealing on Film Properties and Performance of $Cu(In,Ga)Se_2$ Solar Cells. Sheng S. Li, Xuege Wang and Valentin Cracium; Electrical & Computer Engineering, University of Florida, Gainesville, Florida.

The halogen-based rapid thermal annealing (RTA) technique has been widely used in semiconductor industry since it offers several advantages such as short cycle time, reduced thermal exposure and lot size flexibility as compared to conventional furnaces. Strong demand in reducing thermal budget and cycle time has made RTA treatment a popular thermal processing technique for defect reduction in semiconductors. The RTA technique has been successfully applied to the fabrication of low-cost silicon solar cells. In this work, the effects of RTA treatment on film properties and the performance of $Cu(In,Ga)Se_2$(CIGS) solar cells were investigated. RTA experiments were conducted on three CIGS cells fabricated by NREL, and the results show that progressive RTA treatment improves cell performance and overall film uniformity of large area CIGS absorber layers. The photo- J-V results show significant improvement in the performance of three annealed cells after each progressive RTA treatments at temperatures of 100, 200, and 300^{o}C for 30 seconds each. A dramatic increase in the efficiency of cell-1 from 9.52% before RTA to 15.77% after 300^{o}C RTA treatment was obtained from this study. Cell-2 and -3 with pre-annealed efficiencies of 14.73% and 15.51% also increased to 16.65% and 16.42% followed the progressive RTA treatments. The most dramatic improvement of these RTA treated cells is due to the drastic increase in F.F. (fill-factor) for the bad cell. Since the photo- J-V was measured right after each annealing, the light soaking effect could also be a contributing factor to the observed improvement of cell performance Four GIGS cells from a large area CIGS sample prepared by Shell Solar Industry were also characterized by the photo J-V and Q-E measurements before and after RTA at 300^{o}C for 1- and 2-min.and 350^{o}C for 1- and 2-min., respectively. To eliminate light soaking effect, the photo J-V and Q-E measurements were performed again 2 weeks after the initial RTA treatments. The results showed that Voc, Jsc, and conversion efficiency were increased while F.F. decreased after RTA treatments on three cells. From the Q-E measurements, values of quantum efficiency were found to increase over the wavelength range of 400 nm to 1000 nm after RTA treatments. The results of this study clearly show that RTA treatments are indeed beneficial in improving the uniformity of films and performance of CIGS cells. Our estimated optimal annealing temperatures should lie between 200 and 300^{o}C with a 1- minute or less holding time.

F14.32

Effect of Post-Film Deposition and Post-Device Fabrication Treatments on the Performance of $CuInS_2$ Thin Film Solar Cells. Michael H.-C. Jin[1,2], Kulbinder K. Banger[1,2], Jeremiah S. McNatt[2], John E. Dickman[2] and Aloysius F. Hepp[2]; [1]Ohio Aerospace Institute, Brookpark, Ohio; [2]NASA Glenn Research Center, Cleveland, Ohio.

The main objective of this work is the development of thin film space solar cell materials that can be prepared on large-area flexible lightweight substrates, which will make new designs possible for future space applications and minimize the mass-specific power requirements for their missions. The aerosol-assisted chemical vapor deposition (AACVD) is considered to be one of the promising deposition techniques owing to its simplicity, good productivity on a large scale, large process window and inexpensiveness. However, fabricating highly efficient solar cells with AACVD-deposited chalcopyrite absorber layers still remains challenging. They typically show low energy conversion efficiencies primarily due to low open-circuit voltage and poor fill factor [1]. One way to improve the quality of the absorber layer is post- film deposition annealing. The annealing can thermodynamically remove structural defects associated with metal ions and for $CuInS_2$, sulfur vacancies that are undesirable n-type dopants present in both bulk and grain boundaries can be passivated by extra sulfur or oxygen. In this study, the post-deposition annealing of the AACVD-deposited $CuInS_2$ thin films made from single source precursors were optimized by analyzing photoluminescence spectra. The post-deposition annealing under a mixture of Ar and sulfur gas increased S content and improved the crystallinity of the films. The transitions associated with sulfur vacancies were also identified. Post-device fabrication thermal annealing in air was also studied in order to optimize the performance of the solar cells. It was found that humidity has influenced the cell performance and the degradation due to humidity was reversible by heat treatment. It was further verified that the deterioration of the cell performance can be prevented by storing the solar cell under nitrogen environment after annealing. [1] M. H.-C. Jin *etal.*, *Proc.ofthe19thEuropeanPVConference*, 4AV.1.71 (2004).

F14.33

High Efficiency, 0.8 Micron CdS/CdTe Solar Cells. Akhlesh Gupta and Alvin D. Compaan; Physics and Astronomy, The University of Toledo, Toledo, Ohio.

The CdTe thickness (3-8 μm range) in reported high efficiency solar cells is far greater than needed from the optical absorption coefficient and direct band-gap (1.5 eV) of CdTe. High efficiency cells using thinner CdTe layer would be beneficial to increase manufacturing throughput, reduced processing time and material cost, facilitate cell isolation and interconnections, minimize use of toxic (Cd) and rare (Te) materials, and lower waste management cost. Very thin CdTe cells could also be candidates for use as top cells in two-junction tandem solar cells to help in current matching with the bottom cell. In this paper, we present the effect of CdTe thickness reduction, $CdCl_2$ treatment duration and back-contact diffusion on the performance of thinner CdTe solar cells. Cells with CdTe thicknesses from 0.5 μm to 1.28 μm were fabricated using magnetron sputtering at 260^{o}C. The TCO/CdS/CdTe structures were vapor $CdCl_2$ treated at 387^{o}C for 10 to 30 min in dry air, and cells were completed with evaporated Cu/Au or Au back contacts. The back contact was diffused in air at 150^{o}C for 5 to 45 min duration. The films and cells were characterized using XRD, AFM, optical transmission, I-V and QE measurements. When post deposition processing is held constant to standard conditions of 30 min of $CdCl_2$ treatment and 45 min of back contact diffusion, the efficiency decreases by 55% for 0.5 μm in comparison to 2.3 μm CdTe. Similar to thick films, the as-deposited thin CdTe was of (111) preferred orientation that decreased after $CdCl_2$ treatment. XRD patterns also showed the formation of a $CdTe_{1-x}S_x$ alloy to a larger degree than in thick CdTe samples. A 10 min $CdCl_2$ treatment and 10 min of back-contact diffusion were found best to achieve 11.8% efficiency from a $\sim$ 0.8 μm thick CdTe cell. This cell showed V_{OC} of 772 mV, J_{SC} of 21.98 mA/cm^2 and FF of 69.7%. Work is supported by the NREL High Performance PV and Thin Film Partnership Programs.

F14.34

Large Area $Cu(In,Ga)Se_2$ Films and Devices on Flexible Substrates Made by Sputtering. Dennis Hollars, Randy Dorn, P. D. Paulson, Jochen Titus and Robert Zubeck; Miasole, San Jose, California.

$Cu(InGa)Se_2$ (CIGS) thin films have great potential for the fabrication of high efficiency photovoltaic devices. Several research groups routinely fabricate CIGS solar cells with efficiency values greater than 16% using various deposition techniques. However, the laboratory successes are not translated into the manufacturing scenario, mainly because of the complex process steps adopted for the fabrication of high efficiency devices, which may not be suitable for the large-scale manufacturing. Successful commercialization of this technology demands a manufacturing process that is easily scalable, easy to control and that has a large process window. Co-evaporation of the elements and selenization of sputtered metal precursors are the dominant contemporary CIGS preparation methods. With either method, the preparation of compositionally uniform CIGS films over large area requires intelligent process controls. In contrast, with rotary magnetron sputtering the deposition of compositionally uniform films covering large areas is straight-forward. Due to this inherent feature rotary magnetron sputtering is of great interest for the production of CIGS-based solar cells. As of today the dominant substrate material in CIGS manufacturing is glass, but roll-coating of a flexible substrate allows for higher throughput. Reactive rotary magnetron sputtering was used in the production of CIGS films on moving stainless steel substrates, in simulation of the operation of a roll-coater. Cu, In and Ga were sputtered from a single metal target and were reacted in a flow of Se on the heated substrate. Uniform films were deposited on two feet wide stainless substrates. Small area devices of the structure steel/Cr/Mo/CIGS/CdS/ZnO were made on various spots of these samples and were tested for solar cell performance. Film structure and composition as well as device performance were constant over large areas. The dependencies of CIGS film properties and of device performance on various processing parameters were investigated.

F14.35

CdSe Thin Film Preparation by Unipolar Current Pulse Electrodeposition Technique. Kiran Jain[1], M. S. Rashmi[2], K. N. Sood[2], N. Karar[1] and H. Chandra[1]; [1]Electronic Materials, National Physical Laboratory, New Delhi, India; [2]Materials Characterization Division, National Physical Laboratory, New Delhi, India.

CdSe is one of the widely studied II-VI semiconductor materials because of its promising applications as photoanode in photoelectrochemical cell. The conversion of solar light to electrical energy efficiency of 16.7 % has already been realized. More recently a great deal of attention has been focused on the fabrication of nanocrystalline thin films and nanoparticles due to their applications in various areas such as material science, electronic and optoelectronic, magnetic and energy storage devices. Compared to other processing routes the electrochemical route has the advantages in terms of simplicity, relative cost purity and large scale production capability. In electrodeposition, in contrast of chemical synthesis, one can easily control the reaction rate of the system by working at a given current density, or easily select the magnitude of the driving force for the reaction by the adjustment of electrode potentials and temperature. Recently pulsed electrodeposition technique has become an efficient process for the deposition of nanocrystalline materials. Pulse electrodeposition is one of the novel processing techniques utilizing the advantages of high current density. According to the electrodeposition theory, a high cathodic overpotential usually caused by high current density, speeds up the nucleation process and results in fine grained deposit. Even though pulse electrodeposition technique have been utilized to prepare nanocrystalline metallic films but the use of this technique for the fabrication of semiconductor deposition is still scarce. In the present work, unipolar current pulse electrodeposition process was used for CdSe thin films preparation. CdSe films were grown under wide range of variables like applied current density, pulse on time and off time in order to elucidate their effect on film properties. CdSe thin films were prepared on fluorine doped SnO2 coated glass plates. The electrodeposition bath consisted of aqueous solution including CdSO4, SeO2, H2SO4. All samples were prepared at 80 degree centigrade temperature. A systematic study was performed to determine the effect of pulse parameters on the structure and photoluminescence properties of CdSe thin films. The duration of on time and off time were varied within a wide range, from milliseconds to seconds. CdSe samples were also prepared under DC conditions, at constant anodic potentials in the range of 0.5 V to

0.85 Volts for a comparison. The microstructure and morphology were investigated using SEM. Photoluminescence spectra of CdSe thin films prepared under DC deposition and pulse deposition conditions were investigated in detail. The results on CdSe phase and grain size variation were correlated to the pulse parameters to understand the mechanism of CdSe formation using pulse technique.

F14.36

The Effects of Annealing on the Electrical, Optical and Structural Properties of Indium-Zinc-Oxide Thin Films. Matthew P. Taylor[1,2], Dennis W. Readey[1], Maikel F. A. M. van Hest[2], Charles W. Teplin[2], Jeff L. Alleman[2], Matthew S. Dabney[2], Lynn M. Gedvilas[2], Brian M. Keyes[2], Bobby To[2], John D. Perkins[2] and David S. Ginley[2]; [1]Colorado School of Mines, Golden, Colorado; [2]National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, Colorado.

Indium-zinc-oxide (IZO) compounds show very desirable properties as transparent conducting oxides (TCOs) for photovoltaic and display devices. IZO thin films can be deposited at low temperatures and still retain the high conductivity and optical transparency necessary for such applications. The electrical, optical and structural properties of these films were analyzed using high-throughput combinatorial techniques. Compositionally graded "libraries" of IZO were deposited onto glass substrates at 100°C by co-sputter deposition. The composition region studied ranged from 4 to 92 atomic % In for Zn. A conductivity of $\sim$3000 $(\Omega\text{-cm})^{-1}$ was found in amorphous, as-deposited material at a composition of $\sim$70% In. This amorphous region extended from $\sim$45 to 75% In in the as-deposited material, with crystalline regions at lower and high indium contents. Two series of analogous libraries were annealed at one hour intervals at temperatures ranging from 100°C to 600°C in air and argon. A systematic decrease in conductivity with increasing annealing temperature was observed for the air-annealed libraries. The maximum conductivity after the 600°C air anneal was 192 $(\Omega\text{-cm})^{-1}$ at $\sim$66%In. The extent of the amorphous region also decreased and ranged from $\sim$45 to 66% In after the one hour anneal at 600°C. The crystalline, as-deposited indium-rich films (>75% In) recrystallized into the In_2O_3 crystal structure and the conductivity decreased by almost 4 orders of magnitude as they were annealed in air. All of the films retained high optical transparency (>80%) regardless of annealing. The amorphous $In_{0.66}Zn_{0.34}O_y$ compound is the optimal material for devices requiring in-air thermal processing. The results of the argon annealing study will also be presented.

F14.37

Low Temperature Processing of Polymeric Precursor-Derived ZnO Thin Films. Uma Choppali, Michael J. Kaufman and Brian P. Gorman; Dept. of Materials Science & Engineering, University of North Texas, Denton, Texas.

Zinc oxide (ZnO), a wide band gap semiconductor, is a promising transparent conducting oxide material. Although various methods of synthesizing ZnO are available, an uncomplicated and straightforward method of preparing dense, nanocrystalline ZnO thin films at low temperatures has not been previously illustrated. In this paper, we present a novel technique of preparing size-controllable nanoparticle thin films of ZnO at low temperatures from polymeric precursors. The prepared polymeric solution of ZnO nanoparticles was spin-coated onto C-sapphire substrates and annealed at different temperatures. The effect of annealing on film grain size and strain was analyzed by X-ray diffraction. The growth of ZnO nanoparticles along a preferred direction was studied by X-ray diffraction and Electron Backscattered Diffraction in a dual-beam FIB. The surface morphology and interfacial reactions of the as-deposited and annealed ZnO thin films were characterized by SEM and HRTEM. Changes in band gap energy as a function of grain size was investigated by UV-Vis Absorption Spectroscopy. The density of ZnO thin films was analyzed by Ellipsometry.

SESSION F15: Solar Cell Technology

Chairs: Wolfram Jaegermann and Shigeru Niki
Friday Morning, April 1, 2005
Room 2005 (Moscone West)

8:30 AM F15.1

Flexible, Monolithically Integrated Cu(In,Ga)Se2 Thin-Film Solar Modules. Dirk Herrmann, Friedrich Kessler and Michael Powalla; Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung (ZSW), Stuttgart, Germany.

CIGS (Cu(In,Ga)Se2) thin-film solar modules on glass substrates are currently on the verge of commercialization. CIGS modules fabricated on thin and flexible non-glass substrates will on the other hand open entirely new application areas. In addition, roll-to-roll manufacturing of such flexible CIGS modules contains the possibility of low-cost production. The process modifications required to realize the transfer from glass to non-glass substrates will be addressed in this paper. Best suited substrate materials for CIGS solar modules were titanium and stainless steel foils and polyimide films. Transferring the well established CIGS technology on glass to metallic substrates required development work in various fields: An additional Na supply was needed replacing glass as the standard source of sodium. NaF-precursor and -post-treatment as well as Na-coevaporation have therefore been investigated. Furthermore, suitable pretreatment methods and diffusion barriers had to be established. The successful implementation of these processes is demonstrated by CIGS single cells on titanium and stainless steel reaching efficiencies on small area (0.5 cm2) of close to 15% and 13% respectively (AM1.5 measurements). On large area (27 cm2) single cell efficiencies of more than 12% on titanium and more than 10% on stainless steel under AM1.5 illumination could be achieved. Furthermore, for the processing of polyimide substrates a low temperature CIGS deposition method had to be developed. Small area (0.5 cm2) cells on polyimide films with efficiencies of more than 11% (AM1.5) prove the successful establishing of this process. All these values have been achieved using industrial-type in-line deposition machines. The production of CIGS modules on flexible substrates required additional development work: Gentle and selective patterning techniques had to be established and for monolithically integrated modules on conductive metallic foils perfect electrical insulation barriers between substrate and solar module were needed. In this paper we will demonstrate that photolithography is a well suited patterning technique for all scribing lines necessary to produce solar modules on flexible substrates. SiOx barriers deposited by a high-rate microwave plasma-enhanced CVD technique have been proven to work well as electrical insulation barriers on metal foils. With these methods it has been possible to produce small area CIGS modules on flexible substrates reaching efficiencies of more than 7% under AM1.5 illumination.

8:45 AM F15.2

***In − situ* Investigation on Reaction Kinetics of $CuInSe_2$ Formation from Cu-In/Mo/glass Precursor during Selenization.** Woo Kyoung Kim[1], E. A. Payzant[2], S. Yoon[1], T. J. Anderson[1], O. D. Crisalle[1], V. Craciun[3] and S. S. Li[4]; [1]Chemical Engineering, University of Florida, Gainesville, Florida; [2]Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Materials Science and Engineering, University of Florida, Gainesville, Florida; [4]Electrical and Computer Engineering, University of Florida, Gainesville, Florida.

High temperature X-ray diffraction (HT-XRD) was used to investigate the reaction mechanism and kinetics of $CuInSe_2$ formation from Cu-In precursors on Mo/glass substrates during selenization. The precursors were prepared in a migration enhanced molecular beam epitaxial (MEE) reactor on Mo coated ultra thin glass substrates. The combined crystalline and amorphous atomic composition (Cu/In atomic ratio $\sim$ 1) and crystalline structure (Cu_2In and CuIn) of the as-deposited precursor were determined by ICP and XRD, respectively. The surface and cross-sectional structure, and local composition of the precursor were analyzed by SEM and EPMA, respectively. For selenization, selenium powder was placed in wells on the HT-XRD sample holder adjacent to the precursor film. The sample holder containing the selenium and precursor was covered with a thin aluminum or nickel foil and fixed to the holder with a Ni wire to minimize Se vapor loss. During the selenization while ramping temperature, the formation of CuSe followed by its transformation to $CuSe_2$ at higher temperature was observed. The formation of $CuInSe_2$ was initiated at a temperature between 250 and 300°C. Additionally, the production of $MoSe_2$ was clearly detected at temperatures above 400°C. The isothermal selenization experiments were performed at selected temperatures between 260 and 375 °C. The reaction kinetics was analyzed using both the Avrami and parabolic rate models to estimate diffusion limited activation energies of 124($\pm$19) and 100($\pm$14) kJ/mol, respectively.

9:00 AM *F15.3

In-Situ Sensors for CIGS Deposition and Manufacture. Ingrid Repins, ITN Energy Systems, Inc., Littleton, Colorado.

Recent years have seen record laboratory efficiencies for CIGS approach 20%, with multiple groups world-wide reporting small-area results exceeding 15%. A remaining challenge to the CIGS community is transferring these impressive efficiencies to high-yield, low-cost, manufacturing. In situ sensors can be an important aid in achieving this transfer, as they help characterize the process, optimize it in different process spaces, and maintain high yield. This paper presents a review of sensors useful for fabricating CIGS devices. Necessary capabilities, currently-available sensors, recently-introduced technology, and unfilled needs are described. Discussion focuses on sensors useful for CIGS co-evaporation, since it has produced the world-record efficiency small-area devices, and because the requirements it imposes on sensors are among the most rigorous of any deposition process, in terms of simultaneous exposure to multiple flux species, high temperatures, and Se vapor. Sensors to be used in manufacturing must also demonstrate superior stability over long operation times and compatibility with continuous processing. In-situ sensors can be separated into two general categories: those that characterize deposition conditions ("process" sensors), and those that characterize the growing film ("product" sensors). Process sensors comprise the bulk of CIGS sensors to date. Process sensors for CIGS co-evaporation are listed in the first portion of Table 1. To execute a higher level of control, product sensors are also necessary. Product sensors are listed in the first portion of Table 1. Advantages, difficulties, and references associated with each technique will be presented. Implicit in the use of a product sensor is the assumption that one understands what film properties are critical to device performance and what is the acceptable range for these parameters. For some CIGS properties, namely composition and thickness, this is understanding is indeed well-documented. Needs for future product sensors, and the risks associated with utilizing metrics that are not clearly linked to device performance, are discussed.

9:30 AM *F15.4

Rapid Synthesis of Chalcopyrite-type CuInSe2, CuGaSe2 And Their Solid Solution With Self-Heating. Takahiro Wada, Department of Materials Chemistry, Ryukoku University, Otsu, Japan.

Recently, we could successfully prepare chalcopyrite-type CuInSe2 (CIS) in 1 min or less without additional heating. Starting elemental powders, Cu, In and Se, were weighted to give a molar ratio of Cu, In, Se in 1:1:2. The starting powers and some ceramic balls were loaded into a ceramic container. The milling was conducted for only 1 min. A black powder was obtained in the container. The black powder showed a typical x-ray diffraction pattern of a chalcopyrite-type CIS. All the diffraction peaks were sharp and the small characteristic peaks of the chalcopyrite structure were clearly observed. The refined lattice constants were a = 5.79 and c = 11.62 A which were in good agreement with the previously reported data. Next we synthesized CIS from the Cu, In and Se powders in a transparent container. The elemental powders were instantaneously reacted, when the reactor vessel was strongly vibrated. The reaction generated a large amount of heat with a strong light. The product was confirmed to be the chalcopyrite-type CIS by X-ray diffraction analysis. From the results, we understood that the reaction was a kind of Self-propagating High-temperature Synthesis (SHS). In the usual SHS, the ignition is required so that the reaction may start. However the present reaction system, (Cu+In+2Se->CuInSe2), naturally ignites only by the mechanical stimulation. When the reaction starts, the reaction generates a large amount of heat with a strong light, and the reaction continues by the exothermic heat. In order to understand this kind of combustion reaction, we calculated ΔHf(CIS) by a first-principles calculation. The ΔHf(CIS) was obtained by subtracting the total energy of constituent elements from the total energy for CIS. The determined ΔHf(CIS) was -175 kJ/mol. When the exothermic heat of the reaction is all used for heating the produced CIS, the temperature of the CIS rises over the melting point. We have also successfully synthesized the other chalcopyrite-type compounds such as CuGaSe2, and its solid solutions with CIS. This synthesis process is applicable for fabrication of CIGS thin film solar cells. The deposition processes of CIGS thin films will be also discussed from the thermodynamic viewpoint This work was supported by the Incorporated Administrative Agency New Energy and Industrial Technology Development Organization (NEDO) under Ministry of Economy, Trade and Industry (METI). References [1] T. Wada, H. Kinoshita, S. Kawata, "Preparation of Chalcopyrite-type CuInSe2 by non-heating process", Thin Solid Films 431-432, 11-15 (2003). [2] T. Wada and H. Kinoshita, "Preparation of CuIn(S,Se)2 by Mechanochemical Process", Thin Solid Films (Proceeding of E-MRS 2004 Spring Meeting), submitted. [3] T. Wada and H. Kinoshita, "Rapid syntheses of Chalcopyrite-type CuInSe2 With Self-Heating", Proceeding of ICTMC-14, submitted.

SESSION F16: Wide Gap Chalcopyrites

Chairs: Wolfram Jaegermann and Shigeru Niki
Friday Morning, April 1, 2005
Room 2005 (Moscone West)

10:30 AM *F16.1

What is Wrong with Wide-Gap Chalcopyrites? Uwe Rau, Institute of Physical Electronics, University Stuttgart, Stuttgart, Germany.

One of the potential advantages of the $Cu(In,Ga)(Se,S)_2$ alloy system for photovoltaic applications consists in the possibility to build semiconductors with band gap energies Eg in a range between 1 and 2.4 eV. This range covers the relevant part of the solar spectrum and offers the opportunity to construct tandem cells from the same polycrystalline thin-film material system. Single junction $Cu(In,Ga)Se_2$ solar cells with $E_g \sim 1.15$ eV exhibit an excellent photovoltaic quality with a record efficiency in excess of 19 %. Unfortunately, attempts to fabricate solar cells from the wider band gap alloys with an efficiency sufficient to provide a top cell for a tandem structure have failed so far. The contribution yields a review on the differences in the electronic, chemical and structural properties that show up between the standard high efficiency $Cu(In,Ga)Se_2$ devices and their wide-gap counterparts. The differences start with the growth of the absorber layer and the increasing tendency of the material to build secondary phases when choosing increasing Ga or S contents in the alloy. When prepared under identical conditions $Cu(In,Ga)Se_2$, the grain size of the films decreases with increasing Ga-content. Moreover, the general opto-electronic material homogeneity also decreases when increasing E_g via increase of the Ga and/or S content. Large qualitative differences occur also in the concentration of recombination centres and/or their energetic position within the forbidden band gap. All these differences will be evaluated in terms of a quantitative device model demonstrating that the relatively low performance of wide-gap Cu-chalcopyrites results from the sum of many small differences rather than by a single major failure.

11:00 AM F16.2

Band Gap and Interface Engineering of Wide Gap Cu-Containing Chalcopyrite Absorbers by Dry (In,Ga)-S Surface Treatments. David Fuertes Marron, S. Lehmann, Th. Schedel-Niedrig, J. Klaer, R. Klenk and M. Ch. Lux-Steiner; Hahn-Meitner Institut, Berlin, Germany.

Thin-film solar cells based on wide gap Cu-containing chalcopyrite absorbers show poor performances when compared to their low gap counterparts. To a large extent, limitations in their performance have their origin in absorber/buffer interface related issues, in form of a non-ideal band alignment between components and/or due to high densities of interface states. In contrast, the absorber/buffer interface does not seem to represent a fundamental limitation in the performance of low gap, high efficiency chalcopyrite solar cells using the same partner as buffer layer, namely CdS. It can be argued that a single compound may not be the optimal choice for building the interface as buffer layer with the entire family of chalcopyrite absorbers, ranging in gaps between ~1 eV for CuInSe2 and 2.4 eV for CuGaS2. However, also the question arises, how far wide gap chalcopyrites can be forced to work with CdS as partner but with minor electronic losses at their interface. We explore the possibility of overcoming fundamental limitations of wide gap Cu-containing chalcopyrite absorbers related with the performance of the absorber/CdS interface, by means of band gap engineering in the near surface region of the absorbers. As this part of the absorber controls the interface formation and its electronic properties, the approach serves ultimately as a means of interface engineering, aiming at the optimisation of the absorber-buffer heterointerface. Device grade CuGaSe2 (CGSe) and CuInS2 (CIS) thin films for photovoltaic (PV) applications have been subjected to dry surface treatments based on In-S and Ga-S by means of chemical vapor deposition (CVD) carried out in an open system. Structural and electronic characterization of as-grown films and processed devices show the effective incorporation of In and S in the near-surface region of CuGaSe2 thin films and of Ga in that of CuInS2. Film properties have been monitored from time and temperature processing series by means of XRD, SEM, and EDX, revealing the influence these processing parameters have on the formation of alloys and secondary phases in the uppermost part of the absorber film. TEM microstructural analysis of selected samples have helped determining the depth of the modified region, which extends from few to some tens of nanometers, depending on the sample and processing conditions. Related devices based on modified absorbers have shown improved PV performance compared to reference cells, which in the case of CGSe includes the entire composition range from Cu-rich to Ga-rich as-grown absorbers . Numerical simulations of device performance will be presented based on the inputs from the structural characterization. From these results, it is demonstrated that open-tube CVD provides a convenient way for tailoring composition gradients and band gaps in both selenide and sulfide compounds.

11:15 AM F16.3

Characterization of the Electronic Properties of Wide Bandgap $Cu(InGa)(SeS)_2$ Alloys. Adam F. Halverson[1], Peter T. Erslev[1], JinWoo Lee[1], Eric D. Tweeten[1], David Cohen[1] and William N. Shafarman[2]; [1]Physics, University of Oregon, Eugene, Oregon; [2]Institute of Energy Conversion, University of Delaware, Newark, Delaware.

The $Cu(InGa)(SeS)_2$ sulfur containing chalcopyrite alloys are being developed as wider gap materials for possible incorporation into CIGS thin film based solar cells. Of particular interest are the alloys with gaps greater than 1.5eV. Sample devices with these S containing absorbers were deposited on Mo coated soda lime glass using a physical vapor deposition process at the Institute for Energy Conversion (IEC). Films were deposited with Cu-rich compositions and then, to form the devices, the Cu_xS_y on the surface was etched off before finishing the devices with the CdS and ZnO contact and window layers. To determine the electronic properties of these samples we used drive-level capacitance profiling (DLCP) to establish carrier and deep acceptor densities, high frequency admittance measurements to estimate hole mobilities, and transient photocapacitance (TPC) together with photocurrent (TPI) sub-band-gap spectroscopies to obtain the spectra of defect related optical transitions. To date we have been concentrating our measurements on the $CuInS_2$ endpoint sample device. Under AM1.5 illumination these devices exhibited a conversion efficiency between 6.8 and 7.5% with open circuit voltages between 0.62 to 0.64 volts. From DLCP we have determined carrier densities of roughly $1x10^{16}$ cm^{-3} for these $CuInS_2$ absorbers. These are roughly 3 to 10 times higher than typical $Cu(InGa)Se_2$ alloys produced at IEC. However, the hole mobilities appear to be low: below 1 cm^2/Vs. The photocapacitance spectra clearly exhibit optical gaps lying in the 1.50 to 1.55 eV range with very sharp bandtails (the Urbach energies are below 18meV). Unlike the TPC spectra for the $Cu(InGa)Se_2$ alloys that exhibit a single band of optical transitions lying roughly 0.8eV above E_V, the $CuInS_2$ samples exhibit two defect related optical transitions. The first of these appears to lie within 0.5eV of the valence band and gives rise to a positive TPC signal. This means that the detected optical transitions correspond to the excitation of valence band electrons into an empty defect level. Due to the poor signal-to-noise at optical energies below 0.5eV, we have not been able to establish a more accurate energy threshold for this transition. The second defect transition gives rise to a *negative* TPC signal with an energy threshold of 1.0eV. This implies a transition between a filled defect level within the depletion region and the conduction band. It also means that the residual hole in the defect must have a large thermal barrier for emission into the valence band (of at least 0.4eV). This is the first time such a defect transition has been identified in any of the chalcopyrite alloys we have studied to date. A defect density for this transition is hard to estimate, but it appears to lie at or below 3 x $10^{16}cm^{-3}$. The influence of this newly discovered defect band on the performance of these sulfur alloy devices will be discussed.

11:30 AM F16.4

Band Gap Fluctuations in Cu(In,Ga)Se2 Thin Films Analyzed by Absorption and Photoluminescence Measurements.

Julian Mattheis, Thomas Schlenker, Martin Bogicevic, Uwe Rau and Juergen Heinz Werner; Institute of Physical Electronics, University of Stuttgart, Stuttgart, Germany.

Spatial fluctuations of the band gap energy of the photovoltaic absorber material lead to a deterioration of the power conversion efficiency of solar cells. This deterioration is caused by the fact that the photogeneration of charge carriers is determined by the average band gap whereas carrier recombination is enhanced by the low band gap parts of the absorber. This contribution presents an analysis of Cu(In,Ga)Se2 thin-films by room-temperature absorption and photoluminescence measurements. In these films, the absorption spectra exhibit a broadened transition instead of a sharp edge expected from a single-value band gap. Accordingly, the photoluminescence spectra are also relatively broad and are, additionally, shifted towards energies well below the absorption transition. These experimental results fit well to an analytic model that describes spatial band gap fluctuations by a Gaussian distribution of band gap energies [1]. This model computes absorption and luminescence spectra via direct band-to-band transitions in a spatially inhomogeneous semiconductor. Fitting the model to the experimental absorption and luminescence data yields quantitative information on the band gap fluctuations in terms of mean value and standard deviation of the band gap distribution. The standard deviations obtained range from 30 to 70 meV. As a direct consequence of spatial inhomogeneities the achievable open-circuit voltage decreases by 20 to 100 mV as compared to homogeneous absorbers with a single-value band gap that is identical to the mean band gap in the inhomogeneous absorbers. We also investigate the influence of the gallium content on the homogeneity of the Cu(In,Ga)Se2 absorbers. The degree of inhomogeneity increases with increasing gallium content and reaches a maximum for equal amounts of In and Ga in the alloy indicating alloy disorder as one possible source of band gap fluctuations. The contribution will also discuss some implications of our results on the length-scale of the inhomogeneities as well as possible refinements of the theory with respect to free-to-bound transitions. [1] U. Rau, and J.H. Werner, Appl. Phys. Lett. 84, 3735 (2004)

11:45 AM F16.5

Structural, Optical and Electronic Characterization of $CuInS_2$ Solar Cells Deposited by Reactive Magnetron Sputtering.

Thomas Unold, Tobias Enzenhofer and Klaus Ellmer; Hahn-Meitner Institut, Berlin, Germany.

Thin-film chalcopyrite-based solar cells are usually prepared by coevaporation or by a sequential process consisting of the sputtering of metal precursors and annealing in a sulphur or selenium atmosphere at about 500°C. For a large scale production of thin-film solar cells a direct one-step, large area deposition process would be advantageous. Magnetron sputtering is a well established deposition method, which allows low temperature thin film growth on large areas. However, up to now magnetron sputtering has been mainly used for optical (architectural) glass coatings, as well as for the preparation of electronic contacts and for the deposition of metallic precursors layers. In this study CuInS2 absorber films have been deposited directly by reactive magnetron sputtering of copper and indium using an Ar-H2S atmosphere. The Mo and Zn0 contacts as well as the CdS buffer layer were prepared by the standard processes of the Hahn-Meitner-Institut. In order to gain insight in the reactive sputtering process, the substrate temperature, H2S/Ar ratio and Cu/In ratio have been systematically varied. The structural, optical and electronic properties of the solar cells were analysed by transmission/reflection, photoluminescence, Raman, REM, current-voltage and quantum efficiency measurements. We find from Raman and XRD measurements that for substrate temperatures below 450°C Cu-Au defect ordering dominates the crystal structure. When rising the substrate temperatures we find that films prepared above 450°C show dominant chalcopyrite ordering, even for near stochiometric and In-rich compositions. Indeed we have been able to prepare near-stochiometric solar cells with close to 6% conversion efficiency without the need of a KCN etching step, compared to 8% conversion efficiency for Cu-rich deposited cells, for which the typically formed CuS surface layer has been removed by a KCN etching step. Photoluminescence measurements of the films reveal a level structure which is very similar to the level structure found for films from the standard sequential process or coevaporated films. This indicates that the ion bombardment of the growing film in the reactive sputtering process does not introduce fundamental changes to the defect structure of the films. However, the magnitude of the near-band edge photoluminescence signal is weaker than in the sequentially processed films. Also, quantum efficiency measurements indicate a decreased carrier collection in the long-wavelength region pointing to a lower diffusion length in our devices. From these findings we conclude that the approximately 100 meV smaller open-circuit voltage in our reactively sputtered devices is mainly caused by increased number of electronically active defects compared to the sequentially prepared absorbers. It should be possible to further reduce the defect density by optimizing the deposition parameters.