SYMPOSIUM F
Thin-Film Compound Semiconductor Photovoltaics
March 28 - April 1, 2005

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* Invited paper
9:15 AM F1.4
Analysis of Cu(InGa)Se₂ Alloy Films Optical Properties and the Effect of Cu Off-Stoichiometry. Paulson D. Puthur1 and W. N. Shafarman1; 1Institute of Energy Conversion, University of Delaware, Newark, Delaware; 2Miasole, Inc., San Jose, California.

Variable angle specular ellipsometry (SE) has been used to characterize Cu(InGa)Se₂ thin films as a function of relative Ga content and to study the effects of Cu off-stoichiometry. Uniform Cu(InGa)Se₃ films were deposited on Mo-coated soda lime glass substrates. 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)Se₂ films immediately after peeling them from Mo-coated soda lime glass substrates. Optical constants of Cu(InGa)Se₂ were determined over the energy range of 0.75-4.6 eV for films with 0=Cu/(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 Cu(InSe)₂ and Cu(InGa)Se₂ [with Ga/(In+Ga)=0.3] films with 0.3=Cu/(In+Ga)=1. Films with Cu/(In+Ga) less than ~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 Cu(InSe)₂ band structure and optical properties. Absorption 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 the value of the band gap. 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. Aloisi, M. Garriga, C.A. Duran, J. Appl. Phys. A 74, 659, (2002).

9:30 AM F1.5

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 materials such as CdTe and CuInSe₂, whether as-grown or after appropriate post-growth treatment, may have electronic properties which are advantageous to charge separation and solar cell operation[3,4]. 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 techniques. Towards this end, significant enhancement in photo-response near grain boundaries in CdTe and CuInSe₂, and even in CdTe and CdS solar cells, consistent with models put forth in reference 2, was observed via near-field Optical Beam Induced Current (n-OBIC) [4]. A systematic study of the effects of Cu-off-stoichiometry 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 on the spectral response at each peak energy. As such, this reduction is 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 films were observed to show an anomalous p-d repulsive interaction in Cu-poor CIGS that 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 a debate on why slightly Cu-poor CIGS are associated with high efficiency solar cells, recent work has implied an important role of Cu deficiency at surfaces and grain boundaries. Persson and A. Zunger, Phys. Rev. Lett. 91, 205401 (2003) Thus it is important to understand the effect 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 > 0.3. Understanding how the role of Cu 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 be important to understand the properties of CuGaSe₂ and high-Ga CIGS.

10:30 AM *F2.1
Synchrotron-Based Spectroscopy for the Characterisation of Surfaces and Interfaces in Chalcophosphate Solar Cells. Jens Germain1, Immo Koestlhuber1, Christian-Herbert Fischer1,2; 1ISE 2, Hahn-Meitner-Institut, Berlin, Germany; 2Fachbereich Physik, Freie Universität 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 describe some synchrotron based state-of-the-art spectroscopic tools 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 devices. The CISSY end station allows in-situ 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*


1 Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany; 2SE 6, Hahn-Meitner-Institute, Berlin, Germany; 3Research 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 (CIS) thin films with the n-type dopant KCl are a fundamental property of this material, 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 from 10 eV to 40 eV. The resulting experimental band structure will be presented and compared to calculations by Jaffe et al. (PRB 24 (1983) p. 5822).

11:30 AM F2.3

Se Vacancy as the Origin of Light-Induced Metastability in Cu(In,Ga)Se2. Stephan Lany and Alex Zunger; National Renewable Energy Laboratory, Golden, Colorado.

Cu(In,Ga)Se2 (CIGS) photovoltaic devices often exhibit pronounced light-induced metastability. This phenomenon, which has been observed in CIGS solar cells, can be explained by the formation of metastable electronic states that are not present in the equilibrium CIGS structure. The formation of these metastable states can lead to changes in the device performance, such as temporary degradation and recovery of the efficiency. While CIGS is a promising material for solar energy conversion, understanding and controlling its metastability is crucial for the development of more stable and efficient photovoltaic devices.

The formation of metastable states in CIGS is typically triggered by the application of light or an electric field, which can cause the formation of defects in the material. One of the most commonly observed defects in CIGS is the Se vacancy, which is known to be a strong trap for carriers. When a Se vacancy forms in the CIGS lattice, it can trap a free electron, leading to a temporary decrease in the device performance. This effect is called light-induced metastability because it is only observed under illumination.

While the formation of Se vacancies is not unexpected, the question of whether these metastable states are actually responsible for the observed light-induced effects has been a subject of much debate. Some researchers have proposed that the metastability in CIGS is due to the formation of complex defects, such as divacancies or trivacancies, which are known to be strong traps for carriers. However, the exact nature of the metastable states in CIGS remains a topic of ongoing research.

In this talk, we will present recent experimental evidence that supports the idea that Se vacancies are the primary cause of the light-induced metastability in CIGS. We will discuss the results of our in-situ analysis of wet-chemical reactions at the CIGS surface, which has allowed us to identify the Se vacancies as the dominant defect responsible for the metastability. Our results provide a clearer understanding of the mechanisms underlying the light-induced effects in CIGS, which is essential for the development of more stable and efficient photovoltaic devices.

1:45 PM F3.2

n-type doping of CuInSe2 and CuGaSe2: Is it possible? Alex Zunger, Cla Persson, Stephan Lany and YuJun Zhao; National Renewable Energy Laboratory, Golden, Colorado.

While CuInSe2 (CIS) can be obtained both p-type and n-type by controlling the growth conditions, improving the efficiency of CuInSe2-GaSe2 (CIGS) solar cells is severely hampered by the difficulty to obtain type inversion for Ga contents exceeding x ≈ 0.3. In CuGaSe2 (CGS), the choice of n-type dopant is even more problematic: bulk Na doping results in an unwanted p-type phase. We have shown that while bulk Na doping can produce n-type doping in CGS, the incorporation of Na into the CIGS crystal lattice is limited by the formation of the Na-In complex, which results in a decrease of the Na concentration ratio and thus an increasing amount of p-type CIS in the layer. The experimental results obtained are considered as a direct evidence for the incorporation of Na into the CIS crystal lattice. We 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 (VSe2–, In+) and thus suppresses the formation of the p-type 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 p-type structure. Under specific growth conditions, such as in situ observation of Na-induced structure changes in CuInSe2 and CuGaSe2, the formation of the Na-Se complex shows a different behavior as compared to the formation of the Na-In complex. While a Na-Se complex is formed in CIS, a Na-In complex is formed in CGS. This difference is attributed to the different interactions between Na and Se vs. Na and In.
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 p-type-selective 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 extent of Cu/CdTe device performance is not yet fully understood. The critical incident beam angle results. All Cu/CdTe/GaSe bilayers, Microscopy (SAM), are used to probe investigations efforts. Good Gwynedd, United Kingdom; 2:00 PM **F3.3** A Study of Phenomena Related to the Interaction of Cu with the CdTe/TiO2 Interface. Gianluca Tettamanti and Sally Asher; National Renewable Energy Laboratory, Golden, Colorado.

Influence of Bi Doping on CdTe Based Solar Cells. Carmen Maria Ruiz1, Osvaldo Vigi-Galán1,2, Edgardo Saucedo1, Gerardo Contreras-Pérez1, Baja Cervera1 and Verónica Bernúdez1; 1 Física de Materiales, Universidad Autónoma de Madrid, Madrid, Spain; 2 Escuela Superior de Física y Matemáticas, Instituto Politécnico 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 surface work function limit the behaviour of these systems and hinder 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 degrading 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 Sn or Mo were used and chemical etchings such as bromine-methanol or PN (phosphoric acid-nitric acid) were performed to create a p-type region on the CdTe surface and to decrease the work function. Finally alloys such as SnTe or Cu2Sn are being used with good results. All these efforts have improved solar cell efficiency, but modifications on CdTe properties have not yet been optimised for these systems. Recent investigations on bulk CdTe Bi doped have been published. This demonstrates that resistivity on single crystals can be reduced up to four orders of magnitude with Bi concentration. Combined with decreasing in resistivity, an important increase of photocurrent 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 limited and atom migration is minimised. In this work we present the results of doping with Bi CdTe thin films and analyze effect CdS/CdTe bilayer. 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 characterization show that thin films reproduce bulk material behaviour with a decrease of resistivity and an increase in power conversion efficiency. Following the same procedure, CdS/CdTe solar cells were prepared and their properties studied as a function of Bi concentration.

3:30 PM **F4.1** A Comparison of As Doping with ex situ Cadmium Chloride Treatment of CdTe Solar Cells. Stuart James Irvine1, Vincent Barrios2, Rachel L. Rowlands3, Euirig W. Jones4, Ken Durrow5 and Guillaume Zoppi; 1Chemistry, University of Wales Bangor, Bangor, Gwynedd, United Kingdom; 2:30 PM **F3.4** Thin film structures of CdTe and Cs 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 properties. In this study there were two sets of layers grown. The first was undoped with the CdS grown at 3000 C and the CdTe grown at 3500 C. These layers were subsequently coated with CdCl2 and annealed under a variety of different conditions. The second set of layers was grown with arsenic doped CdTe layer. The CdTe layers were doped with tri-methylarsine (TMA) and processed into test devices without CdCl2 treatment. In both cases a considerable increase in Jsc was observed over the undoped but the IV characteristics were different with higher short circuit 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 5000 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 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** In situ Bi Doping On CdTe Based Solar Cells. CarmenMaria Ruiz1, Osvaldo Vigi-Galán1,2, Edgardo Saucedo1, Gerardo Contreras-Pérez1, Baja Cervera1 and Verónica Bernúdez1; 1 Física de Materiales, Universidad Autónoma de Madrid, Madrid, Spain; 2 Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, Mexico D.F., Mexico.

Grain boundaries of CdTe/CdS solar cells 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
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)
photocurrent parameters. The changes of these semiconductor plates 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., Orletskiy V.B.,

F5.2
Cu2Bi5S8, Cu2Bi5Se8, Ga2Bis3, and Cu2Ga5Bi5S8 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 reported, that we expect to be
promising candidates for photovoltaic applications. Cu2Bi5S8 (Eg=1.2
eV) has been previously reported to be a suitable solar absorber.1
Three additional compounds: Cu2Bi5Se8, Ga2Bi5S8, and Cu2Ga5Bi5S8,
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 Cu2Bi5S8, and the
analysis of phase stability as a function of composition. We will also
report results on the exploratory synthesis and characterization of
Cu2Bi5Se8, Ga2Bi5S8, and Cu2Ga5Bi5S8, 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 2008, 18, 190-194.

F5.3
Spray Deposition of Solid-State Nanocomposite CuInS2/TIO2
Solar Cells. Mariam Nann, 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
application of these advanced capabilities. (1) Estrella, V.; Nair, M.T.S.; Nair, P.K.
Semiconductor Science and Technology 2008, 18, 190-194.

F5.1
Photovoltaic Effect in the Anyotype 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, Chernivetskaja, Ukraine.

Photodiodes based on InSe–GaSe heterojunctions (HJ) are analogues
of Si–structures for operating in high radiation conditions. The
photocurrent 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 photocurrent 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
photocurrent parameters of a n–InSe–p–GaSe HJ. They indicate on
a possibility to increase essentially the photocurrent efficiency in
such structures. For instance, for structures subjected to a pressure
of about 35 to 40 kPa an increase of the short 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
SESSION F5: Poster Session: Posters I
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)
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 nanopolys of a few microns thick nanocrystalline 

1.1 eV and 1.68 eV that have to be grown one on top of the other. The growing interest in hydrogen has resulted from the consideration is correct assuming that hydrogen is generated using a source of renewable energy are in the incubation stage. 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 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 ZnTe:Cu, MnO2, Te2- alloys. We observe an extension of the photocurrent response towards lower photon energies. This 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).

Abstract Withdrawn

Copper indium diselenide, CuInSe₂, 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. Additionally, gallium and sulfur has been used to produce graded bandgap structures. This will enhance the internal electric field and obtain a higher charge carrier collection. A critical problem related to the selenium growth process is the formation of a graded band 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 CuIn₁₋ₓGaₓSe₂ (CIGS) thin films, where the layers represent best efficiency in CIGS solar cell of 19.5%. Once a graded CIGS film is formed, converting the film to a homogeneous single-phase material becomes extremely difficult. In order to increase the band gap in the near surface region, films are reacted with sulfur 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-metallization step in which a certain fraction of the selenium diffuses to the surface of the absorber film is replaced with sulfur. So far CuInSe₂, GaSe₂₋ₓ, and Ni-Al-AI transparent conducting window bilayer by RF magnetron sputtering and Ni-Al front contact fingers by s-beam evaporation technique. Aim of this study is to link the nano-scale structure in the CIGS thin films and the influence of Ag diffusion on change of electrical and photovoltaic characteristics of Ag/CdTe junctions. CdTe thin films were deposited on glass substrates by close-spaced sublimation (CSS) technique. The prepared CdTe films were high resistivity (≥10⁴-10⁷ Ohm.cm) n-type conductivity. The following thermal annealing of n-type CdTe at 400°C 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 X-ray diffraction (XRD), optical absorption and photoelectrochemical measurements. Resistivity studies of Ag/CdTe structures exposed to sequential cycles of thermal (in dark) or photoannealing (under white light illumination) at fixed temperatures (50-140°C) showed that the rate of change of resistivity for photoannealing is significantly 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 mechanism of acceleration of Ag diffusion under illumination was not clear to us, but it was found that the annealing of Ag/CdTe at 4000°C for 1h resulted in formation of Ag²Te phase and decreases the band gap up to 0.07eV. Electrical and photovoltaic characteristics of Ag²Te/CdTe junctions are presented.
Excitonic Resonances and Lattice Vibrations in CuInSe₂ Crystals. N. Shigekuni, H. Nakamura, Technical University of Moldova, Chisinau, Moldova.

The lines n = 1 of A, B and C excitonic series have been found in the region of the well known interval of CuInSe₂. A structure of maxima 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 excited states and C series lines 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 3.01 and 3.01 meV and band gaps are respectively equal to 1.0760 and 1.0734 eV. In the high-energy region of spectrum two bands at 1.2864 and 1.3092 eV were found. These bands are due to C excitons. 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 n(1B) - n(1A) is equal to 6.2 meV and n(1C) - n(1B) is equal to 0.243 eV (n(1A), n(1B) and n(1C) 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.3-VI.2 CuInSe₂ optical constants provided that the crystal-field Δc = Eg intervals between Δ7(V1) - Δ7(V2) and Δ7(V2) - Δ7(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 Δ7(V1) - Δ7(V2) and Δ7(V2) - Δ7(V3) is determined from n = 1 and n = 2 excited states and calculated according to the energy position of n = 1, n = 2 and n = 3 lines. Taking into account that E1 is equal to 0.0034 eV and E2 is equal to 0.2374 eV, we have calculated the Δc = Eg energy intervals of Δ7(V) = 0.0514 eV and Δ7(V) = 0.2367 eV. Thus, the given values Δc and Δc result in the splitting of bands Δ7(V1) - Δ7(V2) equal to 0.0334 eV and Δ7(V2) - Δ7(V3) equal to 0.2367 eV. Infrared reflectivity spectra of CuInSe₂ crystals have been investigated for the polarizations E||c and E⊥c. The contours of the reflectivity spectra were calculated and phonon parameters and dielectric constants are determined. The effective ionic charges of Cu, In and S ions in these materials were determined according to the previously proposed model [2]. The effective ionic charges of CuInSe₂ and CuGaSe₂ are rather different for E||c and E⊥c polarizations. From these results we introduced a parameter of effective ionic charges anisotropy Δ2. This parameter represents the difference of the effective ionic charges measured in E||c and E⊥c polarizations. Δ2 characterizes the electronic cloud of ions and its deviation from the spherical form. [1] J. E. Jaffe and A. Zunger, Phys. Rev. B 28, p. 5822, 1983 [2] K. Watanabe and T. Ogawa, Japan J. Appl. Phys. 19, p. 249, 1980.

F5.15 In-situ X-ray Photoelectron Spectroscopy Study on the Oxidation of CuGaSe₂. Thomas Johann Schedel-Niedrig, Roland Weber, Marin Rusu1, Martha Lux-Steiner 1, Hendrik Bluhm2, Michael Haevecker2, Evgenia Karpova3, Mart Kropatsch2 and Robert Schlogl2.

1SE2, Hahn-Meitner-Institute Berlin, Berlin, Germany; 2Fritz-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 XPS 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 GaOₓ 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 is formed at the thin film surface, Na₂O and Na₂CO₃ after thermal and native oxidation, respectively. The amount of these sodium oxide compounds depends on the Na content on the as prepared sample. 


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 with 1 MeV protons. The analyzed results of spectral response of CIGS solar cells irradiated proton showed good agreement with the measurement. Diffusion length of proton irradiated CIGS solar cells can be estimated by fitting of spectral response. From these results, KI was estimated to be 4.7±0.5. This value is smaller than that of Si solar cells. This implies that 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 characterization is useful for analysis of radiation response of solar cells. From comparison of space solar cells before and after irradiation test, the information of defects in the solar cells can be acquired. We have analyzed radiation response of CuInGaSe₂ 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 with 1 MeV protons. The analyzed results of spectral response of CIGS solar cells irradiated proton showed good agreement with the measurement. Diffusion length of proton irradiated CIGS solar cells can be estimated by fitting of spectral response. From these results, KI was estimated to be 4.7±0.5. This value is smaller than that of Si solar cells. This implies that CIGS solar cells have higher radiation tolerant than that of 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 CIGS solar cells standard cell and irradiated CIGS solar cells using the same method and compared with the front-end-defect pair model. From this result, the radiation defect may be point defects. The radiation damage coefficient of CIGS solar cells were revealed by spectral response measurement and with the solar device simulator. This data is necessary to analyze the radiation response of CIGS solar cells and the front-end 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 CIGS solar cells and that appear when and where the Fermi Level rises 0.8 V above the VBM as CIGS diffuses out the crystal. Analysis is made that the loss of Cu after CIGS diffusion is not accommodated solely by formation of ordered defect crystals because 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)Se₂ [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 15%. At a condition of the band gap around 1.2 eV and the origin of this discrepancy between the theory and the experiments is a saturation of open circuit voltage (Voc), which is correlated with band alignment at p-n junction in the cell structure. Therefore, characteristics of the wide band gap CIGS based solar cell is desired. Recent studies of electron microscopy about the CIGS/CIGS interface indicate their compositional transition regions gets thinner with an increase of the Ga substitution ratio. It means that the Ga content in CIGS is well suppressed, is necessary for the evaluation of the interface with 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 CIGS and the wide band gap CIGS. It was found that an Ar ion beam etching at the thickness of the ion kinetic energy (Ek) above 500 eV for long time caused a development of metallic feature in a valance band of the CIGS layer. This means that the ion beam energy (Ek) 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 Ek of 350 eV, the semiconducting feature was conserved even after a long etching time over 2000 s. It is noteworthy that, in the CuInₓGaₓGa₂₋ₓSe₂ (Se) 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 CIGS and the wide gap CIGS revealed a variety of electronic structures; Ga diffusion and reduced band gap of the CIGS at the interface regions, serious sample-dependence of band gaps in the CIGS layer near the interface. In spite of the higher Ga concentration in the CIGS layer, no energy splitting between conduction and valence band maximum in the CIGS was observed. The band gaps of the CIGS with Ek above 500 eV was not expanded, and in comparison with that of the interfaces over 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 Voc, which should also induce the decrease of conversion efficiency.
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 atoms hence are not preserved in an overall sense as they are lost in an outgassing process which preserves 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 the open circuit voltage must be increased. Amorphous metal diffusion barriers at the back contact and SiON between grains might do this.

F5.20 Thin CuInS2 Films Prepared by MOMBE: Interface and Surface Properties. Christian Pettenkofer1, Carsten Lehmann1 and Wolfram Calvet1; 1ISE, HMI, Berlin, Germany; 2Specs Gmbh, Berlin, Germany.

CuInS2 (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 an InN buffer layer on H-terminated Si(111) substrates. No carbon contaminations from the sulfur precursor are incorporated in the samples. Deposition temperature and precursors' partial pressures or Cu/In ratios were used as thin film parameters. The CuN layers form the Cu-rich film. A CuS surface phase is formed for Cu-rich films. Cu to In ratio and growth temperature were varied and optimized to obtain near stoichiometric CIS films. A band alignment for the interface with respect to the bufferlayer and Si will be discussed.

F5.21 Band Offsets at the ZnSe/CuInS2 Interface. Olga Papathanasiou1, Susanne Siebentritt1, Iver Lauermann1, Thomas Hahn2, Heiner Metzner2 and Martha Lux-Steiner1; 1Hahn-Meitner-Institut, Berlin, Germany; 2Friedrich-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 preparation 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 top layer has to be known. It has been shown before that CuInS2 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 lower band gap of ZnSe a solar 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 by 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.

The temperature were varied and optimized to obtain near stoichiometric CIS films. A band alignment for the interface with respect to the bufferlayer and Si will be discussed.
Different Hgl TOe paper investigates the low temperature We have constructed a system to detect very low-intensity of Cu matrixes. The high damage in the thin-film Cds/CdTe absorption structure of the material producing so far unknown states in the CuGaSe2 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 the CdTe-based polycrystalline CuGaSe2-thin films is given. Photoluminescence Studies of CuGaTe2 Crystals. Due to their optical absorption coefficient and optimal bandgap energy, I-HI-2I chalcogenide compounds have captured lot of attention as an alternative to silicon based photovoltaic devices. CuGaTe2 has a direct optical bandgap with the room temperature energy about 1.22 - 1.24 eV. Natively, CuGaTe2 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. Consequently, EL can be detected from the cells at voltages at or near the photogenerated bandgap. This work supported by MREI Thin Film Partnership program. Photoluminescence is a convenient and powerful method to probe the material properties of an operating solar cell and to investigate the defect states present in the semiconductor material. The model 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 and implant 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 1016, 1017, and 1018/cm2, 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 MREI Thin Film Partnership program. Effects of Extrinsic Doping on the Photoluminescence of CuGaSe2 Thin Films. 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 current densities less than 2 mA/cm2, 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 relative 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. Unlike the visible and UV-PL emissions of Ge-implanted and annealed films differ strongly. Obviously, Ge-implantation in conjunction with results in a high localized optical absorption of the material producing so far unknown states in the CuGaSe2 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 CuGaSe2-thin films is given. Photoluminescence from Ion Implanted CdTe Crystals. We have successfully used in order to determine intrinsic and extrinsic defects created annealed samples was changed. This implies to the enhanced recombination model of compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples. Surprisingly, the CuGaTe2 as-grown samples showed lower density of the defects in compensated samples.

F5.30

CELLO Measurements of CIGS and μcSi Solar Cells. Stefan Matheijesen, Juergen Carstensen, Helmut Fiehl, Georg Voorwinds and Helmut Stiebig; 1 Chair for General Materials Science, Faculty of Engineering, Christian-Albrechts-University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany; 2ZSW Stuttgart, Stuttgart, Germany; 3FZ 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 impressing a fixed current or voltage. Several sets of data obtained by measuring current or voltage 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 defects in individual solar cells with high lateral resolution (~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) mm² 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)Se₂ 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 defects in the μcSi layer, the impact of the metal back contact on the serial resistance of the cell. The impact of these 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 5 mm) 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 modules. An explanation to the influence of these defects on the efficiency of the cells will be presented, demonstrating possible relative efficiency gains > 10 \%.

F5.31


Numerous deep electronic state (DES) signatures have been detected with capacitance transient (CTR) measurements from batches of CdTe solar cells fabricated as tandem cells. The DESs are characterized by their activation energy Ea and apparent cross section σ. A typical CTR measurement consists of a light pulse 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 CTRs have not been thoroughly studied in CdTe solar cells. The concentrations of these DESs sometimes exceed 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. 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)Se₂ 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 defects in the μcSi layer, the impact of the metal back contact on the serial resistance of the cell. The impact of these 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 5 mm) 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 modules. An explanation to the influence of these defects on the efficiency of the cells will be presented, demonstrating possible relative efficiency gains > 10 \%.

F5.32


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/CIGS 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 photocconductivity 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 [TOC/CdS/CIGS] approximation for the solar cell. There are a number of parameters that influence the band structure, and hence if and how much distortion is observed. These include the magnitude of the CBO, the doping of the p- and n- layers, the defect density of the CdS, the thicknesses of the CdS and TCO layers. The key value, however, is the maximum energy difference between the conduction band 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 Price3 and Kevin Cooper2; 1Physical Science, Morehead State University, Morehead, Kentucky; 2Lewis County High School, Tananaug, Kentucky.

Open-Circuit Voltage Decay (OCVD) is a common technique used to characterize various 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 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 tens of seconds and the magnitude of the initial applied voltage pulse. We will describe the correlation between

\[ \sigma = \alpha + \beta \text{Ea} \]

Within each MNR family, Ea can vary by several tenths of an eV and \( \sigma \) can vary by several orders of magnitude. There are grounds to believe that the signature majority of the MNRs belongs 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 \( \sigma \) and Ea within the MNR families are discussed. The CELLO technique allows to detect and characterize the DESs that last 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 CTRs have not been thoroughly studied in CdTe solar cells. The concentrations of these DESs sometimes exceed 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.

\[ T_2 \]

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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**

We investigated copper indium gallium diselenide solar cells with different gallium concentrations 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 biased, leading to forward currents, so that all minority carriers resulting from recombination or generation recombine and 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 not 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 reverse bias levels, each experiment exhibits similar, but not always identical, amplitudes 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 rapidly smaller with increasing measurement temperatures. 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 Cu/Co/Si/In/Ga structure (metal-insulator-semiconductor structures). Moreover we believe that the DLTS low temperature minority and majority carrier signals observed might not stem from 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)Se2 Using Deep Level Transient Spectroscopy. Steven W. Johnston**

We have measured the p-type Cu(InGa)Se2 (CIGS) using deep-level transient spectroscopy (DLTS) device characteristics. We have chosen CIGS for our measurements due to the high performance of CIGS solar cells. The use of CIGS as a solar cell material is expected to be more widespread in the future. We have measured the carrier trapping properties of CIGS solar cells using DLTS. The results of these measurements are presented in this paper. We have also measured the CIGS solar cell performance using DLTS, and we have compared the results to the performance of CIGS solar cells that have been manufactured using different deposition parameters. The results of these measurements are presented in this paper.

### F5.37

**Doping by Deposition: Compensating CdS by Tuning rf Sputtering. Jennifer Drayton, Diana Shvydka and A. D. Compaan**

In the recently developed MIS model of a CdTe/CdS solar cell [1], the role of the CdS layer has changed from a window layer to a n-type/heterojunction 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 interface conditions and the CdS (doping) 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 CdS deposition techniques. Here, we deposit CdS by rf sputtering, varying the deposition parameters such as gas pressure. Some films are also exposed to post-deposition CdCl2 treatment, standard in complete PV device preparation. We compare the effect of the deposition parameters on the CdS film properties.

### F5.38

**Native Oxidation of CuGaSe2 Crystals and Thin Films Studied by Electron Paramagnetic Resonance (EPR). Klaus Lipp**

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 CuGaSe2 and to identify strategies for device optimization. Electron paramagnetic resonance (EPR) is a powerful tool for this purpose but only a few EPR investigations of CuGaSe2 crystals and powders have been performed. In this paper the native oxidation of CuGaSe2 crystals and polycrystalline thin films are investigated. We observe an EPR signal assigned to Cu2+ 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 Cu2+ EPR signal disappeared. By comparison with photoelectron spectroscopy (PES) data it is shown that the Cu2+ EPR signal originates from a Cu(OH)2 phase and the activation energy for the thermal reduction of Cu2+ to non-paramagnetic Cu+ is Ea = 0.2eV. A model for the native oxidation of CuGaSe2 will be presented and implications for solar cell device performance discussed.
in the theoretical descriptions of interdiffused heterointerfaces will be deduced. It will be suggested that interdiffusion and extended phase boundaries dominate the formation of the interface when dissimilar and lattice mismatched heterointerfaces are combined.

9:00 AM F0.2
Chemical and Electronic Properties of the Deeply Buried Cu(In,Ga)(S,Se)2/Mo Interface in Thin Film Solar Cells.


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 CIGS/Mo absorber back side as well as the Mo surface with X-ray emission spectroscopy and photobleach spectroscopy. Both techniques give detailed information about electronic and chemical properties, albeit in a different way and with a different information depth (10-200 nm and -1 μm, respectively). We found the formation of MoS2 and MoSe2, but no Mo2O3 on the absorber back side. Furthermore, we observed pronounced composition differences between the external CIGS/Mo surface and the absorber/Mo back side. Based on these findings, an electronic and compositional picture of the CIGS/Mo interface will be discussed.

9:15 AM F0.3

Shingo Ishizuka 1, Keichiro Sakurai 1, Koji Matsubara 1, Akimasa Yamaada 1, Minoru Yonemura 2, Shinpei Kuwamori 2, Sotais Nakamura 2, Yasuyuki Kinuma 3, Hiroyuki Nakarishi 1 and Shigeru Niki 1; 1Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; 2Tokyo University of Science, Noda, Chiba, Japan; 3Tokyo University of Science, Noda, Chiba, Japan.

Cu(In1-xGax)2Se2 (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 higher 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) 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 de-emphasize the possibility of the formation of a hetero pn-junction based at the Cds/CIGS heterointerface.

FURTHERMORE, we observed pronounced composition differences between the external CIGS/Mo surface and the absorber/Mo back side. Based on these findings, an electronic and compositional picture of the CIGS/Mo interface will be discussed.

SESSION FT: TCOS and Window Layers

Chair: Iver Lauermeier and Uwe Rau

Wednesday Morning, March 30, 2005

Room 2005 (Moscone West)

10:45 AM E7.2 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 In2O3 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-spattering 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 on 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 (10-4 Ω cm) and high mobility (>80 cm2/ys) 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 generates less than a carrier per Mo. Films were analyzed by XRD and optical transmission and reflection spectroscopy. The best films are highly crystalline and have high optical transmission across the visible portion of the spectrum (>85%). Comparison of the data obtained for Ti doping with the Ti and Mo metal dopants studied films with very good conductivity and high mobility is shown.


Sn2Zn4O7, SnCd2O4, and CdIn2O4 are ternary compounds that can exist in the spinel structure. They have emerged as promising transparent conducting oxides (TCOs) at deposition temperatures (~1000 °C) 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 (transmittance, reflectance) are not well understood, 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 Sn2Zn4O7, 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 E7.4 Buffer Layers of Zn-Sn-O and Their Influence on the Characteristics of Thin Film CdTe Solar Cells. Chris FerdekDJ, Gayam Sudhakar1, Srilatha Banapalli1, Robert Manasse2, Henhong Zhao1, Linengwei Neman1 and Don Morel3; University of South Florida, Tampa, Florida; 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 latent 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 deposited ZnO as a buffer layer 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 SnO2 targets (in an Ar/O2 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. 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 emorphous and began to crystallize for annealing temperatures of approx. 575 °C. The Zn0.5Sn0.5O2 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 the binary compound with Zn and Sn binary oxides. Solar cells were fabricated using bi-layers of Zn-Sn-O as the 'buffer' with CVD-deposited SnO2:F as the conductive layer. The devices were characterized using standard solar cell techniques. As-deposited Zn-Sn-O as the 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 become crystalline) 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.


Using titanium foil instead of glass as a substrate for Cu(In,Ga)Se2 (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, chalcogenide 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:Al 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 cm2, 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 CIGSe operational parameters. For small area devices (0.5cm2), this technology transfer is considered achieved, with the maximum total area efficiencies on glass and titanium foil substrates being at 16.5% and 16.2% respectively. It is known from Cu(In,Ga)Se2 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 grown on 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 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.
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 spectroscopy, 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 observed that the texture of the MoSe₂ layer is determined by 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 prevent the formation of metal telluride back contacts. Due to their ease of use and fast treatment times, wet chemical etching reagents 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 found to block electrical 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 film, 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 O₂ by conduction band electrons to form H₂O₂, 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) 619.

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 contacts to the absorber layer 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 and 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 N₂/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 photodetector based 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-Through Diode, Yann Roussillon1, Victor G. Karpov2, Diana Shvydka3, Jennifer Drayton4 and Al D. Compaan5; 1Chemistry, University of Toledo, Toledo, Ohio; 2Physics 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 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 reaction strongly affects Voc. Here we show that when the height of the back barrier grows above a certain value (∼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-through 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-through diodes. To verify the above new model, Au, Cu/Au and ZnTe/Ni back contacts were deposited on weak junction devices (with surface photovoltage, SPV ~ 550 mV) and strong junction devices (SPV ~ 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.
physical concepts specific to thin-film devices. In particular, we discuss a model of CdTe-based thin-film PV including such phenomenology and transport through barriers, recombination, and shunting. The effects of lateral nonuniformity are described in the model of Random Diode Arrays (RDA), where weak (low Voc) devices are most detrimental: a) Under forward bias generated eu

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shorter 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 operations 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 the adjacent layers, which in turn reduces the temperature dependent current-voltage (TVD) 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, by creating a thin buffer between the Cu and the CdS surface. These results agree with the calculations of the GBs by the 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 long-standing mystery of (optically inactive) back surface exhibiting 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. This has already led to a number of novel designs and the development of shunting-like phenomena, according to which a conductive path through a thin film device has a precursor in the form of chains of defects that facilitate the electron tunneling. Small film thickness exponentially decreases the shunting probability and our understanding enforces a way of suppressing it.


Solar cells based on Cu(In,Ga)Se2 (CIGS) have demonstrated record conversion efficiencies encouraging exploratory research toward multiple junctions based entirely on these compounds. However, this early effort revealed that CIGS is a small grain size (<50 µm) and 2D material. 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 (60 meV) resolution. The work function values were extracted from the CIGS band offsets and the CIGS/CdS barrier potential. The CIGS/CdS polycrystalline solar cell films cleaved in ultrahigh vacuum.


Cu(In,Ga)Se2 solar cell models have generally been limited to one 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)Se2 solar cell models with grain boundaries. Attractive 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 can separate charge and create current collection channels, which in turn can decrease the overall solar cell efficiency.

10:00 AM 10:10-10:20 Novel Wide-Band-Gap Ag(In1-xGa)xSe2 Thin Film Solar Cells. Tatsuo Nakada, Kenichiro Yamada, Ryota Arai, Hiroki Ishizaki and Naosumi Yamada; Electrical Engineering and Electronics, Aoyama Gakuin University, Sagninaha, Kanagawa, Japan.

Wide band gap chalcogenide materials are required for a top cell of tandem solar cells. Although Ag(In1-xGa)xSe2 (hereafter 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. In order to classify 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). AIG(In,Ga)Se2 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)Se2 phase became predominant as the Ga/(In+Ga) and/or Ag/(In+Ga) atomic ratios increased. The solar cells with a ZnO:Al/ZnO/CDB-AIGS/Mo structure were fabricated. We investigated the influence of carrier generation rate on the efficiency. A high efficiency wide-gap (Eg=1.74eV) AIG(In2Ga3Se8) thin film solar cell with total-area efficiency of 9.3% (10.2% active area efficiency), Voc = 949mV, Jsc = 17.0 mA/cm2, FF = 0.577, and total area = 0.42cm2. 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 Cu(In,Ga)Se2. A very narrow depletion layer near the surface was observed from scanning capacitance microscopy (SCM) analysis revealed a Ag(In2Ga3Se8) 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 films 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 of AIGS, resulting in the formation of n-n+ or n-n-+junctioin due to the substitution of Cd2+ for Ag+1.

11:00 AM E11.2 Surface-modified CuGaSe2 (CIGS) Solar Cells with Improved Performance. Jihad A. AbuShama1,2, Steve Johnston1,2, David Young3, and Rommel Noufi4,5;1 NREL, Golden, Colorado; 2Department of Physics, Colorado School of Mines, Golden, Colorado. We report the growth and characterization of record-efficiency surface-modified CuGaSe2 (CIGS) solar cells. The NREL-confirmed device operating parameters for this cell are: Voc=0.823 volts, Jsc=18.61 mA/cm2, Fill factor = 0.908, and total-area efficiency=10.23%. The recent understanding of the differences in structural and electronic properties between CuxInGaSe2 (CIGS) and CIGS thin films and devices has led to varying the growth process in a way that is likely to make the CIGS surface similar to that of (CIGS) in composition and to minimize defects in the material. This change has led to a gain in the current density of about 3.7 mA/cm2 versus the previous best cell. We examined the new cell using deep level transient spectroscopy (DLTS), scanning capacitance microscopy (SCM) and deep level capacitance profiling (DLCP). The DLTS data exhibit minority traps with activation energies ranging from E-0.3 to E-0.6 eV (where E is the energy of electrons at the conduction band minimum). While varying the filling pulse duration, we also observed an 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 higher reverse current at high forward bias compared to our previous 9.53% CIGS 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 presentiment, we will discuss our data in more details.

11:15 AM E11.3 Effect of Zn and Mg Doping on CuxInS2 Thin Films and Solar Cells. Tobias Enzenhöfer1, Thomas Unold1, Roland Schober1, and Hans-Werner Schock1;1 SESE, Technology, Hahn-Meitner-Institut, Berlin, Germany; 2SEESolar Energy, Hahn-Meitner-Institut, Berlin, Germany. Solar cells based on CuxInS2 will suffer from Voc 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 fabricated a CdS/CIGS cells. For some cells, the responded to a dark-forward-bias step after a dark long soak at zero bias is a complex current flow behavior that exists for the characteristic of the starting voltage at the dark region occurring within about 10 sec, and the other half requiring 1000s of seconds. The effect is completely reversible and a current curve versus time at zero bias after dark bias-on equilibrium 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 fC decays are similar but generally of shorter order in magnitude. Transient data have been observed by McMahon [1] and del Cuesto et al. [2]. 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 is increasing 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.

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 voltages. We found that the CdTe absorber layer is laterally nonuniform on a microscopic scale, showing strong spot-to-spot variations. (iii) Most unexpectedly, the current transients have for accurate measurements of cell efficiency and stability, they provide clues about the current transport mechanisms.

Detailed Study of Metastable Effects in the Cu(In,Ga)Se2: Test of Defect Creation Models. JinWoo Lee, Jennifer T. Heath, David Cohen and William N. Siafarifan; Physics, University of Oregon, Eugene, Oregon; 2Physics, Linfield College, McMinnville, Oregon; 3Institute of Energy Conversion, University of Delaware, Newark, Delaware.

It has been well established that metastable changes in Cu(In,Ga)Se2 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)Se2 material itself. Recent work has also suggested a link between the metastable changes in the concentration of free hole carriers and those of the deep acceptors. 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.

The DLCP method also enables us to clearly distinguish barrier interface from bulk metastable effects. In addition, we have been carrying out measurements on Cu(In,Ga)Se2 solar cells to examine the correlation of the decay of metastable states with solar cell performance, and 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.

The Influence of Traps on Carrier Concentration Profiles Measured by Capacitance-Voltage and Drive Level Profiling in CZTSSe-Based Heterojunctions. Pawel Loeh Zabieiro; Michael Ciwił, Magorzata Igalion and Marika Eno; 1Faculty of Physics, Warsaw University of Technology, Warszawa, Poland; 2Angstrom 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 of 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 the C-V characteristics, 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 metastable 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.

SESSION F13: Discussion Session II

Critical Issues for Thin Film Polycrystalline PV: What Do We Have and Where are We Going?

Discussion Leaders: Uwe Rau, University of Stuttgart

Thursday March 31, 2005
3:00 PM - 5:00 PM
Room 205 (Moscone West)

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**F14.1** Simulation of Polycrystalline Cu(In,Ga)Se_{2} Solar Cells in Two Dimensions. Markus Gloeckler\(^1\), Wyatt K. Metzger\(^3\) and James R. Sites\(^4\); 1Colorado State University, Fort Collins, Colorado; 2National 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 recombination in polycrystalline 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 \(10^7\) 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 it has been thought that the band structure on 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 polycrystalline over single-crystalline CIGS materials.

**F14.2** Photo-Hall-Measurements of Epitaxial and Polycrystalline CuGaSe_{2} Films. Thorsten Rissmann, Siebentritt Susanne, Niklas Regina and Martha Ch. Lux-Steiner; SE2, Hahn-Meitner-Institut Berlin, Berlin, Germany.

In order to achieve high-efficiency wide-band-gap chalcogenide solar-cells a better understanding of basic material properties is necessary. Especially the role of grain boundaries has to be further investigated. Two models have been developed 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 charge transport in the space charge region. The idea of 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 band 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 CuInSe_{2} Solar Cells. Seokhyun Yoon\(^1\), Sheng S. Li \(^2\) and Timothy J. Anderson\(^3\); 1Chemical Engineering, University of Florida, Gainesville, Florida; 2Electrical and Computer Engineering, University of Florida, Gainesville, Florida.

Polycrystalline CuInSe_{2}-based solar cells, in which the absorber layer typically has an average grain size of a few \(\mu\)m, 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 elusive. 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 CuInSe_{2} absorber layer of a cell with the structure ZnO/Mo/CuInSe_{2}/In_{0.2}Ga_{0.8}Se_{2}/CdS/FTO/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 \(\mu\)m. 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 V as a result of injection of carriers by photo generation for the 0.2 \(\mu\)m 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. He Zhou, Xiangyin Wu and Tim Gesse, 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 partial pressures, 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 \(<250^\circ\text{C}\), and few studies exist to guide ITO optimization in this temperature range. In this study, RF-sputtered ITO films deposited at temperatures \(<250^\circ\text{C}\) 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 200-300\(^\circ\text{C}\), actually occurs at \(<230^\circ\text{C}\). Because this temperature is less than 250\(^\circ\text{C}\), high optical and electrical properties may be achieved with a lower temperature, which is essential for fabricating these devices. Recent results have shown that Sn-doped ITO thin films can be readily fabricated in air using standard solid state synthesis thereby making expanded ITO films. Moreover, we have found that optimized deposition conditions for 5% Sn-doped films yield p-type conductivities of 0.033 S/cm. We will report on the electrical, optical, and structural properties of CuInO_{2} films grown from Cu_{2}In_{2}O_{5} targets with different dopants.

**F14.5** Substitutional Doping of the Electrically Bipolar Transparent Conductor CuInO_{2} Using Pulsed-Laser Deposition from Cu_{2}In_{1-x}O_{x} Targets. Charles Iepelin, John D. Perkins, Matthew Dalney, David Young, Tatiana Kuzyanova and David S. Ginley; NREL, Golden, Colorado.

P-type transparent conductors could be used as contacts in organic photovoltaic (PV) cells, in transparent electronic devices 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. Cu-doped CuInO_{2} is p-type and Sn-doped CuInO_{2} is n-type. In this work we report on the electrical, optical and structural properties of CuInO_{2} films grown from Cu_{2}In_{2}O_{5} targets with different dopants.

**F14.6** Wide-Gap CISG Solar Cells with Zn_{1-x}M_{x}O Transparent Conducting Film as a Window Layer. Koji Matsubara, Akimasa Yamada, Shogo Saitou, Keichihiro Sakurai, Hitoshi Tampo, Yasuyuki Kimura, Satoshi Nakamura, Minoru Yonezura, Hisayuki Nakanishi and Shigeru Niki; Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; 2Tokyo University of Science, Noda, Chiba, Japan.

It is well known that the band alignment between the conduction band minimum of CuIn_{1-x}Ga_{x}Se_{2} (CIS) absorber layer and that of the window layer is important for the solar cell performance; the conduction band minimum of ZnO is lower than that of CIS. As the conduction band minimum of Zn_{1-x}M_{x}O is higher than that of ZnO, it is expected that the use of Zn_{1-x}M_{x}O instead of ZnO improves cell performance. So far we have succeeded in fabricating...
Al-doped Zn$_{1-x}$Mg$_x$O transparent conducting films with bandgap of about 4 eV and the resistivity of less than $10^{-2}$ Ω cm. In this study, Al doped Zn$_{1-x}$Mg$_x$O transparent conducting films were deposited by CIGS solar cells with relatively high Ga content: 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$_x$O 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 ~ 0.5) cells with 1-μm thick window layers. At improvements in the Zn$_1-x$Mg$_x$O 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 CuAlO$_2$ Thin Films prepared by RF Reactive Sputtering.** Bruno Karl Meyer and Bin Yang, Physikalisch Institut, Giessen, Germany.

In recent years, p-type transparent conducting oxide compounds based on the delafossite structure have attracted much attention due to their potential in preparing novel transparent p-n junctions for device applications. In this work, transparent conducting CuAlO$_2$ thin films have been deposited by RF reactive sputtering technique on glass and quartz substrates using CuAl alloy target in a molar 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 bandgap, such as 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, 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. HITM 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 of the films was found to increase, and the band gap was 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.** Dhashini 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 chrome contact to the p-type CdTe. This back contact is typically Cu doped to provide both CuTe, essential for low resistance contact, and bulk CdTe doping, essential for higher open circuit voltage. A transparent back contact would allow bifacial device characteristics, with two p-type contacts, 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 efficiencies due to poor ohmic contacts with Cu 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 95% and device efficiencies with ZnTe:Cu contacts of 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, indicating that CuTe 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 back contact has been achieved. 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. Under 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 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 the effects of junction behavior and minority carrier transport previously unavailable with front illumination, and thus allowing a better understanding of the efficiency limiting mechanisms.


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 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 $V_{oc}$ up to 575 mV. In these films a thin layer of Cu is deposited on the ZnTe 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 $J_{sc}$ 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$_2$Se to be an effective p contact as well. As with Cu doped films devices with Cu$_2$Se 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?** Mahildeline Enamzian, Ken Duvall, Douglas P. Halliday, Nicola Romeo and Alesio Bosio; 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$_2$O$_3$:F) layer was used as transparent anti-reflection coating (TACO) 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, S, Cl, Si, In, Sn, Pb, Cu, Cd, Zn and Mg were detected. 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/TACO/glass interface. The results of this study may be useful for understanding the effects 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 towards the TCO for the CdS/TCO/glass structure using both qualitative and quantitative SIMS analysis, CdS relative sensitivity factors (RSFs)
were derived from CdS single crystal wafers. It was shown that before CdTe growth, the impurity elements O, Na, Cl, Sb, In, Zn and Te showed up in the XPS spectra of CIGS ranging from 0.02% to 0.03% for Te and 0 to 2-3×10^17 cm^-2 for Na, Cl, Sb and Te. Si was found to segregate at the CdS/TCO interface with a maximum level of 10^18 cm^-2. However, following CdTe growth, most of the impurities in the CdS layer showed up in the XPS spectra of CIGS, and the concentration of these elements is much lower compared to those before CdTe growth. Furthermore, while the concentrations of Na, Pb and Cu before the CdTe growth were below the detection limit of the SIMS system used, Pb and Cu exhibited a maximum of 8×10^16 cm^-2 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 CIGS 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 Sakurai1, Satoshi Nakamura1, Hajime Shibata1, Shogo Ishizuka1, Akisama Yasuda1, Koji Matsubara1, Minoru Yonenura2, Shinpei Kawanoue2, Yasuaki Kimura2, Hisayuki Nakajima2 and Sugiuru Niki2. 1Research Center for Photovoltaics, AIST Japan, Tsukuba, Ibaraki, Japan; 2Elec. 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, there has been a need for a 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 the a priori stoichiometry of CIGS is the introduction of Fe into the formation of polycrystalline CIGS films via sputtering. It has been reported that the bandgap of bulk CIGS decreases with increasing Fe content, suggesting that the use of iron would help reduce the use of indium. However, to the best of our knowledge, there have been arguments over the effects of Fe doping on the bandgap of CIGS 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 a alumina crucible, and irradiated to the substrate during stage 1 and 2 (together with In, Ga). The Ga / III ratio was varied between 0.3 and 1.0 (15% CIGS). The Fe concentration was varied between 0.0 and 1.2 mol%. The film composition was roughly determined by EPMA. The films were evaluated by EPMA, SIMS, XRDI, 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 uniformity of Fe is about 90%, 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 (~0.6 eV at Fe=1.1%) than the values previously reported for bulk CIGS. The spectral response of the fabricated solar cells deteriorated with higher Fe content, from the long wavelength side. Details would be presented at the conference site.


Molybdenum is used as back contact layer in CuIn+xGa2S3 (CIGS2) absorber thin film solar cells. Mo is deposited using DC magnetron sputtering. The CIGS2 absorber layer was deposited on stainless steel and glass substrates. Earlier studies have shown that film deposition conditions such as the thickness and substrate temperatures can affect the electrical properties of the CIGS2 absorber layer. The objective of the present work was to investigate the effect of the deposition conditions and the nature of stress in the underlying Mo film. All the depositions were carried out on 10 x 10 cm2 glass substrates. Mo film was deposited with four different combinations of deposition parameters. In the first set of experiments molybdenum thickness of approximately 350 nm was deposited at pressure 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. Without using any 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 sputtered at 475°C for 10 cycles. XPS and EDX analysis of Mo/CIGS2:Fe films 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 Roussillon1, Victor G. Karpov2, Diana Shvydka2 and Dean M. Giolando2; 1Chemistry, University of Toledo, Toledo, Ohio; 2Physics 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 of the CdS/Cu layer by EEE and C-V confirms this unexpected effect. To explain this phenomenon, an alternative mechanism of the main junction in CdS/CdTe based devices is proposed, similar to metal-insulator-semiconductor structures. The CdS is believed to be strongly compensated by intrinsic Fe in the structure. The compensation is achieved through either the presence of interfacial defects at the buffer-CdS interface or by Cu doped. This strongly increases the depletion lengths in CdS and thus suppresses the band bending between 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 turn, 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.


The CuInSe2 semiconductor is indisputably the perfect absorber material for solar cells. Engineering its bandgap with S and Ga inevitably perturbs the stoichiometry of the CIGS film. The standard n-type CIGS film is made a 13% efficient cell without any Cu doping, using Au as the back contact. The CuInSe2 semiconductor is indisputably the perfect absorber material for solar cells. Engineering its bandgap with S and Ga inevitably perturbs the stoichiometry of the CIGS film. The standard n-type CIGS film is made a 13% efficient cell without any Cu doping, using Au as the back contact. The CuInSe2 semiconductor is indisputably the perfect absorber material for solar cells. Engineering its bandgap with S and Ga inevitably perturbs the stoichiometry of the CIGS film. The standard n-type CIGS film is made a 13% efficient cell without any Cu doping, using Au as the back contact. The CuInSe2 semiconductor is indisputably the perfect absorber material for solar cells. Engineering its bandgap with S and Ga inevitably perturbs the stoichiometry of the CIGS film. The standard n-type CIGS film is made a 13% efficient cell without any Cu doping, using Au as the back contact. The CuInSe2 semiconductor is indisputably the perfect absorber material for solar cells. Engineering its bandgap with S and Ga inevitably perturbs the stoichiometry of the CIGS film. The standard n-type CIGS film is made a 13% efficient cell without any Cu doping, using Au as the back contact.
Investigations of the effects of Pulsed Laser Annealing (PLA) process on the surface morphology and defect properties of CdS/CuInxGa1-xSe2 (CIGS) films and solar cells are reported in this presentation. CIGS films capped with a CdS layer were laser annealed in air using a Nd:YLF laser emitting at 1064 nm, and permits ~200 nm 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 1064 nm under 70 mJ fluences were characterized by the formation of a 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 CuInSe2 and Cu(In,Ga)Se2 Determined by Cyclic Voltammetry.**

Estela Calixto, Kevin D. Dobson, Brian E. McCandless and Robert W. Birnire; Institute of Energy Conversion, University of Delaware, Newark, Delaware.

CuInSe2-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 alternative deposition techniques that can be used in low cost large area solar cell manufacturing, especially when considering industrial scale-up. Electrodeposition (ED) is one of the best alternatives since deposition equipment is commercially available and film growth is performed at low temperature and the deposition rates are high. To optimize the ED process, CdS/CuInSe2 and Cu(In,Ga)Se2 films were electrically characterized, and it was found that the ratio of bath [Se 4+]/[Cu2+] has a significant effect on composition and morphology of deposited films. The films are generally of 1.5 - 2 μm thickness and exhibit columnar growth. For ED of CuInSe2, a [Se 4+]/[Cu2+] > 2 was found to allow growth of Cu-poor films of ~25 at% Cu, ~25 at% In and ~52 at% Se. For ED of Cu(In,Ga)Se2, a [Se 4+]/[Cu2+] ~ 1.75 was found to be required to maintain appropriate Se and Cu levels, where the In 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 ~25 at% Cu, 17-20 at% In, 6-8 at% Ga and ~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 ~5.5% have been obtained. In order to understand the role of [Se 4+]/[Cu2+] in the film growth, cyclic voltammetry measurements were performed to identify mechanisms leading to the formation of CuInSe2 and Cu(In,Ga)Se2. The study was made using Mo, Mo/ED-CuInSe2 and Mo/ED-Cu(In,Ga)Se2 substrates as the electrodes. Similar mechanisms were observed for deposition of CuInSe2, Cu(In,Ga)Se2, Cu2Se and CuIn2Se3, and gratefully acknowledge the financial support of Davis, Joseph & Hegley.

**F14.18**

**Growth and Properties of HF Magnetron-Sputtered CuInSe2 Thin Films.**

Peter Gorley1, Volodymyr Khomyak1, Yuri Vorobiev1, Estela Gonzalez Hernandez2, Sergiy Bilichyk1, Vadim Grechko1 and Paul Horley1.

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Complex ternary diamond-like semiconductor compounds of A'B'/C'V' 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 CuInSe2 (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 properties. Thin films were deposited using vacuum equipment VUP-5M by HF magnetron sputtering in the atmosphere of high-purity argon using specially-manufactured HF magnetron generator. Crystalline disks of CIS cathodes (4mm in diameter) were made from either copper, indium and selenium or from copper, indium and 10% lithium-grained and 90% 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 48 mm2. 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 1.5-5nm/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 parameter 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 CulnSe2-Solar Cells-Layer using Different Pulse Durations and Wavelengths: A Comparison Aspects.**

Estela Calixto, Lars Petch, Lars Pichler and Sven Albert; 3D-Micromac AG, Chemnitz, Saxony, Germany.

CulnSe2 solar cells consist of multilayer laminates. The reel-to-reel production process of flexible CIS solar cells on 20 μm 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-machining of this type 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 in the 3D-Micromachining layer-composites of CulnSe2 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-machining 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 CuInSe2/In2O3 and CuInSe2/In2O3 Structures.**

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CuInSe2/In2O3 and CuInSe2/In2O3 structures were formed by depositing CuInSe2/CuInSe2 films by stepwise flash evaporation onto DC sputtered In2O3 films. Phase purity of the CuInSe2 and CuInSe2 films was confirmed by Transmission Electron Microscopy. X-ray Diffraction results on CuInSe2/In2O3/glass and CuInSe2/In2O3/glass structures showed sharp peaks corresponding to (112) plane of CuInSe2/CuInSe2 and (222) plane of In2O3. Rutherford Backscattering Spectrometry investigations were carried out on CuInSe2/In2O3/Si and CuInSe2/In2O3/Si structures in order to characterize the interface between CuInSe2 and In2O3. The results show that the CuInSe2 and In2O3 films were near stoichiometric and In2O3 films were oxygen deficient. CuInSe2/In2O3 interface was found to include a ~ 20 to 25 nm thick layer consisting of copper, indium and oxygen. However the interface between CuInSe2 and In2O3 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 CuInSe2 and CuInSe2.

**F14.21**

**Performance of CuGaSe2 Solar Cells Grown by Co-Evaporation Process.**

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CuGaSe2 with band gap 1.98 eV is an attractive absorber material for solar cells to obtain high open circuit voltage and 10-15% efficient solar cells. CuGaSe2 based tandem solar cells have been fabricated with a single cell efficiency of 11% on CdZnTe/CuGaSe2 heterojunction solar cells. In this paper, we deposited CuGaSe2 thin films by physical vapor deposition and fabricated solar cells based on slightly Ga rich absorber. CuGaSe2 thin films were grown by depositing 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 330 °C and 530 °C, respectively. CuGaSe2 films with different Cu:Ga ratios are grown by the Ga flux as 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 80 °C. The window layer consists of a radio-frequency sputtered intrinsic ZnO (50 nm) and Al (100 nm) at 500 nm. Electron beam evaporated Al grids were used as top contact. The cells are tested under AM 1.5 illumination of 100 mW/cm² irradiance. As grown films showed preferred (112) orientation. The grain size of the films decreased with increasing process temperature, 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: SiOx/NixZnOx/Al were fabricated. In optimal condition, we obtained Voc = 0.81 V, Jsc = 11.8 mA cm⁻², FF = 0.635 and FF * = 6.2 %. The absorber film is 1.9 μm thick and slightly Ga-rich, with a bulk composition [Ga] / [Zn] = 0.85. The modification of interface by additional heat treatment and various buffer layer for improvements, fill factor and other junction properties are currently being conducted. And it will be presented at the meeting.

F14.22 Abstract Withdrawn


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 but has produced films with a reproducibility [1]. The new process involves the sprayed deposition of an ionic salt layer 1-10 nm 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 thickness. Thin films grown by spray deposition 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 sulphide buffers on Cu(In,Ga)(S,Se)₂ absorbers from Shell Solar Munich have produced cells exceeding 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 undertreatment was applied. The process is also very reproducible, 48 ±0.05% total area cells were made with a stabilized 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) sulphide and copper indium disulphide (CIS) have also been successfully produced and are of particular interest for non-stoichiometric or ETA cells due to the ability of the gas to penetrate the porous structure of the absorber. In this 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, C.H. Fischer, S. Zweigart, P. Karg and M. Lux-Steiner, Prog. Photovoltaics: Res. Appl. 13, 175 (2005).


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 CdTe to substrate-based composite (CdTe/Si) substrates. This research 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 the CdTe. Although, the growth of CdTe/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 suitable CdTe nucleation. In this work, the surface preparation process of CdTe, CdZnTe, and CdSe layers grown on Si(211) substrates were studied. Several different wet chemical etching processes were employed to prepare the layers for HgCdTe nucleation. Although, the nucleation of CdTe/Si is extensively 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 CdTe/Si material. Initially, the standard Brummel-Metha solution (6.5%) was used to etch CdTe. This etching process is used successfully to prepare both CdTe and CdZnTe layers. However, a vasty different surface is obtained on CdSeTe layers as observed by RHEED, which, with an extremely thin CdTe (211) HRDDE) 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 Brummel-Metha etchant, even for extremely thin CdTe 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 CdZnTe wet-chemical treatment and was not entirely appropriate for nucleation on CdSeTe/Si. This fact is attributed to the difference between various mixing conditions used for 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 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.


High-efficiency thin-film solar cells based on CuIn_xGa_1-xSe_2 absorber material have been developed using CuIn_xGa_1-xSe_2 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_xGa_1-xSe_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 = 72%) and even higher short-circuit current densities (Isc = 32 mA/cm²) as the reference cells with the CBD-deposited CdS. The open circuit voltage of devices with PVD-CdS is, however, lower than could be expected 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_xGa_1-xSe_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 that the PVD-CdS is pinned at the CdS/CdSe interface, inhibiting the absorber grain boundaries. This allows us to suppose that during the initial growth stage a sulfur passivation of the grain boundaries occurs that significantly influences the recombination of carriers in the absorber. The investigation of the ZnO/PVD-CdS/CuIn_xGa_1-xSe_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., Prog. Photovoltaics. 11 (4) (2003) 225.

F14.29 In-Depth Study of Morphological Defects of MBE-Grown CdTe on Si. Eva M. Campo*, Thomas Hierl*, James C. M. Huang*, Gregory Brill*, Yuaping Chen² and Nirib K. Dhar²; Center for Optical Technologies, Lehigh University, Bethlehem, Pennsylvania; U.S. Army Research Laboratory, Adelphi, Maryland.

Morphological defects are known to nucleate during molecular beam epitaxial (MBE) growth of MBE-grown MBE-based composite materials. Presently, any morphological defect present on the surface will remain during any subsequent overlayer MBE growth process and can appear similar to void 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 CdTe/Si deposition processes. To investigate 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 morphology of these defects is related to the Cu/In ratio in the 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 consist of copper-rich CdTe layers embedded into an organic resin. The advantages of the developed CuInSe2 monograin powders. As it is shown in [2], the formation of CuInSe2 monograin takes place in the liquid phase of flux of a certain amount exceeding the limit for crystals sintering. We varied the reaction time from 0.5 to 1 h. The powders were studied by photoluminescence (PL) measurements and characterized structurally by X-ray diffraction and Raman spectroscopy, compositionally by ICP-MS, polychromatically and by energy-dispersive X-ray spectroscopy (EDS). As a result, single-phase powder crystals were synthesized from mixtures of initial components between 1: Cu/In > 0.7. The powders with Cu/In ratios 0.7-0.8 were found to consist of crystals with different compositions: Cu/In = 0.92 and Cu/In = 0.6. 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 0.8 exhibited PL spectrum with one dominant peak at 1.1 eV, typical for single-phase material. The samples with Cu/In = 0.6 exhibited two broad bands with peak position at 0.89 eV and 0.58 eV. [1] M. Altosar, A. Jagomagi, M. Kauk, M. Krunkis, J. Krukstok, E. Melikov, J. Radoja, T. Varema. Monograin layer solar cells, Thin Solid Films 431-432 (2003) 460-469. [2] M. Altosar, E. Melikov CuInSe2 Monograin Growth in CuSe-Se Liquid Phase, Jpn.J.Appl.Phys., 2000, 39, Suppl. 39-1, 65-66.

E14.27
Formation and Characterization of CIS/Buffer Layer Interface in CIS Electodeposited (CISEL) Solar Cells. Negar Naghavi1,2, Cedric Hubert3, Olivier Roussel1, Melanie Lamirot4, Bruno Canav4, Jean-Francois Guillemin1,1, Arnaud Etcheberry4, Daniel Lincln3,2 and Olivier Kerre1,2; CNRS, CISEL, Chatou Cedex, France; 2CNRS, Institut Lavoisier, Villejuif, France; 3CNRS, LEC, Paris Cedex 05, France; 4EDF, CISEL, Chatou Cedex, France.

Our group has shown that electrodeposited CIS solar cells can actually achieve efficiencies over 11%. Photovoltaic properties of CIS 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, namely one of the downfalls 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) on the characterization 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 final 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 optoelectronic techniques.

E14.28
Tailoring the Composition of CuInSe2 Monograin Powders in Growth Process. Mari Kristiim, Mare Altosaar, Jan Raudoja, Kristiim Tamm, Marja Grossberg and Enn Mellikov, Tallinn University of Technology, Tallinn, Estonia.

Monograin powders of CuInSe2 (CIS) have been found application as absorber materials in single layer single-junction cells [1]. The monograin layer consists of a single crystal thick layer of monograin embedded into an organic resin. The advantages of the developed powders materials are single-crystalline structure of every grain, uniform distribution of the thickness of the grains and narrow grain-size distribution. Monograin CIS powders were synthesized from high-purity Cu-In alloys and elements in liquid phase of all components 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 powders of CuInSe2 monograin powders. As it is shown in [2], the formation of CuInSe2 monograin takes place in the liquid phase of flux of a certain amount exceeding the limit for crystals sintering. We varied the reaction time from 0.5 to 1 h. The powders were studied by photoluminescence (PL) measurements and characterized structurally by X-ray diffraction and Raman spectroscopy, compositionally by ICP-MS, polychromatically and by energy-dispersive X-ray spectroscopy (EDS). As a result, single-phase powder crystals were synthesized from mixtures of initial components between 1: Cu/In > 0.7. The powders with Cu/In ratios 0.7-0.8 were found to consist of crystals with different compositions: Cu/In = 0.92 and Cu/In = 0.6. 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 0.8 exhibited PL spectrum with one dominant peak at 1.1 eV, typical for single-phase material. The samples with Cu/In = 0.6 exhibited two broad bands with peak position at 0.89 eV and 0.58 eV. [1] M. Altosar, A. Jagomagi, M. Kauk, M. Krunkis, J. Krukstok, E. Melikov, J. Radoja, T. Varema. Monograin layer solar cells, Thin Solid Films 431-432 (2003) 460-469. [2] M. Altosar, E. Melikov CuInSe2 Monograin Growth in CuSe-Se Liquid Phase, Jpn.J.Appl.Phys., 2000, 39, Suppl. 39-1, 65-66.

E14.29
Abstract Withdrawn.

E14.30
Liquid Phase Deposition of CuInSe2 Films for Photovoltaic Applications. Jonathan Cowan1, Frank Ernst1, Pierou Pierre2, Sheila Bailey3 and Aloysius Hepp1; 1Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio; 2Photovoltaic Branch, NASA Glenn Research Center, Cleveland, Ohio.

Copper Indium Diselenide (c-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 c-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 spray pyrolysis, 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 grain sizes on the order of 10-30 µm or more depending on growth conditions. The study of such films can provide insight into the recently debated issues concerning the effects of grain boundaries and the effects of the buffer layer (usually CdS). Best buffer layers are prepared by liquid phase deposition reactor, and the characterization of the resulting microstructures of deposited films via TEM, XEDS, and SEM.

E14.31
Effects of Rapid Thermal Annealing on Film Properties and Performance of Cu(In,Ga)Se2 Solar Cells. E. Melikov, F. Ernst, and Frank Ernst, Case Western Reserve University, Cleveland, Ohio.

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)Se2(CIGS) solar cells were investigated. RTA experiments were conducted on three CIGS cells fabricated by NREL, and the results show that process 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 treatment at 300°C, 350°C, and 400°C, respectively. The cell performance increased by 1.5% and 15% at 300°C and 400°C, respectively. A dramatic increase in the efficiency of cell-1 from 9.52% before RTA treatment to 15.77% after 300°C RTA treatment was obtained from this study. Cell-2 and -3 with pre-annealed efficiencies of 14.73% and 15.02% were increased to 16.65% and 16.42% after 300°C 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 on F.F. is ruled out by 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 in 150°C for 1-1.5 min. respectively. To eliminate light soaking effect, the photo J-V and Q-E measurements were performed 2 weeks after the initial RTA treatments. The results showed that Voc, Jsc, and conversion efficiency can be increased, albeit F.F. decreases for all 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 1060 nm after RTA treatments. The results of this study clearly show that RTA treatments are indeed beneficial in improving uniformity of films and performance of CIGS cells. Our estimated optimal annealing temperatures should lie between 200 and 300°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 CuInS2 Thin Film Solar Cells, Michael H. -C. Jin1, 2, Kuhlinder K. Hanger1, 2, Jeremiah S. McNatt, John E. Dickman2 and Alyosius F. Hepp2; 1Ohio Aerospace Institute, Brookpark, Ohio; 2NASA 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, low power window and cost effectiveness. However, in 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 fill factor. 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 CuInS2, sulfur vacancies that are undesirable n-type dopants grown in both bulk and grain boundaries can be passivated by extra sulfur or oxygen. In this study, the post-deposition annealing of AACVD-deposited CuInS2 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 high temperature pretreatment and verified the post-deposited performance of the solar cell can be prevented by storing the solar cell under nitrogen environment after annealing. [1] M. H.-C. Jin et al., Proc.ofthe19thEuropeanPVConference, AV.1.171 (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 used 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, CdCl2 treatment and back-contact diffusion on the performance of thin CdTe solar cells. Cells with CdTe thicknesses from 0.5 μm to 1.28 μm were fabricated using magnetron sputtering at 280°C. The TCO/CdS/CdTe structures were vapor CdsCl2 treated at 385°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°C for 5 to 45 min duration. The films and cells were characterized using XRD, AFM, optical transmission, I-V and Q-E measurements. Significant improvements in the stability to standard conditions of 30 min of CdCl2 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 thin films, the as-deposited thin CdTe was of (111) preferred orientation that decreased after CdCl2 treatment. XRD patterns also showed the formation of a CdTe1.2-Sx alloy to a large degree than in thick CdTe samples. A 10 min CdCl2 treatment and 10 min of back-contact diffusion were found being the most optimal. The cells show 11.8% efficiency form a 0.8 μm thick CdTe layer. This cell showed Voc of 772 mV. Jsc of 31.89 mA/cm2 and FF of 0.97%. Work is supported by the NREL High Performance PV and Thin Film Partnership Programs.

F14.34 Large Area Cu(In,Ga)Se2 Films and Devices on Flexible Substrates Made by Sputtering. Dennis Hollars, Randy Dorn, P. D. Macaluso, Jochen Flug and Robert Zubek; Miasole, San Jose, California.

Cu(In,Ga)Se2 (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 scale-up, mainly because of the complex process steps and 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 rotation magnetron sputtering is the great interest of the 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 onto 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 area. The dependencies of CIGS films properties and device performance on various processing parameters were investigated.

F14.35 Cds Thin Film Preparation by Unipolar Current Pulse Electrodeposition Technique. Kiran Jain1, M. S. Rashmi2, K. N. Sood2, N. Karar1 and H. Chandra1; 1Electronic Materials, National Physical Laboratory, New Delhi, India; 2Materials 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 photovoltaic devices. The potential 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 photonic materials. The technique for nanocrystalline CdSe thin films fabrication 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 determine 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 CdS04, SeO2, H2SO4. All samples were prepared at 80 degree centigrade temperature. Pulse 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 overvoltage is matched 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 semiconductor 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 determine 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 CdS04, 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 10 milliseconds to seconds and films were also deposited under DC conditions, at constant anodic potentials in the range of 0.5 V to 1.28 V.
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.


Indium-zinc-oxide (IZO) compounds show very desirable properties as transparent conducting oxides (TCOs) for photovoltaic and display applications. 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 ~3000 (Ohm-cm)^{-1} was found in amorphous, as-deposited material at a composition of ~70% In. This amorphous region extended from ~45 to 75% In in the as-deposited material, with crystalline regions at lower and higher indium contents. Two series of analogous libraries were annealed 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 (Ohm-cm)^{-1} at ~66% In. The extent of the amorphous region also decreased and ranged from ~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_{2}O_{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_{2} compound is the optimal material for devices requiring low-temperature processing. The results of the argon annealing study will also be presented.

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 source 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.

In-situ Investigation on Reaction Kinetics of CuInSe_{2} Formation from Cu-In/Mo glass Precursor during Selenization. Woo Kyung Kim, E. A. Payzant², S. Yoon³, T. J. Anderson¹, O. D. Crissale¹, V. Craciun² and S. S. Li²; ¹Chemical Engineering, University of Florida, Gainesville, Florida; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Materials Science & Engineering, University of Florida, Gainesville, Florida; ⁴Electrical 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 nitrogen enhanced molecular beam epitaxial (MBE) reactor on Mo coated ultra thin glass substrates. The combined crystalline and amorphous atomic composition (Cu_{x}In_{1-x}Se) and crystalline structure (Cu_{2}In and CuIn) of the as-deposited precursor were determined by ICP and XRD, respectively. The surface and cross-sectional structural and local composition of the precursor were analyzed by SEM and EPMA, respectively. For selenization, selenium powder was placed in wells of the HT-XRD sample holder adjacent to the precursor film. The sample holder containing the source 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 CuInSe_{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 closely 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(±19) and 100(±14) kJ/mol, respectively.


Recent years have seen record laboratory efficiencies for CIGS approach 20%, with multiple groups worldwide reporting small-area record exceeding 15%. A remarkable achievement in this 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 unfulfilled needs are described. Discussion focuses on sensors useful for CIGS co-evaporation, since it has produced the world's second 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 fluxes and, in some cases, 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 detail, 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 understood is well-documented. Needs for future product sensors, and the associated characteristics of these sensors that are not clearly linked to device performance, are discussed.

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 1:2:1. The starting powders 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 can be indexed to the chalcopyrite-type CIS with a lattice constant of a = 5.79 Å and c = 11.62 Å 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-Se) (CuIn-Se), 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 the 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) is -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 CuInSe2, quickly and easily. When prepared under identical conditions Cu(In,Ga)Se2, the grain size of the films decreases with increasing Ga-content. Moreover, the general opto-electronic material homogeneity also decreases when increasing the Ga and/or Se content. Large qualitative differences occur also in the combination of recrystallization centres and/or their energetic position with respect to the bands within the forbidden band, as indicated by a number of quantitative model calculations showing that the relative low performance of wide-gap Cu-chalcopyrites results from the sum of many small differences rather than by a single major failure.

SESSION F10: Wide Gap Chalcopyrites
Chairs: Welfran Jagermann and Shigeru Niki
Friday Morning, April 1, 2005
Room 2006 (Moscone West)

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)Se2 solar cells with Eg ~ 1.1 eV exhibit a photovoltaic efficacy 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)Se2 devices and their wide-gap counterparts. The differences start with the structure of the absorber layers and the increasing tendency of the material to build secondary phases when increasing Ga or S contents in the alloy. When prepared under identical conditions Cu(In,Ga)Se2, the grain size of the films decreases with increasing Ga-content. Moreover, the general opto-electronic material homogeneity also decreases when increasing the Ga and/or S content. Large qualitative differences occur also in the combination of recrystallization centres and/or their energetic position with respect to the bands within the forbidden band, as indicated by a number of quantitative model calculations showing that the relative low performance of wide-gap Cu-chalcopyrites results from the sum of many small differences rather than by a single major failure.


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, these limitations in their optoelectronic 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 seems 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(CGS) and CulnS2(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 nanosecond films and films deposited on the surface of the solution of In and S in the near-surface region of CulnSe2 thin films and of Ga in that of CulnS2. 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 CGS includes the entire composition range from CuGaSe2 to Ga-rich as-grown absorbers. Numerical 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 all selected mid-bandgap materials.


The Cu(In,Ga)(Se,S)2 sulfur containing chalcopyrite alloys are being developed as wide gap materials for possible incorporation into CIGS thin film based solar cells. Of particular interest are the alloys with gaps greater than 1.5 eV. 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). Cu(In,Ga)Se2 absorbers were deposited with Cu-rich compositions and then, to form the devices, the Cu2Se 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 (TPP) sub-band-gap spectroscopies to obtain the spectra of defect related optical transitions. To date we have been concentrating our measurements on the Cu2Se 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 \(1 \times 10^{18} \text{cm}^{-3}\) for these Cu2Se absorbers. These are roughly 3 to 10 times higher than typical Cu(InGa)Se2 alloys produced at IEC. However, the hole mobilities appear to be low below 0.005 cm\(^2\text{V}^{-1}\text{s}^{-1}\). The photocapacitance spectra clearly exhibit optical gap lying in the 1.5 to 1.55 eV range with very sharp bandtails (the Urbach energies are below 18 meV). Unlike the TPC spectra for the Cu(InGa)Se2 alloys that exhibit a single band of optical transitions lying roughly 0.8 eV above \(E_v\), the Cu2Se samples exhibit two defect related optical transitions. The first of these appears to lie within 0.5 eV 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 0.5 eV, 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 1.0 eV. 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 0.4 eV). 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 \(3 \times 10^{16} \text{cm}^{-3}\). The influence of this newly discovered defect band on the performance of these sulfur alloy devices will be discussed.

11:30 AM E16.4
Band Gap Fluctuations in Cu(In,Ga)Se2 Thin Films Analyzed by Absorption and Photoluminescence Measurements, Julian Matheis, 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 E16.5
Structural, Optical and Electronic Characterisation of CuInS2 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 applied 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 CdS contacts as well as the Cu2Se 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-stoichiometric and In-rich compositions. Indeed we have been able to prepare near-stoichiometric 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 Cu2Se 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.