

SYMPOSIUM H

II-VI Compound Semiconductor Photovoltaic Materials

April 16 – 20, 2001

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* Invited paper

TUTORIAL

ST H: CHARACTERIZATION OF PHOTOVOLTAIC MATERIALS

Monday, April 16, 2001

1:30 p.m. - 5:00 p.m.

Salon 5/6 (Marriott)

Photovoltaic materials span an immense range of chemical and physical properties from perfect diamond to highly defective amorphous structures and from simple elemental semiconductors to complex alloy ternary compounds. Critical properties cover almost all aspects of normal materials properties - optical, electronic, structural, and chemical. This course covers the most useful methods for characterization of photovoltaic materials. The course is divided into four sections, surface structural and chemical, bulk structural and chemical, optical, and electronic probes. Surface probes are reviewed because surfaces and interfaces are critical to solar cells and determine the effectiveness of carrier collection. Bulk probes are covered because these determine composition and because the bulk properties dominate many aspects of the device. Optical methods describe how light is absorbed and transmitted, determining the generation of current in the device. Finally, electronic properties ultimately determine the performance of a device. Specific topics to be covered are SEM, AES, XPS, scanning probes, XRD, TEM, SIMS, RBS, Absorption/Transmission, PL, ellipsometry, Hall-effect, Capacitance-voltage, DLTS, and EBIC/OBIC. Finally, a discussion of the information that can be gleaned from standard current/voltage and spectral response measurements. Add-on methods such as EDS will be covered during the primary section listed where that add-on is most commonly found. Examples of application of each technique to photovoltaic materials and potential pitfalls and complications relevant to this class of materials are considered.

Instructor:

Angus Rockett, University of Illinois

SESSION H1: MATERIALS AND SYNTHESIS I

Chairs: Reiner Klenk and Douglas H. Rose

Tuesday Morning, April 17, 2001

Salon 5/6 (Marriott)

8:30 AM *H1.1

PHASE EQUILIBRIA IN THE Cu-In-Ga-Se SYSTEM AND ITS IMPLICATIONS FOR SYNTHESIS OF CIS ABSORBER FILMS.

Tim Anderson, B.J. Stanbery, L. Li, W. Zhuang, M. Ider, University of Florida, Dept of Chemical Engineering, Gainesville, FL; C.-H. Chang, Oregon State University, Dept of Chemical Engineering, Corvallis, OR.

The significant advances that have been made in the performance of CIGS cells during the past several years have placed this material system as the leading candidate for second generation thin film technology. Part of the reason for the rapid development of CIGS thin film technology is the discovery of a variety of reaction pathways that lead to efficient absorber layer formation (e.g., co-deposition of elements, stacked elemental layer, and direct compound formation). The large selection of reaction pathways and deposition techniques suggests an inherent stability of Cu(InGa)Se₂ as well as a complex phase diagram. The processes that convert precursor films to efficient absorber layers, however, are not optimized or fully understood. Knowledge of the thermochemistry and phase equilibria of the Cu-In-Ga-Se system is helpful in understanding a variety of process issues in CIGS cell manufacturing, including component segregation, liquid phase assisted reaction pathways, and near surface type conversion. This presentation will review the results of our effort to establish equilibrium phase relations in this system. The work includes structure determinations by XRD and XAFS, Gibbs energy change determinations using solid state electrochemical cells, equilibration studies, and assessment work. The implications of the resulting multicomponent phase diagrams on absorber material processing will be discussed.

9:00 AM H1.2

GROWTH, STRUCTURAL CHARACTERIZATION AND OPTICAL BAND GAP ANOMALY IN Cu-III₃-VI₅, Cu-III₅-VI₈ TERNARY COMPOUNDS. G. Marin, R. Marquez, S.M. Wasim, C. Rincon, G. Sanchez Perez, Centro de Semiconductores, Univ de Los Andes, Fac de Ciencias, Merida, VENEZUELA; R. Guevara, J.M. Delgado, Centro Nacional de Difracción de Rayos X, Fac. de Ciencias, Merida, VENEZUELA; L. Nieves, Dept de Física, Fac de Ciencias, Univ de Los Andes, Merida, VENEZUELA.

It is thought that the ordered vacancy compound (OVC)Cu-In₃-Se₅,

detected as a secondary phase on the surface of In-rich CuInSe₂ thin films, could play an important role in the optimization of solar cells efficiency based on the p-n junction of p-type CuInSe₂ and n-type Cu-In₃-Se₅. On the other hand, recently Zhang et al. have explained the existence and stability of a large number of In-rich OVC as a repeat of multiple units of (In_{Cu} + 2 V_{Cu}) defect pairs in CuInSe₂. This has led to a detailed study of these compounds due to their technological importance as well as to understand the physics involved in these new materials. Hence, in the present work we will report on the growth, phase diagram, crystal structure and a comparative study of the band gap of the selenides and tellurides of the I-III₃-VI₅ I-III₅-VI₈ families of semiconductors. It is established that all compounds have a chalcopyrite-related structure with the exception of Cu-In₅-Se₈ and Cu-Ga₅-Te₈ that has hexagonal and cubic structure, respectively. The band gap E_G of the selenides, higher than that of the corresponding I-III-VI₂ compounds, agrees quite well with the predicted value. However, E_G of the Cu-In-Te system is very nearly the same as of CuInTe₂ and smaller than that of CuGaTe₂ in Cu-Ga-Te system. This behavior will be explained as having its origin in the smaller d-character in the Te p-Cu d interband repulsion. From the analysis of the E_G vs T data of these compounds, values of some of the band parameters are estimated.

9:15 AM H1.3

Cu(In,Ga)S₂ PHASE FORMATION FROM METALLIC Cu-In-Ga PRECURSOR STACKS IN RAPID THERMAL PROCESSES.

A. Neisser, R. Klenk, Th. Matthes, I. Luck, M.-Ch. Lux-Steiner, Hahn-Meitner-Institut Berlin, Dept SE2, Berlin, GERMANY; J. Alvarez-García, A. Pérez-Rodríguez, L. Calvo-Barrio, J.R. Morante, Electronic Materials and Engineering (EME), Department d'Electronica, Universitat de Barcelona, Barcelona, SPAIN.

Open circuit voltages well above 800mV have been reported for CIS/CdS/ZnO solar cells using Cu(In,Ga)S₂ absorber layers sulfurized from evaporated metallic precursors in rapid thermal processing systems. As we have shown earlier, the Gallium-induced open circuit voltage gain in such devices can not be solely explained by electronic properties such as a widened absorber band gap or changes in the dominant recombination mechanism. On the other hand, Raman spectroscopy and transmission electron microscopy indicated larger grains and a reduced defect density. We have therefore investigated the influence of gallium on the reaction kinetics and phase formation in rapid thermal processing. Cu-In and Cu-In-Ga precursor stacks have been sulfurized in a reactive atmosphere containing elemental sulfur or H₂S. Film formation has been studied ex-situ by aborting the sulfurization process at different points during heat up or annealing. X-ray diffraction, SEM and Raman spectroscopy measurements combined with AES depth profiling have been performed for structural characterization and phase identification. Elemental distribution and overall composition have been determined by EDX line scans and ICP spectrometry respectively. Cu-In alloying after deposition and during early stages of film growth is found to be strongly suppressed by the presence of gallium in the precursor stack. This effect is ascribed to a CuGa₂ phase which acts as a diffusion barrier at the Cu/(In,Ga) interface. Without gallium the chalcopyrite phase grows directly from Cu-In alloys. However, the presence of free metallic Indium in the gallium containing precursors leads to intermediate In-rich chalcogenide phases, thereby shifting the formation of Cu(In,Ga)S₂ to higher temperatures at a later stage of the heat-up ramp. A similar shift has been reported for the influence of sodium or gallium in the sequential processing of selenide films and may explain the improved structural quality of the chalcopyrite phase. The observed incorporation of the chalcogen via an intermediate phase as well as the observed delayed Cu(In,Ga)S₂ formation may be responsible for the higher process stability and reproducibility reported for Gallium-containing chalcopyrite films. The inhomogeneous Gallium depth distribution previously reported for sequentially prepared Cu(In,Ga)S₂ films could be assigned to the lower formation temperature of CuGa₂ compared to CuInS₂.

9:30 AM H1.4

GROWTH MONITORING OF Cu-POOR PREPARED CuInS₂ THIN FILMS. I. Luck, A. Werner and D. Bräunig, Hahn-Meitner-Institut

Berlin, GERMANY; J. Alvarez-García, B. Barcones, L. Calvo-Barrio, A. Pérez-Rodríguez, A. Romano-Rodríguez, and J.R. Morante, Electronic Materials and Engineering (EME), Department d'Electronica, Universitat de Barcelona, Barcelona, SPAIN.

The difference in performance of thin film solar cells based on Cu(In,Ga)Se₂ and CuInS₂ has to be attributed to the photovoltage of the latter which is too low when considering the bandgap of the material. This fact is suspected to originate, among others, from the different preparation conditions - Cu-rich for CuInS₂, Cu-poor for Cu(In,Ga)Se₂. However, Cu-poor CuInS₂ film preparation seems to be much more critical compared to Cu-poor Cu(In,Ga)Se₂ and Cu-rich CuInS₂. The purpose of this work is therefore to further elucidate CuInS₂ formation under Cu-poor conditions. A set of Cu-poor CuInS₂

thin films have been prepared sequentially from a sputtered Cu/In precursor stack by a rapid thermal process. For most samples the preparation has been aborted at various stages of the process. Scanning electron micrographs of completely processed samples revealed polycrystalline films with crystal grains in the range of 1 μm . The lateral conductivity of the completely processed samples is in the range of $10^{-5} (\Omega\text{-cm})^{-1}$ which is in accordance with previous results. Information on the film formation was deduced from the characterisation of the partly processed samples. The X-ray diffractograms reveal that the appearance of CuInS_2 is instantaneously accompanied by reflections corresponding to In rich phases as CuIn_5S_8 or $\beta\text{-In}_2\text{S}_3$. Raman scattering measurements on the surface of the processed samples show at the initial anneal stages (up to 30 seconds) the presence of a broad band at $290\text{-}350 \text{ cm}^{-1}$ region, which correlates with the formation of Cu-poor sulphurised phases (likely CuIn_5S_8 and $\beta\text{-In}_2\text{S}_3$). Increasing the annealing time leads to appearance of the A1 CuInS_2 mode, together with an additional mode at about 305 cm^{-1} characteristic for Cu-poor CuInS_2 films. In-depth analyses of these films show a structural improvement of the CuInS_2 phase towards the back interface. The results will be correlated with TEM analysis, and will be discussed with respect to the formation of Cu-rich CuInS_2 and Cu-poor $\text{Cu}(\text{In,Ga})\text{Se}_2$.

9:45 AM H1.5

POST-DEPOSITION SULFUR INCORPORATION INTO CuInSe_2 AND CuGaSe_2 THIN FILMS. Jochen Titus, Institute of Energy Conversion, University of Delaware, Newark, DE; Hans-Werner Schock, Institut für Physikalische Elektronik, Universität Stuttgart, Stuttgart, GERMANY; Robert W. Birkmire, William N. Shafarman, Udai P. Singh, Institute of Energy Conversion, University of Delaware, Newark, DE.

The replacement of Se with S in $\text{Cu}(\text{In,Ga})\text{Se}_2$ results in a widening of the chalcopyrite band gap, which provides a pathway to improve the open circuit voltage of solar cells. In this paper, the focus is on the compositional endpoints of that compound, CuInSe_2 and CuGaSe_2 . Thin films of those materials deposited by co-evaporation were sulfurized in a constant flow atmospheric pressure reactor with the use of a gas mixture containing H_2S , and at times O_2 or H_2Se , with the balance Ar. Reaction temperatures ranged from 475°C to 575°C for times from 10 min to 8 h. Films were analyzed before and after sulfurization to determine elemental and phase composition and their surface and cross sectional morphology. The effects of initial film composition, reaction conditions and substrate were investigated. The films incorporated S in two distinctly different ways. Cu-rich films, in general, took up substantial amounts of S with solid-state diffusion being the dominant mechanism. In Cu-poor films, S reaction resulted in a segregated surface chalcopyrite layer leaving the bulk of the material almost unaffected. S incorporation was correlated with a reduction of the total chalcogen content in the film. The replacement of Se by S is discussed in terms of reaction kinetics at the surface and solid-state diffusion along grain boundaries and in the bulk. $\text{Na}_2\text{In}_2\text{S}_4$ appeared as an additional phase on films grown on Na containing substrates, which complicated both film analysis and modeling of the incorporation process.

10:30 AM *H1.6

THERMOCHEMICAL AND KINETIC ASPECTS OF CADMIUM TELLURIDE SOLAR CELL PROCESSING. Brian E. McCandless, Institute of Energy Conversion, University of Delaware, Newark, DE.

Processing highly efficient CdTe thin-film solar cells requires thermally activated reactions between the semiconducting CdTe/CdS layers and cadmium chloride and oxygen species. Although a wide range of thermal and chemical processing sequences yield small area cells with conversion efficiency up to $\sim 13\%$, obtaining higher efficiencies on a routine basis has only been demonstrated for a narrow processing window. Translating this 'art' to the module scale requires a more detailed science and engineering basis. Thus, elucidating the critical temperature/time/concentration for reaction and diffusion kinetics and quantifying the effects on material properties and device operation is of paramount importance to further development of CdTe based photovoltaic technology. This paper will present thermochemical and kinetic relationships that govern the interaction between the CdTe and CdS layers; and reactions which occur between these and oxygen and cadmium chloride reactants. In particular, the effects of the thermal and chemical history of the CdTe/CdS and the relationship to subsequent treatments will be addressed. Glancing incidence x-ray diffraction of the surface of CdTe and CdS films indicates: 1) the formation of native oxides by reaction with oxygen; 2) formation of CdO by reaction with cadmium chloride and oxygen mixtures; and 3) the degree of penetration of these oxide products. Symmetric x-ray diffraction measurements of individual line profiles indicate the degree of alloying between CdTe and CdS, and modeling these profiles shows that cadmium chloride and oxygen concentration primarily enhance grain boundary diffusion. Formation of native oxides retard grain boundary diffusion of CdS into CdTe.

The paper presents crystallographic and phase data, bulk and grain boundary diffusion coefficients, and diffusion activation energies for CdTe/CdS structures after different treatments in oxygen, cadmium chloride, and combinations thereof using CdTe films evaporated at $\sim 300^\circ\text{C}$ and 500°C with and without oxygen during growth.

11:00 AM H1.7

EFFECT OF CdCl_2 TREATMENT ON THE INTERIOR OF CdTe CRYSTALS. K.J. Price, University of Toledo, Department of Physics and Astronomy, Toledo, OH.

An essential processing step in CdTe/CdS polycrystalline solar cells is heat treatment in CdCl_2 . We present photoluminescence results from single crystals of CdTe that have been exposed to CdCl_2 treatments at 387°C similar to those used in actual cell fabrication. Using sub band gap excitation from a tunable diode laser, we probe states in the interior of the crystal. We show that high-purity (99.998%) CdCl_2 treatment results in the appearance of a 1.456 eV donor-acceptor transition that is likely due to a Cl-Cu center. Low purity (99.7%) CdCl_2 treatment results in the appearance of the 1.456 eV line and a 1.555 eV Cu-related¹ emission. These results indicate that the CdCl_2 treatment has an effect on the interior of CdTe grains, in addition to its already well established effect on grain boundaries in polycrystalline CdS/CdTe devices. They also imply that CdCl_2 treatment may result in the incorporation of Cu into the CdTe grains. The results will be related to the effects of CdCl_2 on polycrystalline CdS/CdTe devices that have been observed by other groups. This work supported by NREL. 1. D. Grecu, A.D. Compaan, D. Young, U. Jayamaha, D.H. Rose, J. Appl. Phys. 88, p. 2490 (2000)

11:15 AM H1.8

PHOTOLUMINESCENCE CHARACTERISATION OF ION IMPLANTED CdTe. D.P. Halliday, M.D.G. Potter, D.S. Boyle, K. Durose, University of Durham, Department of Physics, Durham, UNITED KINGDOM.

We have ion implanted a series of dopants into single crystal CdTe. The impurities studied are: 0, Cl, Cu, S, Na and Sb, and were selected because of their importance in thin film CdTe-CdS photovoltaic devices. Each impurity was implanted at an accelerating voltage chosen to give a smooth gaussian distribution of impurities in the first few microns of material with a doping density of $1 \times 10^{15} \text{ cm}^{-3}$. Low temperature photoluminescence spectra were recorded from each sample and compared with an undoped sample. The features observed in each sample are discussed and the data is compared to an earlier photoluminescence study of thin film CdTe-CdS photovoltaic structures [see: Thin Solid Films 361 (2000) 248].

11:30 AM H1.9

NOVEL 'PHOTOCHEMICAL DEPOSITION' AND CONVENTIONAL 'ELECTROCHEMICAL DEPOSITION' OF CdS AND HgCdTe THIN FILMS AND THEIR CHARACTERIZATION FOR SOLAR CELL DEVICE APPLICATIONS. R. Kumaresan, M. Ichimura, Nagoya Institute of Technology, Dept of Electrical and Computer Engineering, Nagoya, JAPAN; S. Moorthy Babu, P. Ramasamy, Anna University, Crystal Growth Centre, Chennai, INDIA.

Photovoltaic solar cell devices based on semiconductor thin films have been identified as the potential and efficient way of solar energy conversion. Solar cells based on II-VI semiconducting thin films are attaining growing interest for low cost photovoltaic conversion of solar energy due to their high absorption coefficients and therefore low material consumption for their production. In the present research, solar cell structures based on the semiconductor thin films, such as, CdS/CdTe and CdS/ HgCdTe have been fabricated and analyzed. CdS thin films have been deposited by a novel deposition technique, namely, 'Photochemical deposition'. The deposition was carried out from an aqueous bath containing CdSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ and the compound formation takes place by the ultra-violet illumination. Various growth parameters have been identified and optimized for the photochemical deposition of device quality CdS films. The grown films were characterized for their structural, compositional, morphological, optical and electrical properties by means of X-ray diffraction technique, Raman Spectroscopy, SEM, AES, Optical transmission spectra, I-V characteristics etc. The Cd rich HgCdTe films used for the device fabrication have been electrochemically deposited from an aqueous solution, containing CdCl_2 , HgCl_2 and TeO_2 by potentiostatic technique. Different driving parameters such as deposition potential, pH of the electrolyte, concentration of the different species in the bath, temperature of the bath etc., have been optimized for the deposition of device quality films. The grown films were characterized by various techniques such as XRD, SEM, AFM, EDX, XPS, UV-Visible spectra, thickness profiler, I-V characteristics etc. to understand the nature and quality of the films. CdTe single crystal substrate used for the cell fabrication of CdS/CdTe cell structure was analyzed for its quality by X-ray rocking curve

measurement using conventional DCD and DCD with synchrotron radiation. First solar cell devices using photochemically deposited CdS films, of the structures CdS/CdTe and CdS/HgCdTe, were fabricated and the conversion efficiency was analyzed. The results will be discussed in detail at the conference.

11:45 AM H1.10

MICROSCOPIC ANALYSIS OF RESIDUALS ON POLY-CRYSTALLINE CdTe FOLLOWING WET CdCl₂ TREATMENT.

Timothy A. Gessert, Sally E. Asher, Rick Matson, Helio Mountinho, National Renewable Energy Laboratory, Golden, CO; Doug Rose, First Solar LLC, Perrysburg, OH.

The demonstration of a manufacturable, stable, low-resistance, ohmic contact for p-CdTe polycrystalline photovoltaic devices has been a long-standing technology goal. We have demonstrated devices with fill factors approach 77% by incorporating a Cu-doped ZnTe contact interface layer between the p-CdTe and a Ti metallization. Because this process also uses ion-beam milling to prepare the surface (rather than wet-chemical etching), it is expected that the process may provide long-term advantages for large-scale manufacturing. Because nearly all other contacting processes employ an aggressive chemical etch for surface pretreatment, very little information exists detailing the surface condition prior to contacting, or the relevant effects of dry etching. One important issue regards how well dry-etching removes water insoluble residues from the wet-CdCl₂ treatment. Earlier device studies have shown that, for 500 eV Ar ions, a pre-contact mill depth of 100-200 nm is sufficient to establish low-resistance at the CdTe/ZnTe interface. However, subsequent compositional analysis of this interface, using high-resolution secondary ion mass spectroscopy (SIMS), reveals that a significant amount of interfacial Cl remains. To elucidate the nature of the Cl contamination, we have utilized field-emission scanning electron microscopy (FESEM) and atomic-force microscopy (AFM). The microscopic analysis shows that the CdCl₂ residues are contained in surface deposits localized primarily along grain boundaries, and these deposits obscure approximately 20% of the CdTe surface. Similar analysis following various ion-beam milling treatments shows that very little of this residue is removed by what had been previously considered "optimum" ion-beam milling processes. The analysis also shows that the Cl residue may have a significantly lower ion etch rate than the surrounding CdTe surface. This differential ion etching effects surface roughness and impacts estimates of ion mill rate. Moreover, it suggests that higher fill factors may be possible if complete removal of the CdCl₂ residue is achieved.

SESSION H2: MATERIALS AND SYNTHESIS II

Chairs: Tokio Nakada and Ayodhya N. Tiwari
Tuesday Afternoon, April 17, 2001
Salon 5/6 (Marriott)

1:30 PM *H2.1

PHYSICAL VAPOR DEPOSITION OF Cu(In,Ga)Se₂ FILMS FOR INDUSTRIAL APPLICATION. T. Wada, Department of Materials Chemistry, Ryukoku University, Otsu, JAPAN; S. Nishiwaki, Y. Hashimoto, T. Negami, Advanced Technology Research Laboratories, Matsushita Electric Ind. Co., Ltd., Kyoto, JAPAN.

Cu(In,Ga)Se₂ thin films were prepared by physical vapor deposition. The CIGS films were deposited by three kinds of deposition method. The 1st method was "2-stage process" in which the (In,Ga)₂Se₃ precursor layer was deposited on Mo coated soda-lime glass at the first stage, and then exposed to Cu and Se fluxes to form CIGS films at the 2nd stage. The 2nd method was ordinary "3-stage process". The 3rd method was "2-stage deposition and post-annealing process" in which CIGS films were deposited at low substrate temperatures and the obtained CIGS precursor films were annealed in Se flux at high temperatures. Solar cells with our standard structure of ITO/ZnO/CdS/CIGS/Mo/glass were fabricated. A solar cell using a CIGS film prepared at 400°C by the 2-stage process showed an efficiency of 11.8% and that using a CIGS film deposited at 350°C by the "3-stage process" showed an efficiency of 12.4%. The solar cell with an MgF₂/ITO/ZnO/CdS/CIGS/Mo/glass structure using a CIGS film prepared by the "2-stage deposition and post-annealing process" showed an efficiency of 17.5% ($V_{oc}=0.634$ V, $J_{sc}=36.4$ mA/cm², FF=0.756). The quality of the CIGS films are discussed on the basis of the growth mechanism of CIGS crystals during the PVD process.

2:00 PM *H2.2

GROWTH OF COEVAPORATED Cu(In,Ga)Se₂ - THE INFLUENCE OF RATE PROFILES ON FILM MORPHOLOGY. Marika Bodegard, John Kessler and Lars Stolt, Angström Solar Center, Uppsala University, Uppsala, SWEDEN.

Boeing were the first to supersede 10% efficiency for a CuInSe₂ solar cell[1]. The so called Boeing recipe uses coevaporation of the elements and is made in two steps. The first 2/3 of the evaporation is carried out under Cu-rich conditions. In the final 1/3 the Cu evaporation rate is reduced in order to obtain an overall Cu poor stoichiometry.

Variations of this approach have been used in this paper, expressed in different evaporation rate profiles. The influence of the evaporation rate profiles on the microstructure of coevaporated Cu(In,Ga)Se₂ (CIGS), is discussed. The Cu concentration in the film during growth has been varied from Cu excess during the nucleation and main part of the evaporation to a constant ratio between the Cu and group III elements. In the latter and finishing part of the growth, the Cu rate has been decreased gradually or by turning off the source completely, while the group III elemental rates have been increased or kept constant. Bandgap profiles can be obtained by varying the Ga/In ratio during growth. High Ga concentration near the back contact gives improved photovoltaic performance. This can be obtained by having evaporation rate profiles with high Ga content in the beginning of the deposition. This paper discusses the influence on the microstructure using this approach. Another factor which strongly influences the microstructure is the concentration of Na. This influence is studied by using either soda lime glass or soda lime glass with a barrier hindering Na diffusion as substrate materials. Na free growth leads to small grains even when Cu is evaporated in excess during the first part of the deposition. Also the Ga concentration in the beginning of the evaporation has been found to influence the film microstructure regardless of if there is Cu excess or not. [1] R.A. Mickelsen and W.S. Chen, Proceedings of 15th IEEE Photovoltaic Specialists Conference (1981), p. 800

2:30 PM H2.3

EFFECT OF GRAIN SIZE, MORPHOLOGY AND DEPOSITION TEMPERATURE ON EVAPORATED Cu(In,Ga)Se₂ FILMS.

William N. Shafarman, Jie Zhu, Institute of Energy Conversion, University of Delaware, Newark, DE.

The effect of different deposition sequences and temperatures on the grain size and morphology of Cu(In,Ga)Se₂ films deposited by multisource elemental evaporation has been characterized. The deposition processes incorporate different sequences of delivery of the Cu and In Ga fluxes to compare films which nucleate with a Cu-rich layer, a Cu-poor layer, or an In-Ga-Se layer, and to generally determine the effect of Cu-rich growth during the deposition. Using each process sequence, films were deposited at substrate temperatures of T_{SS} = 400, 480, and 550°C. The grain size distribution has been quantitatively determined by analyzing AFM images and is described by a log-normal distribution. The mean grain area increases from < 0.1 μm² for films deposited with T_{SS} = 400°C to 0.5 - 1.0 μm² with T_{SS} = 480°C, independent of whether there is a Cu-rich growth step. However, the grain area does not increase further with higher T_{SS}. The morphology is further described by the surface roughness measured by AFM and by cross-sectional SEM micrographs. The effect of deposition process and temperature on sodium diffusion from the soda lime glass substrate will also be presented. Increasing T_{SS} affects solar cell performance to different extents depending on the deposition sequence. Device performance increases monotonically with T_{SS} independent of deposition sequence, and the temperature dependence is the greatest without a Cu-rich growth step. At T_{SS} = 550°C, device efficiencies of 16.5% are obtained independent of process sequence. The correlation between morphology and grain size, deposition temperature and device performance will be discussed.

2:45 PM H2.4

NEW APPROACH FOR RAPID LOW-TEMPERATURE SYNTHESIS OF DEVICE QUALITY SEMICONDUCTOR FILMS.

Shalini Menezes, InterPhases Research, Thousand Oaks, CA.

The quest for lower cost and higher efficiency continues even as the thin film photovoltaic technology enters the commercial arena. The use of low-cost non-vacuum methods such as electrodeposition that are needed for large-area module manufacturing, lead to low grade absorber layers; these layers require additional cost-intensive vapor phase processing steps to produce efficient devices. Chemical or electrochemical atomic layer epitaxial methods have been recently introduced to produce crystalline films on single crystal substrates. However, the film growth is extremely slow since a separate solution and deposition cycle are needed to produce one atomic layer for each constituent element of the semiconductor compound. This paper outlines a molecular level approach that circumvents the need for two or more separate electrolytes, the rinse cycles between each layer deposition and the elaborate deposition apparatus. The electrochemical molecular synthesis of epitaxial semiconductor films could offer a relatively simple, fast and inexpensive method to fabricate morphologically homogenous absorber layers without further high temperature treatments. The paper will discuss the concepts underlying the electrochemical molecular epitaxy and present the results of initial investigations, involving the synthesis of binary

semiconductors such as, copper selenide on non-crystalline substrates in a flow cell.

This work is sponsored by the California Energy Commission EISG program.

3:30 PM H2.5

IMPROVEMENTS IN NON-VACUUM DEPOSITION OF PARTICULATE MATERIALS. Chris Eberspacher, Karen Pauls, Jack Serra, Unisun, Camarillo, CA.

One of the most promising strategies for lowering the cost of photovoltaics (PV) is the use of thin-film technologies in which thin films are formed from particulate precursor materials deposited by non-vacuum techniques. To date, particles-based non-vacuum techniques have yielded 11.7% cells and 5% monolithic multi-cell modules. These device results have been achieved with particulate layer deposition techniques characterized by particle packing fractions less than half of the theoretical close-packing of uniform spheres, by layer morphologies with short-range thickness variations of 50% or more, and by materials use efficiencies of less than 25%. Low packing fractions and non-planarity of particulate precursor layers can result in sintered films with low densities and poor transport properties, and can result in low device photovoltages due to excessive junction area and to shunting. In order to further increase device efficiencies and to fully realize potential manufacturing cost savings, one must improve particulate layer packing and morphology, and one must increase materials use efficiency. Advanced spraying and printing techniques are capable of the required improvements. Recent progress in improving layer and film quality will be presented.

3:45 PM H2.6

NANOPARTICLE OXIDES PRECURSOR INKS FOR THIN FILM COPPER INDIUM GALLIUM SELENIDE (CIGS) SOLAR CELLS. Vijay K. Kapur, Matthew Fisher and Robert Roe International Solar Electric Technology Inc. (ISET), Inglewood, CA.

High efficiency potential for thin film CIGS solar cells has been clearly demonstrated in a number of labs working on chalcopyrite solar cells. The challenge lies in developing a low cost process that is suitable for low cost mass production of these solar cells. ISET has developed a novel patented process for manufacturing thin film CIGS solar cells. In this novel approach, ISET uses water based precursor inks (colloidal dispersions) made of nanoparticles of mixed oxides to deposit the absorber CIGS layer. Using the ink, a precursor layer (thickness 1.5 -2.5 microns) is deposited on a conducting substrate of choice employing a variety of non-vacuum coating techniques. This precursor layer is then converted to a CIGS layer of desired stoichiometry by annealing it. The solar cell fabrication is completed by depositing a CdS layer from a chemical bath followed by the deposition of a ZnO layer using low pressure MOCVD process. Small area solar cells with efficiency > 13% have been fabricated using this non-vacuum process. The advantages of this versatile process are; composition control in the absorber layer, high material utilization and low cost. This paper will discuss the details of this new process with a special emphasis on the preparation of precursor inks.

4:00 PM *H2.7

NEXT GENERATION TRANSPARENT CONDUCTING OXIDES FOR PHOTOVOLTAIC CELLS. David Ginley, Tim Coutts, John Perkins, David Young, Xiaonan Li, Phil Parilla, National Renewable Energy Laboratory, Golden, CO; Renaud Stauber, University of Colorado, Boulder, CO; Chris Duncan, Colorado School of Mines, Golden, CO.

Transparent conducting oxides (TCOs) represent one of the key components of photovoltaic cells. Traditionally, ZnO and $\text{In}_x\text{Sn}_{1-x}\text{O}_2$ have been the primary TCOs of interest. Recently, considerable activity in the TCO area has led to the development of new materials that will impact PV, flatpanel displays, architectural and electrochromic applications. We will report on key advances in two areas. First is activity in the ternary n-type materials most particularly Cd_2SnO_4 and Zn_2SnO_4 which are already having an impact on CdTe solar cells. These materials offer the promise of being more robust and higher performance. Cd_2SnO_4 especially has demonstrated high mobilities. Most of the phase space for a pyramid with apexes of CdO, In_2O_3 , ZnO, SnO_2 , and Ga_2O_3 has yet to be explored. This offers the potential for a vast array of tailorable n-type materials. The second major area is in the area of p-type TCOs. Until the last couple of years there were no real members in this class. Now there are a number of stoichiometric compounds such as CuAlO_2 and SrCu_2O_2 with good transparency and encouraging conductivities. In addition, ZnO has also been doped p-type through the addition of nitrogen or nitrogen oxides. Though the mechanism of the doping is not entirely clear doping levels up to 10^{20} have been obtained. The existence of p-type TCOs adds a new degree of freedom for PV device design. It also leads to the possibility of developing all oxide heterostructure devices and recently an all oxide diode has been

demonstrated by Ohta and Hosono et.al. We will discuss these results in the context of their future impact on photovoltaic devices. The National Renewable Energy Laboratory is a U.S. Department of Energy Laboratory operated by Midwest Research Institute-Battelle-Bechtel under contract #DE-AC36-99-GO10337

4:30 PM H2.8

CONTROL OF OPTICAL AND ELECTRICAL PROPERTIES OF ZnO FILMS FOR PHOTOVOLTAIC APPLICATIONS. Ralf Hunger, Kakuya Iwata, Paul Fons, Akimasa Yamada, Koji Matsu-bara, Shigeru Niki, Electrotechnical Laboratory, Optoelectronics Div, Tsukuba, Ibaraki, JAPAN; Ken Nakahara, Hidemi Takasu, ROHM Co Ltd, Optical Device R&D Div, Kyoto, JAPAN.

In this study we explore the potential of radical-source molecular beam epitaxy (RS-MBE) for the growth of highly conductive and transparent ZnO window layers. In contrast to the conventionally employed sputtering techniques where highly energetic particles are produced, the RS-MBE of ZnO using an atomic oxygen beam can be considered as a "soft" deposition technique which is potentially advantageous for the deposition of window layers in solar cells. In order to investigate the effect of extrinsic impurity doping on ZnO film properties, we have first developed a growth technique to reduce the native defect density of non-doped ZnO films, achieving $n \leq 1 \times 10^{17} \text{ cm}^{-3}$ and $\mu_e \geq 100 \text{ cm}^2/\text{Vs}$. In a second step, we have employed extrinsic dopants such as Ga and other materials and investigated their effect on the electrical and optical properties of ZnO films for window layer applications. Epitaxial ZnO(001) films were grown in a UHV system on sapphire{1120} substrates at growth temperatures of $\sim 420^\circ\text{C}$. The oxygen beam was produced in a RF-plasma source equipped with an ion trap, and elemental Zn was supplied from a Knudsen cell. ZnO films with thicknesses $\sim 1 \mu\text{m}$ were characterized by four-probe Hall and optical transmission measurements. Preliminary results of the impurity doping experiments indicated that ZnO films with electron mobilities up to $29 \text{ cm}^2/\text{Vs}$, carrier densities of $\sim 5 \times 10^{20} \text{ cm}^{-3}$, and resistivities of $\sim 4 \times 10^{-4} \Omega \cdot \text{cm}$ could be fabricated. In the visible region an optical transmission coefficient of $\geq 80\%$ was obtained. In addition, we have found transmission losses in the near-bandgap and infrared region depending on the dopants in question. The influence of different dopants on the ZnO film properties will be further discussed.

4:45 PM H2.9

INFLUENCE OF CHEMICAL BATH DEPOSITION PARAMETERS ON THE FORMATION OF $\text{CuInS}_2/\text{Zn}(\text{Se},\text{O})$ JUNCTIONS FOR THIN FILM SOLAR CELLS. A.M. Chaparro, M.T. Gutiérrez, J. Herrero, Dept Energías Renovables, CIEMAT, Madrid, SPAIN; J. Klauer, Hahn-Meitner-Institut, Berlin, GERMANY.

The growth of thin films of ZnSe-ZnO composition can be made with controlled properties in a chemical bath. Morphology, composition, band gap and conductivity of the films can be tuned to a certain degree by choosing appropriate bath parameters. These properties are of fundamental importance for their behaviour as buffer layers of thin film solar cells, as they influence properties of the absorber/buffer junction such as interfacial electric fields, band alignment and interfacial states. This absorber/buffer interface being the pn-heterojunction of the solar cell is of major importance for recombination and open circuit voltage and thus for energy conversion efficiency of the cell. We deposit different layers on CuInS_2 absorber layers and fabricate solar cell devices of $\text{CuInS}_2/\text{Zn}(\text{Se},\text{O})/\text{ZnO}$ composition. Characterisation of the resulting solar cells is made with different techniques such as I-V curves, quantum efficiency and electroreflectance, and related to chemical bath deposition conditions.

SESSION H3: THIN FILMS ON ALTERNATIVE SUBSTRATES

Chairs: John M. Merrill and Uwe Rau
Wednesday Morning, April 18, 2001
Salon 5/6 (Marriott)

8:30 AM *H3.1

ATOMIC (IONIC) DIFFUSION AND DRIFT EFFECTS IN CHALCOGENIDE SEMICONDUCTOR-BASED PHOTOVOLTAIC CELLS. David Cahen, Department of Materials & Interfaces, Weizmann Institute of Science, Rehovoth, ISRAEL.

When explaining the mode of action of electronic devices the diffusing species of interests that are considered normally are electronic charge carriers. Over the past few years it has become clear that atomic species, especially in their charged form as ions, can move, from their lattice positions, under normal operating conditions of the device [1]. We will discuss the importance of such effects in photovoltaics, stressing the (opposite) cases of CuInS_2 [2] and CdTe-based [3] cells. In the former type of cells Cu diffusion has been invoked as a cell-stabilizing factor, while in the latter case it is thought to be a

destabilizing factor. In CuInSe₂ such diffusion occurs mostly in the bulk, while in CdTe/CdS cells apparently diffusion is mainly via surfaces and grain boundaries. Such surface diffusion effects also play a role in the very fast distribution of Na throughout CuInSe₂-based cells. As explained elsewhere [4], all other factors being equal, ion diffusion and drift effects will become more pronounced as sample size decreases. As such it is not surprising that diffusion effects are found also in dye-sensitized solar cells, based on films of mesoporous, nanometer-sized particles of wide band gap semiconductors [5]. The talk will address all these mobility issues and point to the different driving forces that underlie them. In such a way controlling ion diffusion and drift becomes possible so as to improve cell performance, especially in terms of reliability. **Acknowledgements:** This work was done in collaboration with the many colleagues, the names of whom appear as co-authors on the following papers. **References:** [1] D. Cahen, L. Chernyak, *Adv. Mater.* 9 (1997) 861; [2] J.F. Guillemoles, U. Rau, H.W. Schock, L. Kronik, D. Cahen, *Adv. Mater.*, 11(1999) 957; [3] K. Dobson I. Visoly-Fisher, G. Hodes, D. Cahen, *Sol. En. Mater. Sol. Cells*, 62 (2000) 295; [4] I. Lubomirski, D. Cahen, *Electro-chem. & Solid State Lett.* 2 (1999) 154; [5] D. Cahen, G. Hodes, M. Grätzel, J.F. Guillemoles, I. Riess, *J. Phys. Chem B* 104 (2000) 2053.

9:00 AM H3.2

HIGH-ENERGY ELECTRON AND PROTON IRRADIATION OF Cu(In,Ga)Se₂ HETEROJUNCTION SOLAR CELLS. A. Jasenek, K. Weinert, M.R. Balboul, H.W. Schock, U. Rau, Institute of Physical Electronics *ipe*, University of Stuttgart, GERMANY.

We irradiate high-efficiency CIGS/CdS/ZnO heterojunction solar cells grown on soda lime glass as well as on 100 μm thin metal foils with high fluences of electrons (0.5, 1, and 3 MeV) and protons (4, 10, and 16 MeV). These CIGS solar cells display a very high radiation resistance compared to other types of solar cells. For example, the efficiency decreases by only 10% for a 1-MeV electron fluence of $\phi_e=10^{17} \text{ cm}^{-2}$, and by only 20% for a unidirectional 4-MeV proton fluence of $\phi_p=10^{13} \text{ cm}^{-2}$. For all irradiations, the degradation of the solar cell conversion efficiency is predominantly caused by a reduction of open circuit voltage V_{OC} . We use a model to describe the loss in V_{OC} by radiation-induced defects enhancing space charge recombination in the CIGS absorber layer. The defect introduction rates $\gamma_{e,p}$ for electron and proton irradiation $\gamma_e=0.02 \text{ cm}^{-1}$ and $\gamma_p=1000 \text{ cm}^{-1}$, as deduced from current voltage analysis, are consistent with results from admittance spectroscopy, where we directly measure the respective defect densities. The generation rate of compensating donors, and hence the reduction of net doping density in CIGS, is calculated from capacitance voltage analysis, both for electron and proton irradiation. In addition to irradiating complete heterostructures, we investigate the radiation resistance of the ZnO window layer and use the results as input for numerical simulation of the degradation of CIGS solar cells. We study the partial recovery of irradiated cells upon storage at room temperature, e.g., a heavily electron-irradiated cell with a $V_{OC}=363 \text{ mV}$ after a fluence of $\phi_e=5 \times 10^{18} \text{ cm}^{-2}$ recovers to a value of 430 mV (initially 595 mV) after 18 months. Partial recovery at room temperature also occurs for all proton-irradiated CIGS solar cells. Elevated temperatures (60°C, 100°C, and 200°C), which are relevant for real space operation, drastically enhance the recovery of V_{OC} . These data significantly contribute to the knowledge base for an efficient and radiation-hard thin-film space solar cell technology.

9:15 AM H3.3

INFLUENCE OF PROTON IRRADIATION AND DEVELOPMENT OF FLEXIBLE CdTe SOLAR CELLS ON POLYIMIDE. A. Romeo, D. Baetzner, H. Zogg, A.N. Tiwari, Thin Film Physics Group, ETH (Swiss Federal Inst of Tech), Zurich, SWITZERLAND; W. Hajdas, PSI, Villigen, SWITZERLAND.

CdTe solar cells are considered promising for space applications. We have investigated the stability of CdTe solar cells against high energy proton irradiation. CdTe/CdS solar cells of 10 to 12% efficiency were developed by a vacuum evaporation method on Na-free and soda-lime glass substrates. Solar cells were irradiated with protons of 5-15 MeV. The proton irradiation causes an increase or a decrease in the open circuit voltage (V_{oc}) and fill factor depending on the energy and fluence of the radiation. However, lower values of the short circuit currents (I_{sc}) are measured for all the irradiated samples, darkening of the glass substrate is a main reason for the decrease in I_{sc} . Optical absorption measurements of the darkened glass and quantum efficiency measurements are used to calculate the actual loss in the photocurrent of solar cells. Flexible and lightweight solar cells are interesting for a variety of applications. We have developed high efficiency CdTe/CdS solar cells on polyimide films, V_{oc} of about 770 mV and I_{sc} of about 21 mA/cm² have been measured. The structural properties of CdTe/CdS layers on TCO coated polyimide have been investigated. Solar cell efficiency and CdTe properties depend on the CdCl₂ and annealing treatments.

9:30 AM H3.4

CIGS2 THIN FILM SOLAR CELLS ON STAINLESS STEEL FOIL. Neelkanth G. Dhere and Shantinath R. Ghongadi, Florida Solar Energy Center, Cocoa, FL.

CuIn_{1-x}Ga_xS₂ (CIGS2) thin-film solar cells are of interest for space power applications because of the near optimum bandgap for AM0 solar radiation in space. Recent studies have shown that CIGS and CIS2 solar cells are expected to be superior to Si and GaAs solar cells for the space missions especially in terms of the performance at the end of low earth orbit (LEO) mission. Ultra-lightweight thin-film solar cells deposited on flexible stainless steel (SS) foils have a potential for achieving high specific power. Cu-rich Cu-Ga/In layers were sputter-deposited on unheated Mo-coated SS foils from CuGa(22%) and In targets. Well-adherent, large-grain Cu-rich CIGS2 films were obtained by sulfurization in a Ar:H₂S 1:0.04 mixture and argon flow rate of 650 sccm, at the maximum temperature of 475°C for 60 minutes with intermediate 30 minute annealing step at 125°C. p-type CIGS2 thin films were obtained by etching away the Cu-rich layer segregated at the surface in a dilute KCN solution. XRD analysis of a CIGS2 film on SS foil showed reflections from a chalcopyrite CuIn_{0.7}Ga_{0.3}S₂ phase having $a_0 = 5.47 \text{ \AA}$ and $c_0 = 10.94 \text{ \AA}$, with $c_0 = 2 a_0$. Positive SIMS depth profile of the CIGS2 film showed gallium and copper concentrations increasing toward the back contact. Solar cells were completed by deposition of CdS heterojunction partner layer by chemical bath deposition, transparent-conducting ZnO/ZnO:Al window bilayer by RF sputtering, and vacuum deposition of Ni/Al contact fingers through metal mask. AM 1.5 PV parameters of a solar cell on SS foil were: $V_{oc} = 743 \text{ mV}$, $J_{sc} = 18.74 \text{ mA/cm}^2$, Fill Factor = 60.09%, efficiency = 8.37%.

9:45 AM H3.5

FABRICATION OF LIGHT WEIGHT FLEXIBLE CIGS SOLAR CELLS FOR SPACE POWER APPLICATIONS. Vijay K. Kapur, Matthew Fisher and Robert Roe International Solar Electric Technology Inc., (ISET), Inglewood, CA.

ISET has developed a patented non-vacuum process for manufacturing low cost thin film CIGS solar cells. Recently this process was used to fabricate CIGS solar cells for space power applications on metallic foils of thickness 25 and 50 microns. Solar cells of area 5.0 cm² were successfully fabricated with AM0 efficiencies about 9.0 %. For the cells fabricated on metallic foil of thickness 25 microns, the specific power density was over 500 watts per kilogram. ISET plans to use its non-vacuum approach to fabricate solar cells on a variety of flexible and light weight substrates. It is estimated that using ISET's non-vacuum process, space quality solar cells can be fabricated to achieve specific power density of 1.25 kilowatts per kilogram and at a significantly lowered cost. This paper will discuss ISET process and some of the results of solar cells measured under simulated AM0 illumination.

10:30 AM H3.6

FLEXIBLE AND MONOLITHICALLY INTEGRATED CIGS-MODULES. Friedrich Kessler, Konrad Herz, Michael Powalla, Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung, Stuttgart, GERMANY; Martin Hartmann, Marion Schmidt, Hans-Werner Schock, Institut fuer Physikalische Elektronik, University of Stuttgart, Stuttgart, GERMANY.

Cu(In,Ga)Se₂-Modules (CIGS) have been fabricated on flexible polyimide as well as on metal foils. Substrate qualification criteria are a temperature stability of at least 450°C, acceptable thermal expansion coefficients, chemical stability, low surface roughness, low costs and suitability for roll-to-roll deposition. Metal foils of acceptable costs and physical properties are ferritic steel, titanium and Ni/Fe-alloys with appropriate thermal expansion coefficients. The metal substrates were electrically insulated by thin ($d < 10 \mu\text{m}$) multiple layers of SiO_x and Al₂O₃ deposited by different methods such as plasma-CVD, sol-gel and sputtering. Best isolating films were obtained by a combination of dense plasma-CVD layers covered by a sol-gel film. The sol-gel film served both as an additional isolation barrier and as a smoothing layer on rough metallic surfaces. Laser scribing was applied for the patterning of the molybdenum back contact on polyimides as well as for the patterning of the absorber layer and worked both on polymer and metal substrates. In contrast to mechanical scribing, which is commonly used for the monolithic cell interconnection on glass substrates, we employed soft techniques on flexible substrates. Photolithography and lift-off were suitable methods for the patterning of molybdenum on insulated metals, as well as of the ZnO window layer. We will report on the fabrication and characterisation of flexible modules on 50 μm thick polymer- and 125 μm thick metal substrates up to a size of 10cm x 10cm. Module efficiencies are still below 10% but small area cell efficiencies exceeding 10% have been obtained on polyimide-, titanium-, Ni/Fe-alloy- and steel foils.

10:45 AM H3.7

LARGE-AREA DEPOSITION OF THIN-FILM Cu(In,Al)Se₂ SOLAR ABSORBERS. Leon Fabick, Lawrence Woods, G. Kleen, Rosine Ribelin, Peter Meyers, ITN Energy Systems, Littleton, CO.

Wide bandgap (≥ 1.5 eV) optical absorbers offer advantages for space PV applications due to the lower temperature dependence of the solar cell device performance and better match to the AM0 spectrum. They can also be utilized as the top junction in a monolithically connected thin film tandem junction based entirely on CIS-alloy technology. This paper presents the advances made in depositing Cu(In,Al)Se₂ CIS-alloy solar cell absorber layers using thermal evaporation from a six source in-line deposition system. Results are presented for deposition on linearly translated glass substrates and on continuous stainless steel web. Statistical process control charts of run-to-run variability for both Cu-ratio, [Cu]/([In] [Al]) and Al-concentration, [Al]/([Al] [In]) demonstrate process control. Morphological characteristics of CIAS films show results similar to those obtained for CIGS alloy films except Cu-ratios for high efficiency devices appear lower than those observed for CIGS thin-films. CIAS thin films with bandgaps between 1.28 eV and 2.04 eV, as measured from α^2 versus $h\nu$ plots, have been produced. Sub-bandgap transmissions (required for the top cell of a tandem junction solar cell) as high as 90% have been measured for these films. Bandgap versus aluminum concentration results show bandgaps are shifted lower than single crystal results reported in the literature. Both the observed difference in morphology transition with Cu-ratio and the shift of bandgap to higher Al-concentrations will be discussed relative to EDS measurement effects. The effect of Fe, Ni, Cr diffused from stainless steel substrates and the effect of Na containing precursor layers on device performance and film morphology will be presented. Results, for Mo/CIAS/CdS/TCO single and tandem junction devices will also be presented.

11:00 AM H3.8

LOW TEMPERATURE GROWTH OF CIGS THIN FILMS FOR FLEXIBLE SOLAR CELLS. D. Rudmann, F.-J. Haug, M. Kaelin, H. Zogg, A.N. Tiwari, Thin Film Physics Group, Laboratory for Solid State Physics, ETH Zürich, Zürich, SWITZERLAND; G. Bilger, Institute of Physical Electronics, University of Stuttgart, Stuttgart, GERMANY.

For the development of flexible solar cells on polymer substrates, a low temperature CIGS deposition process is required, since polymers cannot withstand high temperatures. Also a technique for Na incorporation is needed due to the lack of Na in the polymer substrates. We have developed a CIGS coevaporation process for low substrate temperatures ($< 450^\circ\text{C}$) and attained 14% cell efficiency on soda-lime glass substrates. This process has also been applied to Na-free glass and to polyimide substrates. Na was incorporated into the CIGS films by means of NaF coevaporation or by diffusion from NaCl layers. Morphology, microstructure and composition of the CIGS layers have been investigated using SEM, XRD and SIMS. The cells have been characterized by their quantum efficiency and photovoltaic performance.

11:15 AM H3.9

ION BEAM ASSISTED DEPOSITION OF Cu(In,Ga)Se₂ FILMS FOR THIN FILM SOLAR CELLS. G. Lippold, H. Neumann, A. Schindler, Institute for Surface Modification, Leipzig, GERMANY.

Common Cu(In,Ga)Se₂ (CIGS) thin film deposition procedures utilize selenization by Se vapor, gaseous Se compounds or solid phase reactions, respectively. We report on a novel ion beam selenization process. The reactive chalcogen component Se and a significant part of the thermal energy needed for CIGS formation is delivered directly into the growing surface by a low energy Se ion beam from a broad beam ion source. This highly controllable technique with respect to ion energy, dose and uniformity and with scale-up capabilities can be used in two ways either for selenization of metallic Cu/(In,Ga) thin film stacks or in co-deposition with metal evaporation or magnetron sputtering. In the case of co-deposition two remarkable advantages in contrast to standard techniques exist: (i) The CIGS growth temperature can be reduced to $< 400^\circ\text{C}$ and (ii) The Se partial pressure in the deposition chamber can be decreased by about three orders of magnitude, thus significantly reducing the Se contamination of the vacuum system. Besides the description of the method we present results of Se ion beam analysis and properties of CIGS thin films, produced by the novel selenization process.

11:30 AM H3.10

CURRENT TRANSPORT MECHANISMS IN Cu(In_{1-x}Ga_x)Se₂ AND CIS THIN-FILM SOLAR CELLS ON FLEXIBLE STAINLESS STEEL SUBSTRATES. Gaurav A. Naik and Wayne A. Anderson, State University of New York at Buffalo, Dept. of Electrical Engineering, Buffalo, NY.

Junction transport mechanisms have been studied for various Cu(In_{1-x}Ga_x)Se₂ (CIGS) and CIS thin-film solar cells, fabricated on flexible stainless steel substrates, for space applications. These devices are important because of potential lower cost, light weight and radiation tolerant performance to generate space power. Current density versus voltage (J-V) characteristics have been measured at various temperatures (150°K - 350°K) under dark conditions and standard 0.1 sun broad-spectrum illumination intensity. The light and dark J-V-T characteristics exhibit a significant cross-over in the first quadrant resulting in a loss of open circuit voltage and fill factor. Under dark conditions, in forward operation, space charge limited conduction is the dominant mechanism at higher bias voltages and temperatures below 300°K. At higher temperatures ($\geq 300^\circ\text{K}$) two transport mechanisms are evident: trap assisted transport at lower forward bias and space charge limited conduction at higher bias voltages. Under illumination conditions, space charge limited conduction dominates current transport. Current versus Voltage (I-V) characteristics have also been measured at various illumination intensity levels ranging from 1 sun to 0.05 suns. The ideality factor 'n' and the saturation current density 'J₀' have exhibited a strong dependence on the intensity of illumination resulting in asymmetric cross-over between the different I-V curves.

11:45 AM H3.11

DESIGN, ACTUAL PERFORMANCE, AND ELECTRICAL STABILITY OF CISCUT- BASED QUASI-ENDLESS SOLAR CELL TAPES. Michael Winkler, Jürgen Penndorf, Joachim Griesche, Igor Kononov, and Olaf Tober, IST - Institut für Solartechnologie, Frankfurt (Oder), GERMANY.

Solar cells based on Cu-In-S-phase absorber layers on a quasi-endless copper tape were made in a series of consecutive roll-to-roll processes, for which a base line has recently been set up. The so called "as grown cell absorber", which consists of a stack of CuIn₅S₈ and CuInS₂ layers, is completed to a solar cell by a CuI buffer layer of about 100 nm thickness and a one μm thick ZnO-TCO window layer. The growth of the absorber around the tape edges is avoided by coating them with an isolating glassy material, which is necessary for the further module fabrication. The design of the whole cell including the phase constitution of the absorber layer and the actual standard electrical characteristics will be presented in addition to the best efficiency achieved so far. An outlook will be given concerning the ability and perspectives of using these cell tapes for module production.

SESSION H4: DEFECTS

Chairs: David Cahen and Shigeru Niki
Wednesday Afternoon, April 18, 2001
Salon 5/6 (Marriott)

1:30 PM *H4.1

DEFECTS IN PHOTOVOLTAIC MATERIALS AND THE ORIGIN OF FAILURE TO DOPE THEM. Alex Zunger, National Renewable Energy Laboratory, Golden, CO.

I will first review the basic physical principles underlying the formation energy of various intrinsic defects in common photovoltaic materials (Chalcopyrites, II-VI's), including their dependence on Fermi level and chemical potentials. Second, I will summarize calculated formation energies of basic defects in chalcopyrites, showing how defects stabilize themselves via pairing. Comparison of measured and calculated defect energies will be given. Third, I will use the above principles to explain why doping of semiconductors is, in general limited. Specifically, the highest concentration of electron or hole doping possible in a given material is shown to reflect the position on an "absolute" energy scale, of a "doping pinning energy" $\epsilon_{\text{pin}}^{(n)}$ (for electrons) and $\epsilon_{\text{pin}}^{(p)}$ (for holes). Phenomenological determinations of these energies have shown that they tend to align to constant values in each class of semiconductors (e.g., III-V or II-VI compounds). We have performed pseudopotential total energy calculations to determine $\epsilon_{\text{pin}}^{(n)}$. Our calculations of $\epsilon_{\text{pin}}^{(n)}$ reveal that n-type doping is limited to spontaneously generated, free-carrier-induced "killer defects": e.g., the cation vacancy in AlN, GaN, InP and GaAs and the DX center in AlAs, AlP and GaP. Our calculated $\epsilon_{\text{pin}}^{(n)}$ are in good agreement with those determined from the phenomenological model, thus demonstrating the so-far mysterious but remarkable line-up of the pinning energies in terms of the spontaneous formation of specific "killer defects".

2:00 PM H4.2

IMPURITY COMPENSATION AND CO-DOPING IN CdTe. Su-Huai Wei and S.B. Zhang, National Renewable Energy Laboratory, Golden, CO.

CdTe is one of the strong contenders for low cost, high efficiency

thin-film solar cell materials, having achieved efficiency close to 16%. One of the main issue for the further improvement of CdTe-based solar cell efficiency is the low p-type dopability in this compound. We have systematically calculated the formation energies and transition energy levels of intrinsic and extrinsic defects and defect complexes in CdTe using first-principles total energy and band structure method. We find that (i) the p-type doping in CdTe is limited by the spontaneous formation of Cd interstitial Cd_i^{2+} , while the n-type doping is limited by the spontaneous formation of Cd vacancy V_{Cd}^{2-} . (ii) Na_{Cd} substitution produces a very shallow acceptor level at about 20 meV above valence band maximum (VBM) due to the fact that Na has no occupied d orbital. (iii) N_{Te} and P_{Te} create shallow acceptor levels in CdTe due to the large electronegativity of N and P. We suggest that higher hole carrier density is achievable if one can enhance the incorporation of N or P in CdTe, possibly through non-equilibrium process (e.g., ion implantation, gaseous source, electron beam annealing, etc.). We have also studied the effectiveness of codoping in enhancing the p-type dopability in CdTe. We find that in general, under equilibrium growth condition, co-doping does not reduce the formation energies of the defect complexes below that of the constituent point defects. Furthermore, the acceptor energy level can be lowered only if the defect complex consists of a single donor and a single acceptor, e.g., $V_{Cd} Cl_{Te}$. These observed general trends of doping in CdTe is expected to be applicable in other II-VI semiconductors.

2:15 PM H4.3

STRUCTURE INVESTIGATIONS OF In-RICH COPPER INDIUM SELENIDE COMPOUND SEMICONDUCTOR: FROM LOCAL STRUCTURE TO LONG RANGE ORDER. C.-H. Chang, Oregon State University, Corvallis, OR; J.W. Johnson, B.J. Stanbery, T.J. Anderson, R. Duran, University of Florida; S.P. Ahrenkiel, Su-Huai Wei, S.B. Zhang, M.M. Al-Jassim, National Renewable Energy Laboratory, Golden, CO; G. Bunker, Illinois Institute of Technology, Chicago, IL; E.A. Payzant, Oak Ridge National Laboratory, Oak Ridge, TN.

In this work, a detailed structure investigation of various In-rich Copper Indium Selenide Compounds ($Cu_3In_7Se_{12}$, $Cu_2In_4Se_7$, $CuIn_3Se_5$, and $CuIn_5Se_8$) was performed. The local structure was studied by performing Extended X-ray Absorption Fine Structure (EXAFS) on Cu-K, In-K, and Se-K edges of these compounds. The long range order was studied by electron and powder x-ray diffraction. Convergent Beam Electron Diffraction (CBED) analysis was carried out to obtain the symmetry information (point group, and space group) for these compounds. The resulted space group and unit cell parameters were used in the analysis of powder X-ray diffraction data. The local structure data derived from XAFS were used as building blocks for assigning atomic positions. Rietveld refinement was performed to quantitatively test the possible structure solution. It was found that the Cu and In first nearest neighbor local structures in these compounds are almost identical to those in $CuInSe_2$. The Se first nearest neighbor local structures, however, are quite different. For example, the least-square fitting of Se-K edge EXAFS spectra indicated $CuInSe_2$ consists of Se-centered tetrahedron with average 2 Cu and 2 In as nearest neighbors. On the other hand, $CuIn_3Se_5$ consists of Se-centered tetrahedron with average 0.8 Cu and 2.4 In as nearest neighbors. These results directly indicate In-rich copper indium selenide compounds belong to the defect tetrahedral structural family, which can be described as a normal tetrahedral structure with a certain fixed number of unoccupied structure sites. The data are consistent with the models proposed by first-principle calculations, which suggested that the structure of In-rich copper indium selenide compounds consist of three types of local tetrahedral cationic clusters around each Se: $VCu Cu_2In$, $2Cu_2In$, and VCu_3In . The analysis of CBED and X-ray diffraction results indicated these compounds could not be well described by any long-range order structure model, especially the selenium position.

2:30 PM H4.4

COMPOSITION DEPENDENT DOPING AND TRANSPORT PROPERTIES OF $CuGaSe_2$. S. Siebentritt, A. Gerhard, A. Bauknecht, U. Fiedeler, S. Brehme, M.C. Lux-Steiner, Hahn-Meitner-Institut, Berlin, GERMANY.

The occurrence of intrinsic defects in chalcopyrites and thus the doping and transport properties of the material depend strongly on the composition. To investigate this influence in detail epitaxial layers of $CuGaSe_2$ on GaAs and polycrystalline layers on glass/Mo with varying [Cu]/[Ga]-ratios have been grown by MOVPE (metal organic vapor phase epitaxy). Defect spectroscopy is performed by means of temperature dependent PL (photoluminescence) and Hall measurements. Doping levels in polycrystalline layers are determined by capacitance measurements on complete solar cell devices. The effect of the individual solar cells preparation steps on surface and interface recombination is investigated by PL. PL on Cu-rich samples reveals two acceptor levels 60 and 110 meV deep and a shallow

acceptor 10meV deep. Hall measurements confirm the existence of two acceptor levels with corresponding activation energies. Even on the Cu-rich side the degree of compensation is high, above 50% in most samples. From the temperature dependence of the mobility acoustic phonon scattering is determined as the dominant scattering mechanism. The luminescence spectrum of Ga-rich $CuGaSe_2$ is determined by compensation effects and fluctuating potentials due to a high density of charged defects in agreement with room temperature Hall investigations that reveal a strong decrease in netto carrier concentration and mobility with increasing Ga content. First experiments indicate a reduction of surface and interface recombination due to KCN etch and ZnO deposition.

2:45 PM H4.5

STRUCTURAL AND ELECTRONIC PROPERTIES OF POLYCRYSTALLINE $Cu(In,Ga)(S,Se)_2$ ALLOYS.

Immo M. Kötschau, Mircea Turcu, Uwe Rau, Hans W. Schock, Institute of Physical Electronics, University of Stuttgart, Stuttgart, GERMANY.

We present a systematic study on the polycrystalline $Cu(In,Ga)(S,Se)_2$ alloys with a gallium to indium ratio of $Ga/(Ga+In) < 0.3$ and a sulfur to selenium ratio varying in the range between $0 < S/(S+Se) < 1$. All samples were grown by coevaporation of the elements at constant rates under high vacuum conditions. The formation of island-like $Cu_x(S,Se)_y$ segregations correlate with the sulfur to selenium ratio in the layer and is only found in the copper rich growth region. These segregations are related to a preferred incorporation of sulfur in the copper rich growth mode. We obtain solar cell grade material from an indium rich growth mode up to a sulfur to selenium ratio of $S/(S+Se) = 0.9$. We report further a detailed analysis of the electronic properties by current voltage measurements and quantum efficiency analysis of $Mo/CIGSSe/CdS/ZnO:Al$ solar cell devices. Our results of admittance spectroscopy confirm that the concentration of the dominant deep acceptor defect in $Cu(In,Ga)(S,Se)_2$ at an energy distance of approximately 300 meV from the valence band is reduced by the addition of small amounts of sulfur ($S/(S+Se) < 0.2$). At the same time the energy of this acceptor increases with increasing sulfur to selenium ratio up to an energy of about 600 meV above the valence band at $S/(S+Se) = 0.7$. Keeping in mind that alloying of $Cu(In,Ga)Se_2$ up to $CuGaSe_2$ does not change the acceptor energy level, we conclude that the energy change in the (S,Se)-system is due to the decrease of the valence band energy with increasing sulfur to selenium ratio in the alloy. Thus, taking the deep level energy as a reference allows us to determine the energetic position of the bands within the $Cu(In,Ga)(S,Se)_2$ alloy system.

3:30 PM DISCUSSION SESSION – SUBSTRATES

Panel:

V. Kapur - ISET
A. Tiwari - ETH Zurich
F. Kessler - ZSW

SESSION H5: POSTER SESSION
GROWTH, JUNCTION FORMATION
Chairs: Rommel Noufi and Daniel Lincot
Wednesday Evening, April 18, 2001
8:00 PM
Salon 1-7 (Marriott)

H5.1

CdTe THIN FILM SOLAR CELLS: THE SnO_2 / CdS FRONT CONTACT. J. Fritsche, S. Gunst, A. Thissen, A. Klein and W. Jaegermann, Darmstadt University of Technology, Darmstadt, GERMANY.

SnO_2 coated glass is the substrate for many thin film solar cells based on CdTe absorbers. We have studied the properties of the SnO_2/CdS interface by surface science techniques using photoelectron spectroscopy (PES), scanning probe microscopy (STM/AFM), high resolution scanning electron microscopy (HRSEM) and X-ray diffraction (XRD). SnO_2 coated glass substrates as used for solar cell preparation were cleaned by different procedures such as derinsing, sputtering, heating and annealing in oxygen atmosphere. Different surface properties with a strongly dependent number of defects in the SnO_2 bandgap are identified. CdS films were deposited stepwise by thermal evaporation to determine the electronic interface properties for different surface preparation conditions.

H5.2

XPS STUDIES OF BURIED INTERFACES IN CIGS SOLAR CELLS. Bruno Canava, Jacky Vigneron, Arnaud Etcheberry, Université de Versailles, Versailles, FRANCE; Jean François Guillemoles, Denis Guimard, Daniel Lincot, Ecole Nationale Supérieure de Chimie de Paris, Paris, FRANCE; Georg Voerwinden, ZSW, Stuttgart, GERMANY.

The active interface of CIGS solar cells is the key to further improvements of their performance, yet this interface is quite complex and its formation not well understood. The present work is a contribution to its understanding using XPS studies of buried interfaces (i.e. in the device), with a special attention to CIGS/CdS interfaces. Studies have been conducted on technologically relevant material, i.e. coevaporated CIGS prepared on 30x30 cm plates. The presentation aims specially at a clarification of the formation and the role of the various segregated/intermixed phases at the interface.

H5.3

ELASTIC RECOIL DETECTION ANALYSIS OF $ZnS_x(OH)_y$ BUFFER LAYERS FOR CHALCOPYRITE SOLAR CELLS. Sven Neve, Wolfgang Bohne, Joerg Roehrich, Roland Scheer, Hahn-Meitner Institut, Berlin, GERMANY.

Chemical bath deposition of Zn-compound buffer layers is investigated for high efficiency chalcopyrite solar cells. The bath contains different amounts of ammonia, hydrazine, thiourea, and a Zn salt in aqueous solution. We use elastic recoil detection analysis (ERDA) in order to investigate the influence of the complexing agents and the pH of the solution on film growth and composition. A strong effect of the pH of the solution is revealed: At high pH (>11.5) mainly ZnS growth occurs while at lower pH Zn(OH)₂ is the dominant product. Hence, the pH of the solution can be used to adjust the film stoichiometry. With respect to the pH effect, the influence of the thiourea concentration is of minor importance. Deposition of Zn-compound films is possible without NH₃ while OH⁻ and N₂H₄ are necessary. We propose that ZnS film formation is mediated via the Zn-complex Zn(N₂H₄)₂(OH)₂. Other complexes are certainly present in the chemical bath. Their concentration determines the abundance of Zn(N₂H₄)₂(OH)₂ and thereby influences the formation of ZnS.

H5.4

CHARACTERIZATION OF THE ZnSe/CuGaSe₂ INTERFACE USING KELVIN PROBE FORCE MICROSCOPY. S. Sadewasser, Th. Glatzel, Hahn-Meitner Institut, Berlin, GERMANY; M. Rusu, State University of Moldova, Dept of Physics, Chisinau, MOLDOVA; U. Fiedeler, S. Siebentritt, A. Jäger-Waldau, M.Ch. Lux-Steiner, Hahn-Meitner Institut, Berlin, GERMANY.

To improve the efficiency of heterostructure solar cells based on chalcopyrite semiconductors a good understanding of the interface properties is crucial. By Kelvin Probe Force Microscopy it is possible to obtain laterally resolved (resolution down to 20 nm) images of the work function of semiconductor surfaces in addition to the topographical information usually obtained by non-contact AFM. We studied the ZnSe/CuGaSe₂ interface prepared by growing CuGaSe₂ onto the (110) face of freshly cleaved ZnSe single crystals by different growth processes, i.e. CVD and MOCVD. On single CuGaSe₂ grains we observed different work function values for different facets. An insulating layer developing at the interface during the growth was identified by studying the cross section through the heterojunction. From the obtained work function data a schematic band diagram for the ZnSe/CuGaSe₂ heterostructure is proposed.

H5.5

MICROSTRUCTURAL ANALYSIS OF CuGaSe₂ EPITAXIAL FILMS. S. Siebentritt, K. Gartsman, R. Scheer, U. Fiedeler, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Berlin, GERMANY; Weizmann Institute of Science, Rehovoth, ISRAEL.

CuGaSe₂ is a promising material for thin film solar cells. Applications include high open circuit voltage solar cells and tandem devices. For material characterization epitaxial films of CuGaSe₂ have been grown on GaAs(100) by MOVPE (metal organic vapor phase epitaxy). EBIC (electron beam induced current) measurements have been performed on the pristine CuGaSe₂ films as well as on CuGaSe₂/CdS/ZnO heterojunctions. In both cases electric fields in the film are discovered. EBIC contrast revealed lamella-shaped structures parallel to the (011) direction. These structures are most pronounced for Cu rich preparation. Current collection is influenced by the lamella boundaries serving as recombination planes in heterojunction samples. The lamella boundaries correspond with topographic lines along (001) which are depicted in SEM micrographs. The boundaries are tentatively assigned to plane dislocations. X-ray topography is used to identify the microstructural nature of these defects.

H5.6

CHARACTERIZATION OF THE SURFACE PHASE OF POLYCRYSTALLINE COPPER-INDIUM-GALLIUM-DISELENIDE THIN FILMS USING SPECTROSCOPIC ELLIPSOMETRY. Dean Levi, Jehad AbuShama, and Rommel Noufi, National Renewable Energy Laboratory, Golden, CO.

Solar cells based on thin polycrystalline films of

copper-indium-gallium-diselenide (CIGS) have recently achieved nearly 19% efficiency. Further advances in this technology will depend upon improved understanding of the complex quaternary CIGS material. It has been found that CIGS thin films grow in different phases, depending upon the Cu:In:Ga ratio. Recent research has shown that an In-rich layer may form at the surface of the CIGS film. This surface phase may be only one or two hundred nanometers thick. It is believed that this surface layer may be n-type, forming a homojunction with the p-type bulk of the CIGS film. Hence this surface layer could be a crucial element of a CIGS PV device. In this study, we will apply spectroscopic ellipsometry (SE) to characterization of CIGS thin films grown using the NREL 3-stage evaporation method for fabrication of thin-film solar cells. We have prepared CIGS films at various points along the Cu₂Se - In₂Se₃ tie line. Two control films have been grown with 6 at.% and 12 at.% Cu, respectively. The composition of these films may correspond to the gamma and beta phases, respectively. One hypothesis is that the surface layer that forms on CIGS device films is a mixture of gamma and beta phases. A third film has been grown exactly as it would for a high-efficiency CIGS PV device. This film is slightly Cu-poor, and corresponds to the alpha phase of the CIGS material. This device-quality film is expected to exhibit the surface phase in question. All three of these films will be characterized using variable-angle SE, or VASE. Optical properties of the beta- and gamma-like films will be utilized in the analysis of VASE data for the device film. This analysis should determine the nature and thickness of the surface layer in CIGS PV device films.

H5.7

SIGNIFICANT COMPOSITIONAL CHANGES AND FORMATION OF A Ga₂O₃ PHASE AFTER OXYGEN-ANNEALING OF Ga-RICH CuGaSe₂ FILMS. Akihiko Nishio, Hisayuki Nakanishi, Science Univ. of Tokyo, Faculty of Science and Technology, Chiba, JAPAN; Akimasa Yamada, Paul J. Fons, Ralf Hunger, Hiroshi Matsubara, Kakuya Iwata, Shigeru Niki, Electrotechnical Laboratory, Ibaraki, JAPAN.

CuGaSe₂ (CGS) is a promising material for high efficiency thin film solar cells though predicted device performance has not been realized. Understanding the difference in the chemical nature between CuInSe₂ (CIS) and CGS is critical for improving Cu(In, Ga)Se₂ solar cells with high Ga concentrations. In this work, we have investigated the effects of oxygen-annealing on CGS films focusing on compositional changes and secondary phase formation. CGS films with [Cu]/[Ga] = 0.85 - 0.90 were epitaxially grown on GaAs (001) at T_{sub} = 490 °C. The films were then annealed in an oxygen atmosphere for 1 hour at 250 - 470 °C. Before and after oxygen annealing the films were characterized by electron probe microanalysis (EPMA), photoluminescence (PL), X-ray diffraction (XRD) and atomic force microscope (AFM). The PL spectrum of Ga-rich CGS films after annealing always changed into a spectrum characteristic of Cu-rich CGS; similar effects have been reported for In-rich CIS films. XRD measurements indicate the formation of Ga₂O₃ after oxygen annealing. Selective etching of the Ga₂O₃ phase by H₂SO₄-etching showed the composition of CGS became close to stoichiometry. AFM images of annealed films showed a large number of pits ~ 100 nm in depth and ~ 2.5 μm in width. EPMA analysis using a focused e-beam showed a Ga₂O₃ is founded in a columnar form from the bottom of the pits to the film/substrate interface. The above results suggest that excess Ga in Ga-rich CGS tends to react with oxygen to form Ga₂O₃, thus the composition of the remaining CGS approaches stoichiometry consistent with the changes observed in PL.

H5.8

BACK-CONTACT EFFECTS ON CADMIUM TELLURIDE DEVICE PERFORMANCE: BEYOND THE ONE DIMENSIONAL MODEL. D. Grecu, U. Jayamaha, V.G. Karpov, G. Rich, D.H. Rose and G. Dorer, First Solar, LLC, Perrysburg, OH.

While the metal-CdTe contact is considered essential for manufacturing high-efficiency solar-cell devices, a thorough understanding of the ways in which the back-contact can affect the electrical characteristics of these devices has not been achieved. In our study, "bad" and "good" devices were created intentionally by a slight modification of the CdTe surface-preparation procedure. An extensive set of measurements was performed to characterize the two types of contacts; these include temperature-dependent current-voltage measurements in the -45 to 45°C interval, light-intensity dependent current-voltage measurements and capacitance-voltage measurements. We show that the back-contact treatment affects all of the above properties strongly in a nontrivial way. Among the surprising results was that starting with nominally identical substrates, the open circuit voltage of the "bad" cells was considerably reduced and showed little dependence on the light intensity; however the saturation value of the forward-bias current was found strongly dependent on the illumination. Neither the standard one-dimensional model (main diode junction plus back diode), nor its conceivable modifications were sufficient to explain our observations. When we took into

account in-plane variations in device parameters (beyond the one-dimensional model) we were able to explain the whole set of our data. The resulting picture is an array of many microscopically small "bad" and "good" devices connected in parallel, where the back-contact treatment is critical for reducing the relative contribution from the "bad" device component.

H5.9
PROPERTIES OF RF SPUTTERED ZnTe:N FILMS FOR BACK CONTACT TO CdS/CdTe SOLAR CELLS. Jennifer Drayton, Akhlesh Gupta, Konstantin Makhratchev, Kent Price, Randy G. Bohn and Alvin D. Compaan, Department of Physics and Astronomy, University of Toledo, Toledo, OH.

Most of the low resistance back contacts formed on high efficiency CdS/CdTe solar cells involve copper either in elemental form (such as Cu/Au back contacts) or as dopant in other material (such as Cu doped ZnTe). But, copper is also suspected to be a cause of degradation of devices in long term stability tests due to its high diffusion coefficient in polycrystalline CdTe. In this paper, we present our results on the development of Cu-free N-doped ZnTe back contact for CdS/CdTe solar cells. Reproducible N-doped p-ZnTe films were prepared using reactive RF magnetron sputtering with Ar/N₂ gas mixtures. The presence of neutral and ionized nitrogen species in the sputter plasma is monitored for various deposition conditions by using optical emission spectroscopy. The conductivity of the doped ZnTe films was about five orders of magnitude higher than that of intrinsic ones. The effect of heat treatments and etching of the films to form low resistance back contacts on high efficiency CdS/CdTe solar cell has also been studied. Efficiency of over 10% has been achieved with ZnTe:N/Ni back contact. This work was supported by NREL.

H5.10
ELECTRONIC PROPERTIES OF POLYCRYSTALLINE THIN FILM CdS AND CdTe UNDER VARYING POST DEPOSITION TREATMENTS. A.S. Gilmore, V. Kaydanov, T.R. Ohno, Colorado School of Mines, Dept of Physics, Golden, CO.

CdTe and CdS are the absorber and window layers of CdTe/CdS solar cells. The electrical properties of these films influence the performance and degradation of the completed cells. Chemical Bath Deposition is a widely used method for preparation of the CdS window layers. Electrodeposition, closed space sublimation, and vapor transport are common methods of CdTe deposition. Results of the electrical characterization of differently prepared CdS and CdTe films are presented herein. Standard post deposition treatments of both CdS and CdTe include anneals with and without CdCl₂ and copper diffusion throughout the films. Annealing provides recrystallization under elevated temperatures, while annealing with CdCl₂ promotes both recrystallization and diffusion of species throughout the film. Copper treatment is given to CdTe/CdS cells to provide a low resistance back contact on the film. This copper migrates quickly through the CdTe and accumulates in the CdS layer. Hall effect measurements provided mobility and carrier concentration of the films. Temperature dependent Hall measurements provided dominant dopant energy levels. Impedance spectroscopy (IS) has been used to show that the grain boundaries dominate the film resistivity. Temperature dependent IS has provided an estimate of the grain boundary potential barrier height. Suppression of the grain boundary resistance under illumination has been observed in these films. Capacitance measurements as a function of applied bias have provided estimates of the "doping level", or space charge density, in the vicinity of the grain boundary, which are used to explore the distribution of dopants in the films. Copper treatment has been shown to lower the CdTe film resistance, and increase the CdS film resistance. Results of the post deposition treatment studies suggest that these treatments have a large effect on the film's electrical properties, and hence the cell's performance and degradation.

H5.11
DEGRADATION OF CdS/CdTe SOLAR CELLS. S.W. Townsend, T.R. Ohno, V. Kaydanov, Colorado School of Mines, Dept of Physics, Golden, CO.

Much effort is assigned to studying the degradation of CdS/CdTe solar cells. The influence of Cu in the device structure is of particular interest. Cu is added to the CdTe device so as to obtain a near ohmic back contact. However, Cu can migrate from the back contact, and its presence is observed in the CdS layer. As such, it is important to know how Cu migrates from the back contact, since redistribution may cause device degradation. Bias dependent degradation studies can contribute to the understanding of how Cu migrates. Devising a technique that indicates Cu migration with bias stressing can aid the understanding of device changes with the presence of Cu in the CdS. Photoluminescence (PL) is a technique that can do this. So far, cells degraded at 100°C in dark under forward, open circuit, and reverse biases show different behavior in the Current-Voltage (IV),

Capacitance-Voltage (CV), and Quantum Efficiency (QE) characterization. Although reverse bias degradation provides the poorest cells, it is unclear why. Also, it is unclear which bias condition results with the largest Cu concentration in the CdS layer. Correlating the IV, CV, and QE results with stress dependent PL data can help to reveal the nature of this. CdS thin films, doped and undoped with Cu, are characterized using PL. Among the changes in the PL spectrum, an increase in the peak intensity at ~1.6 to 1.7 eV is observed when Cu is added. In solar cells, stress induced changes in the PL spectrum of CdS are also characterized. The intensity of the dominant structure in the luminescence at ~2.1 eV, known as the Yellow Band, shows a dependence on the stress condition. Moreover, some degraded cells show additional structure in the band edge luminescence that is not seen in the CdS films.

H5.12
TRAPPING MECHANISM FOR TRANSIENT CURRENT-VOLTAGE BEHAVIOR IN CIGSS-BASED CELLS. Pamela Johnson, Alexei Pudov and James Sites, Department of Physics, Colorado State University, Fort Collins, CO; Dale Tarrant, Siemens Solar Industries, Camarillo, CA; Kannan Ramanathan, National Renewable Energy Laboratory, Golden, CO.

As with many thin-film CIS photovoltaic devices, cells made using CIGSS absorbers made at Siemens Solar Industries (SSI) exhibit a modest level of reversible transient behavior in electrical properties. This modest transient behavior is not an instability, since it is reversible and long-term outdoor stability has been demonstrated for devices that exhibit the behavior. Nonetheless, the changes are a complicating factor when trying to measure or certify the photovoltaic parameters of devices or modules. The transient behavior of the cells is manifested through dark heat and moderate-temperature light soaking cycles. Typically, I-V performance declines somewhat after dark heat exposure and recovers with light soaking. C-V measurements generally reveal a wider depletion width after dark heat exposure and a decreased depletion width after light soaking. Experiments utilizing devices produced with varying buffer layers on nominally identical SSI CIGSS absorbers have shown that (1) annealing immediately following CdS deposition reduces the degree of transient behavior in SSI absorber cells and (2) fill factor improvements and a decrease in depletion width are likely caused by the same mechanism. All cells with the nominally same absorber showed similar behavior, while cells with an NREL absorber (with a similar buffer layer) showed different behavior. The changes in the depletion width within the absorber coupled with the similarities among same-absorber cells strongly suggest the transient behavior is caused by changes in the absorber. Through more extensive characterization during the transient cycle, including admittance spectroscopy, we investigate the energies of trap states in the absorber with long lifetimes being charged and discharged by the light soaking and dark heat exposure. Complementary to the more extensive characterization, AMPS modeling, developed at Pennsylvania State University, confirms that reasonable variations in trap occupation between light and dark are consistent with the I-V and C-V changes observed.

H5.13
THEORETICAL AND EXPERIMENTAL STUDY OF SHUNT EFFECTS IN THIN FILM PHOTOVOLTAICS. V.G. Karpov, G. Rich, D.H. Rose and G. Dorer, First Solar, LLC, Perrysburg, OH.

We present an analytical model that quantitatively describes the physics behind shunting in thin film photovoltaics and predicts size-dependent effects in the I/V characteristics of solar cells. The model consists of an array of micro-diodes and shunt in parallel between the two electrodes, one of which mimics the TCO and has a finite resistance. We introduce the concept of the screening length L , over which the presence of the shunt is felt in the system. The nature of this screening is that the system generates currents in response to the point perturbation caused by the shunt. L is expressed explicitly in the terms of the system parameters. We find the spatial distribution of the electric potential in the system and its I/V characteristics. The measured I/V characteristics depend on the relationship between the cell l size and L , being markedly different for the cases of small ($l \ll L$) and large ($l \gg L$) cells. Our theory predicts how the shunt related current loss area depends on the buffer-layer resistivity and thickness. This model was verified both by numerical modeling and experimentally: good agreement is obtained.

H5.14
CuGaSe₂ BASED THIN FILM SOLAR CELLS WITH DIFFERENT BUFFER LAYERS. S. Schuler, S. Nishiwaki, M. Dziedzina, W. Eisele, A. Ennaoui, S. Siebentritt and M. Ch. Lux-Steiner, Hahn-Meitner-Institute Berlin, Berlin, GERMANY.

Due to its high bandgap of 1.68eV CuGaSe₂ (CGS) is an ideal candidate for the top cell of a chalcopyrite based tandem device with

a CuInSe₂ bottom cell. However, considerable optimisation of the CGS device is still necessary for this purpose. Polycrystalline CGS thin films were grown by co-evaporation of the elements in high vacuum. Presently a two-stage process is used for achieving best results. Mo/CGS/CdS/ZnO devices with such absorbers show open circuit voltages well above 800mV (under AM1.5 illumination) which is comparable to the best CGS devices grown by co-evaporation. Our standard CBD recipe of the CdS buffer layer deposition, which is optimised for Cu(In,Ga)Se₂ solar cells, was adapted for efficient CGS devices. However, a CdS buffer layer limits efficiencies in high gap chalcopyrite based solar cells due to a negative conduction band offset leading to increased interface recombination. A promising material for buffer layers in high gap chalcopyrite solar cells is ZnSe due to the formation of a favourable spike in the conduction band. Based on results of our Mo/CGS/buffer/ZnO devices the suitability of various buffer layers in CGS solar cells is discussed. The different devices are optically and electrically characterised by I/V analyses and quantum efficiency measurements. The absorber and buffer layer compositions are precisely analysed by X-ray fluorescence and the influence on the device performance is shown.

H5.15
ELECTRONIC PROPERTIES OF Cu-In-S SOLAR CELLS ON Cu-TAPE SUBSTRATE (CISCUT). Igor Konovalov, Jürgen Penndorf, Reinhard Brückner, Olaf Tober, Institut für Solartechnologien, Frankfurt (Oder), GERMANY.

Thin film solar cells obtained by "CIS on copper tape" fabrication technique (see e.g. Jacobs et al., Proc. 2nd WCEPSEC (1998), 409) are being investigated. This technique promises a high throughput capability, but the efficiency of the cells is still about 5-6%. The aim is to introduce the model of the band structure of the absorber discussed in the previous work (Konovalov et al., Solar Energy Materials and Solar Cells (2000), 67-49) into the model of the whole cell and to determine the parameters of the model quantitatively using methods like quantitative EBIC profiling (Konovalov, Breitenstein Semicond. Sci. Technol. to appear in December 2000), DSR measurements, C-V doping profiling, I-V measurements, etc. Parameters like the position of the space charge region, the net doping profile, and the band offset at the heterojunction are being determined. The benefits and drawbacks of such a cell structure and its parameters are discussed.

H5.16
THE QUANTIFICATION OF THE EFFECT OF TRANSIENTS AND TEMPORAL STABILITY ON THE PERFORMANCE MEASUREMENTS OF CdTe AND CIGS SOLAR CELLS AND MODULES. Gabi Friesen, Ewan D. Dunlop, Francesco Merli, European Commission, Joint Research Centre, Environment Institute, ESTI, Ispra, ITALY.

Several groups have shown that IV-measurements of CdTe and CIGS devices exhibit large variations in repeatability, making inter comparison measurements between different laboratories difficult. The European Solar Test Installation (ESTI) as part of its development and quality assurance programme has experimented over the past year with the effects of pulsed solar simulators on accurate and repeatable measurement of large area thin film solar modules. Several inconsistencies in measurements have been found, and as a result the group has executed a systematic study of how feasible different IV characterisation methods are for CdTe and CIGS technologies. In this paper the main emphasis is put into transient effects introduced by different IV systems. A comparison of the results obtained on different CdTe and CIGS solar cells and modules by different flash simulators and steady state simulators are presented. For the pulsed measurements two different Large Area Pulsed Solar Simulator (LAPSS) systems were used a SpectroLab LAPSS and a PASAN LAPSS. The first simulator is characterised by a trapezoidal pulse with duration of approximately 1.5 ms and a temporal irradiance stability of better than ±2%. The second by a poisson type distribution of the light pulse and a temporal irradiance stability, which depends on the sweep speed of the IV curve (faster sweep = more stable). For a better understanding the pulsed measurements are compared to quasi steady state and transient measurements made under continuous illumination on a WACOM WXS-140S-Super tandem-light source and outdoor measurements.

H5.17
VOLTAGE DEPENDENT CARRIER COLLECTION IN CdTe SOLAR CELLS. Derk L. Bätzner, Swiss Federal Institute of Technology Zurich, Thin Film Physics Group, Zurich, SWITZERLAND; Jutta Beier, ANTEC GmbH, Kelkheim, GERMANY.

The IV-characteristics of CdTe solar cells often show a roll-over behaviour, which is a current limitation in the forward bias direction. This current limitation is due to a second diode in series with the pn-junction, but of opposite orientation. The onset of this reverse-diode is voltage dependent and therefore the IV-characteristics

cannot be modelled with a two-diode equation. The roll-over and therefore the IV-characteristics, i.e. the diode behaviour, shows a dependence on the spectral part of the irradiation. We present an investigation of this spectral dependent carrier collection at different work points of the diode. The so obtained voltage dependent quantum efficiency is analysed and correlated with the diode parameters derived from CV-characteristics. The reverse-diode is usually attributed to a barrier at the back contact. A set of cells with different back contacts are investigated and the origin of the reverse-diode is discussed.

H5.18
Cd-DIFFUSION IN Cu(In,Ga)Se₂ POLYCRYSTALLINE FILMS. M. Schmidt, Q. Nguyen, H.W. Schock, U. Rau, Institute of Physical Electronics, University of Stuttgart, GERMANY; W. Bohne, J. Röhrich, Hahn-Meitner-Institute, GERMANY.

High efficiency Cu(In,Ga)Se₂ solar cells, in general, use CdS buffer layers deposited by a chemical bath at 60-80°C. The CdS/Cu(In,Ga)Se₂ heterojunction is an electrically active interface and of primary importance for the solar cell operation. According to recent investigations the chemical bath deposition process implies some intermixing and interdiffusion between the Cu(In,Ga)Se₂ absorber material and the CdS buffer layer. This contribution focuses on the role of Cd diffusion into the absorber on the electronic properties of the heterojunction solar cells. We treat bare absorber layers with a cadmium containing solution prior to the deposition of the CdS buffer layer. We examine these absorber layers by means of elastic recoil detection analysis (ERDA) and solar cells made from the Cd-treated thin-films with admittance spectroscopy. First results of ERDA indicate that after the prolonged treatment large quantities of Cd (the equivalent of a 25 nm thick layer of pure CdSe) are accumulated in the surface region of the Cu(In,Ga)Se₂ film. Air-annealing of the absorbers at 200°C for up to 1 h does not change the spatial distribution of the Cd as it is detected by ERDA. This implies that the amount of Cd diffusing deeper into the absorber is below the detection limit of 10¹⁹ cm⁻³. However, capacitance data gained from admittance measurements show that the effective doping density in the Cu(In,Ga)Se₂ film decreases by the Cd treatment and even more if the samples are air-annealed at 200°C. Extensive air-annealing of Cd-treated absorber layers leads even to a removal of the pn-junction by completely compensating the p-type doping (of initially several 10¹⁶ cm⁻³) of the Cu(In,Ga)Se₂ absorber layer. We explain this fact by a diffusion of a small fraction of cadmium from the close to surface reservoir through the whole depth of the absorber.

H5.19
STUDIES OF CuInSe₂ USING CONVENTIONAL SOLID-STATE MAGNETIC RESONANCE TECHNIQUES. P.E. Stallworth, S.G. Greenbaum, Dept. of Physics, Hunter College of CUNY, New York, NY; V. Aubin, L. Binet, J.F. Guillemales, ENSCP, Paris, FRANCE; G. Voewinden, M. Powalla, ZSW, Stuttgart, GERMANY.

An overview of recent experiments employing conventional solid-state magnetic resonance studies of CIS and CIGS is presented. The measurement of properties relevant to the electronic characteristics of the material by magnetic resonance is particularly challenging due to the dilute nature of intrinsic defects, yet several interesting observations have been made. The ⁶³Cu NMR displays temperature dependent chemical shifts whereas the ¹¹⁵In lineshapes are susceptible to quadrupolar interactions. The rich detail observed in the ¹¹⁵In responses provides information pertaining to structural defects near indium sites. Additionally, ESR data, which provide evidence for trapped electronic spins at defect sites, are presented for the first time for pilot-line coevaporated CIGS. All results will be discussed for various systematically modified compositions in relation to electrical properties, impurities and intrinsic defects.

H5.20
INFLUENCE OF ATOMIC HYDROGEN ON INTRINSIC DEFECTS IN Cu(In,Ga)Se₂. Karsten Otte, Gerd Lippold, Wilfried Frank, Axel Schindler, Institut für Oberflächenmodifizierung, Leipzig, GERMANY; Alois Weidinger, Johann Krauser, Hahn-Meitner-Institut, Berlin, GERMANY.

The ternary chalcopyrite semiconductor Cu(In,Ga)(Se,S)₂ is currently used as absorber layer in high efficiency thin film solar cells. It is known that the electrical properties of the absorber layer are mainly determined by stoichiometry deviations. Post-growth treatments to modify the defect population can yield valuable results for a better understanding of the complex defect chemistry and might help to optimize the device performance. We present the results of the modification of the defect population in the near-surface range of Cu(In,Ga)Se₂ samples under the influence of atomic hydrogen. The hydrogenation was performed by low energy H ion implantation at elevated temperature. Despite the removal of surface oxide and contaminations, atomic hydrogen causes compositional changes, i.e. a Cu and Se-deficiency within a depth range of a few hundred nm,

corresponding to the hydrogen depth profile in the investigated samples. The depth as well as the magnitude of the changes can be influenced by varying the implantation dose and temperature. In addition, initially p-type CuInSe₂ can be type converted to n-type conductivity due to the low energy hydrogenation. We suggest as explanation that hydrogen passivates Cu-vacancy V_{Cu} (acceptor) and produces additional V_{Cu} induced by the Fermi level shift towards the conduction band. The resulting in-diffusion of Cu causes the Cu-deficiency corresponding to the hydrogen dose. Other effects discussed in the model are a re-activation of Se-vacancies (donor level) formerly passivated by oxygen and the possible production of additional Se vacancies as an result of the atomic hydrogen. The experimental data for the discussion have been acquired by X-ray photoelectron spectroscopy, RAMAN- spectroscopy, nuclear reaction analysis (NRA) as well as total-reflection X-ray fluorescence spectroscopy (TXRF) on beveled sections of the samples.

H5.21

PREPARATION AND CHARACTERIZATION OF CdS_xTe_{1-x} ALLOY FILMS. R.G. Dhere, D.S. Albin, S.E. Asher, H.R. Moutinho, and T.A. Gessert, National Renewable Energy Laboratory, Golden, CO.

Intermixing at the CdS/CdTe interface is considered crucial for the performance of CdTe-based solar cells. High efficiency devices have been fabricated in spite of large lattice mismatch between CdS and CdTe. Intermixing and formation of CdS_xTe_{1-x} alloys in present generation devices results from high temperature CdTe deposition and post-deposition CdCl₂ treatment. In this paper, we present our work on preparation of CdS_xTe_{1-x} alloy powders and films and the results of their structural, optical, and electrical characterization. Our previous attempts to deposit CdS_xTe_{1-x} films from mixed CdS and CdTe powders by close spaced sublimation (CSS) were unsuccessful because of the significant difference in the vapor pressure of individual components. We have collaborated with CERAC Corporation to fabricate CdS_xTe_{1-x} alloys with different compositions. The CdS and CdTe powders are sized and mixed, isostatically pressed into a bar, sealed into closed-quartz ampoules, annealed at temperatures >1000°C, and water quenched. X-ray Diffraction (XRD) analysis showed that, although the powders were not single phase, they contained only distinct phases on S-rich and Te-rich sides of the phase diagram. Recently, two new batches of CdS_xTe_{1-x} material, produced by the improved process at CERAC, have been obtained (x=0.71 and x= 0.35 in CdS_xTe_{1-x} alloy). Initial XRD results from the films deposited by CSS using these powders reveal that both samples of bulk powders (prior to CSS deposition) are single-phase and demonstrate CdS-like characteristics (hexagonal). We will present the results on the structural properties of these powders. We have deposited CdS_xTe_{1-x} alloy films using these powders. These alloy powders evaporate more congruently as opposed to mixed powders of CdS and CdTe. We will also present results on the preparation, as well as the structural, optical, and electrical characterization of thin CdS_xTe_{1-x} alloy films deposited using these powders by close spaced sublimation and sputtering.

H5.22

A DETAILED STUDY OF Cu(In,Ga)Se₂ THIN FILMS BY ELECTRON BEAM INDUCED CURRENT AND CATHODOLUMINESCENCE. M.J. Romero, F.S. Hasoon, M.M. Al-Jassim, R. Noufi, National Renewable Energy Laboratory, Golden, CO; D. Araujo, R. Garcia, Universidad de Cadiz, Departamento de Ciencia de los Materiales e IM y QI, Cadiz, SPAIN.

Thin-film Cu(In,Ga)Se₂ (CIGS) is the most promising candidate for photovoltaic modules of improved efficiency and low-cost terrestrial applications. Among its advantages, CIGS absorption limit can be tailored to the solar spectrum with the Ga/(In Ga) ratio and its large optical absorption coefficient ensures that the solar spectrum is captured within thinner (1 to 2 μm) films. However, the further development of high-efficiency CIGS cells will critically depend on a better understanding of fundamental material parameters and their impact on solar cell performance and reproducibility of fabrication. Most of the CIGS absorbers for high-efficiency cells have been fabricated with the three-stage process. The initial stage of this procedure consists of deposition of In-Ga-Se precursors. They are then exposed to Cu and Se fluxes in the second stage to form Cu-rich CIGS. In the final stage, a slightly In-rich CIGS thin film is obtained by the addition of In, Ga and Se. In this work, CIGS thin films were obtained with the three-stage process at two different temperatures during the third stage and different addition of Indium in the final stage. Cross-sectional observations of the electron beam induced current (EBIC) and cathodoluminescence (CL) were made to investigate the influence of both temperature and In excess on the electronic and optical characteristics of CIGS films and their impact on the efficiency of the CIGS cells. On the whole, we observed higher efficiencies for CIGS thin films deposited at higher temperature. Indeed, we show that the luminescence behavior of CIGS is mostly dependent on the

temperature, with enhanced nonradiative recombination at grain boundaries and improved spectral purity. On the other hand, the In addition has a major effect on diffusion lengths and carrier collection efficiencies across the CIGS films, as EBIC measurements revealed.

H5.23

ILGAR OVERCOMES CBD WITH RESPECT TO EFFICIENCY OF CHALCOPYRITE SOLAR CELLS. Christian-H. Fischer^a, Marcus Bär^a, Hans-J. Muffler^a, Franz Karg^b, Siegmund Zweigart^b, Martha C. Lux-Steiner^a; ^aHahn-Meitner-Institut Berlin, Dept. SE 2; Berlin, GERMANY, ^bSiemens Solar GmbH, Munich, GERMANY.

The sequential and cyclical ILGAR process (Ion Layer Gas Reaction) has recently been introduced as a rough, economic and versatile method for the deposition of sulfidic and oxidic thin layers. In CIGSSe solar cells it has been applied for the preparation of ZnS buffer layers as well as ZnO window extension layers (WEL). The concept of WEL means a layer consisting of the same material as the transparent window but prepared by a soft chemical process and therefore exhibiting excellent buffer properties. Application of an ion pretreatment of the absorber (Zn²⁺ for ZnS, Cd²⁺ for ZnO, both in aqueous ammonia) as well as further optimization of the ILGAR process now resulted in efficiencies superior to those of corresponding cells with CBD-CdS buffer (14.6 % ZnO; 14.2% ZnS; reference cell with CBD-CdS buffer 14.1 %; total area 0.5cm²). In the ZnO-WEL devices the other cell parameters were similar to the data of CBD-CdS cells (given in brackets): V_{OC} = 587 (588) mV, J_{SC} = 35 (33) mA/cm², FF= 72 (73) %. One device with ZnO-WEL was certified with η=14.1% by ISE (Freiburg, Germany). Furthermore, the conventional dip application of the precursor salt is being replaced by spraying. Moreover, first results will be shown for extending the typical ILGAR layer thickness of 10-100nm to the μm-range.

SESSION H6: SURFACES AND INTERFACES I

Chairs: Susanne Siebentritt and Peter V. Meyers

Thursday Morning, April 19, 2001

Salon 5/6 (Marriott)

8:30 AM *H6.1

THE PROPERTIES OF DEFECTS AND INTERFACES IN CdTe SOLAR CELLS. M.M. Al-Jassim, Y. Yan, M.J. Romero, K.M. Jones, R. Dhere, National Renewable Energy Laboratory, Golden, CO.

CdTe is among the most promising candidates for cost-effective terrestrial photovoltaics. Although efficiencies up to 15.8% have been achieved, many material issues remain ambiguous. This is particularly the case with the nature, origin and effects of structural defects. In this work CdTe thin films deposited by close-spaced sublimation were investigated. The microstructure was examined by conventional and high resolution TEM, with particular emphasis on the generation mechanism of the defects. The chemical properties of the CdS/CdTe interface were investigated by small spot energy dispersive spectroscopy. Cathodoluminescence was used to study the luminescent behavior of the defects. The films were heavily faulted with a high density of planar defects. Our results showed that the effect of the crystallinity of the underlying substrate on the defect density in the CdTe films is minimal. Under most growth conditions the majority of the defects was generated at the CdS/CdTe interface. Lattice mismatch between the CdS and CdTe, interface irregularities and the nucleation mode all played a major role in defect generation. The mechanisms by which the defects are generated and the recombination characteristics of these defects will be discussed.

9:00 AM H6.2

ABSORPTION AND PHOTOLUMINESCENCE STUDIES OF LIGHTLY ALLOYED CdTe(S) AND CdS. Diana Shvydka, K.J. Price and A.D. Compaan, University of Toledo, Dept. of Physics and Astronomy, Toledo, OH.

The formation of a CdS_xTe_{1-x} mixed crystal layer at the CdS/CdTe interface of thin-film solar cells based on CdTe is an unavoidable result of post-growth CdCl₂ heat treatment which is crucial to cell performance. Due to the large miscibility gap at 415°C, which extends from about x = 0.06 to x = 0.97, it is very important to study the optical properties of light alloys. For this work CdTe-rich and CdS-rich alloy films were deposited at temperatures less than 300°C using rf sputtering. Transmission-reflection and photoluminescence measurements were conducted to study the near-band edge properties of this ternary system for films of different compositions at room temperature and at 10K. Results from the polycrystalline films were compared to data on defect states introduced in single crystal CdTe by annealing at several different overpressure conditions, including CdS overpressure. Understanding the nature and density of these defect states in the forbidden energy gaps of CdTe and CdS is important for electrical properties of solar cells, since these defects can control the

minority carrier lifetime. The effects of different steps in the production of complete solar cells on band-gap states of CdS_xTe_{1-x} alloys, CdTe, and CdS was studied with below-band-gap-excitation photoluminescence. This work was supported by NREL.

9:15 AM H6.3

OPTICAL PROPERTIES OF HIGHLY EFFICIENT 2- μ m THICK CdS/CdTe THIN FILM SOLAR CELLS. K. Nakamura, M. Gotoh, T. Fujihara, T. Toyama, H. Okamoto, Osaka Univ, Graduate School of Engineering Science, Dept of Physical Science, Toyonaka, Osaka, JAPAN.

Highly efficient CdS/CdTe thin film solar cells with thinner photovoltaic (PV) active layers are required from a view point of reduction of production cost as well as toxicity of Cd. Up to the present, we have achieved the conversion efficiency of 13.5% (Voc: 0.799 V, Jsc: 24.8 mA/cm², F.P.: 0.679, area: 0.42 cm²) using 2.0- μ m thick PV active layers without antireflection coating. The CdTe film was deposited on the CdS film by close-spaced sublimation (CSS) growth technique, and the PV active layer thickness was reduced by the decrease of the source temperature and the deposition time. To achieve the high efficiencies, annealing temperature and oxygen concentration at CdCl₂ treatment are found to be crucial parameters. We here report results on the detail characterization of the 2- μ m thick solar cells made with the different conditions at the CdCl₂ treatment by spectral response, electrorreflectance (ER), and photoluminescence (PL) measurements. With an increase in the annealing temperature, the spectral response above 2.4 eV increases and the bandgap of the CdTe_{1-x}S_x mixed crystal layer revealed by the ER measurements decreases. These facts suggest that the CdCl₂ treatment enhances the interdiffusion at the CdS/CdTe interface, which would correspond to a decrease in Voc at the higher annealing temperatures. We will also discuss the influence of the oxygen concentrations on the PV performances in conjunction with the spectral shift in 1.38-eV PL band taken at 80K.

9:30 AM H6.4

EFFECT OF CdTe THICKNESS REDUCTION IN HIGH EFFICIENCY CdS/CdTe SOLAR CELLS. Akhlesh Gupta, Ilvydas Matulionis, Jennifer Drayton, Mitra Shabesteri and Alvin D. Compaan, Department of Physics and Astronomy, The University of Toledo, Toledo, OH.

High efficiency CdTe solar cells are typically grown with CdTe thicknesses from 3 to 15 μ m. Although the thickness required for 90% absorption of the incident irradiation at 800 nm, is approximately 1 μ m. In this paper, we present the effect of CdTe thickness reduction on the performance of CdS/CdTe solar cells. Both, CdS and CdTe films were grown using sputtering. We produced a series of cells with different CdTe thickness (from 2.5 to 0.5 μ m), and held the CdS thickness and back contact-processing constant. The effect of CdTe thickness reduction on the diffusion of CdS into CdTe, crystallographic, and morphological properties were studied using optical absorption, photoluminescence, XRD, and SEM techniques. The performances of the solar cells with different CdTe thickness were evaluated using current voltage and quantum efficiency measurements. While there is not much reduction in open circuit voltage, the short circuit current and fill factor decreases a little with the decrease in CdTe film thickness up to 1.0 μ m. However, more than 10% efficient cells were obtained with 1 μ m CdTe. All cell parameters decrease rapidly when CdTe thickness decreases below 1 μ m, and 8.5 and 3.3% efficiencies were obtained for 0.73 and 0.47 μ m thick CdTe cells. The red response of the cells also suffers rapidly with the reduction in CdTe thickness, especially for cells with CdTe thickness of less than 1 μ m. This work was supported by NREL.

9:45 AM H6.5

CHARACTERIZATION OF GRAIN BOUNDARIES AND THEIR ROLE IN POLYCRYSTALLINE APCVD CdTe THIN FILM PV DEVICES. Peter Meyers, Lawrence Woods, ITN Energy Systems, Littleton, CO; James Kestner, Colin Wolden, Dept. of Chem. Engr., Laxminarayanan Raja, Robert Kee, Engineering Division, Viktor Kadanov, Tim Ohno, Eli Mateeva, Physics Dept., Colorado School of Mines, Golden, CO; Rick Matson, Brian Keyes, Steve Johnston, NREL, Golden, CO; Alan Fahrenbruch, ALF, Stanford, CA.

The role of grain boundaries is a fundamental issue in determining the operating characteristics of polycrystalline thin film solar cells. As the record efficiency for CdTe PV devices is 16% - was achieved with polycrystalline films, it is reasonable to conclude that grain boundaries in CdTe can have characteristics which do not severely degrade PV device performance, i.e., that grain boundaries can be benign. It is also possible, however, that grain boundaries may be beneficial. For example grain boundaries may serve as n-type walls which penetrate into the CdTe from the n-type CdS window layer or as p-type walls which extend inward from the back contact. Thus grain boundaries could result in enhanced collection of minority

carriers, reduced internal series resistance and mitigate effects of low minority carrier diffusion length. In order to investigate the role of grain boundaries, researchers are employing a variety of electrical and microscopic methods to characterize film and device performance. In-plane impedance is used to characterize grain boundary energy band structure in thin films while in-plane Hall measurements determine mobility and carrier concentration. TEM and EDS provide microscopic characterization of the physical and chemical nature of grains and boundaries while EBIC provides information on the two-dimensional minority carrier collection in devices. Measured material properties are employed to model device performance including measurements of device I-V, C-V, C-f and QE. CdTe films employed in this study are deposited by atmospheric pressure chemical vapor deposition (APCVD), which has been used to deposit >10% AM1.5 efficient CdTe PV devices. APCVD employs the same reaction chemistry as close spaced sublimation (CSS), which was used to deposit record (16% efficient) CdTe devices, but employs forced convection rather than diffusion for transport of the Cd and Te₂ gasses to the substrate.

10:30 AM *H6.6

INTERFACE ENGINEERING OF CHALCOGENIDE SEMICONDUCTORS IN THIN FILM SOLAR CELLS. Wolfram Jaegermann, Institute of Materials Science, Darmstadt University of Technology, Darmstadt, GERMANY.

Thin film solar cells of chalcogenide semiconductors as CIGS or CdTe are strongly determined by their interface properties in heterojunction and ohmic contact formation. For well defined heterointerfaces well accepted mechanisms are operative which govern the contact properties. We will present experimentally determined band line-ups for chalcopyrite and CdTe heterojunctions formed either by UHV deposition experiments or by the standard solar cell production process. Also a comparison of the back contact formation after deposition of the contact material in UHV and by the standard procedure will be given. These results show that chemically based interface engineering is evidently important in device preparation. We will present our approach to investigate the involved processes on a molecular level by applying integrated preparation chambers also for wet chemical processing in combination with surface science techniques also to be used with synchrotron radiation.

11:00 AM H6.7

DIRECT EVIDENCE FOR A FLAT CONDUCTION BAND ALIGNMENT AT THE REAL CdS/Cu(In,Ga)Se₂ THIN FILM SOLAR CELL HETEROJUNCTION. M. Morkel, B. Lohmüller, A. Möglinger, U. Groh, R. Fink, C. Heske, E. Umbach, Experimentelle Physik II, Universität Würzburg, GERMANY; W. Riedl, S. Zweigart, Siemens ZFE, Munich, GERMANY; F. Karg, Siemens Solar, Munich, GERMANY.

The band alignment at internal interfaces in Cu(In,Ga)Se₂ (CIGS)-based thin film solar cells is one of the fundamentally important properties for the electronic performance as well as for the modeling of such devices. In recent years the CIGS-community has settled on models containing a significant (approx. 0.3-0.7 eV) conduction band spike at the CdS/CIGS-interface. We will report on a combined Photoemission (PES) and Inverse Photoemission (IPES) study on samples which have been prepared by chemical bath deposition of CdS on RTP-processed polycrystalline CIGS absorbers. From the IPES and PES data we directly derive that the conduction band offset in real samples is, on the contrary, very small. Hence, a step-free description is more appropriate. Furthermore, we will demonstrate that such a revision of the existing model is made necessary (1) by an increased (1.4 eV) band gap of the CIGS absorber surface and (2) by the influence of intermixing effects at the CdS/CIGS interface on the electronic structure of the heterojunction. The current findings will be compared with various other results and models for the CdS/CIGS interface. A discussion of implications for the electronic structure of the solar cell device will be given.

11:15 AM H6.8

INTERFACE INVESTIGATION OF ZnO/CdS/ CuIn_{1-x}Ga_xSe₂/Mo SOLAR CELLS. F.S. Hasoon, K. Ramanathan, H.A. Althani, K.M. Jones, Y. Yan, H.R. Mounho, J. Alleman, M.M. Al-Jassim R. Noufi, National Renewable Energy Laboratory, Golden, CO.

CuIn_{1-x}Ga_xSe₂ is the most promising chalcopyrite semiconductor compound for polycrystalline photovoltaic devices due to its suitable bandgap and high absorption coefficient for solar radiation. CIGS devices have been fabricated on a variety of substrates including polymers, microsheet (F 45 corning glass), and stainless steel. In these cases the addition of sodium (in the form of NaS, NaSe, or NaF) is required to achieve high performance devices. Incorporation of Na into the CIGS films enhances the quality, the grain size and the electrical conductivity of the CIGS. To date, ZnO/CdS/CIGS deposited on Mo-coated soda lime glass substrates has demonstrated the highest

conversion efficiencies for all polycrystalline thin films solar cells for both laboratory small area (18.8%) and modules (12%). However, limited investigations have been performed on the chemistry and microstructure of the Mo/CIGS interface and how these may affect device performance. In this work we have studied the influence of the microstructure of Mo films on the growth and the microstructure of the bulk of CIGS films and the Mo/CIGS interface. We explored a wide parameter space that correlates the Mo deposition conditions with its microstructure, and in turn with the properties of the overlying CIGS films. We also investigated the CIGS/CdS interface. We made a comprehensive use of XRD, TEM, SEM and AFM, as well as other material and device characterization tools in this study. The results of this comprehensive study will be presented and discussed.

11:30 AM H6.9

HOW DO BUFFER LAYERS AFFECT SOLAR CELL PERFORMANCE AND STABILITY? Bolko von Roedern, National Renewable Energy Laboratory, National Center for Photovoltaics, Golden, CO.

Buffer layers are commonly used in the optimization of thin film solar cells. For CuInSe₂- and CdTe-based solar cells, usually multi-layer transparent conductors (TCO, e.g., ZnO or SnO₂) are used in conjunction with a CdS heterojunction layer. Optimum cell performance is usually found when the TCO layer in contact with the CdS is very resistive or almost insulating. It has been previously shown that buffer layers enhance the open-circuit voltage (V_{OC}) of solar cells by optimizing the profile of the carrier-gradient derived potential such that the potential is maximized near the metallurgical junction, but far enough away from it to reduce the potential-lowering effect of the contact itself [1]. In addition to affecting V_{OC} , it is commonly reported that buffer layers affect stress-induced degradation and transient phenomena in CdTe- and CuInSe₂-based solar cells. A recent study of electron beam induced stress in CdTe [2] reported that, upon removal of the stress, two components of degradation became evident, one partially recoverable and the other non-recoverable. The overall degradation was described with rate equations also used to describe Staebler-Wronski degradation of amorphous silicon. Because of the similarity of transients and degradation in dissimilar material systems it is suggested that degradation and recovery are driven by carriers rather than by diffusing atomic species. To understand the degradation phenomena, the influence of excess carriers on the structural or diffusive properties of the semiconductor and buffer layers must first be understood. The question must be addressed why, not how, species diffuse and atomic configurations relax differently in the presence of excess carriers. Often, excess carriers may be confined to localized regions ("filaments") and buffer layers limiting current flow into such filaments may thereby control the rate and amount of degradation (or recovery). A detailed model will be presented and compared with experimental stress and transient data. [1] B. von Roedern and G.H. Bauer, Mat. Res. Soc. Symp. Proc. Vol. 557 (1999), 761. [2] R. Harju, V.G. Karpov, D. Grecu, and G. Dorer, J. Appl. Phys. 88 (2000), 1794

11:45 AM H6.10

TEM STUDY OF THE MICROSTRUCTURE OF THE SURFACE LAYER OF Cu(In,Ga)Se₂ THIN FILMS. Y. Yan, K.M. Jones, F.S. Hasoon, H. Althani, J. Alleman, M.M. Al-Jassim, and R. Noufi, NREL, Golden, CO.

Cu(In,Ga)Se₂ (CIGS) is a promising candidate for high efficiency solar cells. It is reported that the CIGS has a homo-junction, beside the CIGS/CdS hetero-junction. In this work, we present transmission electron microscopy (TEM) observation of an approximately 250 nm thick surface layer on the bulk CIGS. The microstructure of this layer was studied by high-resolution TEM imaging and conversion beam electron diffraction. The chemical composition was investigated by high spatial resolution energy dispersive x-ray spectroscopy. The surface layer could form a homo-junction with the bulk CIGS. The structure and composition of the surface layer and the structure of the intra-interface will be discussed.

SESSION H7: SURFACES AND INTERFACES II

Chairs: Wolfram Jaegermann and Peter Sheldon

Thursday Afternoon, April 19, 2001

Salon 5/6 (Marriott)

1:30 PM *H7.1

DIFFUSION BEHAVIOR AND MICROSTRUCTURAL PROPERTIES AT THE CBD-ZnS/CIGS INTERFACE BOUNDARY. Tokio Nakada, Department of Electrical Engineering & Electronics, Aoyama Gakuin University, Tokyo, JAPAN.

The diffusion behavior and micro structural properties at the CBD-ZnS/Cu(In,Ga)Se₂ (CIGS) interface of high efficiency Cd-free

CIGS thin film solar cells with efficiencies exceeding 17% have been investigated using energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). CIGS thin films were grown by three-stage process using molecular beam epitaxy (MBE) system. ZnS layers were deposited on CIGS thin films by chemical bath deposition (CBD) using ZnSO₄-thiourea-ammonia solution at 80°C. Micro-EDX analysis with spatial resolution of 3nm revealed that Zn and S diffused into CIGS thin layer approximately 50 nm and 10 nm, respectively, from the interface boundary after annealing at 200° for 10 minutes. On the other hand, no diffusion of Zn and S was observed before annealing process. These results showed that the main role of annealing process is not substituting of Se vacancies by oxygen atoms but the diffusion of Zn into CIGS which may result in the formation of pn homojunction. The diffusion depth of Zn and S in CIGS thin layers, which affects a cell performance, on Ga/(Ga+In) atomic ratio of CIGS thin films was investigate by SIMS and AES analyses. The results were discussed in connection with the cell performance and compared to the diffusion behavior at the interface between CBD-CdS and CIGS thin films with different Ga contents. Details of the CBD-ZnS/CIGS interfacial microstructure which might play an important role in the diffusion properties are also presented.

2:00 PM H7.2

AN EXAMINATION OF THE INTERMEDIATE PHASE DEVELOPMENT DURING Cu(In,Ga)Se₂ THIN FILM GROWTH FROM (In,Ga)2Se₃ PRECURSORS. Jehad AbuShama, Rommel Noufi, Falah Hasoon, Rick Matson, Amy Swartzlander, Jeff Alleman, James Keane, National Renewable Energy Laboratory, Golden, CO.

In our approach, the process used to deposit Cu(In,Ga)Se₂ (CIGS) thin films consists of: (1) the formation of an (In,Ga)2Se₃ layer on Mo-coated soda-lime glass substrates heated to 400°C, followed by (2) the deposition of Cu and Se at about 550°C, at which point the compound formation and crystallization of Cu(In,Ga)Se₂ takes place with the additional formation of Cu₂-xSe as a secondary phase; and (3) additional In, Ga, and Se is added at the same temperature, so that the final composition expected is slightly Cu-poor. In this presentation, we examine the intermediate evolution of the microstructure, the phase development, and the distribution of the cations, using two substrate temperature profiles and Ga/In Ga concentrations of 0.3 and 0.6. We will attempt to show that: (1) the phase formation path does not necessarily coincide with the pseudobinary section between Cu(In,Ga)Se₂ and (In,Ga)2Se₃, possibly because the Cu, In, and Ga components exhibit different diffusivities as compared to CuInSe₂; (2) the Ga distribution is influenced by the local conditions, i.e., the concentration of Cu₂-xSe; and (3) the make-up of the surface region is influenced by the degree of overlap between the second and third stages. The objective is to determine the factors in the growth of CIGS film that may limit its performance as the absorber in a CdS/CIGS-based solar cell.

2:15 PM H7.3

LASER LIGHT SCATTERING IN-SITU STUDIES ON THE GROWTH OF CHALCOPYRITE THIN FILMS. Roland Scheer, Christian Pietzker, Dieter Brauning, Hahn-Meitner Institut, Berlin, GERMANY.

Optical real time monitoring is a valuable tool for quality assessment and process control for thin film deposition. Diffuse reflectivity of laser light (LLS) can give information about structural and optoelectronic properties of a film. In this work, we use LLS for the inspection of sequential and simultaneous film formation processes of CuInSe₂ and CuInS₂ thin films. For the sequential process (the chalcogenisation of Cu/In precursor layers), we find the formation of chalcogenide phases at an early stage of the process. This finding is in accordance with structural ex-situ measurements such as Raman spectroscopy and XRD. The influence of process dynamic and precursor composition has been studied. The effect of Ga addition is to shift the transition temperatures to higher values. Critical temperatures of surface phase transitions are clearly dependent on the ramp dynamic. This may be interpreted in terms of material transport processes within the precursor layer. Cu-rich films exhibit phase transitions also in the cool-down period of the process. LLS experiments are also performed during coevaporation of chalcopyrite films (simultaneous process). Growth assistance by Cu-excess is nicely revealed. We found that this growth assistance depends on a critical density of accumulated Cu excess at the surface.

2:30 PM H7.4

A COMPARATIVE STUDY OF CdS THIN FILMS GROWN BY CHEMICAL-BATH DEPOSITION AND CLOSE-SPACED SUBLIMATION. H.R. Moutinho, Y. Yan, D. Albin, R.G. Dhere, and M.M. Al-Jassim, National Renewable Energy Laboratory, Golden, CO.

Cadmium sulfide is the material of choice to function as window layer in CdTe and Cu(In,Ga)Se₂ solar cells. The most common deposition techniques used for CdS production are chemical-bath deposition

(CBD) and close-spaced sublimation (CSS). At the present, CBD CdS has produced the best devices, but the reason for this is not known yet. Furthermore, CBD CdS presents several problems, including high density of pinholes. Recently, CSS CdS has received attention as a possible substitute. We have studied both materials using two structures: Si/SnO₂/CdS and glass/SnO₂/CdS. We have also analyzed the films before and after heat treatment in CdCl₂ vapor, which is considered to be an efficient agent in the recrystallization process of this material. In this work, we present a detailed analysis of the differences between the films produced by these two techniques, and try to understand how these differences influence device performance. The properties of the films were studied with atomic force microscopy (surface morphology and roughness), X-ray diffraction (crystalline structure), and transmission-electron microscopy (internal structure and defects). The X-ray analysis was performed using θ - 2θ setup, and also using grazing-angle incidence technique, to allow the top-most layers of the films to be analyzed. The AFM results showed that the CdCl₂ treatment did not significantly affect the surface morphology of the films deposited on Si/SnO₂. These results, in conjunction with the XRD analysis, indicated that the CBD and CSS films did not recrystallize during the treatment. Nevertheless, the CSS CdS had grain size approximately 50% larger than the CBD CdS. At the same time, the roughness of the CSS films was approximately 3 times larger. This higher roughness implies that a thicker CdS film is needed for complete coverage of the SnO₂, and may be related to the lower efficiencies obtained in devices using CSS CdS.

2:45 PM H7.5

ELECTRONIC PROPERTIES OF CHEMICALLY ETCHED CdTe THIN FILMS: ROLE OF Te FOR BACK CONTACT FORMATION. D. Kraft, A. Thissen, T. Mayer, A. Klein and W. Jaegermann, Dept of Materials Science, Darmstadt University of Technology, Darmstadt, GERMANY; R. Wendt, ANTEC GmbH, Kelkheim, GERMANY.

Improvement of electric back contact formation is one of the major issues of the CdTe thin film solar cell research. Chemical etching of CdTe before metallization is accepted to improve contact formation. It is believed that a CdTe/Te contact is formed by this procedure leading to a Fermi level position in the CdTe close to the valence band maximum for low contact resistance. We have studied the electronic properties of chemically etched CdTe surfaces with photoelectron spectroscopy. Etching of the samples was performed in air (ex-situ) as well as in an electrochemical setup directly attached to the UHV system (in-situ). The formation of a Te layer is clearly shown by XPS. In contrast to previous studies we could not detect the formation of a p-CdTe surface for different experimental conditions. The detected Fermi level position indicates still strong band bending and hence a blocking Schottky barrier. For comparison we have also studied the interface formation of thermally evaporated Te with CdTe.

3:30 PM DISCUSSION SESSION – NATURE OF JUNCTION, INTERNAL SURFACES

Panel:

J. Sites - Colorado State Univ
U. Rau - Univ of Stuttgart
K. Ramanathan - Natl Renewable Energy Lab

SESSION H8: POSTER SESSION CHARACTERIZATION

Chairs: Hans-Werner Schock and R. W. Birkmire
Thursday Evening, April 19, 2001
8:00 PM
Salon 1-7 (Marriott)

H8.1

CHARACTERIZATION AND PHOTOELECTROCHEMISTRY OF LAYER-BY-LAYER SELF ASSEMBLED FILMS OF CdS QUANTUM DOTS IN POLYELECTROLYTE MATRIX.

Lara I. Halaoui, Department of Chemistry, American University of Beirut, Beirut, LEBANON.

We report a fast and novel procedure for growing thin films (10-50 nm) of CdS nanoparticles (Q-CdS) from aqueous solutions. This is accomplished by imparting a negative surface charge to Q-CdS by capping it with polyacrylate in-situ. The polyacrylate-capped particles are then self assembled layer-by-layer in poly(diallyldimethylammonium chloride) matrix on different surfaces (Si, quartz, Au, indium tin oxide) by means of electrostatic attraction between the negatively charged capping agent and the polyelectrolyte cation. The characterization of Q-CdS particles and films, and the processes of light-induced charge separation, recombination, and transfer to solution species will be discussed. Q-CdS particles are characterized by UV-visible absorption, high-resolution TEM, electron diffraction, and emission measurements. Results show quantum confined

nanocrystals of 4 nm average diameter (110 particles sample size; cubic or hexagonal crystal structure depending on preparation temperature). Assembled films are imaged by TEM, showing the distribution of particles in the films, and its dependence on the deposition times. The layer-by-layer assembly through consecutive surface charge reversal was characterized using Fourier-transform infrared spectroscopy, UV-visible absorption, and emission measurements. Results show a linear growth, representative of a reproducible charge reversal, and reveal the dependence of film growth on the deposition parameters (i.e., time of dipping, ionic strength of solution). The photoluminescence at 560-570 nm (red shifted from the absorption edge), for instance, measured as 10 bilayers were grown on quartz, increased linearly with number of bilayers with R² of 0.995. The photoelectrochemical properties of films thus formed are also investigated. Significant photocurrents are measured (e.g., 1.4 μ A/cm² at 100 mV vs. SCE for 4 layers of Q-CdS), and the feasibility of charge transport through the matrix is reported. Electron-hole recombination is studied by following the photocurrent decay with time, following the initial light absorption, before reaching a steady state.

H8.2

ALLOYING AND SELENIZATION OF Cu-In STACKED LAYERS EVAPORATED ONTO LARGE AREAS. R. Caballero, C. Guillén, Rocio Bayon, Departamento de Energías Renovables (CIEMAT), Madrid, SPAIN.

CuInSe₂-related compounds are an attractive option for PV power market with actual laboratory scale efficiencies up to 18.8% which are record for thin film photovoltaic devices. High material quality on large areas has to be achieved to combine as high efficiencies with low costs. There are various growth techniques (mainly evaporation and sputtering processes) which are being tested for the up-scaling and production lines.

In our work, Cu and In thin films, as precursors for CuInSe₂ formation, were deposited on glass substrate up to 30 x 30 cm² area using an electron beam evaporator, in sequential processes. Thin films of the Cu-In alloys have interest because of the structural uniformity of them affects the quality of the semiconductor after the chalcogenization. In this sense the order of the several deposition steps can affect to final sample properties.

Obtaining the same global composition, we have tested three types of sequential processes of evaporation: Cu/In/Cu/In, Cu/In/Cu/In/Cu/In and In/Cu/In/Cu. Previous to the selenization, the alloy phases of sequentially deposited films are studied at room temperature and at 120°C, which is a temperature that keeps the properties stable. After alloying, thin films are selenized in the range 400°C-500°C in vacuum with elemental selenium vapour.

The structural properties as determined by XRD, the compositional and morphology by EDAX and SEM, and the electrical properties, are compared before and after selenization, to obtain how they depend on the different conditions used.

H8.3

CBD-In(OH)_xS_y THIN FILMS: AN APPROACH TO THE GROWTH MECHANISM. Rocio Bayon, José Herrero, Departamento de Energías Renovables (CIEMAT), Madrid, SPAIN.

For some years now our group has been involved in the study of chemical bath deposited indium hydroxide sulphide (CBD-In(OH)_xS_y) as an alternative compound to replace CdS in chalcopyrite-based solar cells and we have found that film properties strongly depend on deposition conditions (reactant concentrations, deposition time, bath temperature, etc). At the moment we are more concerned with the chemical reactions taking place in the solution and the growth kinetics mechanism of the films. In this way we have undertaken a deep study of the surface morphology of CBD-In(OH)_xS_y thin films in order to propose a descriptive model for their mechanism of growth, which, in principle, could be extended to other CBD-semiconductors. It has been found that the surface morphology strongly depends on deposition conditions such as solution pH, reactant concentrations and bath temperature. These differences in surface morphology can be explained in terms of nucleation rate. Nevertheless in all cases the so called cluster-by-cluster is the thin film growth mechanism.

H8.4

FABRICATION OF SOLAR-CELL-QUALITY CADMIUM SULFIDE LAYERS VIA LASER-ASSISTED CHEMICAL VAPOR DEPOSITION (LCVD). Johnnie L. Hixson, Christopher S. Cassidy, Robert L. Stewart, Robert M. Taylor, Lowell R. Matthews and Kenneth H. Church, CMS Technetronics, Inc., Stillwater, OK; Robert Mamazza and Christos S. Ferekides, Dept. of Electrical Engineering, University of South Florida, Tampa, FL.

The laser-assisted chemical vapor deposition (LCVD) technique has proved to be an effective means of depositing cadmium sulfide layers in a well-controlled manner over select small areas. Observations of favorable conditions for deposition and typical pitfalls in the process

are discussed. Analysis of the LCVD CdS layers is presented in conjunction with comparisons to conventionally grown CdS layers. The stoichiometry, thickness, and grain structure of the LCVD CdS layers have been suitably optimized for use in solar-cell applications.

H8.5

CdS AND CdTe LARGE AREA THIN FILMS PROCESSED BY RADIO-FREQUENCY PLANAR-MAGNETRON- SPUTTERING. H. Hernandez-Contreras, G. Contreras-Puente, J. Aguilar-Hernandez and O. Vigil-Galan^a, Escuela Superior de Física y Matemáticas, Unidad Profesional Adolfo López Mateos del Instituto Politécnico Nacional, MEXICO; ^aPermanent address: Facultad de Física-IMRE, Universidad de la Habana, Cd. Habana, CUBA.

The processing of large area thin films solar cells represents a challenge, due mainly to the optimal setting of the different critical growth parameters in this scaling-up process, than can guarantee a homogeneous-surface-photovoltaics-response in the subminimodule architecture. We have been working for this purpose with a Radio-Frequency Planar Magnetron Sputtering (RF-PMS) system, processing 450 cm². CdS and CdTe thin films grown on conducting glasses (SnO₂ of 7 Ω), using for it a two 6" balanced gun. The films have been processed with a substrate temperatures (Ts) of 250°C, Ar chamber-pressure of 20 mTorr, radio frequency power of 300 watts. The films were characterized by optical, and electrical techniques, presenting in this work the corresponding measurements. Our results show that the samples grown on conducting glass present good polycrystalline perfection, adherence and pinholes free surfaces. Work partially supported by CONACyT, Mexico, project No. G27713A

H8.6

PREPARATION OF THE Cu₂S - CuAlS₂ SYSTEM AND ITS T(X) PHASE DIAGRAM. Klaus Bente, Leipzig University, Institut fuer Mineralogie, Kristallographie und Materialwissenschaft, Leipzig, GERMANY; Barys V. Korzun, Ruslan R. Mianzelen, Institute of Physics of Solids and Semiconductors, Minsk, BELARUS.

In recent years growing interest has been shown to complex semiconducting compounds I-III-VI₂ (where I-Cu, Ag; III-Al, Ga, In; VI-S, Se, Te). These chalcopyrite semiconductors are considered to be possible candidates for application in photovoltaics, optoelectronics and devices for transferring and processing of information. The CuAlS₂ semiconductor is one of these compounds and has a wide direct gap of 3.5 eV making it suitable for the use as window material for solar cells. CuAlS₂ has been studied largely but there is not the information about its region of homogeneity in the literature. The aims of this paper are (i) the preparation of alloys of the Cu₂S - CuAlS₂ system and (ii) the construction of T(x) phase diagram by differential thermal analysis and X-ray diffraction. To obtain Cu₂S and CuAlS₂ compounds and their alloys two methods were developed. One of them was the melting from the constituent elements of 99,999% (copper) and 99,9999% purity (aluminium, sulphur). The charges were sealed in evacuated double quartz ampoules and then placed into electric furnace. The crucible from BN with the metallic components was heated to the temperature higher above 20-30 K that the melting point of corresponding alloy. The second method was the sintering of alloys from the powders of previously obtained Cu₂S and CuAlS₂ compounds. The procedure was similar to the above described one. The phase equilibrium in the Cu₂S - CuAlS₂ system was investigated by means of X-ray diffraction and differential thermal analysis. The melting point was 1386 K for Cu₂S and 1493 K for CuAlS₂. Cu₂S has two solid state transformations at 383 and 713 K. The T(x) phase diagram of the Cu₂S - CuAlS₂ has the eutectics at 0,34 molar part of CuAlS₂ and 1280 K. The region of formation of solid solutions on Cu₂S side does not exceed 0,10 molar part of CuAlS₂ at the room temperature.

H8.7

NEW APPROACH TO THE CuInSe₂ - CuGaSe₂ PHASE DIAGRAM. Barys V. Korzun, Institute of Physics of Solids and Semiconductors, Minsk, BELARUS.

Thin film solar cells based on the CuInSe₂ and CuGaSe₂ chalcopyrite semiconductors are ones of the most promising candidates for a large scale low cost application of photovoltaic solar energy conversion. The good results were achieved using different compositions of the Cu(Ga, In)Se₂ multinary compounds. To develop the methods of single crystal and thin films growth the information on phase equilibria in this system is necessary but up to now the knowledge of the T(x) phase diagram of the CuInSe₂ - CuGaSe₂ system is still incomplete because the peritectic melting of CuGaSe₂ has been not taken into account. The purposes aims of this paper are the preparation of alloys of the CuInSe₂ - CuGaSe₂ system and the construction of T(x) phase diagram by differential thermal analysis and X-ray diffraction using the knowledge of the Cu₂Se - In₂Se₃ and Cu₂Se - Ga₂Se₃ phase diagrams. To obtain CuInSe₂ and CuGaSe₂ compounds and their

alloys two methods were developed. One of them was the melting from the constituent elements of 99,999% (copper, gallium, indium) and 99,9999% purity (selenium). The charges were sealed in evacuated double quartz ampoules and then placed into electric furnace. The ampoules were heated to the temperature higher above 20-30 K that the melting point of corresponding alloy. The second method was the sintering of alloys from the powders of previously obtained CuInSe₂ and CuGaSe₂ compounds. The procedure was similar to the above described one. The phase equilibrium in the CuInSe₂ - CuGaSe₂ system was investigated by means of X-ray diffraction and differential thermal analysis. The melting point was 1370 K for CuGaSe₂ and 1259 K for CuInSe₂. CuGaSe₂ melts incongruently and the temperature of peritectics is 1315 K, and the melting of the CuGaSe₂-rich solid solutions has also the peritectics' character. CuInSe₂ has the solid state transformation at 1083 K. The melting of the CuGaSe₂-rich solid solutions has the peritectics character. The complete series of solid solutions are formed in the CuInSe₂ - CuGaSe₂ system. The lattice constants are changed linearly from a=5,606 and c=11,01A for CuGaSe₂ to a=5,782 and c=11,62 A for CuInSe₂.

H8.8

FABRICATION OF CuInSe₂ SOLAR CELLS BY THE EVAPORATION OF BINARY SELENIDE COMPOUNDS.

Doon Youl Lee, Jae Ho Yun, Byung Tae Ahn, Korea Advanced Institute of Science and Technology, Dept of Materials Science and Engineering, Taejeon, KOREA; Kyung Hoon Yoon, Jinsoo Song, Korea Institute of Energy Research, New Energy Department, Taejeon, KOREA.

CuInSe₂ films were prepared by the three stage process using the evaporation of In₂Se₃, Cu₂Se and Se. In₂Se₃ layer was deposited at 150°C substrate and a Cu-rich CuInSe₂ film was formed at 440°C by the reaction between the incoming evaporated Cu₂Se and the pre-deposited In₂Se₃ layer. CuInSe₂ film had a bi-layer morphology where the top layer has small grains and the bottom layer has large grains. The CuIn₃Se₅ layer was formed on the top of CuInSe₂ film by adding a small amount of Cu₂Se at 440°C. The morphological difference between CuIn₃Se₅ and CuInSe₂ was not observed, but only the compositional change occurred. The CuInSe₂ solar cell with a thin CuIn₃Se₅ layer, showed the best active area efficiency of 9.6% with V_{oc}=417 mV, J_{sc}=37.9 mA/cm² and FF=0.606. As the thickness of CuIn₃Se₅ layer increased further, the efficiency decreased.

H8.9

EFFECTS OF SURFACE TERMINATION ON CuIn_{1-x}Ga_xSe₂ PREPARED FROM MIXED Cu-In-Ga-Se PRECURSORS.

Markus E. Beck, Jeff Alleman, Amy Swartzlander-Guest, Rick Matson, Rommel Noufi, National Renewable Energy Laboratory, Golden, CO.

We have recently reported on the material and device properties of the first thin film CuIn(Ga)Se₂ samples prepared by a novel formation process [1]. This two-stage absorber formation method involves mixed amorphous or nano-crystalline Cu-In-(Ga)-Se precursor structures deposited onto unheated substrates and subsequent compound formation at elevated temperatures. This approach was found to be thermodynamically favorable and avoids the formation of intermetallics associated with the selenization of Cu/In/Ga metallic layers. Precursor growth in the employed hybrid sputter-evaporation technique could be described with a slightly modified Thornton Structure Zone Model. Deposition of Cu Se layers as a function of substrate temperature (T_{sub}) revealed the onset of detectable crystal structures in XRD measurements at 100°C - CuSe for T_{sub} < 250°C; Cu₃Se₂ and Cu_{2-x}Se for T_{sub} ≥ 250°C. Similar studies for the In Se system resulted in diffraction peaks of In₂Se₃ and In₆Se₇ to evolve at T_{sub} ≥ 200°C with In₂Se₃ dominating at T_{sub} > 300°C. Upon compound formation it was found that III VI first layers resulted in excellent adhesion while Cu Se first precursors did not adhere well upon thermal treatment. CuIn_{1-x}Ga_xSe₂ devices (x ≈ 0.25) based on recrystallized precursor structures of Ga Se/In Se/Cu Se yielded efficiencies in the 12 - 13% range. Current focus encompasses the study of surface termination schemes with the objective to enhance open-circuit voltage (V_{oc}). This publication addresses the structural, morphological, compositional, and device results on the use of Ga Se, In Se, Ga Se/In Se, and In Se/Ga Se terminating layers in the precursor structure with varying amounts of Ga and In. Schemes studied to date have resulted in an increase in V_{oc} at the expense of short-circuit current. Future work is directed at understanding and overcoming these limitations. [1] M.E. Beck, A. Swartzlander-Guest, R. Matson, J. Keane, and R. Noufi, *Sol. Energy Mater. Sol. Cells*, 64 (2000) 135-165.

H8.10

CuIn_{1-x}Ga_xSe₂-BASED PHOTOVOLTAIC CELLS FROM SOLUTION-BASED PRECURSOR FILMS. Raghu N. Bhattacharya, NREL, Golden, CO.

Photovoltaic solar cells are a very attractive source of energy. At present, the photovoltaic industry primarily uses wafers of single-crystal and polycrystalline silicon, which generally have a wafer thickness in the range of 150 to 330 μm . The wafers must go through several processing steps and then be integrated into a module. The high material and processing costs make these modules relatively expensive. The modules prepared from thin-film semiconductor materials are expected to lower costs by significantly reducing the material and processing costs. The thickness of the semiconductor films can be as little as a few microns. The development of photovoltaic device structures based on $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) has advanced rapidly during the last few years. The direct energy gap of CIGS results in a large optical absorption coefficient, which in turn permits the use of thin layers (1 - 2 μm) of active material, and also allows the use of a material with a modest diffusion length. CIGS solar cells are also known for their long-term stability. In this meeting, I will discuss new results on the development of device quality stoichiometric CIGS films by electrodeposition and electroless deposition method. Non-vacuum electrodeposition and electroless deposition techniques with a potential to prepare large-area uniform precursor films using low-cost source materials and low-cost capital equipment are very attractive for the growth of compound materials for photovoltaic applications. We have already fabricated 15.4%- and 13.4%-efficient CIGS-based devices from electrodeposited and electroless deposited precursors, respectively. As-deposited precursors are Cu-rich films and polycrystalline in nature. Additional In, Ga, and Se are added to the precursor films by physical evaporation to adjust the final composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$. Our primary goal is to minimize or eliminate the physical evaporation step. The stoichiometric films deposited using new improved deposition bath is very promising to meet this goal. The films/devices have been characterized by inductive-coupled plasma spectrometry, Auger electron spectroscopy, X-ray diffraction, electron-probe microanalysis, current-voltage characteristics, and spectral response.

H8.11

OPTIMIZATION OF THE MATERIAL PROPERTIES OF $\text{Cu}(\text{In,Ga})\text{Se}_2$ THIN FILMS BY CONTROLLED SULFUR INCORPORATION. V. Alberts, Department of Physics, Rand Afrikaans University, Johannesburg, SOUTH AFRICA.

The efficiency of $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{CdS}/\text{ZnO}$ solar cells produced by classical two-step growth processes are significantly lower than those in which co-evaporated absorbers are used. This phenomenon is mainly attributed to the reported segregation of Ga towards the Mo back contact during the precursor formation step and/or reaction step, resulting in separated CuInSe_2 and CuGaSe_2 phases. Although this problem can to a certain extent be solved by optimizing the growth parameters, it remains problematic to optimise the Ga gradient (and hence the band gap) in samples prepared by standard two-step growth processes. In this study, selenium-containing metallic precursors (e.g. $\text{InSe}/\text{Cu}/\text{GaSe}$, $\text{Cu}/\text{InSe}/\text{GaSe}$ and $\text{GaSe}/\text{Cu}/\text{InSe}$) were prepared by thermal evaporation, followed by a sulfurization step in $\text{H}_2\text{S}/\text{Ar}$. The reaction temperatures, reaction periods and gas concentrations were optimised in order to ensure homogeneous and controlled incorporation of sulfur into these structures. The surface/bulk concentrations and in-depth distribution profiles were calculated from X-ray fluorescence $L_{\alpha 1}$ and $K_{\alpha 1,2}$ line scans. The optical properties (band gap and PL response) of the films were correlated against the gallium and sulfur surface concentrations of the respective samples. The material properties of these films were also compared with that of thermally evaporated selenium-free precursors (e.g. $\text{In}/\text{Cu}/\text{Ga}$, $\text{Cu}/\text{In}/\text{Ga}$ and $\text{Ga}/\text{Cu}/\text{In}$) reacted at low temperatures to $\text{H}_2\text{Se}/\text{Ar}$, followed by a sulfurization step in $\text{H}_2\text{S}/\text{Ar}$. These low temperature (below 400°C) reaction processes are beneficial, not only in terms of ensuring low thermal budgets, but also for the deposition of chalcopyrite thin films on flexible substrates (e.g. kapton). The controlled surface treatment of two-step processed thin films in $\text{H}_2\text{S}/\text{Ar}$ can also raise the band gap of CIGS thin films in order to obtain an optimum match with the solar spectrum.

H8.12

Abstract Withdrawn.

H8.13

EFFECT OF CdCl_2 TREATMENT CONDITIONS ON THE DEEP LEVEL DENSITY, CARRIER LIFETIME AND CONVERSION EFFICIENCY OF CdTe THIN FILM SOLAR CELLS. A. Sandhu, K. Kobayashi, Tokai Univ, Dept of Electrical Engineering, Hiratsuka, JAPAN; T. Okamoto, A. Yamada, M. Konagai, Dept of Physical Electronics, Tokyo Institute of Technology, JAPAN.

There is intense interest in the development of low cost, high efficiency solar cells using p-CdTe/n-CdS/TCO/glass structures. During fabrication, the post deposition CdCl_2 treatment of the CdTe layer is very important for realizing conversion efficiencies over 15%.

However, a deeper knowledge of the relationship between CdCl_2 treatment conditions and device performance will be critical in order to achieve efficiencies approaching the theoretically predicted value of 29%. We have studied the effect of the CdCl_2 annealing conditions of p-CdTe/n-CdS/TCO/glass solar cell structures on the deep level density and carrier lifetime of the p-CdTe layer and correlated these results with the solar cell conversion efficiency. CdTe thin film solar cells with a glass/ITO/CVD-CdS/CSS-CdTe/Cu-doped graphite/Ag structure were fabricated using a wide range of growth ($T_g=595\text{-}650^\circ\text{C}$) and CdCl_2 treatment ($370\text{-}460^\circ\text{C}$) temperatures. The CdTe layers (6-8 μm thick) were deposited by close-spaced sublimation (CSS) on Corning 1737 substrates with a 250nm thick ITO film and a 60-80nm thick CdS layer deposited by chemical vapor deposition (CVD). DLTS measurements were carried out between 100-500K using a Biorad DL-8000 system. The carrier lifetimes were determined by laser induced and microwave detected photoconductive decay measurements using a Semilab WT-85 system set-up for measuring thin films. Our results showed a clear correlation between trap density, carrier lifetime, conversion efficiency and the post deposition CdCl_2 annealing conditions. Un-annealed structures had a conversion efficiency of 5.7%, a lifetime of 0.15 μs , a hole trap energy of 0.37 eV, and a hole trap density of $4 \times 10^{14} \text{cm}^{-3}$. The optimum post deposition CdCl_2 treatment temperature was found to be 415°C for structures grown at $T_g=595^\circ\text{C}$, where the conversion efficiency, lifetime, trap energy and density were 13.4%, 4.0 μs , 0.44 eV and $8 \times 10^{12} \text{cm}^{-3}$, respectively. The physical and industrial implications of these results will be discussed.

H8.14

IMPROVED ROUTES TO NANOCRYSTALLINE METAL OXIDE FILMS FOR DYE-SENSITISED SOLAR CELLS AND RELATED APPLICATIONS. Iain P. O'Hare and Paul O'Brien, The University of Manchester, Department of Chemistry and the Materials Science Center, Manchester, UNITED KINGDOM.

Nanoporous metal oxide thin films are currently attracting interest for a wide range of electronic applications, such as dye-sensitised photovoltaic cells. However, limited, and poorly controlled, film fabrication routes represent a key factor impeding the development of such devices. To date, device applications have been limited largely to sol-gel-fabricated nanocrystalline films of TiO_2 . Such studies have recently been extended to the application of an alternative film fabrication technique, notably that of chemical bath deposition (CBD), to the growth of an alternative metal oxide, ZnO. CBD is a simple, and potentially inexpensive, method by which thin films of semiconductors may be deposited. One interesting feature of CBD-fabricated films of ZnO is that, under specific conditions of undersaturation, highly reticulated layers may be obtained, such an observation suggesting that control of morphology is possible. Thick nanoporous films of ZnO have been deposited upon conducting glass substrates, under alkaline conditions, from a solution containing the metal ion, added base and a chelating agent, such as ethylenediamine or triethanolamine. The deposition rate is controlled by systematic adjustment of both temperature and pH, together with the nature, and relative concentration, of the reactants in the solution (chelating agent or metal ion). The material properties of the resulting films have been routinely characterised, through the use of a broad range of techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD), conventional Raman spectroscopy, band gap measurements, pore size distribution and photoluminescence spectroscopy. It is proposed to undertake studies of the function of the deposited films, within nanocrystalline devices, with respect to such characteristics as dye binding and photovoltaic performance.

H8.15

CHEMICAL BATH DEPOSITION OF ZINC SULFIDE FROM ACIDIC SOLUTIONS. Iain P. O'Hare and Paul O'Brien, The University of Manchester, Department of Chemistry and the Materials Science Center, Manchester, UNITED KINGDOM; David Smyth-Boyle, The University of Durham, Department of Physics, Durham, UNITED KINGDOM.

At present, the soft processing of materials attracts considerable interest. Zinc sulfide is a wide, direct band gap semiconductor, which exists in both cubic and hexagonal forms. A diverse range of applications exists for thin films of this material, including as waveguides, heterojunction devices and within electroluminescent displays, within which ZnS represents the most commonly used host material. Applications of the material within optoelectronic, or photovoltaic, devices is another area receiving attention, but one which has yet to be fully developed. The chemical bath deposition (CBD) process employs a controlled chemical reaction to effect the deposition of a thin film by precipitation. Adherent, uniform and reproducible films of ZnS have been deposited, upon low iron-content microscope slides, under acidic conditions, from a solution containing zinc chloride, urea and thioacetamide. Film thickness measurements, obtained using the quartz crystal microbalance (QCM) technique,

suggest that film growth occurs in two stages, an initial rapid phase being followed by a slower process. X-ray diffraction provides evidence of the crystalline nature of the ZnS films, indicating formation of the hexagonal wurtzite structure. Scanning electron micrographs of the deposited layers, obtained at regular intervals, suggest that, as the reaction proceeds, uniform growth of ZnS films is associated with increasing particle size, rather than continuous nucleation and deposition of new primary particles during the CBD process. EDAX spectra are typical of CBD-deposited films of ZnS, whilst signals attributable to elements within the glass substrate are also detected, an observation consistent with the thin nature of the films. Grain size distributions have been investigated using computational image analysis, and an average grain growth rate of 33.7 nanometres per hour has been calculated.

H8.16

STRATEGIES FOR ACHIEVING HIGH YIELD IN CHEMICAL BATH DEPOSITION OF SEMICONDUCTOR THIN FILMS. P.K. Nair, O. Gomez Daza, A. Arias-Carbajal, M.T.S. Nair, Universidad Nacional Autónoma de México, Centro de Investigación en Energía, Temixco, Morelos, MÉXICO; V.M. Garcia, Universidad Autónoma de Zacatecas, Faculty of Chemical Sciences, Zacatecas, MÉXICO; P. Parmananda, Universidad Autónoma del Estado de Morelos, Faculty of Science, Cuernavaca, Morelos, MÉXICO.

Chemical bath deposition has been used to deposit a range of I-VI, II-VI, IV-VI, V-VI compound semiconductors. The integration of chemically deposited CdS thin film into the structure, Mo-(p)Cu(Ga/In)Se₂-(i)CdS-(I)ZnO-(n)ZnO, is an example of its use in solar cells. Annealing the chemically deposited thin films in air or nitrogen at 200°C to 500°C leads to chemical and physical changes of interest to solar cell applications. For example, when semiconductor-metal films of the type, MX-In, are annealed at 200-350°C, heterostructures of the type, MX:In-In₂O₃-x (M = Zn, Cd; X = S, Se) result and annealing in air at 450°C of CdS and ZnS films results in CdS-CdO and ZnS-ZnO. In solar cell technology, the deposition of films of thickness 0.05 micrometer (for window layers) and 0.5-1.5 micrometer (for absorber layers or precursors to produce absorber layers) at an acceptable thin film yield is a matter of importance. Thin film yield is high when very low concentration of metal ions, typically < 0.01 mol/liter, is used since the metal ions lost in precipitation is a super-linear function of the ionic concentration or ionic product. Use of small substrate spacing, typically 2 to 5 mm, is recommended in batch production so that complex ions participating in the film formation possess sufficient range to collide with the growing film surface. At larger substrate separation, the ions are lost in precipitate formation in a 'passive' layer away from the substrate surface. Thin film yield of > 50% may be achieved through this approach for a terminal film thickness of > 0.5 micrometer. Thin film thickness (d) can be simulated as a function of substrate separation (x): $d(x) = d_{max}[1 - \exp(-bx)]$, and the thin film yield (Y) is: $Y(x) = Y_{max}[1 - \exp(-a/x)]$. At very small substrate deposition (0.1 mm), films of 0.05 micrometer as required for window layers is deposited, with thin film yield approaching 100%. The different cases are illustrated using CdS, CdSe, CuS and Cu₂xSe thin films as examples.

H8.17

CONDUCTIVE CdO LAYER FORMED ON CHEMICALLY DEPOSITED CdS THIN FILM DURING AIR-ANNEAL: PERSPECTIVE AS A WINDOW LAYER. P.K. Nair, O. Gomez Daza, A. Arias-Carbajal Reidigos, J. Campos, M.T.S. Nair, Universidad Nacional Autónoma de México, Centro de Investigación en Energía, Temixco, Morelos, MEXICO.

CdS thin films of approximately 400 nm in thickness were deposited from a chemical bath containing citratocadmium(II) complex and thiourea. When annealed in air for 5 min - 120 min at 370°C to 500°C, a thin layer of CdO is formed. Consequently the sheet resistance of the film drops from about 10¹³ ohm/square to 3.5 k ohm/square (370°C) and 470 ohm/sq (500°C). X-ray diffraction studies showed the formation of a thin layer of CdO occurring at temperatures above 370°C. From the optical transmittance and reflectance spectra, the thickness of the CdO layer was found to be about 10 nm. Crystalline grain size of CdO is 12 nm - 25 nm, depending on the temperature and duration of air-anneal and its electrical resistivity, 10⁻⁴ to 10⁻³ ohm cm. The optical band gap of the CdS-CdO layer is effectively that of the underlying CdS thin film, about 2.45 eV in the annealed film. The CdS, which remains under the conductive CdO top layer, is photosensitive - with photo-to-dark current ratio of 10³ - 10⁴, which is inferior to that of the as prepared CdS films (> 10⁶). Essentially the air annealing converts the highly resistive and highly photosensitive intrinsic (i) CdS thin film into a (i)CdS-(n)CdO layer. The technique offers prospects to convert the top part of a chemically deposited CdS thin film window layer of high photosensitivity, deposited on an absorber layer, to a conductive layer. The brief processing time at the elevated temperature would inhibit mixing of the window layer with the underlying absorber layer

already produced. Further work is required to establish this possibility. It is possible to reduce the sheet resistance to about 100 ohm/square by annealing at 500°C for a longer duration.

H8.18

COMPARATIVE STUDY OF THE STRUCTURAL AND OPTICAL PROPERTIES OF CIS FILMS PREPARED BY RF-MAGNETRON SPUTTERING AND SELENIZATION OF ELEMENTAL LAYERS. A.F. Cunha, M.M. Pereira de Azevedo, R.I.O. Ferrão, A.A.C.S. Lourenço and Claude Boemare, Departamento de Física, Universidade de Aveiro, Aveiro, PORTUGAL.

Solar cells based on CuInGaSe₂ (CIGS) grown by co-evaporation have been demonstrated in laboratory with efficiency around 18% and high material stability. Growth methods better suited to large-scale production are, currently, object of intense study. Here we report on a study where the properties of films obtained by RF-magnetron sputtering and by Selenization of elemental precursor layers are analysed by Raman scattering, x-ray diffraction and reflectivity measurements. Three routes were followed to prepare CIS films on glass. First we sputtered CIS onto a glass slide at room temperature and then annealed the films at 450°C in air to adjust its crystal structure to chalcopyrite (type-I CIS). Secondly we sputtered the CIS films onto a glass slide at 400°C (type-II CIS). Thirdly we selenized stacked elemental layers of Cu/In/Cu obtained by RF-magnetron sputtering. RF-magnetron sputtered films showed Raman modes at 128cm⁻¹(tentatively assigned to E¹_{TO}), 147cm⁻¹(unassigned), 175cm⁻¹ (A₁) and at 214cm⁻¹ (E¹_{TO} or B¹_{2TO}). These four peaks were observed in several points of the same films but their relative intensity changed from point to point, perhaps, indicating different crystal orientation of the grains along the film. On the other hand the selenized films show a strong Raman mode at 175cm⁻¹ (A₁) and two others much less intense at 213cm⁻¹ (E¹_{TO} or B¹_{2TO}) and 231cm⁻¹(unassigned). This is a characteristic of all the selenized films and it is, perhaps, a consequence of the anisotropic diffusion of Se from the surface down. X-ray diffraction shows that type-I films have essentially chalcopyrite structure but diffraction peaks corresponding In₂Se₃ have also been observed. On the other hand type-II films have a crystal structure of pure chalcopyrite. The selenized films, however, although essentially made up of a dominant chalcopyrite phase also contain In₂O₃ and Cu₂In as revealed by the X-ray diffraction analysis. The number and the relative intensity of the Raman peaks observed must be related to microstructure differences between the films.

H8.19

EFFECTS OF Na AND Se ANNEALING ON CuInSe₂ SINGLE CRYSTALS. Vera Lyakhovitskaya, Ishay Feldman, David Cahen and Konstantin Gartsman, the Weizmann Institute of Science, Rehovoth, ISRAEL.

We report on scanning electron microscopy, energy dispersive X-ray fluorescence, electron-beam induced current, secondary ion mass spectroscopy and X-ray photoelectron spectroscopic studies of high quality, travelling heater-grown single crystals of CuInSe₂, that were subjected to controlled heat treatments from 300°C upwards for varying times, in Se atmosphere, in Na atmosphere and in a mixture thereof. We find that with Na the surface of the crystals is gradually destroyed, while with Se a gradual topotactic type conversion takes place, controlled by Cu diffusion towards the surface, rather than by Se diffusion into the bulk. This is accompanied by formation of a separate Cu-Se phase on the surface. The implications of these findings for the effects of Na on the performance of CuInSe₂-based solar cells will be considered, in terms of both possible surface and bulk effects.

H8.20

ATOMIC LAYER DEPOSITION OF INDIUM SULFIDE LAYERS FOR CIGS SOLAR CELLS. Frederique Donsanti, Benno Weinberger, Pierre Cowache, Daniel Lincot, Ecole Nationale Supérieure de Chimie de Paris, Paris, FRANCE.

Indium sulfide layers deposited by Atomic layer epitaxy are promising interfacial buffer layers for cadmium free, all vacuum processed, CIGS thin film solar cells with efficiencies up to 13.5% achieved with device quality CIGS. These layers are deposited at low temperature (100-180°C) by using alternatively indium acetylacetonate and hydrogen sulfide vapor pulses. This study aims first to a better understanding of the growth mechanism. This is carried out from a parametric study where parameters are varied in a wide range (sources and substrate temperatures, precursors and purging gas pulse durations) and their effects immediately followed by in situ microgravimetric measurements. This allows to evidence the importance of adsorption/desorption effects in this system as compared to the zinc oxide one. Films are then characterized (composition, structure, optical prop.). The properties are influenced by the deposition conditions. The main effect is a widening of the band gap value which can reach 3.5 eV instead of about 2 eV for bulk indium sulfide. These

results will be presented and further discussed. Results on solar cells will complete the study.

H8.21

OBSERVATION OF INTERDIFFUSION IN ZnO/CuInSe₂ HETERO-STRUCTURES AND ITS EFFECT ON FILM PROPERTIES. Ralf Hunger, Paul Fons, Kakuya Iwata, Akimasa Yamada, Koji Matsu-bara, Shigeru Niki, Electrotechnical Laboratory, Optoelectronics Div, Tsukuba, Ibaraki, JAPAN; Ken Nakahara, Hidemi Takasu, ROHM Co Ltd, Optical Device R&D Div, Kyoto, JAPAN.

We have investigated the direct growth of ZnO on epitaxial CuInSe₂(001) (CIS) by radical-source molecular beam epitaxy (RS-MBE). CIS substrates with a cation ratio [Cu]/[In]≈0.82 were grown on GaAs(001) at T_{sub} = 450°C. Subsequently, ZnO films were deposited by RS-MBE at growth temperatures of 250°C and 450°C. In RS-MBE, oxygen is supplied as an atomic beam from a RF-plasma source, whereas Zn is supplied from a conventional effusion cell. The ZnO film structure was characterized by XRD texture measurements, and a possible substrate interaction was investigated by low temperature photoluminescence of the CIS before and after ZnO growth. For T_{sub} = 250°C, ZnO exhibits multiple-domain epitaxial growth characterized by eight distinct orientations of individual ZnO crystallites relative to the substrate lattice. For the higher T_{sub} = 450°C, a c-axis orientated ZnO domain with only a weak in-plane preferential orientation becomes dominant. Another significant difference of ZnO growth is revealed by PL: the CIS signal is dominated by a broad DAP transition at hν ≈0.86 eV, which remains essentially unchanged for ZnO growth at T_{sub} = 250°C. The ZnO growth at T_{sub} = 450°C, however, induces a shift to higher PL emission energies. By exposure of the CuInSe₂(001) surface at T_{sub} ≈ 450°C to only a Zn flux, a similar spectral change was observed. SIMS measurements of the CIS/ZnO structures on the other hand do not reveal any oxygen indiffusion into CIS. These results suggest that the ZnO growth at T_{sub} = 450°C is accompanied by Zn indiffusion into the CIS substrate. The role of Zn in regard to changes in the optical and electronic properties of CIS is further investigated.

H8.22

A STUDY ON THE FRONT CONTACT MODIFICATION IN CdS/CdTe SOLAR CELLS. Hokyun Ahn, Jangeun Heo, Younggun Han and Donghwan Kim, Korea Univ, Div of MS&E, Seoul, KOREA.

The performance of CdS/CdTe solar cells was improved by applying a thin resistive indium-tin oxide (ITO) between CdS and conducting ITO layers. The surface of resistive ITO was hydrophilic and the heterogeneous nucleation and growth of CdS seemed to be enhanced in the chemical bath deposition. The CdS layers had smaller grains, smoother surfaces and a denser microstructure when deposited on this type of ITO. The numbers of the absorbed surface particles and the pores observed at CdS/CdTe interface also decreased. Current-voltage measurements revealed that the reverse saturation current (J₀) decreased and the cell performance improved. This implied that the shunt paths of the diode decreased. Effect of Ar or O₂ ion-beam sputtering of ITO on the performance of CdS/CdTe solar cells was also investigated. Changes of the work function and the surface composition of ITO were correlated with the device performance using x-ray and ultraviolet photoelectron spectroscopy.

H8.23

CADMIUM TELLURIDE SOLAR CELLS ON MOLYBDENUM SUBSTRATES. Ilvydas Matulionis, Sijin Han, Jennifer A. Drayton, Kent J. Price, and Alvin D. Compaan, The University of Toledo, Toledo, OH.

We report on the development of Mo/CdTe/CdS/Indium-Tin-Oxide thin film solar cells grown by radio frequency sputtering in an 18 mTorr argon plasma. This is an inverted configuration compared to the conventional glass/tin-oxide/CdS/CdTe/metal cells. The molybdenum or stainless steel substrates are clearly advantageous compared to glass - they are flexible, can withstand much higher processing temperatures and are at least 10 times lighter. Molybdenum has been chosen as a substrate because its thermal expansion coefficient and the work function are close to those of CdTe. We have achieved the conversion efficiencies of 7.8 percent on 0.05 cm² area devices. The highest efficiency previously reported by the group at the University of Texas at El Paso was 5.3 percent[*]. Our best cells had a nitrogen doped ZnTe layer between the molybdenum and the CdTe for an improved ohmic contact. We observe a significant rollover in the IV curve under the forward current that indicates a back-diode effect. This implies the need for improvement of the electronic properties of the molybdenum - CdTe and CdS - ITO interfaces. [*] V.P. Singh, J.C. McClure, G.B. Lush, W. Wang, X. Wang, G.W. Thompson, and E. Clark. Solar Energy Materials and Solar Cells 59 (1999) 145-161.

H8.24

WHEN, WHY AND WHERE ARE CdTe/CdS SOLAR CELLS STABLE? Kevin D. Dobson, Iris Visoly-Fisher, Gary Hodes and David Cahen, Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, ISRAEL.

Efficient CdTe/CdS thin-film solar cells require formation of reliable ohmic contacts to p-CdTe. Use of various metals, particularly Cu, in the contact material improves contact properties and initial cell performance. Unfortunately, cell stability then decreases under accelerated (200°C) stress testing. Even if empirically the problem can be overcome, it is important to understand the fundamental scientific issue(s) involved, also for public acceptance of such cells. Present understanding connects the instability with Cu diffusion into CdTe and with poisoning of the cell junction. [Note: large-area, encapsulated modules can be stable in the field for years, at typical module efficiencies].

Earlier studies (here and elsewhere) showed that Cu from the back contact indeed diffuses into the cell. This can lead to loss of contact, expressed in I-V rollover. More surprisingly, with longer stress times Cu is found to accumulate in the CdS region and near the CdS/TCO interface. We find that Cu dopes the CdS. As a result, and especially by co-doping with Cl (from CdCl₂ treatment used for sintering), CdS becomes photoconductive. This, by itself, mainly affects the cell's dark I-V characteristics and, at least initially, will NOT affect cell performance (for which it is actually beneficial). However, if the cell is exposed also to air (oxygen), then degradation, in terms of loss of V_{OC} and fill factor, is accelerated substantially.

We used a combination of methods on thermally stressed cells, including light-beam induced current, secondary ion mass spectroscopy and photoluminescence, to understand this. Based on our results we conclude that while Cu diffusion is not much affected by O₂, IN THE PRESENCE OF Cu, OXYGEN IS A DETERMINING FACTOR FOR CELL DEGRADATION. We present a simple model explaining this and provide experimental results that support the model.

We thank Reshef Tenne for help with PL and acknowledge NREL support.

SESSION H9: FILM AND DEVICE CHARACTERISTICS

Chairs: Takahiro Wada and James R. Sites
Friday Morning, April 20, 2001
Salon 5/6 (Marriott)

8:30 AM *H9.1

DEVICE ANALYSIS OF Cu(In,Ga)Se₂ HETEROJUNCTION SOLAR CELLS. U. Rau, Institute of Physical Electronics, University of Stuttgart, GERMANY.

The steady improvement of the Cu(In,Ga)Se₂ based solar cell performance and process reproducibility over recent years together with the development of sensitive analysis methods and detailed electronic transport models has led to a conclusive picture of the basic electronic properties of these devices. This contribution summarizes our present understanding on the electronic transport of ZnO/CdS/Cu(In,Ga)Se₂ heterojunction solar cells with a special focus on high-efficiency devices. The range of material parameters which allows to describe devices with efficiencies above 18 % is relatively narrow if one considers not only the bare photovoltaic output parameters but also results from additional characterization methods like quantum efficiency and admittance analysis. Such a rather complete device modeling allows to determine densities of bulk and interface defects as well as their capture cross sections for both kinds of charge carriers. Starting from such a standard model for high-efficiency devices we discuss the dependence of the electronic properties on absorber composition and the potential for improving the device performance by compositional gradings. The contribution further proposes electronic models for the reversible changes of the electronic properties that occur by illumination (i) and by application of reverse voltage bias (ii). Both types of metastabilities are - to a larger or a smaller extend - present in all Cu(In,Ga)Se₂ solar cells, and, thus represent fundamental properties of the bulk material (i) and of the defective close-to-surface region of the polycrystalline absorber layer (ii). Especially the explanation of the metastability upon reverse biasing sheds some light on the not yet fully understood electronic properties of the Cu(In,Ga)Se₂/CdS interface and its extreme sensitivity to chemical and physical conditions during heterojunction formation.

9:00 AM H9.2

DEEP CENTERS AND FILL FACTOR LOSSES IN THE CIGS DEVICES. M. Igalson, P. Zabierowski, Warsaw University of Technology, Faculty of Physics, Warszawa, POLAND.

Fill factor deficiency is a frequently observed source of efficiency loss in some of the ZnO/CdS/Cu(In,Ga)Se₂ devices. It is most pronounced if the light characteristics are examined under the red illumination (absorbed in CIGS). A blue component of the white light (absorbed in CdS) in large extent reduces that loss. The widely accepted interpretation of that effect attributes it to the deep centers in the window layer. In this work we will show, that a distribution and charge state of deep centers in the absorber affects strongly fill factor of CIGS devices. The experimental procedure applied here has been introduced earlier [1] and is based on a producing of a "frozen" non-equilibrium charge distribution within the absorber by the illumination or voltage bias and a subsequent characterization of the device at the low temperature. Thus we can study in detail junction electronic characteristics avoiding relaxation effects present around the room temperature. The methods used include dark and light IV, CV and DLTS measurements. We demonstrate, that fill factor loss similar to that present in some devices in the equilibrium state might be produced also in the high efficiency structures by introducing a negative charge close to the heterointerface. The fill factor losses are correlated to the worse transport properties of the device indicating higher contribution of a trap-assisted tunneling to the carrier transport. The results are interpreted in terms of a model of np p junction in which a charge state and concentration of deep midgap centers plays a crucial role. The contribution of these states to the metastable phenomena encountered in CIGS is also discussed. [1] M. Igalson, L. Stolt, 12th Int. Conf. On Ternary and Multinary Compounds, Hsinchu, Taiwan 2000; Jpn. J. Appl. Phys., in press

9:15 AM H9.3

OPTICAL PROPERTIES AND PHOTOLUMINESCENCE OF CuInGaSe₂ THIN FILMS AND DEVICES. Thomas Unold, Karsten Bothe, Gottfried H. Bauer, Dept. of Physics, University of Oldenburg, GERMANY.

Several CuInGaSe₂ devices and thin films with thicknesses ranging from 0.7 to 6 microns have been studied by temperature dependent direct and diffuse reflection/transmission and photoluminescence measurements. We find a strong subgap absorption that is almost independent of the thickness of the films, indicating that it arises from depth inhomogeneities common to all films. A multilayer analysis of the spectra allows us to deduce the bulk absorption coefficient for our films. The temperature dependence and intensity dependence of the photoluminescence measurements indicates that the main feature observable at room temperature arises from free-to-bound transitions. Spatially resolved photoluminescence measurements show inhomogeneities which can be correlated with the morphology of the films as determined by atomic force microscopy. From the analysis of the spectral shape of the photoluminescence we estimate the diffusion length, surface recombination velocities and the splitting of the quasi-Fermi levels. These results are consistent with estimates of the recombination lifetime from time-resolved photoluminescence measurements.

9:30 AM H9.4

CURRENT TRANSPORT IN CuInS₂ SOLAR CELLS DEPENDING ON ABSORBER PREPARATION. Joachim Reiss, Axel Werner, Imke Hengel, Reiner Klenk, Martha Ch. Lux-Steiner, Hahn-Meitner-Institute, Berlin, GERMANY; Jonas Malmström, Ångström Laboratory, Uppsala, SWEDEN.

Improved understanding of the current transport in CuInS₂/CdS/ZnO solar cells will help to overcome the observed limitation of their open circuit voltage V_{oc} to about 750 mV which is a moderate value in view of the absorber band gap E_g of 1.5 eV. According to our model presented previously, the dominant recombination under illumination occurs at the CuInS₂/CdS interface. In this contribution we refine this model by using results from jV curve measurements performed at varied temperature and illumination. We compare CuInS₂/CdS/ZnO solar cells where the absorber has been prepared in sequential processes: evaporated or sputtered Cu/In precursors sulphurised with 3 different methods. All cells show qualitatively the same behaviour of the dominant recombination mechanism. The temperature dependence of the diode quality factor indicates a change from tunnelling enhanced recombination in the dark to thermally activated recombination under illumination. The latter is believed to be located at the CuInS₂/CdS interface, since both, extrapolation of the V_{oc} to 0 K as well as the activation energy E_a in the $\ln(J_0)$ arrhenius plot under illumination are significantly below E_g ($qV_{oc}(0\text{ K}) \approx E_a \approx 1.1$ eV). However, in the dark E_a increases and correlates well with E_g . This suggests that not only the mechanism of the main recombination changes, but also the location shifts from the CuInS₂ bulk in the dark to the CuInS₂/CdS interface under illumination. Doping with silver has the capability to change this general behaviour. The E_a extracted from the diode characteristics of CuInS₂:Ag/CdS/ZnO solar cells can reach values up to 1.5 eV (i.e. E_g) even under illumination in contrast to the $qV_{oc}(0\text{ K})$ which still remains at about 1.1 eV. This discrepancy between E_a and $qV_{oc}(0\text{ K})$ is not easily understood in

terms of the models presented in the literature for chalcopyrite solar cells. We will discuss these findings using also our results from measurements of Cu(In,Ga)Se₂ and CuGaSe₂ based solar cells as well as numerical modelling.

9:45 AM H9.5

IMPORTANCE OF ELECTRON CURRENT IN P-TYPE CdTe IN CdS/CdTe THIN FILM SOLAR CELLS AT FORWARD BIAS. Jutta Beier, ANTEC GmbH, Frankfurt, GERMANY; Marc Köntges, ISFH, Hanover, GERMANY; Peter Nollet, Stefaan Degraeve and Marc Burgelman, Ghent University, Dept of Electronics and Information Systems, Ghent, BELGIUM.

In previous work, we explained the cross-over of the $I - V$ curves of thin film CdS/CdTe solar cells, with the assumption of surprisingly high values of the bulk minority carrier diffusion length L_n in p -type CdTe: L_n in the order of 3 μm . In this work, we measured such high values under low injection circumstances by combining spectral response measurements and $C - V$ measurements at reverse bias voltage. The measured values are discussed and compared to results of other (totally) different diffusion length measurements reported in literature: time resolved photoluminescence (TRPL), EBIC, etc. We then shortly present a series of new measurement results obtained on CdS/CdTe thin film solar cells, that basically look at the current flow at forward bias. They mainly describe the wavelength dependence of the current flow at forward bias. Illuminating the cell through the front and through the back surface shows typical wavelength dependent behavior. This behavior can be understood and modeled very accurately by adopting the long diffusion length hypothesis in the p -type CdTe. Using modeling, we then go into more detail concerning the necessity of this assumption: what assumptions are really necessary to be able to model the measured $I - V$ and spectral response curves. The results presented strengthen the previously stated model. This model gives a more realistic description of the CdTe back contact region: not only describing the hole contribution (which can account for roll-over and for a decrease in fill factor FF), but also the electron contribution (which decreases V_{oc}). Our measurements stress the importance of the electron current contribution at the back contact at forward polarization of the solar cell.

10:30 AM H9.6

IMPROVEMENT IN DIFFUSION LENGTH ESTIMATION USING THE PHOTOCURRENT-CAPACITANCE METHOD IN CuInSe₂-BASED CELLS. C.H. Champness, Department of Electrical and Computer Engineering, McGill University, Montreal, Quebec, CANADA.

A convenient non-destructive method of determining the minority diffusion length L_n in a photovoltaic cell, without requiring precise values of the optical absorption coefficient α , is the photocurrent-capacitance method. This method depends on the increase of photo-generated current in an illuminated cell as the depletion width W is widened by increasing reverse bias. The method requires incident long wavelength penetrating light, for which $1/\alpha$ is much greater than W , so that $\alpha W \ll 1$. In a successful technique, chopped light from a monochromator is incident on the cell and, with increased applied reverse bias, the illuminated-to-dark current change ΔI is measured, along with the junction capacitance C_p . Next, if ΔI is plotted against $1/C_p$ and extrapolation from the linear region is made to the abscissa, cutting it at the negative intercept $1/C_i$, then the diffusion length is given by $L_n = -\epsilon_0 \epsilon_r A / C_i$, where A is the cell area, ϵ_r is the relative dielectric constant of the absorber and ϵ_0 is the permittivity of a vacuum. For high quality cells, where the diffusion length is the order of micrometers, such as in CuInSe₂-based devices, the method works well. However, serious errors arise for devices with significant junction shunting, as can occur in developing cell fabrication techniques. Therefore, efforts were made to make the method more tolerant to device imperfections, where needed, by changing some of the measuring techniques. This was done by measuring the capacitance values at lower frequencies, ensuring that the readings were obtained under the same illumination as the ΔI measurements and replacing the monochromator with a high wavelength pass optical filter. It was found that a silicon wafer, with a 1.1 μm edge, acted as an excellent filter for cells with a CuInSe₂ absorber. However, in the case of Cu(In,Ga)Se₂ cells, this wavelength was too long and experiments will need to be carried out with shorter wavelength edge filters at 0.9 and 1.0 μm .

10:45 AM H9.7

PHOTOELECTROCHEMICAL CHARACTERIZATION OF STATE OF ART CIGS THIN FILMS. Elisabeth Ciolus, Daniel Lincot, Jean Francois Guillemoles, Anouk Galteyries, Ecole Nationale Supérieure de Chimie de Paris, Paris, FRANCE; Georg Voerwinden, ZSW, Stuttgart, GERMANY.

Schottky like diodes are formed when CIGS thin films are brought in

contact with an electrolyte. This provides a very easy way to characterize bulk and interface properties of CIGS films. Bulk properties are not affected by the contact with the electrolyte allowing measurements of doping level by electrochemical impedance measurements. Interface properties are very sensitive to the reaction with the electrolyte and can be followed by flat band potential measurements and further correlated to composition by XPS ex situ analysis. Under illumination, photocurrent is generated allowing to make spectral response measurements. Mapping the lateral properties is made by local illumination. In this presentation device quality CIGS films are studied and the characteristics compared with solid state devices. The effect of surface modifications on the photoelectrochemical response is also studied, using for instance noble metal deposition at the surface by ion exchange, in order to catalyze the photoreduction of protons in acidic aqueous solutions.

11:00 AM H9.8

MICRON-RESOLUTION PHOTOCURRENT OF CdTe SOLAR CELLS USING MULTIPLE WAVELENGTHS. Jason F. Hiltner, James R. Sites, Colorado State Univ, Dept of Physics, Fort Collins, CO.

The apparatus developed recently at Colorado State University utilizes a diffraction limited optics system and a high resolution translation system to measure the laser-induced photocurrent at resolutions up to 1 μm , with equivalent incident laser intensities of 1 sun. Multiple lasers in the 635-830 nm range are now easily selected by changing the fiber-optic connectors. The spot profile and location are unchanged when different lasers are selected. In addition, a laser temperature tuned through the 830-857 nm range allows variation of the quantum efficiency with wavelength to be measured near the CdTe bandgap, also with micron resolution. Sulfur incorporation in CdTe leads to a lower bandgap, corresponding to absorption of higher wavelength photons by the material, so that CdS-CdTe intermixing can be investigated. This capability extends the previous analysis, which includes the separation of series resistance and shunting effects. The effect of post-deposition processing on local variations in electrical and optical parameters, especially using the near-bandgap wavelengths, are examined using a series of prepared samples.

11:15 AM H9.9

ANNEALING TIME AND COLLECTION EFFICIENCY IN ELECTRODEPOSITED CdS/CdTe SOLAR CELLS. G. Agostinelli, E.D. Dunlop, B. Ebner, N. Gibson, European Commission, Joint Research Centre, Ispra, ITALY.

This paper presents a detailed analysis of the spatially resolved evolution of External Quantum Efficiency of electrodeposited CdS/CdTe solar cells as a function of the duration of the post-deposition annealing process which promotes n to p-type conversion of electrodeposited CdTe. Strips of 30x4 cm were cut from deposited plates at various stages of the fabrication process and processed into cells. Annealing treatments were carried out on these strips at 400°C for times ranging from 1 to 120 minutes. 130 spectral response curves (in the range of 300 to 900 nm) have been measured to trace temporal evolution and spatial non-uniformity of the materials and extrapolate parameters such as effective diffusion lengths, evolution of the collection profiles, junction depth. Correlation between these parameters suggests that recrystallisation does not take place uniformly but progresses through the film. The analysis of structural vs. optical parameters differences along the cells evidence spatial non-uniformities of the state of crystallisation of as-deposited and annealed material. Poor performance has been observed near the edges of the cells where material is resistant to recrystallisation.

11:30 AM H9.10

COMPREHENSIVE STUDY OF LIGHT-SOAKING EFFECT IN ZnO/Cu(InGa)Se₂ SOLAR CELLS WITH Zn-BASED BUFFER LAYER. Sutichai Chaisitsak, Akira Yamada and Makoto Konagai, Dept. of Electrical and Electronic Engineering, Tokyo Institute of Technology, Tokyo, JAPAN.

In our previous works, Zn-based materials fabricated by "dry process", such as ZnIn_xSe_y and i-ZnO, have been investigated as alternative buffer layers to CBD-CdS in CIGS solar cells. Devices with these buffer layers have demonstrated well in efficiency. However, light-soaking effect is observed clearly in these devices compared to devices with CBD-CdS. In this work, we attempt to clarify the light-soaking effect and to improve device stability for the Zn-based buffer layer solar cells. We found that device stability can be controlled by modifying absorber surface; 1) CIGS absorbers treated with the chemical bath, such as dipping in NH₄OH, almost do not show light-soaking effect; 2) Zn-doping of CIGS surface by Diethylzinc is beneficial in limiting light-soaking effect without any kinds of chemical treatments. A relative higher initial v_{oc} and FF, and shorter time to become fully efficient is achieved. According to experimental results, the origin of this phenomenon is assumed to locate at/near

the interface and correlate mainly with the absorber surface/grain-boundary properties. The proper engineering of absorber surface is important, not only for conversion efficiency but also device stability.

11:45 AM H9.11

EFFECTS OF POLYCRYSTALLINITY ON THE PHOTOVOLTAIC PERFORMANCE OF CdTe SOLAR CELLS. Iris Visoly-Fisher, K. Gartsman^a, S. Cohen^a and D. Cahen, Departments of Materials & Interfaces and ^aChemical Services, Weizmann Institute of Science, Rehovot, ISRAEL.

To study the relations between polycrystallinity (PX) and photovoltaic (PV) performance of chalcogenide solar cells, we examine the effects of selective chemical changes of the grain external and internal surfaces (grain boundaries, GBs) on the material's electrical properties and PV cell performance. Below a grain size of a few μm , the density of surface electronic states in most PX materials approaches the bulk density of states. Thus, chemical changes of the grain surface properties may result in significant changes of carrier concentration and mobility, hence affecting PV cell performance. We measure **electrical properties of a single GB and a single grain**, to detect whether charge separation and current collection are changed in GBs and/or near GB/cell junction intersections. Such measurements are also used to determine the effect of chemical treatments on the electronic properties of the grain boundaries and surfaces. **Surface photovoltage measurements** show that adsorption of certain organic molecules changes the onset of the photo-response of CdTe/CdS cells. I-V measurements of these cells (after ohmic contact application) show that the molecules affect their photovoltaic behavior. **Scanning Kelvin Probe microscopy**, using AFM with conductive tip, showed that a sample with adsorbed molecules gave smaller differences in surface potential between grain surfaces and inner GBs, than a Br₂/MeOH etched sample. In the dark, the inner GBs show higher CPD than the outer grain surfaces, while under illumination the GBs show lower CPD. **Spatially controlled I-V measurements** show a change in the current collection with increasing distance from the GB. These results may indicate that GBs are more electrically active than the surface, with a higher band bending (due to surface charge) and recombination velocity, and that GB electronic states are affected by chemical treatments. Inorganic surface treatments, such as surface passivation and reduction, will also be discussed. We thank USDOE/NREL for support.