



Strasbourg (France)

E-MRS Spring Meeting 2004  
May 24-28, 2004

## SYMPOSIUM O

Thin film chalcogenide photovoltaic materials

### Symposium Organizers:

Daniel Lincot, Ecole Nationale Supérieure de Chimie de Paris, France

Hans-Werner Schock, University of Stuttgart, Germany

Ayodhya N. Tiwari, CREST Loughborough University, UK

Alvin D. Compaan, University of Toledo, USA

Takahiro Wada, Ryukoku University, Japan

Papers will be published in Thin Solid Films

# E-MRS 2004 SPRING MEETING

## SYMPOSIUM O

Tuesday, May 25, 2004

Morning

Session I: High efficiency cells & modules

Session chairs: Rommel Noufi, Takahiro Wada

**O-I.1** 09:00 -Invited-

### PROPERTIES OF HIGH EFFICIENCY CIGS HETEROJUNCTIONS

**K. Ramanathan**, M.J. Romero, C.S. Jiang and R. Noufi, National Center for Photovoltaics, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden CO 80401, USA

We describe the unique features of the three-stage process that allows us to control the structural and compositional properties of CIGS absorbers. The sequential nature of the process permits good control of the bulk and surface properties of the absorbers. We shall present quantitative data on the properties of the ZnO and CdS window layers, and determine the losses in the window layers in the short and long wavelength regions. This leads to an accurate estimation of the collection efficiency of the junction and the losses that are inherent to the device. We shall present related information about the structural and chemical properties of the absorbers surface region, the nature of grain boundaries, and the variation of surface potential as a function of chemical treatments. A general review of the current understanding of the junction formation will also be given.

**O-I.2** 09:30 -Invited-

### APPROACHES TO FLEXIBLE CIGS THIN-FILM SOLAR CELLS

**Friedrich Kessler** and Dirk Herrmann, Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg, ZSW Industriestrasse 6, 70565 Stuttgart, Germany

As CIGS is a direct semiconductor, it is possible to fabricate thin solar cells in the thickness range of about 5  $\mu\text{m}$ . The real potential of this type of material can only be met if the ballast of the substrate and the cover glass is abandoned. The advantages of lightweight, flexible, and robust (unbreakable) modules are evident, especially with regard to novel applications. Proven high efficiencies, very high stabilities against proton and electron radiation, potentially low weight, high flexibility, and cost-effective roll-to-roll manufacturing have even attracted the interest of space suppliers. However, due to the relatively high CIGS deposition temperature of about 550°C, the substitution of the commonly applied glass substrate by a suitable flexible and low cost material and the direct transfer of process technologies is not as straightforward as expected and not all aspects mentioned could be combined to date.

We will briefly introduce some special approaches - especially from European laboratories - to fabricate flexible CIGS-based modules and discuss their respective features. Furthermore, the approaches on metal and polymer foils at ZSW will be presented. Functioning monolithically integrated modules were fabricated on an area of up to 20 cm  $\times$  30 cm on both polyimide and metal substrates. Important challenges which were solved are the electrical insulation of titanium or steel substrates and the patterning process on thin foils. Suitable dielectric barriers are, for example, SiO<sub>x</sub> layers which were deposited pinhole-free and which withstand both the CIGS process and the structuring procedures. Adequate patterning methods such as direct laser scribing and mask-free photolithography were successfully applied to interconnect more than 30 cells.

**O-I.3** 10:00

### THE EFFECT OF GA-GRADING IN CIGS-BASED THIN FILM SOLAR CELLS

**O. Lundberg**, M. Edoff, L. Stolt, Ångström Solar Center, Solid State Electronics, Uppsala, Sweden

In this paper the effect of an in depth variation of the Ga/(In+Ga) ratio in CIGS based thin film solar cells is presented. In order to obtain an as complete picture as possible the effect of Ga-grading is studied in CIGS layers grown at different conditions. The conclusions made are based on a review of earlier publications in combination with the results from a large set of new devices.

For standard devices with normally thick CIGS films (1.5-2  $\mu\text{m}$ ) deposited at a relatively long deposition time (60 minutes) an improved efficiency of around 0.4 % units for the devices with an increased Ga/(In+Ga) ratio towards the back contact is observed. This improvement is due to a field assisted carrier collection resulting in an improved QE response at long wavelengths. When the CIGS thickness is reduced the importance of the increased Ga/(In+Ga) ratio towards the back contact is enhanced and at a CIGS thickness of 0.5  $\mu\text{m}$  a gain of 2.5 % units is obtained. For these devices an improved Voc and FF is obtained. The main reason for the improvement is passivation of the back contact, which becomes increasingly detrimental for the device performance as the CIGS thickness is reduced. Also for pure CIS a significant improvement of the device performance is obtained by introducing an increased Ga concentration towards the back contact. This improvement is, however, more related to the introduction of Ga itself than the gradient of the Ga-concentration. From many simulations the largest gain is predicted for an increased Ga/(In+Ga) ratio towards the CIGS surface. However, neither in the literature nor from our own experiments we can find evidence for an improved device performance due to an increased Ga-concentration towards the CIGS surface.

- O-I.4** 10:15 TRANSFER OF Cu(In,Ga)Se<sub>2</sub> THIN FILM SOLAR CELLS TO FLEXIBLE SUBSTRATES  
C.A. Kaufmann, A. Neisser, R. Klenk, R. Scheer, Hahn-Meitner-Institut Berlin GmbH, Glienickestrasse 100, 14109 Berlin, Germany  
 Lately the development and the investigation of flexible thin film technologies are attracting increased attention. The translation of high, small area efficiencies from rigid glass substrates to flexible substrate materials, upscaling the solar cell area and device optimisation on low-temperature substrates are all of crucial interest.  
 Using co-evaporated Cu(In,Ga)Se<sub>2</sub> as absorber layer material, so far we have reached an efficiency of 16.7% (AM1.5) for laboratory scale cells on glass. This contribution reports on advances in performance optimisation, which have been achieved for single solar cells, produced on Ti-foil and polyimide substrates with a total area of up to 30cm<sup>2</sup>. A major loss in open circuit voltage on Ti-substrates can be prevented through adjustment of the sodium content, resulting in an efficiency of 16.2% on laboratory scale devices. Thus the transfer of the small area efficiency from glass to titanium foil as substrate material is basically achieved. Optimisation of large area efficiencies and of the low-temperature process are under way. Device efficiencies till date are 12.2% for a 16.5cm<sup>2</sup> total area device on Ti-foil and 10.8% for a small area device on polyimide.
- O-I.5** 10:30 CIGS SOLAR CELLS AND MODULES BY AN ELECTRODEPOSITION PROCESS  
S. Taunier(a), J.F. Guillemoles(a), J. Sixx-Kurdi(a), A. Chaumont(a), P.P. Grand(a), O. Roussel(a), O. Ramdani(a), D. Guimard(a), C. Hubert(a), J.P. Fauvarque(a), N. Bodereau(a), L. Parissi(a), P. Panheleux(a), P. Fanouillère(a), N. Naghavi(a), M. Ben-Farah(a), P. Mogensen(2) D. Lincot(a), O Kerrec(a), (a)Laboratoire Commun « Cellules Solaires en Couches Minces » EDF-CNRS/ENSCP, Plateau CISEL, 6 Quai Watier-BP 49, 78401 Chatou Cedex, France, (b)Saint-Gobain Recherche, Aubervilliers, France  
 The electrochemical deposition offers attractive possibilities for the mass production of CIGS solar cells at lower cost. There are however certain difficulties to allow the industrial development of this method : (1) obtaining sufficiently high conversion efficiencies on small area cells, (2) extending the electrodeposition process to larger areas. These are the main goals of the current CISEL project (Copper Indium Selenide by Electrodeposition)\*.  
 To date, a record cell efficiency of up to 11.3 % was obtained with the combination of the electrodeposition process and a thermal annealing treatment at atmospheric pressure. It appears as the best result to date for the electrodeposition method without any vacuum step for the realization of the active part of the device. We will present an analysis of the best cells, in particular by admittance spectroscopy vs temperature, spectral response and temperature dependant I-V curves, allowing to determine the origin of the losses in the cells, and to carry out a comparison with devices prepared by classical vacuum methods. Then we will present some results on the scaling-up of the electrodeposition step, up to 30 by 30 cm<sup>2</sup> substrates. Lateral composition homogeneity on single plates, dispersion from plate to plate will be presented based of tens of preparations. First results on efficiencies from modules configurations will be presented. \*between Electricité de France (EDF) and CNRS, together with Saint-Gobain Recherche and the support of the ADEME.

10:45

**BREAK**

Session chairs: A. Tiburcio-Silver, Chris Ferekides

- O-I.6** 11:15 -Invited- HIGH-EFFICIENCY Cu(InGa)Se<sub>2</sub> THIN FILM SOLAR CELLS WITH Zn-BASED NOVEL BUFFER LAYER  
**A. Yamada**, H. Miyazaki, Y. Chiba and M. Konagai, Research Center for Quantum Effect Electronics, Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1 O-Okayama, Meguro-ku, Tokyo 152-8552, Japan  
 Zn-based materials has been investigated as a novel buffer layer for Cu(InGa)Se<sub>2</sub> solar cells. The deposition of Zn<sub>1-x</sub>Mg<sub>x</sub>O was studied by both chemical-bath deposition (CBD) and metal-organic chemical vapor deposition (MOCVD). ZnO was successfully fabricated by the CBD method with zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>) and ammonia (NH<sub>4</sub>OH). The films were applied to the buffer layer of the solar cell and an efficiency of 14.3% was obtained. The concentration of chemical species in the solution was numerically calculated in order to clarify the growth mechanism of ZnO and it was found that Zn(OH)<sub>2</sub> is a possible precursor for the CBD-ZnO growth. We have also tried to grow Zn<sub>1-x</sub>Mg<sub>x</sub>O from an aqueous solution to control the bandgap of a buffer layer and Mg(OH)<sub>2</sub> could be grown by the CBD technique, but the efficiency of the solar cells with this buffer layer was still low. Zn<sub>1-x</sub>Mg<sub>x</sub>O have been successfully grown by the MOCVD method. Bisethylcyclopentadienyl-Mg, diethylzinc and water were employed as reactant gases. The growth temperature was about 300°C. The bandgap of the films was varied from 3.30eV (x=0.0) to 3.57eV (x=0.15) by changing the ratio of reactant gases. As a preliminary experiment, we applied the films to Cu(InGa)(SSe)<sub>2</sub> solar cells and an efficiency of 6.57% was achieved.

- O-I.7** 11:45 SPUTTER-DEPOSITED ZINC-MAGNESIUM OXIDE AS CADMIUM-FREE BUFFER LAYER IN CIGSSE SOLAR CELLS AND MINIMODULES  
S. Visbeck, K. Stießberger, T.P. Niesen, J. Palm, V. Probst and F. Karg, Shell Solar GmbH, Muenchen, Germany  
 RF-sputtered (Zn,Mg)O has successfully been used as buffer layer in CIGS<sub>Se</sub>-based solar cells. So far, efficiencies up to 12,5% have been reached for small laboratory cells. Motivated by these results, we installed a mixed-oxide (30 at% Mg) ceramic (Zn,Mg)O-target in our pilot line sputter machine capable of coating substrates up to 30x90cm<sup>2</sup>. In this contribution, we present first results of layers deposited at Shell Solar. The influence of different sputter parameters like pressure and power on the film growth will be shown, covering electrical, optical and compositional thin-film properties. Additionally, first experiments employing (Zn,Mg)O as buffer layer in 10x10cm<sup>2</sup> series-integrated mini-modules will be presented. We used different wet pre-treatments as well as untreated absorbers from the standard pilot line selenization/sulfurization. To further clarify the role of the absorber-buffer interface for the solar cell performance, we used additional absorbers from different selenization experiments, employing different levels of sulfur at the hetero-interface.
- O-I.8** 12:00 -Invited- SOLAR CELLS BASED ON CuInS<sub>2</sub> - AN OVERVIEW  
**R. Klenk**, J. Klaer, R. Scheer, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Glienickerstr. 100, 14109 Berlin, Germany, I. Luck, N. Meyer, U. Rühle, SULFURCELL Solartechnik GmbH, Barbara-McClintock-Str. 11, 12489 Berlin, Germany  
 Over the last years, selenium-free chalcopyrites based on CuInS<sub>2</sub> have emerged as promising candidates for thin-film photovoltaic modules. We shall give an overview concerning the preparation, properties and perspectives of CuInS<sub>2</sub>-based solar cells and modules as well as the status of pilot production. In preparation, the most obvious difference to the more widely researched selenium-based materials is the general use of an over-stoichiometric copper content which provokes the formation of Cu-S phases. They assist in gathering and incorporating the sulphur and act as an inherent surfactant. This growth mechanism allows very fast compound formation and reproducibly yields films with low defect density and high effective doping independently from the sodium content. Implementation in a two-step process using sputtered metal precursor films and rapid thermal sulphurisation results in a process which is very attractive for industrial production through its use of standard equipment, high throughput and high yield. The company SULFURCELL has been founded to implement the first pilot production for large area modules, currently under construction in Berlin. The band gap of 1.5 eV of the gallium-free compound allows a comparatively simple structure for single-junction devices, results in high open circuit voltages and limits efficiency losses at higher operating temperatures of the module. We have shown that it is also a good starting point for the development of wide-gap cells as required for tandem configurations.

12:30

**LUNCH**

Tuesday, May 25, 2004

Afternoon

14:00

POSTER SESSION I

Heterojunctions, window layers

Session chair: Ayodhya Tiwari

O/PI.01

INTERFACE FORMATION BETWEEN Cu(In,Ga)Se<sub>2</sub> AND CdS: COMPARISON BETWEEN Cu-RICH AND Cu-POOR SURFACE CONDITIONS

T. Schulmeyer(a), R. Hunger(a), R. Kniese(b), M. Powalla(b), W. Jaegermann(a) and A. Klein(a), (a)Darmstadt University of Technology, Department of Materials Science, Surface Science Division, Petersenstrasse 23, 64287 Darmstadt, Germany, (b)Zentrum für Sonnenenergie und Wasserstoffforschung, Industriestrasse 6c, 70565 Stuttgart, Germany

The interface with CdS is important for Cu(In,Ga)Se<sub>2</sub> thin film solar cells, which have achieved energy conversion efficiencies above 19 %. Record efficiencies are obtained with Cu(In,Ga)Se<sub>2</sub> films, which have a Cu-poor surface composition. We have investigated the chemical and electronic properties of the Cu(In,Ga)Se<sub>2</sub>/CdS interface for Cu-poor and Cu-rich surface conditions using photoelectron spectroscopy. These Cu(In,Ga)Se<sub>2</sub> absorbers were prepared by the selenium capping and decapping process. This procedure enables a preparation of clean Cu(In,Ga)Se<sub>2</sub> surfaces in ultra high vacuum. The unavoidable Cu<sub>2</sub>Se segregation of the Cu-rich grown absorbers was removed by an in situ KCN etching process. The difference of the valence band offsets for the two substrates is reproducibly smaller than predicted from theory. This might be due to a change in Cu concentration, which is induced by interface formation and directly observed by photoemission intensities.

O/PI.02

FABRICATION AND CHARACTERIZATION OF In<sub>2</sub>S<sub>3</sub> THIN FILMS DEPOSITED BY THERMAL EVAPORATION TECHNIQUE

A. Timoumi, H. Bouzouita, M. Kanzari and B. Rezig, Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs, Ecole Nationale des Ingénieurs de Tunis (E.N.I.T), BP 37 Belvédère, 1002 Tunis, Tunisie

Indium sulphide In<sub>2</sub>S<sub>3</sub> Thin films present an alternative to conventional CdS films as buffer layer for CIS-based thin film solar cells. The objective is to eliminate toxic cadmium; to widen the energy gap. Indium sulphide is synthesized and deposited by single source vacuum thermal evaporation method on glass substrates. The films are examined by X-ray diffraction (XRD), electron probe microanalysis (EPMA), Scanning electron microscopy (SEM) and optical absorption measurements. The XRD spectra confirmed the initial amorphous nature of the as-deposited films and showed transition phase into crystalline In<sub>2</sub>S<sub>3</sub> form upon annealing at 250°C. X-ray diffraction analysis and Scanning Surface morphology of the samples showed that the number of the spots decreases with increasing annealing temperature. The EPMA results show S-poor in all samples. The optical constants of the deposited films were obtained from the analysis of the experimental recorded transmission and from reflectance spectral data over the wavelength range 300-1800 nm. We note that the films annealed at 150 °C during 2 hours show a good homogeneity with 80% transmission. An analysis of the optical absorption data of the as-deposited films revealed an optical direct band gap energy in the range of 2.0-2.2 eV.

O/PI.03

COMPARISON STUDY OF ITO THIN FILMS DEPOSITED BY SPUTTERING AT ROOM TEMPERATURE ONTO POLYMER AND GLASS SUBSTRATES

C. Guillén and J. Herrero, Departamento de Energías Renovables, CIEMAT, Avenida Complutense 22, 28040 Madrid, Spain

Indium tin oxide (ITO) thin films onto glass substrates are widely used as transparent and conductive electrodes for various displays, sensors and photovoltaic devices. The replacement to flexible polymer substrates is gaining a great interest because can give advantages such as lightweight, higher shock resistance and scalable roll-to-roll preparation procedures. For chalcogenide-based solar cells, the structure, morphology and electro-optical characteristics of the transparent conductive layer play an important role on the final device performance, aiming to increase the light collection. Thus, it is needed to take into account the influence on the ITO characteristics of the chemistry, roughness, stability and thermal expansion coefficient of the selected polymer substrate. In this contribution we present a comparative study of ITO thin films grown by sputtering at room temperature onto glass and polymer substrates. The structure, morphology and electro-optical characteristics of the ITO/glass and ITO/polymer samples have been analysed by x-ray diffraction, atomic force microscopy, four points electrical measurements and spectrophotometry. The final objective is to get a better understanding on the ITO-substrate interactions during the deposition process that can modify (improving or worsening) the material properties for thin film photovoltaic applications.

O/PI.04

OPTOELECTRONICAL PROPERTIES OF INDIUM SULFIDE THIN FILMS PREPARED BY SPRAY PYROLYSIS

M. Calixto-Rodriguez, A. Tiburcio-Silver\*, and A. Sanchez-Juarez, Centro de Investigación en Energía, UNAM Apto. Postal 34, 62580 Temixco, Mor. Mexico, \*Instituto Tecnológico de Toluca, SEP

In this work we are reporting the formation of tin sulfide thin films prepared by the spray pyrolysis technique using indium acetate and N-N dimethyl thiourea as precursor's compounds. Corning glass substrates and single-silicon slides were used as substrates. Samples with different substrate temperatures and indium to sulfur ratio, in the starting solution, have been synthesized and characterized using different techniques. XRD studies have shown that substrate temperature affect the crystallinity of the deposited materials as well as the optoelectronic properties. For substrate temperature bigger than 350°C, XRD studies have revealed that the deposited materials are In<sub>2</sub>S<sub>3</sub>. For a In/S=1, the optical band gap increases from 2.1 eV up to 2.65 eV, and dark electrical conductivity increase up to 1.1x10<sup>-1</sup> (cm)<sup>-1</sup>, when substrate temperature increases from 350°C up to 450°C. Dark electrical conductivity and optical band gap can be controlled by changing either the substrate temperature or the In/S ratio. The characterization results show that the In<sub>2</sub>S<sub>3</sub> thin films prepared under these conditions have a big potential use as a window material for photovoltaic heterojunctions devices.

**O/PL05****BARRIER FORMATION AND CHANGES OF IT PARAMETERS DURING THE OXIDE LAYER GROWTH PROCESS ON THE SURFACE OF INDIUM MONOSELENIDE**

S.I. Drapak, S.V. Gavryluk, Z.D. KovalyukFrantsevich Institute of Materials Science Problems, the National Academy of Sciences of Ukraine, Chernivtsi Department, 5 Iryna Vilde Str., Chernivtsi, 58001, Ukraine

The thermal oxidation process of cleft surface of p-InSe, which is a potential material for photovoltaic, at 673 K have been investigated using X-ray diffraction method in the time range from 10 to 180 minutes. We established that the formed oxide layer, in fact, consists of two chemically different sublayers: one with oxygen on the surface (mainly In<sub>2</sub>(SeO<sub>4</sub>)<sub>3</sub>) and another transitional &#8211; without it. The last one consists of different phases of In<sub>2</sub>Se<sub>3</sub>. The thickness and homogeneity of these layers are not constant during the thermal oxidation process and lead to the changes of electrical, photoelectric, and noise characteristics of p-InSe-intrinsic oxide heterojunction. The minimum values of dark saturation current as well as the maximum value of the signal to noise ratio were observed for the structures obtained after oxidation for 1.5 h when the thickness of the interface layer decreases and its homogeneity becomes higher. A further increase of oxidation time leads to the appearance of micro cracks on the surface of oxide, the inversion of the InSe conductivity type and, as a result, to the decrease of built-in potential. The main photoelectric parameters also become worse.

**O/PL06****GROWTH AND CHARACTERIZATION OF ITO THIN FILMS DEPOSITED ON PET SUBSTRATES**

Jaehyeong Lee, Hakkee Jung, School of Electronics and Information Engineering, Kunsan National University, Junsin Yi, School of Information and Communications Engineering, Sungkyunkwan University, Korea

ITO films are highly degenerated, wide gap semiconductors with a relatively low resistivity and a high transmittance in the visible range of the spectrum. Because of these characteristics, ITO films are widely used in optoelectronic applications, such as transparent electrodes in liquid crystal displays, ferroelectric photo-conductor storage devices, and photovoltaic devices. There is a strong current commercial requirement that the high-quality ITO films for color LCDs or flexible solar cells should be deposited at substrate temperature (Ts) of about room temperature (RT) -150 oC because of the restricted thermostability of color filters or flexible polymer substrates such as PC or PET. (Ts=300-400 oC for conventional processes to deposit the low-resistivity ITO directly on a glass substrate.) In order to deposit the ITO films on these polymer substrates with certain properties and good adhesion, detailed study on structural and electrical properties of the films is important. In present work, ITO films on PET substrate have been prepared by magnetron sputtering method using powdery target with different deposition conditions. The structural, optical and electrical properties of the obtained films depending on deposition parameters, such as sputtering power and working pressure, have been investigated. As the sputtering power and working pressure were higher, the sheet resistance of ITO films increased. The optical transmittance deteriorated with increasing sputtering power and thickness. As the working pressure increased, however, the optical transmittance improved at visible region of light. High quality films with sheet resistance as low as 100 ohm/sq and transmittance over 80% have been obtained by suitably controlling the deposition parameters.

**O/PL07****MATERIAL ANALYSIS OF PVD GROWN INDIUM SULFIDE FOR Cu(In,Ga)Se<sub>2</sub> ABSORBERS**

S. Gall, S. Harel, N. Barreau, J.C. Bernède, J. Kessler, LPSE University of Nantes, France

Recently it has been shown that indium sulfide thin films can replace the standard Chemical Bath Deposition (CBD) cadmium sulfide buffer layers in Cu(In,Ga)Se<sub>2</sub>-based solar cells and achieve comparable device performance. Although the best reported efficiencies using indium sulfide buffer layers [1] are grown by Atomic Layer Chemical Vapor Deposition (ALCVD), we have deposited similar layers by a simple Physical Vapor Deposition (PVD) process. Nevertheless, a difference is found in that the oxygen content in our PVD grown layers is higher than for those grown by ALCVD. Found to be on the order of 10%, this oxygen has been observed to substitute sulfur and results in an increased band gap. Optimization of the deposition parameters has allowed us to achieve devices up to 12.5% efficient [2]. In order to improve our understanding of the influence of the deposition parameters on device performance, we have investigated our indium sulfide material by XPS and TEM studies, and in particular its interface with the Cu(In,Ga)Se<sub>2</sub>. We have systematically observed the presence of copper in the buffer layer which clearly plays a role on the device performance. This copper content strongly depends on the deposition conditions. The better devices being those which contain less copper in the indium sulfide buffer layer. [1] N. Naghavi, S. Spiering, M. Powalla, B. Canava, A. Taisne, J.-F. Guillemoles, S. Taunier, A. Etcheberry and D. Lincot, Mat. Res. Soc. Symp. Proc. Vol. 763 © 2003 Materials Research Society [2] S. Gall, S. Harel, N. Barreau, J.C. Bernède, J. Kessler, Influence of indium sulfide buffer layer growth conditions on Cu(In,Ga)Se<sub>2</sub> solar cell performance, submitted to the 19th European Photovoltaic Solar Energy Conference and Exhibition, Paris, France, June 2004

**O/PL08****P- TYPE COPPER (I) IODIDE AS HETEROJUNCTION PARTNER FOR CISCuT OBSERVED BY TEM, SPV, XPS, AND ERDA TECHNIQUES**

B.R. Sankapal, A. Ennaoui, Th. Dittich, W. Bohne\* and M.Ch. Lux-Steiner, Division Solar Energy Research (SE2), \*Division Structure and Dynamic (SF4), Hahn-Meitner-Institut, Glienicke Strasse 100, 14109 Berlin, Germany

In contrast to the standard p-type CuInS<sub>2</sub> (CIS) based thin films solar cell techniques, the roll-to-roll CISCuT technology leads to the formation of n-type CIS absorber. Therefore, a p-type buffer layer is necessary to form the junction. In this paper, we used p-type CuI as buffer layer synthesized at room temperature by successive ionic layer adsorption and reaction (SILAR) method. Device efficiency up to 4 % was achieved with p-CuI as heterojunction partner for CISCuT. Quantum efficiency above 60 % was observed. SEM, TEM, SPV, XPS and ERDA have been used for the characterization. SEM of CuI film deposited on CISCuT at room temperature shows a fibrous surface morphology. However by dipping in ethanol solution containing iodine, the film showed small crystallites with an average size of 50-100 nm. TEM of CuI deposited on carbon coated gold grids shows small crystallites (20-40 nm). Analysis of SPV measurements reveals that surface states at n-CIS/p-CuI are reduced as compared to bare CIS. A pronounced increase in PV amplitude is observed around 1.5 eV mainly attributed to the band gap of CIS. The amplitude decreases at 3.0 eV, which corresponds to the absorption in CuI. The iodine treated n-CIS/p-CuI heterojunction shows enhancement in PV. XPS survey spectrum of CuI on CIS shows that only Cu and I. C and O impurities are also observed, mainly from surface contamination. ERDA analysis revealed a diffusion of iodine into CIS. The optimization of n-CIS/p-CuI properties in relation to the device efficiency and the role of CuI are in progress.

ACKNOWLEDGEMENT: This work is supported by the European Commission, FP5, contract ENK6-CT-2001-00519. Our project partner IST GmbH provided the CISCuT absorber samples.

- O/PL.09** COMPARISON OF CdS FILMS DEPOSITED FROM CHEMICAL BATHS CONTAINING DIFFERENT DOPING IMPURITIES  
M. Altosaar, K. Ernits, J. Hiie, M. Danilson, J. Krustok, L. Kaupmees, T. Varema, J. Raudoja, E. Mellikov, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia  
The characterization results obtained for CdS films chemically deposited from solutions containing different impurities: chlorine, iodine, boron or In, which all are known as donor type dopants for CdS, are reported. CdS films were deposited on pure glass and ITO covered glass substrates at 85°C. CdCl<sub>2</sub>, CdI<sub>2</sub> and Cd(CH<sub>3</sub>COO)<sub>2</sub> were used as Cd sources respectively. The baths contained 0.001 M Cd and 0.02 M ammonium compound and 0.002 M thiourea in ammonia solution of different pH: 9.5, 10 and 11.5. The samples were heated at 200 °C for 30 minutes in vacuum. The films were characterized by XRD, EDS, SEM, current-voltage and capacitance-voltage measurements using ITO/CdS/gold structures. I-V characteristics of electrochemically deposited CuInSe<sub>2</sub>/CdS/ZnO solar cells with CdS deposited from chemical baths with different dopants are measured and compared.
- O/PL.10** STUDY OF THE ELECTRODEPOSITION OF In<sub>2</sub>S<sub>3</sub> THIN FILMS  
B. Asenjo, A.M. Chaparro, M.T. Gutiérrez, J. Herrero, C. Maffiotte, CIEMAT, Madrid, Spain  
In<sub>2</sub>S<sub>3</sub> is a semiconductor with interest for photochemical and photovoltaic energy conversion. Among thin film deposition techniques, aqueous solution based are low temperature, soft processes, most adequate to leave unaltered the subsurface of the substrate, which is a requirement in photovoltaic technology. In previous studies, we have reported on the chemical solution deposition of In<sub>2</sub>S<sub>3</sub> thin films. This process produces thin films of In<sub>2</sub>S<sub>3</sub>- In<sub>2</sub>O<sub>3</sub> mixed composition as a consequence of parallel chemical and electroless reactions. Being the electroless reaction based on reduction reactions on the surface of the substrate induced by sulphide anions, we want to study the films obtained directly by cathodic polarisation of a conductive substrate immersed in a proper solution bath. The electrochemical route may provide better control over the composition of the films than a pure chemical or electroless process. Two strategies are studied for obtaining In<sub>2</sub>S<sub>3</sub> films, the sequential deposition of the atomic components (S, In), and the one step cathodic deposition. The growth of the films is monitored with an electrochemical quartz-crystal microbalance, and subsequent film analysis is carried out to determine composition and structure.
- O/PL.11** PREPARATION OF NANOCRYSTALLINE ZINC SULFIDE BY A NEW CHEMICAL BATH DEPOSITION ROUTE FOR CuInS<sub>2</sub> SUPERSTRATE THIN FILM SOLAR CELL  
S.D. Sartale, A. Ennaoui and M. Lux-Steiner, Department of Heterogeneous Material Systems (SE2), Hahn-Meitner-Institut, Glienicke Strasse 100, 14109 Berlin, Germany  
Zinc sulfide (ZnS) is a wide band gap material with n-type conductivity. It is a promising material in powder form for catalysis and as a barrier material for chalcopyrite based solar cells. Numerous expensive methods have been applied to obtain zinc sulfide thin films. In the present study, new chemical bath deposition route (CBD) has been used to obtain thick ZnS films up to 500 nm. The as-deposited films are either amorphous or nanocrystalline. After annealing in Ar atmosphere at 400 °C broad peaks corresponding to nanocrystalline ZnS starts to appear. After annealing, the collected byproduct shows a mixture of ZnS and ZnO with cubic and hexagonal structures, respectively. Optical measurements show a band gap of 3.7 eV for as-deposited films, which decreases with annealing temperature. In order to develop ITO/ZnS/CuInS<sub>2</sub> and ITO/(Zn,Cd)S/CuInS<sub>2</sub> superstrate solar cell, we have performed a series of treatments involving immersion of ZnS film deposited on ITO in the aqueous solutions containing Cd(II) and Cu(I) ions. Structures such as ZnS/CdS and ZnS/CdS/CuxS are formed by ion exchange. The ITO/ZnS/CuInS<sub>2</sub> or ITO/(Zn,Cd)S/CuInS<sub>2</sub> heterostructures are formed by electroplating Cu-In alloy followed by exposure to H<sub>2</sub>S vapor at 500°C. Films containing particles of different sizes are produced. Transmission electron microscopy (TEM) has been used to investigate the microstructure of the different interfaces. Surface photo-voltage has been used to characterize the devices.  
Acknowledgement: One of us (SDS) acknowledges Alexander von Humboldt Foundation, Germany for the financial support.
- O/PL.12** CHEMICAL AND ELECTRONIC PROPERTIES OF ZNO SURFACES IN DEPENDENCE ON THE DEPOSITION PARAMETERS  
Frank Säuberlich, Andreas Klein, Surface Science Division, Materials Science Department, Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany  
Surfaces of the transparent conducting oxide (TCO) zinc oxide (ZnO) are investigated with X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS) and X-ray diffraction (XRD) to observe the chemical, electronic and structural properties of the prepared thin films. These films are deposited by magnetron sputtering in an ultra high vacuum analysis and preparation system (DAISY-MAT) which allows in-situ XPS and UPS analysis. We have varied sputtering pressure, oxygen partial pressure, sample temperature, sample-target distance and plasma power densities with DC or RF excitation. Intrinsic ZnO (i-ZnO) and aluminium-doped ZnO (ZnO:Al, 2 wt-%) targets were used. Those parameters, which mainly affect the deposition rate do not have a major impact on the electronic properties of the surfaces but are clearly observable in the structural properties of the film. The surface Fermi level is mainly affected by the oxygen partial pressure.  
The XPS and UPS measurements give also information about the growth mechanisms of the films. We present evidence for the contribution of metastable peroxo-like surface species to the growth process. Concerning the doping mechanism of ZnO:Al our measurements indicate highly oxygen coordinated Al atoms.

- O/PI.13** EFFECTS OF THIOUREA CONCENTRATION ON CdS THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION FOR CdTe SOLAR CELLS\*.  
 Rogelio Mendoza-Pérez(a), Guillermo Santana-Rodríguez(b), Jorge Sastre-Hernández(a), Gerardo Contreras-Puente(a), Arturo Morales-Acevedo(c), Aime Arias-Carbajal(b) and Osvaldo Vigil-Galan(b), (a)Escuela Superior de Física y Matemáticas del I.P.N.; Edificio 9, U.P.A.L.M., 07738 México D.F., (b)Instituto de Materiales y Reactivos, U. de la Habana, Cd. de la Habana, C.P. 10400, Cuba, (c)CINVESTAV-IPN, Depto. de Ingeniería Eléctrica, Av. IPN 2508, 07360 México D.F.  
 We study the effects of thiourea concentration on CdS thin films grown by the chemical bath deposition (CBD) technique, processed with different thickness and submitted to post-thermal treatments of CdCl<sub>2</sub>. We compare these films with similar CdS-films grown by closed space vapor transport (CSVT) technique, by analyzing the I-V characteristics of CdS/CdTe solar cells fabricated with these CdS films. The CdS-CBD cells showed higher open circuit voltage (V<sub>oc</sub>) and fill factor (FF), while the short circuit current remains without change, as the ratio of S to Cd in the CBD solution goes from 0.5 to 5.0. This dependence changes when there is also a variation of the CdS-CBD layer thickness. We have obtained cells with more than 12% efficiency when the CdS layers are deposited by CBD as compared to cells with 11% efficiency for the CdS layers prepared by CSVT. Other measurements such as spectral response were performed and their results are correlated to the I-V characteristics of the cells so that the best performances of CdS-CBD solar cells are explained in terms of the chemical composition of this layer. (\*) Work partially support by CONACYT-México.
- O/PI.14** PROPERTIES OF BANDGAP MODIFIED Zn<sub>1-x</sub>Mg<sub>x</sub>O TRANSPARENT CONDUCTING FILMS  
 K. Matsubara, H. Shibata, A. Yamada, H. Tampo, S. Ishizuka, K. Sakurai, P. Fons, K. Iwata and S. Niki, National Institutes of Advanced Industrial Science and Technology (AIST), Japan  
 Bandgap engineering of ZnO films using the solid solution of ZnO with another materials such as MgO have been studied by several groups. Improvement of the efficiency of CIGS solar cells is expected with the bandgap engineering of window layer. We propose the use of the bandgap modified Zn<sub>1-x</sub>Mg<sub>x</sub>O as transparent conducting films and the controlling of the band lineup at a heterojunction. Low resistivity and transparent Al-doped Zn<sub>1-x</sub>Mg<sub>x</sub>O films were deposited by pulsed laser deposition system. Al-doped Zn<sub>1-x</sub>Mg<sub>x</sub>O target was fabricated by mixing ZnO, MgO, and Al<sub>2</sub>O<sub>3</sub> powder, pressing them into a pellet, and sintering in air. Films were deposited in oxygen ambient by a KrF excimer laser. Transparent and low resistivity Al-doped Zn<sub>1-x</sub>Mg<sub>x</sub>O films were obtained on glass substrates with the substrate temperature less than 200 °C. Energy bandgap of the films with the electrical resistivity of 1 x 10<sup>-3</sup> Ohm cm or less could be varied from about 3.5 eV to 4 eV with different Mg content. The relation between bandgap energy and resistivity was found to be trade-off; i.e. larger the bandgap energy, higher the resistivity. Carrier mobility tended to decrease with increasing Mg content, while the carrier concentration was almost constant for the films with low Al concentration. The increase in resistivity was attributed to increased effective mass in good agreement with theoretical investigation.
- O/PI.15** AN INVESTIGATION INTO THE INFLUENCE OF VARIOUS METALORGANIC SOURCES ON THE QUALITY OF MOVPE-GROWN CuGaS<sub>2</sub>  
 M.S. Branch(a), P.R. Berndt(a), A.W.R. Leitch(a), J. Weber(b), J.R. Botha(a), (a)University of Port Elizabeth, South Africa, (b)Institute for Low Temperature Physics, University of Technology, Dresden, Germany  
 The chalcopyrite semiconductor CuGaS<sub>2</sub> has a direct band gap of 2.49 eV at room temperature<sup>1</sup> making it a potential material for optoelectronic devices operating in the green part of the visible spectrum. In this paper we report on the epitaxial growth of CuGaS<sub>2</sub> on (100) GaAs and (100) Si by means of metalorganic vapour phase epitaxy (MOVPE). This method of growth offers greater control over the composition of individual epilayers, which will in turn help create a better understanding of how deviations from stoichiometry affect the defect chemistry of the material. The new metalorganic (MO) source hexafluoroacetylacacetate-copper triethylamine ((hfac)<sub>2</sub>CuEt<sub>3</sub>N) was used, which has a higher vapour pressure than that of existing copper MO sources<sup>2</sup>. Trimethylgallium and triethylgallium were compared as gallium sources and di-tert-butylsulfide was used as a sulphur source. Structural and optical properties, as obtained by X-ray diffraction, transmission electron microscopy (TEM) and photoluminescence spectroscopy, relating to growth parameters such as the [Cu]/[Ga] and [S]/([Cu]+[Ga]) ratios will be presented. The formation of other crystal structures such as the zinc-blende and Cu-Pt type ordering will also be illustrated from TEM analysis.
- O/PI.16** COMPARISON OF CDS FILMS DEPOSITED BY TWO TECHNIQUES: EFFECTS ON CdTe SOLAR CELL  
 Jaehyeong Lee, Hakkee Jung, School of Electronics and Information Engineering, Kunsan National University, Junsin Yi, School of Information and Communications Engineering, Sungkyunkwan University, Korea  
 Cadmium telluride (CdTe) is recognized as a most promising thin-film photovoltaic material. Polycrystalline thin-film solar cells are normally of the heterojunction configuration because of the short optical absorption length in CdTe and difficulty of forming a shallow junction with a high-conductivity surface layer. Cadmium sulfide (CdS) has been found to be best suited as the heterojunction partner or "window" for thin-film CdTe solar cells.  
 For solar cells applications, CdS films need to have a suitable conductivity (>10<sup>16</sup> cm<sup>-3</sup>), and adequate thickness to allow high transmission and good uniformity to avoid electrical short-circuit effects. The electrical and optical properties of the films depend strongly on the preparation technique and conditions. CdS films can be deposited by low cost techniques such as vacuum evaporation, sputtering, spray pyrolysis and chemical bath deposition (CBD). Among these deposition methods, CBD is rather simple and really inexpensive, added to the advantage to produce reproducible, uniform and adherent films. In present work, we will characterize differences in the structural and optical properties of as-grown CBD and vacuum evaporated CdS films. In addition, we will fabricate CdS/CdTe solar cells using these films and investigate the electrical properties of solar cells with two type layers.

**O/PL17**

STABILITY BEHAVIOUR OF Cd-FREE CU(IN,GA)SE<sub>2</sub> SOLAR MODULES WITH ALD In<sub>2</sub>S<sub>3</sub> BUFFER LAYER

S. Spiering, D. Hariskos, S. Schröder, M. Powalla, Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg, Industriestrasse 6, 70565 Stuttgart, Germany

The IV characteristics of Cd-free CIGS thin-film solar modules using an In<sub>2</sub>S<sub>3</sub> buffer layer indicate that they are a good alternative to modules using the CdS buffer. An efficiency of 12.9 % has already been realised for a substrate area of 30 cm x 30 cm. For implementation in industrial production, however, the lifetime of the solar modules is very important. In this work we present the results from the stability testing of Cd-free devices as compared to references with the CdS buffer layer. Indoor and outdoor lifetime tests were performed with 15 cm x 30 cm and 30 cm x 30 cm CIGS modules with a In<sub>2</sub>S<sub>3</sub> buffer layer deposited by the Atomic Layer Deposition (ALD) technique. Indoor Damp Heat, Thermocycling, and UV tests were carried out in the ZSW laboratories, outdoor testing at the Widderstall solar test field in Germany. The results show comparable stability behaviour of the CIGS modules with different buffer layers and that way reinforce the qualification of In<sub>2</sub>S<sub>3</sub> as buffer material for high efficiency CIGS modules.

**O/PL18**

ON THE PHOTOVOLTAIC EFFECT IN ITO-CdS-Cd<sub>1-x</sub>Zn<sub>x</sub>Te-NI HETEROSTRUCTURES

P. Gashin(a), I.I.Rusu(b), Iuliana Caraman(b), Iulia Salaoru(c), G.I.Rusu(c), (a)State University of Moldova, Faculty of Physics, Kishinau 2009, Moldova , (b)University of Bacau, Physics Department, 700506 Bacau, Romania, (c)“A.I.Cuza” University, Faculty of Physics, 700506, Iassy, Romania

Cadmium telluride (CdTe) and its ternary alloys (Cd<sub>1-x</sub>Zn<sub>x</sub>Te, Cd<sub>1-x</sub>Mn<sub>x</sub>Te, etc) are intensively studied in the last years due to their interesting characteristics (very high light absorption coefficient, large band gap, remarkable photoconductivity, etc), which are considered relevant for its applications in photovoltaic conversion devices of solar energy. The efficiency of the thin-film photovoltaic cells on the basis of heterojunctions with these compounds strongly depends on the characteristics of active trapping state located at heterojunction interfaces. In the paper, the experimental results on the generation and separation mechanisms of excess carriers in CdS-Cd<sub>1-x</sub>Zn<sub>x</sub>Te, heterojunction interfaces are reported. CdS and Cd<sub>1-x</sub>Zn<sub>x</sub>Te films were deposited by vacuum evaporation and ITO by spray pyrolysis. The short-circuit current, drift mobility of excess carriers in heterojunction region, surface state density, and efficiency are studied as a function of preparation conditions of component films and post-deposition heat treatment. The monochromatic radiation (in the spectral range from 300nm to 1400nm) and also a standard A-type source were used for illumination.

**O/PL19**

REDUCTION OF IMPURITY INCORPORATION IN ZnO THIN FILMS FOR PHOTOVOLTAIC DEVICES GROWN BY REACTIVE PLASMA DEPOSITION

K. Iwata(a), H. Sakemi(b), K. Awai(c), T. Yamamoto(d), A. Yamada(a), P. Fons(a), K. Matsubara(a), K. Sakurai(a), H. Tampo(a), S. Ishizuka(a) and S. Niki(a), (a)National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba 305-8568, Japan, (b)Research & Development Center, Sumitomo Heavy Industries Ltd., 5-2 Soubiraki-cyo, Niihama, Ehime 792-8588, Japan, (c)S.H.I. Examination & Inspection Co. Ltd., 5-2 Soubiraki-cyo, Niihama, Ehime 792-8588, Japan, (d)Department of Electronic and Photonic System Engineering, Kochi University of Technology, Tosayamada, Kochi 782-8502, Japan

Reactive plasma deposition (RPD) is a technique for depositing a thin film on a substrate using a pressure-slope type plasma ion gun. This method offers the advantage of low-ion damage, low deposition temperature, large area deposition and high growth rates. In order to achieve high throughput development, Ga-doped ZnO thin film growth was done dynamically on a moving glass substrate using a 3% Ga content ZnO target. ZnO thin film growth was performed at a substrate temperature of 200 degrees C. Samples were grown using argon gas for the plasma source and oxygen gas for stoichiometric control. The electrical properties of as-grown films were measured using Hall effect measurements. A dependence of the resistivity of the Ga doped ZnO thin films on unintentionally incorporated impurities was found. Incorporation of carbon impurity resulted in an increase in resistivity of Ga-doped ZnO films due to both decreasing carrier concentration and mobility in oxygen flow growth condition. On the other hand, incorporation of tungsten impurity resulted in an increase in resistivity of Ga-doped ZnO thin films due to a decrease in only the mobility. In order to prevent the incorporation of carbon impurity, we developed a carbon free system around the target and succeeded in reducing the previous observed decrease in carrier concentration and mobility in oxygen flow conditions. In addition, in order to prevent tungsten incorporation during growth, we developed a water-cooling system around the target. After installation of the cooling system, increase of only the mobility (38 cm<sup>2</sup>/Vsec) was observed and the lowest resistivity (2.1e-4 Ohm cm) film was grown.

**O/PL20**

STUDIES OF SPUTTERED ZnTe FILMS AS INTERLAYER FOR THE CdTe THIN FILM SOLAR CELL

B. Späth, J. Fritsche, A. Klein and W. Jaegermann, Institute of Materials Science, Surface Science Division, Darmstadt University of Technology, Germany

The properties of sputtered ZnTe and its interfaces have been investigated using in-situ photoelectron spectroscopy (XPS, UPS), atomic force microscopy (AFM), x-ray diffraction and electric characterisation. Nitrogen doped p-ZnTe films were prepared using reactive RF magnetron sputtering with N<sub>2</sub>/Ar gas mixtures with a maximum electrical conductivity of 2.5 Ohmcm<sup>-1</sup>. The electronic interface properties of sputtered ZnTe with CdTe and ZnO have been characterized using XPS. For the CdTe/ZnTe interface a valence band offset of 0.09±0.1 eV has been found, which is in agreement to previous investigations of ZnTe films deposited by physical vapor deposition onto CdTe substrates. A chemical reaction or a formation of an interlayer compound has not been observed. The ZnO/ZnTe interface is of great interest as tunneling barrier in tandem solar cells. We have found a type II band alignment with a valence band offset of 2.42±0.1 eV and a conduction band offset of 1.42±0.05 eV, which should be almost ideal for tunneling contacts.

- O/PL.21** UNIFORM LOW RESISTIVITY Ga-DOPED ZnO THIN FILMS PREPARED BY A REACTIVE PLASMA DEPOSITION METHOD ON LARGE SUBSTRATES  
Tetsuya Yamamoto, Kochi University of Technology; Toshiyuki Sakemi, Sumitomo Heavy Industries, Kiyoshi Awai, Sumiju Technical; Sho Shirakata, Ehime University, Kakuya Iwata, AIST; Shigeru Niki, AIST; Tetsuo Ikari, Miyazaki University, Kenji Yoshino, Miyazaki University, Tokio Nakada, Aoyamagakuin University; Tetsuo Yano, AIST, Japan  
 We have succeeded in the fabrication of uniform low resistivity ZnO thin films doped with Ga species (GZO) prepared by reactive plasma deposition method (RPD) on large glass substrates with a size of up to  $\sim 1\text{m} \times 1\text{m}$  at the high deposition rate. ZnO thin films have attracted attention because of a transparent conductive layer and antireflection coating for Cu(InGa)Se<sub>2</sub>-based solar cells. A pressure gradient type plasma source was used. In mass production level of using the double plasma sources described above, the GZO films deposited at almost 200 °C and at a high rate of 67 nm/min exhibited uniform distributions of both resistivity and thickness with an average transmittance above 80 % in the visible range on the large area glass substrates. Average thickness was 180 nm in the range of width 1m and the dispersion was within less than  $\pm 5\%$ . The electrical resistivity, Hall mobility, and carrier concentration of the GZO films at room temperature were determined by the van der Pauw method and by Hall-effect measurements. Average resistivity, carrier concentration and Hall mobility were  $2.8 \times 10^{-4} \Omega\text{cm}$ ,  $9 \times 10^{20} \text{cm}^{-3}$  and  $24 \text{cm}^2/\text{Vs}$ , respectively. And those dispersion were in order within less than  $\pm 5\%$ ,  $\pm 8\%$ , and  $\pm 7\%$ , respectively.
- O/PL.22** ELECTRODEPOSITION OF ZINC TELLURIDE FILMS ON CUPPER SUBSTRATES  
E. Beltowska-Lehman, P. Ozga, Z. Swiatek, Polish Academy of Sciences, Institute of Metallurgy and Materials Science, Reymonta 25 Str., 30-059 Cracow, Poland, E. Kusior, AGH University of Science and Technology, Mickiewicz Avenue 30, 30-059 Cracow, Poland  
 Thin polycrystalline films of zinc telluride (ZnTe), AIBVI - type compound, are an important material for heterojunction semiconductor structures and till now, they are prepared by expensive vacuum techniques. Electrodeposition is an alternative method for the preparation of such semiconducting films. The aim of investigation is the determination of electrocrystallisation conditions for deposition of p-type ZnTe layers with the most favourable optoelectronic properties. The preparation of electrolytes as well as determination of their stability domain was worked out. The potentiodynamic polarization curves of tellur cathodic reduction from solution containing HTeO<sub>2</sub><sup>+</sup> ions, at different pH values, in constant and controlled hydrodynamic condition were determined. The result obtained with data of separate Zn(II) reduction allowed to indicate the cathode potential range for co-deposition of ZnTe layers. For optimised electrodeposition parameters, the XRD measurements show the formation of a single-phase, cubic ZnTe.
- O/PL.23** CuInS<sub>2</sub> THIN FILMS PREPARED BY ILGAR  
N.A. Allsop, H.-J. Muffler, M. Bär, M.C. Lux-Steiner and Ch-H. Fischer Hahn-Meitner-Institut Berlin, Dept. SE2, Glienicke Str. 100, 14109 Berlin, Germany  
 ILGAR (Ion Layer Gas Reaction) is a new non-vacuum technique for the deposition of chalcogenides, capable of producing high quality thin films with potentially low production costs. Previous ILGAR studies have focussed on ultrathin films of 10-100nm for applications such as solar cell buffer layers and the new window extension layer concept. In the current study we examine the deposition of CuInS<sub>2</sub> thin films between 100nm and 1-micron in thickness. IGLAR CuInS<sub>2</sub> is prepared by the deposition of copper and indium salts onto molybdenum and TiO<sub>2</sub> substrates, followed by conversion of the salt to Cu<sub>x</sub>S, In<sub>2</sub>S<sub>3</sub> and CuInS<sub>2</sub> by H<sub>2</sub>S gas. The resulting dense films completely cover the underlying substrate and subsequent annealing at 500°C can be used to increase the grain size. The composition and microstructure of the films are analysed using SEM, XRD and XRF, and efficiencies from the first sputtered Mo/ILGAR CIS/CBD CdS/sputtered ZnO solar cells are presented.
- O/PL.24** RECOMBINATION MECHANISMS IN THIN-FILM CIGS AND CIS SOLAR CELLS WITH ALD-ZNO BUFFER LAYER  
Ulf Malm, Jonas Malmström, Charlotte Platzer-Björkman and Lars Stolt, Uppsala University, Ångström Solar Center, Sweden  
 Cu(In,Ga)Se<sub>2</sub> (CIGS) and CuInSe<sub>2</sub> (CIS) thin-film solar cells, with ZnO buffer layers deposited with Atomic Layer Deposition (ALD), are examined with respect to dominant recombination mechanism. They are compared with reference cells with CdS buffer layers. The principal method of examination is temperature dependent IV characterization (IVT), and the analysis of these data have been modified in order to more reliably discern the dominant recombination mechanism. Compared to the CIS cells with the traditional CdS buffer layer, the cells with ALD-ZnO buffer layer exhibit the same dominant recombination mechanism, i.e. recombination in the bulk of the absorber. For the CIGS cells (with  $[\text{Ga}]/([\text{Ga}]+[\text{In}]) = 0.3$ ) the situation is, however, different and these cells with ALD-ZnO buffer exhibit evidence pointing to dominant interface recombination, while the CdS ones are dominated by bulk recombination. For CIGS, the difference between the recombination in ALD-ZnO and CdS cells is consistent with the negative conduction band offset found in these ALD-ZnO cells in a previous study. This offset leads to increased interface recombination. For CIS, it was previously found that there is no negative conduction band offset, since the conduction band minimum of the absorber is lower. Consistently there is no difference in dominant recombination mechanism between ALD-ZnO buffer cells and traditional CdS buffer cells.
- O/PL.25** CHEMICAL BATH DEPOSITION OF QUANTIZED CdS/CdSe ABSORBERS INSIDE MESOPOROUS, NANOCRYSTALLINE TiO<sub>2</sub> FILMS  
Sven Rühle, Olivia Niitsoo, Shaibal Sarkar, Christophe Pejoux, Gary Hodes and David Cahen, Weizmann Institute of Science, Dept. of Materials and Interfaces, Rehovot 76100, Israel  
 Solar cells based on mesoporous, nanocrystalline TiO<sub>2</sub> films, covered with an extremely thin absorber (ETA) layer, electrically connected to a liquid redox electrolyte or a solid state hole conductor present a promising alternative to conventional p-n junction solar cells. The very large interface area and the small absorber layer width are the key features of such cells. These guarantee that electrons and holes are always generated close to the interface so that bulk recombination within the absorber is minimized. ETA cells are meant as cheap alternatives to conventional solar cells. This should be kept in mind in the search to identify and develop ways for the deposition of the extremely thin absorber inside the mesoporous, nanocrystalline structure of the TiO<sub>2</sub> film. We present here such a simple method for homogeneous CdS/CdSe deposition inside the pores of nanocrystalline TiO<sub>2</sub> films. The cells give a short circuit current of about 3 mA/cm<sup>2</sup> and an open circuit voltage of 600 mV under 1 sun illumination. The deposition process is based on illumination of the TiO<sub>2</sub> semiconductor inside the deposition solution. We will discuss the details of the process and the importance of the initial CdS layer, which is essential for the subsequent CdSe deposition process. SR acknowledges partial financial support provided by the Minerva Foundation and SR, ON and CP acknowledge support from the European Union's Human Potential Program under contract HPRN-CT-2000-00141, ETA Solar Cells.

**O/PL26**

**METAL CONTACTS TO CdTe AND ZnTe**

D. Kraft, B. Späth, J. Fritsche, A. Klein, W. Jaegermann, Surface Science Division, Materials Science Department, Darmstadt University of Technology, Petersenstrasse 23, 64287 Darmstadt, Germany

Photoelectron spectroscopy (PES) and I-V measurements have been used to study the electronic and chemical properties of different CdTe/metal and ZnTe/metal interfaces, respectively. In general metal-deposition causes decomposition of the semiconductor and formation of metal-tellurides and elemental Cd or Zn. For noble metals a broad reacted region is created which is explained by Te-segregation at the surface and the dissolution of the cation in the noble metal (alloying). In contrast to that the deposition of transition metals causes the formation of a metal-telluride and elemental Cd or Zn at the interface. For all contacts to CdTe barrier heights of around 1eV have been observed which correspond to calculated defect energies for Cd on interstitial sites. Nevertheless, results from electrical measurements indicate linear current-voltage characteristics. Because of the insufficient doping concentration and the large barriers for hole transport neither thermionic emission over the barrier nor tunneling can be the dominant carrier transport mechanism. It is rather supposed that deep defect states in the space charge zone ensure carrier transport. The concentration and distribution of defects are assumed to depend on the interface chemistry.

**O/PL27**

**SXPS INVESTIGATION OF THE CdS CBD PROCESS AND THE Cd PARTIAL ELECTROLYTE TREATMENT OF CIGS ABSORBERS**

R. Hunger, T. Schulmeyer, M. Lebedev, A. Klein, W. Jaegermann, Darmstadt University of Technology, Surface Science Division, 64287 Darmstadt, Germany, K. Sakurai, S. Niki, AIST, Thin Film Solar Cells Group, Tsukuba 305-8568 Japan

The fabrication of high-efficiency CIGS thin film solar cells generally involves a wet-chemical process step, either the chemical-bath deposition of a buffer layer or a so-called Cd partial electrolyte (PE) treatment. With this study we investigated the specific chemical modifications induced by the wet processes and their benign electronic consequences. The chemical and electronic modification of CIGS surfaces by the Cd PE was characterised by synchrotron x-ray photoelectron spectroscopy (SXPS). CIGS/CBD-CdS heterointerfaces were formed by the stepwise CBD deposition of CdS onto preoxidised CIGS. The wet-chemical interface formation was investigated by SXPS and compared to the well-defined model CIGS/CdS interface, which was prepared by the physical vapour deposition of CdS onto clean CIGS surfaces. The observed wet-process-induced interface modifications are discussed in relation to solar cell operation.

**O/PL28**

**TRANSPARENT CONDUCTORS AND BUFFER LAYERS FOR CdTe SOLAR CELLS**

C.S. Ferekides, R. Mamazza, U. Balasubramanian and D.L. Morel, University of South Florida, Tampa, USA

Thin film CdTe solar cells are typically of the superstrate configuration where the junction is fabricated on a glass substrate coated with a transparent conducting oxide that serves as the front contact. The most commonly used transparent contacts are SnO<sub>2</sub> and ITO, due to their electro-optical properties and chemical and thermal stability. Binary and ternary transparent oxides of Cd, In, Zn, Sn have been prepared by sputtering and chemical vapor deposition, and their structural and electro-optical properties have been investigated. Most sputtered oxides were deposited at room temperature and subsequently annealed in order to improve their structural and electrical properties. The performance of CdTe solar cells has been studied for various combinations of transparent oxides that included the use of bi-layer structures, where a resistive or buffer layer was deposited on top of the conductive oxide. The use of a buffer layer is beneficial to solar cell performance in particular when the CdS thickness is relatively small. Several resistive oxides have been found to be effective buffer layers. These include SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, and Zn<sub>2</sub>SnO<sub>4</sub>. Conductive oxides utilized in this work include SnO<sub>2</sub>, CdIn<sub>2</sub>O<sub>4</sub> and Cd<sub>2</sub>SnO<sub>4</sub>.

**O/PL29**

**OXIDATION OF CUGASE<sub>2</sub> CRYSTALS AND THIN FILMS STUDIED BY ELECTRON PARAMAGNETIC RESONANCE AND X-RAY PHOTOELECTRON SPECTROSCOPY**

R. Würz, A. Meeder, D. Fuertes Marrón, Th. Schedel-Niedrig, I. Lauer mann, M. Vogel, M. Ch. Lux-Steiner, Hahn-Meitner-Institut, Abteilung SE2, Glienicke Strasse 100, 14109 Berlin, Germany, K. Lips, Hahn-Meitner-Institut, Abteilung SE1, Kekuléstrasse 5, 12489 Berlin, Germany, H. Bluhm, Fritz-Haber-Institut der Max Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

The oxidation of bulk and thin-film CuGaSe<sub>2</sub> was investigated by low temperature electron paramagnetic resonance (EPR). Independent on the morphology of the samples a broad EPR signal that is assigned to Cu<sup>2+</sup> is observed only when the specimens were stored in air under ambient conditions for a few months. It is shown that by etching in KCN or annealing at 200°C in He-atmosphere the Cu<sup>2+</sup> EPR signal disappears. This is assigned to the reduction of Cu<sup>2+</sup> to non-paramagnetic Cu<sup>+</sup>. The activation energy for the reduction was determined to be  $E_a = 0.25\text{eV}$ . X-ray photoelectron spectroscopy (XPS) measurements on the oxidized thin film specimens revealed the formation of a CuO phase at the surface of the films. This CuO phase is removed by annealing in vacuum at 200°C or etching in KCN. We therefore conclude that the EPR signal originates from this CuO phase. Implications on device performance will be discussed.

**O/PL30**

**CADMIUM SULFIDE/INDIUM SULFIDE AS A MODEL SYSTEM FOR UNDERSTANDING INDIUM RELATED CHEMICAL REACTIVITY AT CIGS/CDS INTERFACES: XPS, ELECTRICAL AND IN-SITU LUMINESCENCE INVESTIGATIONS**

B. Canava, I. Gerard, A. Etcheberry, IREM-Université de Versailles-Saint Quentin, 45 ave des Etats Unis, 78035 Versailles Cedex, France J.F. Guillemoles, D. Lincot, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

In thin film polycrystalline Cu(In,Ga)Se<sub>2</sub>/CdS solar cells, the active interface is the key to further improvements of their performance. However this interface is complex and its formation still not well understood. In this paper, we focus our attention on the indium which can present different chemical bindings at this interface (Se,O,S). An important question is to know what is the real shift of binding energy on this element after the deposition of CdS by CBD. To answer this question, we decided to study the interface between single crystalline InP wafers and CdS. CBD CdS Layers on InP are already known to give extremely high quality devices, for solar cells (17%) but also for high speed field effect transistors. As a consequence we have considered this system as a model system for CIGS/CdS interfaces. The fact the InP surface is specular also allows a precise use of the XPS profiling technique. In this study we have investigated the effect of the oxidation state of the InP surface on the growth of the CdS layer. During the first steps the surface is deoxidated. For later stages, the composition profile from CdS to InP is obtained by sputter etch profiling, with a special attention to the oxygen signal. These measurements have been completed by in situ electro-luminescence measurements using different excitation sources to evaluate the correlations between chemical and electronic properties. The relevance of these results to CIGS/CdS interfaces will be discussed.

**O/PI.31**

A PRELIMINARY STUDY OF CdS FOR SOLAR CELLS USING COMBINED TEM AND CATHODOLUMINESCENCE  
K. Mam, D.P. Halliday, K. Durose, Dept. Physics, University of Durham, South Road, Durham DH1 3LE, U.K.  
This study uses a JEOL 200CX TEM fitted with an Oxford Instruments MONOCL2 cathodoluminescence (CL) light detector and monochromator. This combination allows diffraction contrast imaging to be directly correlated with spectroscopy and imaging at 77K. In this work the combined TEM-CL method has been qualified for investigations of CdS in CdTe/CdS solar cells, and preliminary device results are reported. Firstly, the effect of both Ar<sup>+</sup> and I<sup>+</sup> ion beam thinning of the TEM foils was investigated. Photoluminescence spectra taken at 4K showed that the red luminescence (~1.7eV) characteristic of Ar<sup>+</sup> ion milling was significantly reduced by I<sup>+</sup> ion milling. I<sup>+</sup> milling also had the effect of avoiding the stacking fault loops resulting from Ar<sup>+</sup> thinning. Secondly the influence of electron beam damage on CL brightness and spectral features was investigated as a function of beam current and voltage. Curves of luminescence intensity vs. dose could be fitted to a simple model describing the increase of quenching centres with irradiation. Conditions of electron beam voltage, current and scanning appropriate for studying CdS by TEM-CL were identified. Finally, we present results obtained from complete CdTe/CdS solar cell devices. In the device context combined TEM-CL reveals unique information about the relationship between microstructure and the optoelectronic quality of the material at a local level.

**O/PI.32**

STRUCTURAL AND CHEMICAL INVESTIGATIONS OF CBD- AND PVD-CdS BUFFER LAYERS AND INTERFACES IN Cu(In,Ga)Se<sub>2</sub>-BASED THIN-FILM SOLAR CELLS  
D. Abou-Ras, G. Kostorz, ETH Zürich, Institute of Applied Physics, 8093 Zürich, Switzerland, A. Romeo, D. Rudmann, A.N. Tiwari\*, ETH Zürich, Thin Film Physics Group, Laboratory for Solid State Physics, Technoparkstrasse 1, 8005 Zürich, Switzerland, \*also at: Centre for Renewable Energy Systems and Technology, Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire LE11 3TU, U.K.  
Thin-film solar cells based on Cu(In,Ga)Se<sub>2</sub> (CIGS) with high efficiencies of 15 - 19% have been developed using CdS buffer layers grown by chemical bath deposition (CBD). For industrial production, an in-line vacuum deposition, e.g., physical vapor deposition (PVD), of the CdS buffer layer is preferred. However, the highest efficiencies achieved by PVD-CdS buffer layers hardly exceed 13%. To understand the reasons, structural and chemical properties of CBD- and PVD-CdS buffer layers and their interfaces with CIGS were investigated. The CdS buffer layers and interfaces in CIGS-based solar cells were examined by means of bright-field transmission electron microscopy (BF-TEM), high-resolution TEM, energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM). For the investigation, CdS buffer layers were deposited on a CIGS-Mo-soda lime glass substrate by CBD or PVD. Both samples were exposed to air before CdS deposition; thus, the effect of CBD and PVD on the formation of oxide phases on the CIGS surface could be investigated. In contrast to prevailing expectations, PVD-CdS layers show a uniform conformal coverage of the CIGS surface, similar to the CBD-CdS coverage. Both BF-TEM and SEM images show significantly larger grain sizes for the PVD-CdS layer than for the CBD-CdS layer. By means of EDX, an oxygen-containing surface layer was identified at the CIGS/PVD-CdS interface, whereas such a layer was not found at the CIGS/CBD-CdS interface. This indicates that the oxide on the CIGS surface is etched away in-situ in the CBD solution prior to the CdS deposition, while it has a detrimental effect on the photovoltaic properties of the cells with PVD-CdS.

**O/PI.33**

EFFECTS OF BIAS VOLTAGE ON THE PROPERTIES OF ITO FILMS PREPARED ON POLYMER SUBSTRATES  
Jaehyeong Lee, Hakkee Jung, School of Electronics and Information Engineering, Kunsan National University, Donggun Lim, Keajoon Yang, Department of Electronic Engineering, Chungju National University, Junsin Yi, School of Information and Communications Engineering, Sungkyunkwan University, Korea  
Transparent conducting indium tin oxide (ITO) thin films on polymer substrates have many merits such as light weight, small volume and can make the obtained devices folded, easily carried. They can be used in plastic liquid crystal display devices, transparent electrostatic discharge and electromagnetic shielding materials, flexible photovoltaic devices, unbreakable heat reflecting mirrors. However, it is necessary for ITO films to be deposited at very low substrate temperature for the poor thermal endurance of polymer substrates. The low substrate temperature is not in favor of depositing good quality films. A bias applied to the substrate can attract cations in the plasma to bombard the growing film. This bombardment gives an additional energy to the molecules and clusters condensed on substrate and peel off the molecules with weak bonding from the film. In this study, the ITO films were deposited on polycarbonate (PC), polyethylene terephthalate (PET), and acrylic, at room temperature by magnetron sputtering. The effects of bias voltage on the deposition rate, electrical and optical properties of the films were evaluated. ITO films have been deposited by dc reactive magnetron sputtering by using metal In-Sn alloy target in an Ar-O<sub>2</sub> gas mixture. The substrate bias voltage was changed from - 80 to 0 V. The study demonstrated that the rf bias improved the electrical and optical properties of ITO films, regardless of substrate types. The lowest sheet resistance of ~30 Ohm/sq and visible transmittance of about 80% was achieved by applying a negative bias of -60 V for PET substrate.

**O/PI.34**

HIGH TRANSMITTANCE AND LOW RESISTIVE ZnO:Al FILMS FOR THIN FILM SOLAR CELLS  
Jinsu Yoo, Jeongchul Lee, Seokki Kim, Kyunghoon Yoon, I Jun Park, S. K. Dhungel, Junsin Yi, Korea  
Transparent conductive oxide (TCO) are indispensable as front electrode for most thin film solar cell. Aluminum-doped Zinc oxide films (ZnO:Al) were prepared by rf magnetron sputtering on glass (Corning 1737) substrate as a function of the deposition condition. Argon gas pressure during deposition was in the range 0.3-10 mTorr at RT-400 oC. As argon gas pressure was increased, the deposition rate and the grain size were decreased and the surface roughness and the etch rate were increased. The smooth films have excellent electrical properties ( $\rho = 1.9 \times 10^{-4} \Omega\text{cm}$ ) and high transmittance(>80%) in the wavelength of 400-800nm. Also, the maximum spectral haze( $T_{\text{diffuse}}/T_{\text{total}}$ ) as an indicator for scattering properties of the etched ZnO:Al films achieved above 70% at the wavelength of 400-800nm. As a function of substrate temperature and gas pressure, the surface morphology and thereby the light scattering properties can vary over wide range. In low pressure (0.2mTorr) and high substrate temperature (300oC), the surface morphology of films exhibited a more dense and compact film structure with effective light-trapping to apply for the fabrication of thin film silicon solar cells.

## Session II: Heterojunctions

Session chairs: Tokio Nakada, Andreas Klein

- O-II.1** 16:00 -Invited- **BUFFER LAYERS IN CIGS BASED SOLAR CELLS AND MODULES**  
**D. Hariskos**, Zentrum für Sonnenenergie- und Wasserstoff- Forschung (ZSW), Industriestr. 6, 70565 Stuttgart, Germany  
The most efficient CIGS-based solar cells and modules are realised with a chemical-bath-deposited CdS buffer layer. In the last decade several laboratories have made serious efforts to replace the “conventional” CdS buffer layer. As an alternative, materials based on In and Zn chalcogenides are deposited by different solution and gas-phase growth methods. Several processes demonstrate efficiencies comparable with the standard. Despite these positive results, Cd-free buffer layer processes are still not implemented in pilot production lines. Depending on the material or the process, there are different problems (e.g. availability of appropriate large area deposition systems, reproducibility, stability) which still must be solved. In this contribution we will present an overview of the different buffer layer materials and technologies, and discuss issues concerning the transfer to an in-line CIGS module production line.
- O-II.2** 16:30 **RE-ENGINEERING OF CIGS NATURAL SURFACES BY CHEMICAL ETCHING FOR BETTER UNDERSTANDING AND CONTROLLING INTERFACE CHEMISTRY IN HIGH EFFICIENCY CIGS SOLAR CELLS-AN XPS STUDY**  
**B. Canava**, A. Etcheberry, IREM-Université de Versailles-Saint Quentin, 45 ave des Etats Unis, 78035 Versailles Cedex, France, J.F. Guillemoles, D. Lincot, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France  
Although Cu(In,Ga)Se<sub>2</sub> is a technologically important material for thin film photovoltaic devices, the control of the interfacial chemistry is still an open question and crucial for further improvements. of the devices. The interface depends on various parameters such as the initial chemical state of the CIGS surface or the CBD conditions used to form the CdS layer. The originality of our approach is to re-engineer the surface by chemical etching, instead of using as grown surfaces which are good but not deliberately controlled. The etching process is based by oxidation in aqueous bromine solutions. We focus our attention on the chemical structure of CIGS/CdS hetero-interface using mainly XPS profiling. Bromine treatments lead to the formation of a Se<sup>o</sup> film on the CIGS surface, leaving a specular surface. This film is completely removed by KCN treatment.  
The Se3d core level was used to follow a chemical reactivity of interface during CdS growth. In this work, we present a detailed study of the evolution of Se signal, at CIGS surface but too at the CIGS/CdS interface and discuss problems of nucleation and growth of CdS layer on well defined CIGS surfaces, as a function of initial surface preparation conditions. Solar cell parameters have been correlated to the etching conditions/surface conditions. Efficient devices can be obtained for specific surface chemistry conditions.
- O-II.3** 16:45 **IN-LINE DEPOSITION OF In<sub>x</sub>S<sub>y</sub> LAYERS FOR EFFICIENT ZnO/In<sub>x</sub>S<sub>y</sub>/-Cu(In,Ga)Se<sub>2</sub> SOLAR CELLS**  
**A. Strohm**(a), T. Schlotzer(a), K. Gebhardt(b), A. Harding(a), H.W. Schock(a), (a)Universität Stuttgart, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70569 Stuttgart, (b)Institut für Angewandte Physik, Heinrich-Heine-Universität Duesseldorf, Universitaetsstr. 25, 40225 Duesseldorf, Germany  
Coherent in-line processing of the complete heterojunction is desirable for the fabrication of CIGS-based solar cells. Materials and processes compatible with the absorber layer are essential for replacing the wet chemical bath deposition of the CdS buffer layer. Evaporation of In<sub>x</sub>S<sub>y</sub> as a compound from a boron nitride crucible at temperatures of 600-800oC turned out to be a well controllable and reproducible process. No significant changes of the evaporation behaviour with time indicate congruent evaporation of the compound. In contrast to the amorphous structure of the layers from earlier experiments with co-evaporation of In and S, grazing-incidence X-Ray diffraction patterns of the 30-200 nm thick layers show a distinct tetragonal In<sub>2</sub>S<sub>3</sub> phase, even at substrate temperatures below 120 oC. Quantification of X-Ray photoemission spectra of the surface of the films leads to a slightly S-deficient composition. No elements from the substrates are found in the XPS spectra indicating a complete coverage of the underlying absorber layer. From In<sub>x</sub>S<sub>y</sub> reference films on glass a similar bandgap compared with CdS of 2.4 eV can be estimated. Nevertheless, the spectral quantum efficiency shows an improved blue response, resulting either from a lower absorption coefficient or an improved carrier collection in the In<sub>x</sub>S<sub>y</sub> layer. Solar cells show a reproducible total area efficiency of >14 % with top values approaching 15%. A short annealing in air at 200oC improves the photovoltaic parameters. The devices feature superior stability during long-term annealing and no metastable behaviour of the current-voltage characteristics is found.
- 17:00 **DISCUSSION I**  
**Akira Yamada, Dimitri Hariskos, Susanne Siebentritt**  
**Is CdS the best material for heterojunctions?**

14:00

## POSTER SESSION II

Absorbers, new materials, novel devices and concepts

Session chair: Daniel Lincot

**O/PII.01**

## GROWTH OF POLYCRYSTALLINE II-VI CHALCOGENIDE THIN FILMS BY ELECTROCHEMICAL SYNTHESIS

R. Chandramohan(a), D. Kalyanaraman(b) and T. Mahalingam(c), (a)Department of Physics, Sree Sevugan Annamalai College, Devakottai-630 303, India, (b)Sudharshan Engineering College, Pudukottai, India, (c)Department of Physics, Alagappa University, Karaikudi-630 003, India

The II-VI semi conductors like ZnSe and CdSe are important for photovoltaic solar cell applications. In this work the thin films of one micron thick ZnSe and CdSe with crystallites in the order of 100-300 nm were grown via electrochemical route from an aqueous acidic bath. The physical properties of these films were estimated and reported. The results of the Nitrogen ion implantation studies carried out onto the surface of these films are also reported.

**O/PII.02**PHYSICO-CHEMICAL CHARACTERISATION OF Cu(In,Al)Se<sub>2</sub> THIN FILM FOR SOLAR CELLS OBTAINED BY SELENISATION PROCESS

E. Halgand, J.C. Bernède, S. Marsillac, LPSE FSTN, Université de Nantes, 2 rue de la Houssinière, BP 9220, 44320 Nantes Cedex 3, France

Cu(In,Al)Se<sub>2</sub> thin films are investigated for their application as absorber layer material for solar cells. Films were elaborated by selenization of multilayer metallic precursor deposited by thermal evaporation. In order to minimize the aluminium oxidation during the precursor deposition, alternative method like Cu-Al(15 at.%) eutectic or Al-flash evaporation were used. Films have been characterized by X-ray diffraction, electron probe analysis, secondary electron microscopy and X-ray photoelectron spectrometer measurement, electrical and optical measurement were done too. These measurements show that the films are well crystallized and homogeneous, they have good electrical and optical properties and that the films are not oxidized during the aluminium evaporation (less than 0.5 at.% of O<sub>2</sub>).

**O/PII.03**STRUCTURE, MORPHOLOGY AND OPTICAL PROPERTIES OF CuInS<sub>2</sub> THIN FILMS PREPARED BY MODULATED FLUX DEPOSITION

C. Guillén(a), J. Herrero(a), M.T. Gutiérrez(a) and F. Briones(b), (a)Dep. Energías Renovables, CIEMAT, Av. Complutense 22, 28040 Madrid, Spain, (b)Instituto de Microelectrónica de Madrid, CNM-CSIC, Isaac Newton 8, Tres Cantos, 28760 Madrid, Spain

CuInS<sub>2</sub> thin films have the potential to attain high photovoltaic conversion efficiencies due to a high absorption coefficient and an optimum direct bandgap of 1.5 eV. Besides of the optical characteristics, the structure and morphology of the CuInS<sub>2</sub> layers should be optimised to obtain an efficient absorber material. In general, large chalcopyrite grains are achieved by using Cu excess that resulting in a Cu-S alloy at the surface which promotes the CuInS<sub>2</sub> crystallisation. The Cu-S phase has to be removed by KCN treatment. In order to avoid this additional etching step, other approximations are being investigated to obtain Cu-poor absorbers with the required crystallinity and morphology. In our laboratory, CuInS<sub>2</sub> thin films are grown by Modulated Flux Deposition in a custom-designed chamber in which glass substrates are cyclically transported through different zones for successive metal deposition, heating and chalcogen incorporation. This technique can provide high quality material films since it allows for an accurate control of the deposition conditions. The structure, morphology and optical properties of the CuInS<sub>2</sub> layers are analysed as a function of the substrate temperature and the ratio of the Cu, In and S fluxes during deposition. The final objective is to develop a novel procedure to obtain an optimised material for thin film photovoltaic applications.

**O/PII.04**

## FIVE SOURCE PVD FOR THE DEPOSITION OF CIGSS ABSORBER LAYERS

Mario Gossla(a,b) and William N. Shafarman(a), (a)Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark DE 19716, USA, (b)Institut fuer Festkoerperphysik, Friedrich-Schiller-Universitaet Jena, Max-Wien-Platz 1, 07743 Jena, Germany

CuIn(1-x)Ga(x)(Se(1-y)S(y))<sub>2</sub> (CIGSS) films are being investigated as absorber layer materials for the wide-band-gap cell in a tandem or multijunction thin-film solar cell. To become a viable option for high performance photovoltaics, tandem or multijunction solar cells based on polycrystalline thin films will require a wide band gap top cell with at least 15% efficiency, optical band gap in the range  $1.7 < E_g < 1.9$  eV, and small sub-band gap absorption. A new five-source deposition system was developed for the deposition of CIGSS thin films. Thin films within the complete compositional range of  $0 < x < 1$ , and  $0 < y < 1$  were deposited on Mo-coated soda lime glass. Single layer and two layer processes were used at different substrate temperatures. The films were analyzed by means of IR, SEM, XRD RBS, and AES. The incorporation of sulfur in the films depends strongly on the sulfur concentration in the vapor phase, substrate temperature, and Cu/In ratio. The two layer deposition processes used result in an incomplete interdiffusion of sulfur and selenium, depending of the respective layer composition. Complete Mo/CIGSS/CdS/-ZnO/NiAl solar cells with a typical area of 0.5 cm<sup>2</sup> were prepared. Cell performance was monitored by QE and I-V measurements.

- O/PII.05** GROWTH OF BRIDGMAN INGOTS OF  $\text{CuGa}_{1-x}\text{In}_x\text{Se}_2$  FOR P.V. CELLS  
 T. Cheung, H. Du, C.H. Champness and I. Shih, Electrical and Computer Engineering Dept., McGill University, 3480 University St., Montreal H3A 2A7, Quebec, Canada  
 Following the successful growth of ingots of the ternary compound  $\text{CuInSe}_2$  by the vertical Bridgman method, work has now begun on the preparation of the quaternary alloys  $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ . The growth conditions initially have been those used for the ternary compound. Thus, the one-ampoule process was employed, whereby the same sealed ampoule was used for both synthesis and crystal growth. This minimizes loss of selenium at the high furnace temperatures and results in more uniform ingots. Prior to charging the ampoule with the high purity elements, the inner surface was coated with flamed-in boron nitride, whose oxygen gettering effect prevents sticking of the final ingot to the quartz ampoule and minimizes the formation of voids. X-ray diffraction on material from an ingot with  $x = 0.3$  confirmed the lattice spacing reported previously for this composition and a photovoltaic cell, fabricated with the same material, as a p-type substrate, indicated a photoresponse edge shift to shorter wavelengths consistent with the composition. The ingots prepared from stoichiometric proportions, (i.e.  $[\text{Cu} : \text{Ga} + \text{In} : \text{Se}]$  in the ratio of 1:1:2), were all p-type. The powder X-ray peaks corresponded only to the chalcopyrite phase, with no evidence of the sphalerite phase. Observation of pieces fractured from the ingot showed the crystallographic facet features of chalcopyrites. However, in the quaternary material more multi-cracks were observed than in the ternary, indicating that the presence of the Ga requires further changes to the growth parameters to eliminate such defects.
- O/PII.06**  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  THIN FILMS AND JUNCTIONS  
C.S. Ferekides, G. Sivaraman, S. Subramanian, M. Ramalingam, J. Gaduputi and D.L. Morel, University of South Florida, Department of Electrical Engineering, Clean Energy Research Center, 4202 E. Fowler Ave., Tampa FL 33620, USA  
 $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  has a tunable band gap in the 1.45-2.26 eV range and is therefore a suitable candidate for the top cell in tandem solar cell applications. The aim of this work is to investigate the potential of thin film polycrystalline  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  deposited by two co-deposition technologies, as a solar cell material.  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  films have been deposited by co-sputtering and co-close-spaced sublimation using CdTe and ZnTe sputtering targets and powders respectively. Both processes were optimized for a band gap of 1.65-1.75 eV, the optimum range for tandem solar cells. Single-phase  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  films were obtained with both technologies. Films deposited by co-sublimation exhibited larger grain size and overall better microstructure than films deposited by sputtering.  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ -based junctions of the superstrate configuration were fabricated on glass and flexible polyimide substrates. Various compounds such as CdS, ZnO, CdO and ZnSe were utilized as window layers. Junctions with CdO yielded the best overall performance. Junctions with CdS and ZnSe yielded high open-circuit voltages but low short-circuit currents. In general, as-deposited junctions exhibited rather poor photovoltaic properties primarily due to low short-circuit currents as a result of inefficient collection in  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ . Improvements in the SR have been attained by subjecting the devices to a post-deposition heat treatment. The most significant improvements have been attained for junctions heat-treated in  $\text{H}_2$  ambient.
- O/PII.07** SYNTHESIS OF  $\text{CuInGaSe}_2$  NANOPARTICLES BY SOLVOTHERMAL ROUTE  
Young-Gab Chun, Ki-Hyun Kim\* and Kyung-Hoon Yoon, Korea Institute of Energy Research, 71-2 Jang-dong, Yusong-gu, Daejeon, 305-343 Korea, \*Dept. of Inorganic Materials Engineering, Kyungpook National University, 1370 Sankyuk-dong, Puk-ku, Deagu, 702-701, Korea  
 Chalcopyrite  $\text{CuInGaSe}_2$  (CIGS) nanoparticles for solar cell were directly synthesized by a solvothermal route in an autoclave with ethylenediamine as a solvent. The CIGS nanoparticles with diameter in the range of 30-120 nm were obtained from the reactions of elemental Cu, In, Se and Ga powders under the temperatures in the range of 180-250°C for 36h. The products were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution scanning electron microscopy (HRSEM). The role of Ga in the formation of the CIGS nanoparticles was discussed with the SLS (Solution-Liquid-Solid) mechanism.
- O/PII.08** PREPARATION AND CHARACTERIZATION OF  $\text{CuInS}_2$  THIN FILMS COMPLETELY CONVERTED FROM  $\text{CuInSe}_2$  BY SULFURIZATION  
G.P. Liu and B.H. Tseng, Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan  
 Thin films of  $\text{CuInSe}_2$  can be completely converted to  $\text{CuInS}_2$  after annealing in a  $\text{H}_2\text{S}$  gas flow or sulfur vapor. In this work, we conducted the conversion process in an MBE chamber and the film was exposed to a heated sulfur source. We found that complete conversion of a 0.5- $\mu\text{m}$ -thick  $\text{CuInSe}_2$  film into  $\text{CuInS}_2$  was achieved when the film was annealed in a sulfur beam flux of  $4.5 \times 10^{16}$  atoms/cm<sup>2</sup>-sec at 450°C for 5 min. The speed of conversion process depended on the sulfur vapor flux, annealing temperature, film crystallinity, and original film composition. Both the TEM observations for the conversion process occurred in a polycrystalline film and the kinetics of sulfide conversion will be reported in this paper. The PL spectrum of a converted Cu-rich  $\text{CuInS}_2$  film showed a broad emission peak at about 1.33 eV which was caused by the donor-acceptor transition and might be associated with the S-vacancy and the In-vacancy.
- O/PII.09** CONTROL OF STRUCTURE OF CdS/CdTe IN PULSE LASER EPITAXY  
I. Stefaniuk(a), A. Blahut(b), M. Kuzma(a), (a)University of Rzeszow, Institute of Physics, Rejtana 16a, 35-959 Rzeszow, Poland, (b)Rzeszow University of Technology, Department of Physics, Wincentego Pola 2, 35-959 Rzeszow, Poland  
 CdS/CdTe structure is very promising for thin-films solar cells. The quality of such devices depends strongly on the interface between CdTe and CdS layers. Therefore, to reduce the lattice mismatch between the CdS and CdTe films, high-temperature device fabrication processes should be used. We propose to replace this method by pulsed laser deposition of layers. Using the Monte Carlo procedure the initial stage of the CdTe layer growth on CdS substrates was simulated. The results allow to determine the proper choice of the layer growth parameters in the real process. A model for the layer growth included: surface diffusion, absorption and desorption of adatoms, kinetic energy of atoms or ions in the plasma plume and the time distance between consecutive pulses. The shape of the clusters formed clearly depends on these conditions. The structure of CdS/CdTe interface was demonstrated for various parameters of layer deposition. The interdiffusion of the CdS and CdTe films resulted in an intermixed layer  $\text{CdTe}_{1-x}\text{S}_x$  was achieved for suitable parameters of the layer deposition.

**O/PIL.10****SODIUM INCORPORATION STRATEGIES FOR CIGS GROWTH AT DIFFERENT TEMPERATURES**

D. Rudmann(a), D. Brémaud(a), A.F. da Cunha(b), M. Kaelin(a), H. Zogg(a), A.N. Tiwari(a,c), (a)Thin-Film Physics Group, ETH Zürich, Switzerland, (b)Dep. de Física, Univ. de Aveiro, Portugal, (c)Dept. of Electronic and Electrical Eng., Loughborough Univ., U.K.

Incorporation of sodium into Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber layers and low-temperature absorber growth processes are important issues in the processing of flexible CIGS solar cells, particularly when polymeric substrates are used. Na present during growth of CIGS is known to influence the growth kinetics and lead to structurally and electronically modified absorber material. With post-deposition Na incorporation, predominantly electronic absorber properties are altered. Therefore, we compared the performance of solar cells processed with the two Na incorporation methods and thus obtained an indication of the significance of the structural Na effects for cell efficiency. When the absorbers were grown at high substrate temperatures (580°C), we found that the presence of Na during CIGS growth is beneficial for cell performance. At medium substrate temperatures (500°C), the two Na incorporation methods led to comparable cell results. When substrate temperatures were decreased further (down to 370°C), the presence of Na during growth was found to become a hindrance. With post-deposition Na incorporation, a cell efficiency of 13.8% was achieved at 400°C substrate temperature.

**O/PIL.11****TWO STAGE GROWTH OF SMOOTH Cu(In,Ga)Se<sub>2</sub>**

J. Schöldström, J. Kessler, M. Edoff, University of Uppsala, Ångström Solar Center, Box 534, 75121 Uppsala, Sweden

For solar cells with absorbers made of co-evaporated Cu(In,Ga)Se<sub>2</sub>, the two stage process, originating from Boeing is a well known recipe. A key issue for the Boeing process is that the film during the 1st stage is grown Cu rich, whereafter the composition in the 2nd stage ends up to be Cu poor. In our extreme version of the Boeing recipe, CURO, the 2nd stage is performed completely without Cu. In this paper we examine another two-stage process, where the Cu(In,Ga)Se<sub>2</sub> film is grown in the opposite way. In the 1st stage the rates of the metals are constant and with such magnitude that a Cu poor film is created. In the 2nd stage the In and the Ga sources are turned off, and the film evolves less and less Cu poor until the final composition is reached. For both processes, End Point Detection, EPD, is used to achieve a predetermined composition of the CIGS layer. Comparing the films from the two processes the grains from the reversed process are smaller and the top surface is smoother and exhibits no crevices. The crevices from the CURO process have been explained by transport of Cu from Cu<sub>x</sub>Se which is segregated in the grain boundaries and consumed during the 2nd stage. This Cu<sub>x</sub>Se emanates from the Cu surplus in the first growth stage. For the reversed process no such material transport is observed.

**O/PIL.12****THE FORMATION OF THIN CdSe LAYERS PREPARED BY THE CHEMICAL REACTION OF CADMIUM FILMS AND SELENIUM VAPOUR**

G. Sáfrán, O. Geszti and G. Radnóczy, Research Institute for Technical Physics and Materials Science, HAS, Konkoly-Thege út 29-33, 1121 Budapest, Hungary

The formation of Cd-Se thin films was studied by the chemical reaction of the successively deposited constituents by TEM, SAED and EDS. 30-60nm Cd was vacuum deposited on (001) (011) and (111) NaCl and on carbon foil. 5-120nm Se was deposited subsequently at 0.01-0.1 nm/s and at 100-200°C substrate temperatures. The Cd-Se reaction occurred during Se deposition. Partly selenized layers exhibited very small grains of hexagonal CdSe, high amount of crystal defects and strong stress field. Kirkendall voids in the film represented a diffusion transport of Cd. The layers showed (0001) orientation with two azimuths on (001) and (011), one azimuth on (111) NaCl and random orientation on the carbon. The CdSe exhibited epitaxy on the Cd grains i.e. the reaction was topotactic. Fully selenized CdSe layers showed stoichiometry (50/50at%). A recrystallization, grain coarsening and reorientation of the CdSe was observed on all substrates at a certain stage of the selenization. It can be related to the transfer from a two-phase (Cd/CdSe) to a one-phase (CdSe) system and that the new orientation is determined by the free surface energy of CdSe instead of the interface energy of Cd/CdSe. A polymorphic phase transition including cubic structure is also considered. The results may suggest an alternative technology for the preparation of films and devices based on II-VI semiconductors. We acknowledge the support by the Hungarian National Science Foundation (OTKA T-035270)

**O/PIL.13****THE EFFECT OF SULFUR PRESSURE ON THE DEPTH DISTRIBUTION OF IMPURITIES IN Cu(In,Ga)S<sub>2</sub> FILMS**

R. Kaigawa(a), T. Wada(b), S. Bakehe(c), R. Klenk(c), (a)Department of Electronics and Informatics, Ryukoku University, Seta, Otsu 520-2194, Japan, (b)Department of Materials Chemistry, Ryukoku University, Seta, Otsu 520-2194, Japan, (c)Hahn-Meitner Institut, Abteilung SE2, Glienickestr.100, 14109 Berlin, Germany

We have been studied deposition of Cu(In,Ga)S<sub>2</sub> films for thin film solar cells [1]. In this study, Cu(In,Ga)S<sub>2</sub> films have been prepared with varied sulfur pressure. A sequential multi-source evaporation process has been employed. Deposition of an In-Ga-S precursor layer was followed by the diffusion of Cu and S into the precursor layer. The depth profiles of In, Ga and impurities (O and C) were investigated by secondary ion mass spectroscopy (SIMS). When coevaporated films were measured for comparison, the In, Ga, C and O concentrations were almost constant throughout the film. In the case of the sequential process, a higher Ga concentration inside the Cu(In,Ga)S<sub>2</sub> layer and a lower one towards the surface were observed. X-ray diffraction data also indicate the existence of two Cu(In,Ga)S<sub>2</sub> layers with different Ga content. It has been found that the O concentration was constant in the bulk, and maximum at the surface, with a decreased concentration next to the surface. On the other hand, C was also nearly constant in the bulk, but tended to increase in a layer close to the surface. A model of the incorporation of impurities will be proposed. The changes of In, Ga, O and C concentrations become less expressed with increasing sulfur pressure. This indicates that higher sulfur partial pressure promotes the diffusion in the film. The efficiency of a solar cell from our Cu(In,Ga)S<sub>2</sub> film showed 9.3% (total area, no antireflection coating).

[1] R. Kaigawa et al., "Improved performance of thin film solar cell base on Cu(In,Ga)S<sub>2</sub>, Thin Solid Films 415, 266-271 (2002).

- O/PIL.14** ELECTRODEPOSITION OF CADMIUM TELLURIDE THIN FILMS ON MO AND TCO/GLASS SUBSTRATES FOR SOLAR CELLS: MATERIAL CHARACTERISATION AND FLUX RECRYSTALLIZATION  
 J. Hiie, J. Kois, V. Valdna, Department of Materials Science, and V. Mikli, Tallinn Technical University, Centre for Materials Research, Ehitajate tee 5, 19086 Tallinn, Estonia  
 Nanosize dimensions of electrodeposited CdTe grains are favorable for fast recrystallization and doping in the presence of liquid fluxes like CdCl<sub>2</sub> and Te. CdTe films have been electrodeposited at low rates around 0.5 microns/h at room temperature without stirring, potentiostatically on stationary Mo foil and ITO/glass substrates from acidic solutions containing 0.3M CdCl<sub>2</sub>, TeO<sub>2</sub>, NH<sub>4</sub>Cl and HCl. Te anode was used to keep a constant saturated concentration of TeO<sub>2</sub> in solution. The Cd/Te ratio in as-deposited films was controlled by pH of solution (regulated at 1.4 - 2 by addition of NH<sub>4</sub>OH) and potential (400 – 800 mV, reference Ag/AgCl). The as-deposited films were amorphous with decreasing of Te content from 80 at% to 53at% with increasing pH and potential. The films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and X-ray diffraction (XRD). Intensive reaction of elemental tellurium with Mo at temperatures over 450 degC in evacuated quartz ampoules eliminates the possibility to use liquid Te as a flux for Mo substrates. For as-deposited films recrystallization and sintering vs temperature and concentration of CdCl<sub>2</sub> were investigated.
- O/PIL.15** CRYSTAL QUALITY STUDIES OF CuInS<sub>2</sub> FILMS PREPARED BY SPRAY PYROLYSIS  
 I. Oja, A. Katerski, A. Mere, O. Kijatkina, M. Krunks, Department of Materials Science, Tallinn Technical University, Ehitajate 5, Tallinn 19086, Estonia, M. Nanu, A. Goossens, Laboratory for Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands  
 Raman spectroscopy and XRD methods were applied to determine the phase composition and crystalline quality of copper indium sulfide (CIS) films grown by spray pyrolysis. The aim of the study was to develop a low-cost preparation technique for solar cell quality materials. The Cu/In molar ratio in spray solution (0.8-1.1) and post-deposition treatment conditions were taken as variables. According to XRD, Cu-rich solutions result in well-crystallised CuInS<sub>2</sub>, whereas In-rich solutions yield multiphase films, containing an additional phase of CuIn<sub>5</sub>S<sub>8</sub>, as confirmed by Raman measurements. CIS films prepared at 370 °C consist of chalcopyrite (CH) and Cu-Au (CA) ordered phases of CuInS<sub>2</sub> as is conducted from the A1 phonon modes at 294 and 305 cm<sup>-1</sup> in Raman spectra. A broadening and blue shift of 4 cm<sup>-1</sup> of both A1 modes is observed by increasing the Cu/In molar ratio in solution. The A1 modes intensity ratio CA/CH>1 was found to be independent of copper content. It is found that thermal treatment of CIS films at 450 °C in H<sub>2</sub> and H<sub>2</sub>S atmospheres effectively increases crystallinity and purity of the films. The CH phase fraction can be increased by heating in sulphur containing atmospheres above 500 °C. Rietveld refinement along with careful analysis of XRD spectra allows quantification of the CA/CH ratio, which is of vital importance for further improvement of spray-CIS solar cells.
- O/PIL.16** GROWTH STUDIES OF Cu-In-S THIN FILMS USING IN-SITU RAMAN SPECTROSCOPY  
 E. Rudigier, R. Scheer, Hahn-Meitner Institute, Dep. SE3, Glienicke Str. 100, 14109 Berlin, Germany and Beatriz Barcones, Alejandro Pérez-Rodríguez, Ingeniería i Materials Electrònics (EME), Departament d'Electrònica, Universitat de Barcelona, Martí Franquès 1, 08028 Barcelona, Spain  
 The growth of CuInS<sub>2</sub> thin films is investigated using in-situ Raman spectroscopy. This allows a detailed insight in the formation of the different CuInS<sub>2</sub>-orderings. The growth processes (sulfurization of metallic precursors) are investigated in dependence on the stoichiometry and doping of the starting precursors. For all the samples it is found that, independent from their starting composition, the CuAu ordering of CuInS<sub>2</sub> initially forms as the dominating ordering. A transformation of this primarily formed CuAu-ordering into the chalcopyrite is observed for temperatures above 380°C. This transformation is strongly dependent on the precursor composition and high temperatures are found to be advantageous. The linear temperature dependence of the phonon branch has been determined to around -2 cm<sup>-1</sup>/100 K.
- O/PIL.17** E-BEAM ABLATION TECHNOLOGY: PROPERTIES OF CIGS LAYERS AND JUNCTIONS ON THEIR BASE  
 Ac. A.M. Andriesh(a), V.I. Verlan(a), L.A. Malahova(b), (a)Center of Optoelectronics of IAP, (b)Institute of Mathematique, Academy of Sciences of Moldova  
 The new and rather cheap two step technology process of deposition of good quality polycrystalline films of a quaternary structure CuIn<sub>1-x</sub>GaxSe<sub>2</sub> (CIGS), CdS and junctions on their base was developed. In this method the deposition was implemented by a pulsed high current and magnetically self pinched electron-beam (e-beam) produced in a low pressure channel spark camera at the obtained optimally operation conditions. The crystalline and the optical properties of the initial target bulk and film materials are practically identical. X-ray diffraction and microscopy analysis of CIGSE thin films are found to have a strong preferential (112) orientation, the chalcopyrite structure, columnar grain microstructure, and surface morphology consisting of a smooth background of closely arranged grains as well as precipitates and spherical particulates disposed on the film surface. Thin films have optical absorption coefficient in the 10<sup>4</sup> cm<sup>-1</sup> range and the band gaps are 1.0, 1.4 and 1.65 eV for x = 0, 0.25, 1.0. The method of admittance spectroscopy was applied for monitoring of density of concentration of deep states and optimization of deposition process and photovoltaic properties. The obtained heterostructures CdS/CuIn<sub>1-x</sub>GaxSe<sub>2</sub> display good photovoltaic properties. Localized centers with a discrete energy and the quasicontinuous distribution of density of states in a forbidden band of amorphous CuIn<sub>1-x</sub>GaxSe<sub>2</sub> films down to 0.5 eV have been found. The current of free carriers takes place by the use their capture and release in dispersion transport.
- O/PIL.18** PREPARATION OF CuIn(Se,S)<sub>2</sub> BY MECHANOCHEMICAL PROCESS AND PREPARATION OF THEIR THIN FILS  
 T. Wada and H. Kinoshita, Department of Materials Chemistry, Ryukoku University, Seta Otsu 520-2194, Japan  
 We prepared CuIn(Se<sub>1-x</sub>S<sub>x</sub>)<sub>2</sub> solid solution by using mechanochemical process (MCP). The MCP is a process which causes physical and/or chemistry change by mechanical energies, such as pulverization, friction and compression [1]. The starting powders were milled using planetary ball mill. The phases in the products were analyzed by X-ray diffraction and their microstructure were observed in an SEM. The crystal structures were refined by Rietveld analysis of x-ray diffraction data. Both optimum rotational frequency and mixing time for preparation of CuIn(Se<sub>1-x</sub>S<sub>x</sub>)<sub>2</sub> solid solutions were increased with increasing S content. All the x-ray diffraction peaks could be indexed on the basis of tetragonal unit cell. The characteristic peaks of chalcopyrite structure such as 110 peak near 2θ#952;=17° and 211 peak near 2θ#952;=35° are clearly observed. The determined lattice constants, a and c, were continuously decreased with increasing the S content. The S content dependences of c/a and x coordinate of Se/S atom change at x = 0.4. The reaction mechanism for preparation of chalcopyrite-type CuInSe<sub>2</sub> by MCP will be proposed on the basis of our recent results. We will also show the preparation of CuIn(Se<sub>1-x</sub>S<sub>x</sub>)<sub>2</sub> thin films from the obtained powder by a screen printing technique. [1] T. Wada, H. Kinoshita, S. Kawata, "Preparation of Chalcopyrite-type CuInSe<sub>2</sub> by Non-Heating Process", Thin Solid Films 431-432, 11-15 (2003).

**O/PII.19**RESULTS ON MONOCRYSTALLINE CuInSe<sub>2</sub>-BASED CELLS

H. Du, C.H. Champness and I. Shih, Electrical and Computer Engineering Dept., McGill University, 3480 University St., Montreal H3A 2A7, Quebec, Canada

Using wafers cut from Bridgman-grown ingots of p-type CuInSe<sub>2</sub>, photovoltaic cells have been fabricated in the laboratory having the layer structure Au-CuInSe<sub>2</sub>-CdS-ZnO-In. Here the CuInSe<sub>2</sub> substrate was first annealed in flowing argon for 2 hours at a temperature of 350 °C. This treatment, carried out prior to the deposition of the other layers, has been found to increase the performance of monocrystalline photovoltaic cells. The CdS buffer layer was deposited by a standard chemical bath method, the Au and the In contacts by vacuum evaporation and the ZnO was deposited by rf sputtering from a ZnO target containing 2 % (wt.) of Al<sub>2</sub>O<sub>3</sub>. Among the cells fabricated, one device yielded an effective area efficiency of 12.5 % under sunlight with a measured irradiance of 90.5 mW/cm<sup>2</sup>, representing the highest efficiency reported for a monocrystalline chalcopyrite cell. The cell total area was 0.138 cm<sup>2</sup>, some 50 % larger than for previous cells and the total area efficiency was 11.3 % , without an antireflection coating. Comparing the different cells, there was a tendency towards better photovoltaic performance with decrease in the substrate resistivity, as determined by four point probe and hot probe prior to fabrication and from dark current-voltage characteristics and Mott-Schottky data after fabrication. The performance of all the devices degraded somewhat with time over the months after fabrication. However, the total area efficiency of the best cell after 3 months was 9.6 % , as measured at NREL, in agreement with our own measurements at this time.

**O/PII.20**FORMATION OF TRANSPARENT AND OHMIC ZnO/MoSe<sub>2</sub>/Cu(In,Ga)Se<sub>2</sub> CONTACTS FOR BIFACIAL Cu(In,Ga)Se<sub>2</sub> SOLAR CELLS

P.J. Rostan, J. Mattheis, U. Rau, and J.H. Werner, Stuttgart, Germany

Transparent, ohmic back contacts to Cu(In,Ga)Se<sub>2</sub> absorber layers are a prerequisite for producing bifacial solar cells. Moreover, this type of contact allows the enhancement of light trapping by a dielectric back side mirror and substrate texturing. ZnO:Al is a transparent, highly conductive material and is therefore a potential back contact. If Cu(In,Ga)Se<sub>2</sub> solar cells are fabricated on ZnO:Al back contacts the p-Cu(In,Ga)Se<sub>2</sub>/n-ZnO:Al interface forms a pn-junction with diode characteristic, whereas an ohmic back contact is achieved by insertion of a thin Mo interlayer. The Mo forms MoSe<sub>2</sub> during the growth of the absorber and the optical and electric properties of the opaque Mo change to the characteristics of a MoSe<sub>2</sub> semiconductor which is transparent in the visible range of the light. This study shows that the formation of such a MoSe<sub>2</sub> interlayer strongly depends on the existence of NaF. Mo films with approximately 10 nm thickness and 5-15 nm thick NaF precursor layers are deposited by evaporation on the ZnO:Al covered soda lime glass substrates. The 1 μm thick ZnO:Al layer forms a transparent diffusion barrier that prevents Na diffusion from the glass into the Cu(In,Ga)Se<sub>2</sub> absorber. Cu(In,Ga)Se<sub>2</sub> absorber layers are grown by thermal co-evaporation on samples with and without NaF-precursors. Quantitative evaluation of reflection measurements of samples with and without NaF-precursors unveils selenisation of Mo only in the presence of NaF whereas without NaF the interlayer remains metallic. The combination of a thin Mo interlayer and a NaF precursor allows us to produce bifacial Cu(In,Ga)Se<sub>2</sub> solar cells with efficiencies up to 13 % under front side illumination and thus, ZnO/MoSe<sub>2</sub> back contacts open a new avenue to fabricate bifacial Cu(In,Ga)Se<sub>2</sub> solar cells.

**O/PII.21**

## MATERIALS ISSUES IN VERY THIN FILM CdTe FOR PHOTOVOLTAICS

S.J.C. Irvine, V. Barrioz, E. Jones, University of Wales, Bangor, U.K.

This paper explores the prospect for very thin CdTe photovoltaics, below the normal absorber layer thickness of approximately 2 - 4 μm. Thin films of CdTe and CdS were deposited onto ITO coated glass substrates by metal-organic chemical vapour deposition (MOCVD) in a continuous process. In a series of experiments, the thickness of the absorber CdTe layer was progressively reduced from 2 μm down to 100 nm. At this thickness the quantum efficiency should be low due to poor absorption across the available spectrum from 550 to 850 nm. The thicker layers did not show any degradation in the I-V characteristics but the layers below 0.5 μm indicated that the shunt resistance reduced and the devices effectively became shorts. The layers were examined in an atomic force microscope (AFM) which clearly showed the grain structure of the CdTe films and the effects of coalescence. These results are related to the in situ laser interferometer monitoring of the MOCVD film growth which monitors the film growth rate, thickness and morphology. Reduced growth temperature (below the usual 350 °C) results in smoother layers but a finer grain structure that could lead to more rapid coalescence. Results will be shown on I-V characteristics on layers with different morphology achieved by growing the films at different temperature and different II/VI ratios.

**O/PII.22**NUMERICAL MODELING OF GRAIN BOUNDARY EFFECTS ON Cu(In,Ga)Se<sub>2</sub> THIN-FILM SOLAR CELLS

K. Taretto, U. Rau and J.H. Werner, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70569 Stuttgart, Germany

Solar cells made from polycrystalline Cu(In,Ga)Se<sub>2</sub> have the highest efficiency of all thin-film photovoltaic technologies. These devices are made from an absorber material that has a grain size of 1-2 μm, i.e., of the same order as the thickness of the device. The record efficiency for Cu(In,Ga)Se<sub>2</sub> solar cells is over 19 %, i.e., almost as high as the best efficiency obtained from polycrystalline Si with grain sizes in the range of several mm exceeding the absorber thickness by a factor of more than ten. Hence, Cu(In,Ga)Se<sub>2</sub> must have grain boundaries that are much less electronically active than those of Si. The description of electronic losses in Cu(In,Ga)Se<sub>2</sub> solar cells, up to now, was restricted to one dimensional analytical or numerical models. However, proper modeling of a polycrystalline material, with grain sizes in the range of its thickness, even for weakly active grain boundaries, requires at least two-dimensional (2D) models. The present contribution presents results from numerical 2D-simulations using the finite difference method for Cu(In,Ga)Se<sub>2</sub> solar cells with grain sizes between 1 and 2 μm. We find that even moderate grain boundary defect concentrations  $N_{gb} = 2 \times 10^{11} \text{ cm}^{-2}$  are sufficient to push the cell efficiencies  $\eta$  below 18 % irrespective of the electronic quality of the grain volume. With  $N_{gb} > 5 \times 10^{11} \text{ cm}^{-2}$  only devices with  $\eta < 15 \%$  are possible. We show further that in some cases one-dimensional modeling introduces errors of more than 2 % (absolute) into the prediction of device efficiencies from averaged defect concentrations.

**O/PII.23**

## STUDY OF CHARGE-CARRIER DYNAMIC IN 3D INORGANIC SOLAR CELLS

Marian Nanu, Joop Schoonman and Albert Goossens, Laboratory for Inorganic Chemistry, Julianalaan 136, 2628 BL Delft, The Netherlands

The transport of charges in nanostructured 3D inorganic solar cells has been investigated. In this new solar cell concept a CuInS<sub>2</sub>(CIS) p-type semiconductor absorber layer fills the pores of an n-type nanostructured TiO<sub>2</sub> film. Investigation of the native defects, which introduce energy levels in the band gap of CIS, is necessary for optimisation of solar cells. The presence of sub-bandgap electronic states is related to anti-site point defects, that form the Cu-Au disordered structure in CIS films. In this study we apply different characterization methods to elucidate whether these electronic states in the band-gap are involved in the transport of holes. The possible presence of a macroscopic field inside the nanocomposite is also investigated. In order to elucidate the charge-carrier dynamics, Current-Voltage (IV), Time of Flight (TOF), Impedance Spectroscopy (IS), and Deep-Level Transient Spectroscopy (DLTS) studies are performed as a function of temperature. Preliminary results provide strong indications that these cells behave differently compared to dye-sensitised solar cells. The IV curves recorded in the dark show a space-charge limited current in forward direction. The activation energy for the mobility is found to be 0.15 eV. The energy levels of electron and hole traps derived from IV, IS, and DLTS techniques agree with those found in our previous PL study. At room temperature, hole transport is governed by trapping (i.e., ) with an activation energy of about 0.15 eV above the valence band. TOF results suggest the presence of a built-in electric field, which leads to a predominantly drift type transport. We conclude that TOF, IS, and DLTS, data are in good agreement and that hole transport is a hopping type migration via antisites, driven by the built-in electric field.

**O/PII.24**CHEMICAL TREATMENT OF CuInSe<sub>2</sub> MONOGRAIN POWDER SURFACE

M. Kauk, K. Ernits, T. Varema, M. Altosaar, E. Mellikov Tallinn Technical University. Ehitajate tee 5, 19086 Tallinn, Estonia  
Results of chemical etching of CuInSe<sub>2</sub> monograin powders with HCl, KCN, KOH in ethanol (KOH-EtOH) and NH<sub>3</sub> and the effect of etching on solar cell parameters are presented. CuInSe<sub>2</sub> powders were synthesized from Cu-In alloy and Se in molten fluxes and post treated in Se or S vapors. The chemical compositions of untreated and etched powders and leaching solutions were determined polarographically and by EDS. Surface composition was characterized by XPS and Raman spectroscopy. In the monograin layer design of solar cell the absorber crystals are embedded in polyurethane, which is removed from the crystallite surfaces in the contact areas by etching with KOH-EtOH. CIS powder etching with KOH-EtOH results in metal-rich surface and leads to lowered values of Voc and short circuit currents. The KCN or HCl etching after KOH-EtOH treatment did not restore the origin surface state. So we conclude, that etching time with KOH-EtOH is a crucial step in monograin layer performance. KCN etching before CdS deposition resulted in improved FF and higher currents regardless the In-rich powders were used. Short time etching with conc. HCl leads to higher currents, but lower values of Voc in comparison with KCN etched samples. NH<sub>3</sub> etching alone showed undesirable influence: lower values of Voc, short circuit currents and FF. Only combination of above-mentioned chemical treatments before chemical deposition of CdS leads to improved parameters of CuInSe<sub>2</sub> monograin layer solar cells.

**O/PII.25**

## PREPARATION AND CHARACTERIZATION OF TIN SULPHIDE THIN FILMS BY SPRAY PYROLYSIS TECHNIQUE

H. Ben Haj Salah, H. Bouzouita and B. Rezig, Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs, Ecole Nationale des Ingénieurs de Tunis (E.N.I.T), BP 37, Belvédère 1002 Tunis, Tunisie

Tin sulphide SnS which has the band gap of 1.2 -1.4 eV and absorption coefficient over 10<sup>4</sup>cm<sup>-1</sup> in visible light range, is suitable for absorbing layer of thin film solar cells. It has potential applications in thin film photovoltaic materials. SnS<sub>2</sub>, a wider band gap semiconductor, is a much less intensively studied material; it has potential application as an optical window layer in thin film photovoltaic materials. Spray pyrolysis technique has the merits of simplicity of its apparatus and good productivity in large area film formation. This essentially fits for solar cell production. In this study, first we have attempted the preparation and characterization of SnS, SnS<sub>2</sub>, and Sn<sub>2</sub>S<sub>3</sub>, thin films by using the spray pyrolysis technique. Starting with acidic aqueous solutions including tin (II) chloride and thiourea were atomized with compressed air gas. The Sn-S ( SnS, SnS<sub>2</sub> and Sn<sub>2</sub>S<sub>3</sub> ) thin films were obtained on glass substrate. Thin layers of Sn-S have been grown at various temperatures in the range 200-300°C and various [S/Sn] ratios .The structural properties have been determined by using X-ray diffraction and scanning electron microscopy to evaluate the crystalline phases present and the surface topography of the grown layers .The changes observed in the structural phases with the growth temperature during film formation are reported and discussed. The optical constants of the deposited films were obtained from the analysis of the experimental recorded transmission and from reflectance spectral data over the wavelength range 300-1800 nm. An analysis of the optical absorption data of the as deposited films revealed an optical indirect band gap energy of 0.9eV for Sn<sub>2</sub>S<sub>3</sub> layers; 1.2eV for SnS layers and 2.4 eV for SnS<sub>2</sub> layers.

**O/PII.26**FABRICATION OF SnS<sub>2</sub>/SnS HETEROJUNCTION THIN FILM DIODES BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

A. Sanchez-Juarez(a), A. Tiburcio-Silver(b), and A. Ortiz(c), (a)Centro de Investigación en Energía, UNAM Apto. Postal 34, 62580 Temixco, Mor. Mexico, (b)Instituto Tecnológico de Toluca, SEP, (c)Instituto de Investigaciones en Materiales, UNAM P. O. Box 70-360, 04510 Coyoacan, D.F. Mexico

Heterojunction based on Sn-S compounds, SnS and SnS<sub>2</sub>, has been prepared by plasma enhanced chemical vapor deposition. The semiconductor materials SnS and SnS<sub>2</sub> were obtained by the decomposition of the gas precursors SnCl<sub>4</sub> and H<sub>2</sub>S in a capacitive coupled RF plasma-deposition chamber. Corning glass with a transparent conductor oxide thin film was used like a substrate. The heterojunction was fabricated depositing on the TCO surface a thin film of SnS<sub>2</sub> with a thickness of 0.15 μm, followed by the deposition of 0.35 μm thick layer of SnS. Aluminum dots deposited on the SnS layer by vacuum thermal evaporation were used as back contact. Thus, the structure for the diode was glass/ TCO/n-type SnS<sub>2</sub>/p-type SnS/ Al. The contact between the n-type and p-type Sn-S compounds was found to be rectifying. The estimate reverse saturation density current was 1.2x10<sup>-5</sup> A/cm<sup>2</sup>. The ratio of forward current to the reverse current exceeded 300 within the range of applied voltages of -1.0 to 1.0 V and the estimated diode factor was 2.7. A photovoltaic effect was observed under standard test conditions with an open circuit voltage of 0.35 V and a small short circuit current density with a value of 1.5 mA/cm<sup>2</sup>. These results open the opportunity to use this structure for studying the electrical behavior of photovoltaic devices based in these materials.

- O/PIL.27** SYNTHESIS AND CHARACTERISTICS OF NANOSTRUCTURED  $\text{CuInS}_2$  FILMS  
 Xianghui Hou and Kwang-Leong Choy, School of Mechanical, Materials, Manufacturing Engineering and Management, The University of Nottingham, University Park, Nottingham NG7 2RD, U.K.  
 Ternary compound  $\text{CuInS}_2$  is one of the most popular and promising materials for high-efficiency solar cell applications. This paper reports the successful deposition of uniform  $\text{CuInS}_2$  films with well controlled stoichiometry, using a novel Electrostatic Spray Assisted Vapour Deposition (ESAVD) method. Precursor solution based on non-chlorinated copper and indium salts and thiourea were used for the deposition of  $\text{CuInS}_2$  films. The deposition has been preformed using ESAVD process which involves the atomization and charging of the precursor to form charged aerosol, the control of chemical reactions and the growth of films under electric field. This paper presents the influence of precursor composition and processing parameters on the phases, morphology, and properties of  $\text{CuInS}_2$  films. The deposition mechanism will also be described.
- O/PIL.28** DEVICE CONFIGURATION AND PROCESSING FOR n-CIS FLEXIBLE SOLAR CELL  
Shalini Menezes, Yan Li, Sharmila J. Menezes InterPhases Research, 166 N. Moorpark Rd, #204, Thousand Oaks CA 91360, USA  
 Lightweight, flexible solar cells based on p-CIGS offer distinct advantages over conventional PV modules in space. Adapting the CIGS cell for high-volume manufacturing is complicated by specific material and processing requirements. This paper investigates an alternative PV cell configuration based on  $(\text{Cu}_2\text{Se})(\text{In}_2\text{Se}_3)_n$  compounds and an electrochemical fabrication method that could considerably simplify the process steps, reduce the number of cell components and hence its cost. It examines the role of substrates, process parameters and alternate deposition sequences on CIS film formation mechanism, growth, composition and morphology, using voltammetry, X-ray diffraction and composition analysis. The results indicate a new route for controlling the grain growth for CIS films. They lead to a simple three-step method for roll-to roll fabrication of n-CIS PV cell on a continuous metal foil. The n-CIS PV solar cell potentially avoids the complexity, expense, safety and scale-up issues of the p-CIGS PV cell while retaining its high efficiency, reliability and radiation hardness. It is also totally cadmium free.
- O/PIL.29** PHOTOELECTROCHEMICAL WATER SPLITTING FOR HYDROGEN PRODUCTION USING MULTIPLE BANDGAP COMBINATION OF PHOTOVOLTAIC CELL AND THIN-FILM-PHOTOCATALYST  
Neelkanth G. Dhere, Anant H. Jahagirdar and Upendra S. Avachat, Florida Solar Energy Center, University of Central Florida, 1679 Clearlake Road, Cocoa FL 32922, USA  
 FSEC photovoltaic (PV) Materials Lab has developed a photoelectrochemical (PEC) cell setup consisting of two-illuminated  $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$  (CIGS<sub>2</sub>) cells, a  $\text{RuO}_2$  anode deposited on titanium sheet for oxygen evolution and a platinum foil cathode for hydrogen evolution. With this setup, a PEC efficiency of 4.29% has already been achieved. Further improvements in the PEC efficiency are being carried out by aiming the research at development of better photoanode illuminated with photons not absorbed by the PV cell for oxygen evolution, improvements in the efficiencies of CIGS<sub>2</sub> thin film PEC cells, etc. This effort is different and distinct from development of two-junction thin-film PV tandem cell typically with individual absorber bandgaps of 1.1 eV and 1.68 eV that have to be grown one on top of the other. The proposed PEC cell has the potential of being as efficient as III-V tandem cells while being significantly cheaper. Over the last several years FSEC PV Materials Lab has developed excellent facilities for the development of  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2\text{-ySy}$  (CIGSS) thin film PEC cells. Large area (10 cm x 10 cm) CIGS<sub>2</sub> solar cells with a configuration Glass/Mo/CIGS<sub>2</sub>/CdS/ZnO/ZnO:Al/Ni-Al contact fingers are being prepared routinely. The CIGS<sub>2</sub> layers are being characterized with scanning electron microscopy, X-ray diffraction, Auger electron spectroscopy and secondary ion mass spectrometry. This paper presents the development of PEC cell by multiple bandgap combination of thin-film CIGS<sub>2</sub> PV cell and photocatalyst for production of hydrogen and oxygen by water splitting.
- O/PIL.30** EFFECT OF HYDROGEN PLASMA TREATMENT ON THE ELECTRICAL PROPERTIES OF SPUTTERED N-DOPED CUPROUS OXIDE FILMS  
Yang-Ming Lu, Jun-Yuan Chen, Tzue-Shaang Wey, Ming Hong Lin, Kun Shan University of Technology, Yung-Kang City, Tainan, Taiwan  
 Cuprous oxide ( $\text{Cu}_2\text{O}$ ) is a direct-gap semiconductor with a band gap of 2.0 eV and has been regarded as one of the most promising materials for application to photovoltaic cells. The attractiveness of cuprous oxide as a photovoltaic material due to the fact that the constituent materials are nontoxic and abundantly available on the earth, and that the cuprous oxide has a high absorption coefficient and low-cost producibility. The practical application have not been achieved to date because of the difficulty in controlling its electrical properties. It is necessary to investigate the controllability of the electrical properties and reduce the resistivity of cuprous oxide for practical applications. In previously study, a pure phase of cuprous oxide can be obtained by adjusting the sputtering parameters. It is also found that nitrogen doping is effective to deduce the resistivity of cuprous oxide films. The N-doped cuprous oxide films were deposited onto corning 1737 using a magnetron co-sputtering process in a mixture of oxygen and argon gases with a constant substrate temperature of 350°C. The flow rate of nitrogen was kept at 12 ml/min while others sputtering parameter were kept constant. It is found that the hole carrier concentration of nitrogen doped cuprous oxide films increase from  $9.0 \times 10^{17} \text{ cm}^{-3}$  to  $4.0 \times 10^{18} \text{ cm}^{-3}$  resulting in a lowest resistivity of  $9.1 \times 10^3 \Omega \cdot \text{cm}$  after 60 seconds of hydrogen plasma treatment. The XRD analysis reveals no obvious structural change but the roughness analysed by AFM is obviously depressed after hydrogen plasma treatment. Because the mobility of carrier almost keeps constant, it is believed that hydrogen plasma treatment can induce point defects in the films and results in effective decreasing the resistivity of cuprous oxide.
- O/PIL.31** LOW COST CIGS SOLAR CELLS BY PASTE COATING AND SELENIZATION  
M. Kaelin(a), D. Rudmann(a), F. Kurdesau(a), H. Zogg(a), T. Meyer(b), A.N. Tiwari(a,c), (a)Thin-Film Physics Group, ETH Zürich, Switzerland, (b)Solaronix SA, Rue de l'Ouriette 129, 1170 Aubonne, Switzerland, (c)Dept. of Electronic and Electrical Eng., Loughborough Univ., U.K.  
 $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) solar cell production cost can be lowered by using simple and fast precursor deposition techniques and reactive sintering by rapid thermal processing. Materials costs are reduced by the high material utilization yield of paste coating techniques and the reduction of the layer thickness to a minimum required for good light absorption properties. The challenge is to find a suited precursor material which allows uniform thin film deposition and a fast chemical conversion to ~ 1 micron thin CIGS layers. A novel low-cost precursor material was deposited by the doctor blade technique and selenized in a quartz tube at 10mbar for about 10min. at 550°C. No dangerous  $\text{H}_2$  and toxic  $\text{H}_2\text{Se}$  gases were used for the chemical reaction. The conversion to the CIGS phase was confirmed by X-ray diffraction, while grain size and morphology were characterised with electron microscopy. Thin CIGS layers grown on Mo/glass were processed to solar cells by applying a CdS buffer and  $\text{ZnO/ZnO:Al}$  front contact, a maximum efficiency of 6.7% was achieved with ~0.5 micron thick absorber layer.

**O/PII.32****ELECTRON TRANSPORT IN CuInS<sub>2</sub>-BASED NANOSTRUCTURED SOLAR CELLS**

Catelijne Grasso(a), Marian Nanu(b), Albert Goossens(b) and Marc Burgelman(a), (a)University of Gent (UGent), St. Pietersnieuwstraat 41, 9000 Gent, Belgium, (b)Delft University of Technology (TUD), Laboratory of Inorganic Chemistry, Julianalaan 136, 2628 BL Delft, The Netherlands

In dye-sensitized solar cells (DSSCs), a nanostructured TiO<sub>2</sub> electrode is made sensitive for visible light by grafting dye-molecules onto the surface. The pores are filled with a redox electrolyte, in which positive carriers are transported to the back electrode. It is generally accepted that in DSSCs electron transport is predominantly governed by diffusion, because the electrolyte screens the electric field. Recently the transport of charge carriers in all solid-state DSSCs has been investigated as well. Here, we present a transport study on so-called 3-dimensional cells (3D-cells): nanocomposites of an n-type and a p-type semiconductor, in particular, nanoporous TiO<sub>2</sub> filled with CuInS<sub>2</sub> [1]. Intensity Modulated Photocurrent Spectroscopy (IMPS) has been used to investigate the nature of electron and hole transport in 3D-cells. IMPS is sensitive to small variations in the charge carrier dynamics, and relies on small amplitude modulation of the irradiation intensity. First results show that 3D-cells show a much faster response than DSSCs; differences up to four orders of magnitude are measured. Since the same type of TiO<sub>2</sub> is used for 3D-cells and DSSCs, this is very surprising and strongly suggests completely different charge carrier dynamics. Different recombination mechanisms but also the presence of a macroscopic electric field inside 3D-cells might be responsible for it. Future investigations will focus on these important issues. IMPS-measurements will therefore be carried out at a range of bias voltages and as a function of temperature. [1] M. Nanu, J. Schoonman and A. Goossens, to be published in Adv. Mat.

**O/PII.33****ELECTRICAL AND OPTICAL CHARACTERIZATION OF AgInSnS<sub>4</sub> THIN FILMS GROWN BY SPRAY PYROLYSIS**

J.J. Cayente-Romero(a), J.M. Peza-Tapia(a), M.L. Albor- Aguilera(b), L.R. De León- Gutiérrez(a), M. Ortega- López(a), (a)Electrical Engineering Department - SEES, CINVESTAV-IPN, 07360 México D.F., (b)E.S.F.M.-I.P.N., U.P.L.M., Zacatenco, 07738 México D.F.

AgInS<sub>2</sub> and SnS<sub>2</sub>, and related compounds, are interesting materials for diverse optoelectronic applications, including solar cells. In an earlier paper Ohachi and Pamplin prepared the AgInSnS<sub>4</sub> quaternary compound by annealing (AgInS<sub>2</sub>) and (SnS<sub>2</sub>) at 680 °C. They reported that such a material has spinel-like structure and is a promissory ionic conductor. In this work, we have grown AgInSnS<sub>4</sub> polycrystalline thin films by the spray-pyrolysis method, using an alcoholic solution comprising silver acetate, indium chloride, tin chloride and thiourea. The samples were grown on glass substrates at deposition temperatures of 375 and 400 °C. The X-ray diffraction analysis revealed a cubic structure for the sprayed films, with lattice parameter of 10.77 Å. Hot-probe measurements indicated p-type conductivity with room temperature resistivity ranging from 10<sup>-1</sup> to 10<sup>-2</sup> S/cm. Conductivity versus 1/T plots showed an Arrhenius-like behavior, from which two activation energies of Ea1=0.15 eV and Ea2 = 0.23 eV were found. These results suggest that the charge carrier transport could be due to the drift and jumps of Ag<sup>+</sup> ions through sulfur vacancies. The AgInSnS<sub>4</sub> absorption spectrum revealed an energy gap around Eg = 1.8 eV, which was associated to direct - allowed transitions.

**O/PII.34****GRAIN AND CRYSTALLITE SIZE IN FeS<sub>2</sub> THIN FILMS**

J.R. Ares\*, A. Pascual, I.J. Ferrer, C. Sánchez. Dpto. de Física de Materiales, C-IV, U.A.M., Cantoblanco, 28049 Madrid, Spain, \*Laboratoire de Chimie Metallurgique des Terres Rares, ISCA-CNRS, Rue Henri Dunant 2-8, 94320 Thiais Cedex, France

Iron disulphide thin films have been deposited on glass substrates by sulphurisation of Fe layers thermally evaporated. The dependence of the morphological and structural parameters on the sulphurisation temperature (in the range from 523 K to 773K) by profilometry, Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) techniques, have been investigated. Measured parameters were basically: crystallite and grain size, thickness, roughness and lattice parameter. From these measurements several facts can be observed and they are described at once. Results of grain size and crystallite size obtained from AFM and XRD, respectively, are compared. Both of them show an increasing trend with the sulfurisation temperature. However, crystallite size is always lower than grain size. By comparing these results, it is concluded that the grains are formed by several crystallites. The number of crystallites forming a grain depends on the sulphurisation temperature. In addition, thickness of the film after sulfurisation increases between 3 and 3,5 times, in the range of temperatures studied. Roughness of the surface shows an increasing trend, which is very similar with data proceeding from AFM and from profilometry, although the values obtained from AFM are always higher. On the contrary, the lattice parameter has a decreasing dependence on the sulphurisation temperature, which hints lattice contraction. In the paper, the crystallisation of FeS<sub>2</sub> films will be discussed with the data here presented.

**O/PII.35****SINGLE-STEP LIGHT ASSISTED PATTERNING OF PHOTONIC PROPERTIES OF CHEMICAL-BATH-DEPOSITED CDSE NANOCRYSTALLINE FILMS**

M. Šimurda, P. N'mec, F. Trojánek, P. Maly, Charles University in Prague, Ke Karlovu 3, 121 16 Prague 2, Czech Republic, T. Miyoshi, K. Kasatani, Yamaguchi University, 2-16-1 Tokiwadai, 755-8611 Ube, Japan

We report on the effect of light illumination of nanocrystalline CdSe film during its deposition from chemical bath. Light illumination by above-band-gap light leads to larger nanocrystal size, which means that the single-step nanocrystal size patterning (with the spatial resolution of tens microns as given by illumination light masking) is possible. Resulting films with thickness ≤ 300 nm contain CdSe nanocrystals the diameters of which can be modulated so that the corresponding lowest absorption transition can be adjusted from 540 nm to 600 nm. The illumination has also an effect on PL efficiency (higher efficiency for illuminated parts of the film) and carrier dynamics as studied by ultrafast luminescence (negligible effect on PL decay) and absorption laser spectroscopy (a pronounced subpicosecond decay component for non-illuminated regions). Possible mechanisms of the effect are discussed.

## Session III: Widegap and novel devices

Session chairs: Jim Sites, Neelkanth Dhere

- O-III.1** 16:00 -Invited- MATERIAL AND DEVICE ISSUES IN WIDEGAP CHALCOGENIDE SOLAR CELLS  
**S. Niki**, K. Sakurai, S. Ishizuka, K. Matsubara, P. Fons, K. Iwata, H. Tampo and A. Yamada, AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan, T. Baba, Y. Kimura, S. Nakamura and H. Nakanishi Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-0022, Japan, R.T. Widodo, K. Ohki, K. Fujita, N. Terada, Kagoshima University, 1-21-40 Korimoto, Kagoshima, Kagoshima 890-0065, Japan  
Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (CIGS)-based solar cells have emerged as one of the most promising candidates for high-efficiency low-cost thin-film solar cells, and a significant improvement in solar cell performance has been reported with conversion efficiencies as high as  $\text{eff}=19.2\%$ . The high-efficiency cells have been demonstrated using the CIGS films with their bandgaps of  $E_g \sim 1.2\text{eV}$  (Ga:  $x \sim 30\%$ ). The conversion efficiencies drop when the bandgap is further increased ( $E_g \sim 1.3\text{eV}$ ) though theoretical analysis indicated that highest efficiency should be achieved at  $E_g = 1.4\text{--}1.5\text{eV}$ . The device structures and material properties have to be optimized specifically for widegap CIGS solar cells in order to improve the solar cell performance. We first developed the in-situ growth monitoring techniques during the CIGS film deposition. It made possible the improvement in reliability and reproducibility for the CIGS deposition. In addition, some differences in growth mechanisms have been observed when high Ga-content CIGS films were grown. The CdS/CIGS interface has been investigated extensively by means of conventional and inverse photoemission spectroscopy. The conduction and valence band offsets, bandgaps, and the electronic structure of the CIGS surface have been investigated systematically as a function of Ga composition. All the CIGS solar cell processes have been under investigation for improving the widegap cell performance. The characteristics of the CIGS ( $x \sim 0.48$ ) and CGS solar cells have been improved up to  $\text{eff}=15.8\%$ ,  $\text{VOC}=0.724\text{V}$ ,  $\text{JSC}=29.8\text{mAcm}^{-2}$ ,  $\text{FF}=0.73$  and  $\text{eff}=8.4\%$ ,  $\text{VOC}=0.80\text{V}$ ,  $\text{JSC}=16.0\text{mAcm}^{-2}$ ,  $\text{FF}=0.66$  (active area, without AR coating), respectively.
- O-III.2** 16:30 -Invited- Cu<sub>2</sub>ZnSnS<sub>4</sub> THIN FILM SOLAR CELLS  
**Hironori Katagiri**, Nagaoka National College of Technology, 888 Nishikatai, Nagaoka, Niigata, 940-8532, Japan  
Aiming to develop the solar cells free from the environmental contaminants, promising solar cell of a thin film type could be produced by using Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) film as the absorber. The CZTS film possesses promising characteristic optical properties; band-gap energy of about 1.5 eV and large absorption coefficient in the order of 10<sup>4</sup> cm<sup>-1</sup>, which means large possibility of commercial production of the most suitable absorber by using the CZTS film. Also as the CZTS film contains neither rare metals nor toxic materials, combining this film with Cd-free buffer layer we can expect coming solar cells with non-toxic thin films in the near future. CZTS thin films could be successfully produced in our previous work by vapor phase sulfurization of the stacked precursors that were prepared by sequential vacuum evaporation of Cu, Sn and ZnS. The best conversion efficiency with the heterojunction of ZnO:Al/CdS and CZTS was 5.45 %, which showed the possibility of a very low cost solar cell. It has been, however, quite difficult to prepare CZTS film with high reproducibility. The present study adopted a new type precursor that was prepared by co-sputtering technique with Cu, ZnS and SnS target. As this precursor consists of the mixture of those three targets, large improvement of the uniformity of the composition could be attained compared with that of our previous precursor. The measurement results of EDS showed that we can control the atomic ratio with high reproducibility.
- O-III.3** 17:00 -Invited- SEMI-TRANSPARENT AND BIFACIAL CIGS THIN FILM SOLAR CELLS FABRICATED USING TRANSPARENT CONDUCTING OXIDE BACK CONTACTS  
**Tokio Nakada**, Takehito Tokado and Daisuke Ohmori, Department of Electrical Engineering and Electronics, Aoyama Gakuin University, Kanagawa, Japan  
Understanding of interfacial properties at the Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (CIGS)/transparent conducting oxide (TCO) boundary is a most important issue for achieving high efficiency semi-transparent and bifacial devices. Nano-structural and diffusion properties at the CIGS/TCO interface of these devices have been investigated using TEM, EDX, SIMS and XPS. CIGS thin film solar cells have been fabricated using TCO back contacts such as ITO, SnO<sub>2</sub>:F, and ZnO:Al. The influence of the substrate temperature, Ga content in CIGS, and thickness of CIGS on the cell performance of semi-transparent and bifacial CIGS devices has been investigated. High efficiency CIGS devices were obtained using ITO and SnO<sub>2</sub>:F back contacts at a substrate temperature of 520 C. In contrast, almost no photovoltaic effect was observed for the device using ZnO:Al back contact. After optimizing growth conditions, a CIGS thin film solar cell with over 15% efficiency was obtained using ITO back contact. The best bifacial cell at present showed a 12%, 5% and 17% for front, rear and both side illuminations. The details of the cell performance of these devices are presented in connection with nano-structural and diffusion properties and Ohmic behavior at the CIGS/TCO interface.

- O-III.4** 17:30 **TRANSPARENT HIGH PERFORMANCE CdSe THIN-FILM SOLAR CELLS**  
P. Mahawela, S. Jeedigunta, S. Vakkalanka, C.S. Ferekides and D.L. Morel, University of South Florida, Tampa, USA  
Simulations indicate that efficiencies of 25% can be attained with compound semiconductor based tandem structures. The bottom cell is assumed to be CIGS with a bandgap of 1.0 eV and efficiency of about 15%. The key to reaching this performance level for the tandem is development of a transparent top device with bandgap in the 1.6 – 1.8 eV range and efficiency of 16 - 18%. We have been developing CdSe-based devices for this application and have made significant progress toward achievement of the performance objectives. Our devices are of configuration ZnSe:Cu/CdSe/SnO<sub>2</sub>/glass, and CdSe has an ideal bandgap of 1.7 eV. While both contacts are transparent, highest output is attained for ZnSe:Cu incidence. This is due to superior transport properties for electrons and that ZnSe:Cu is the effective p-type contact. Voc's are typically in the 300 – 350 mV range for this structure. While Cu doping is important to the contact, a combination of Au with Cu produces about a 100 mV increase in Voc. Still higher Voc's approaching 500 mV have been attained with ZnTe:Cu as the p-contact due to its greater inclination toward being p-type. Jsc's for the baseline structure have exceeded 17 mA/cm<sup>2</sup> which is a record for this device structure. Transmission to the bottom cell is 80% which is close to the target value of 85% used in the simulations. We have thus nearly attained the current densities needed to achieve the needed performance level for the CdSe device as well as the overall optical performance to reach the 25% tandem objective.
- O-III.5** 17:45 **MODELING AND DESIGN OPTIMIZATION OF EXTREMELY-THIN ABSORBER SOLAR CELLS**  
K. Taretto and U. Rau, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70569 Stuttgart, Germany  
Extremely-thin absorber (ETA) solar cells are a concept to overcome the poor electronic quality of low-cost semiconductor materials and to maintain a good photovoltaic performance of the solar cell. The ETA design uses absorber layers that have a thickness of only several tens of nm. To achieve the necessary volume of light-absorbing material the absorber is folded in such a way that the light path transverses the absorber material a number of times. Despite of considerable effort to develop such ETA devices using, e.g., thin CdTe or CuInS<sub>2</sub> layers, there is up to now no conclusive theoretical model that allows to estimate the photovoltaic potential of the ETA concept or to find design rules to optimize these devices for a given set of material parameters. This contribution proposes an analytical model for the current/voltage characteristics of the ETA solar cell. Due to its simplicity, the model is a viable tool to optimize the solar cells in terms of the thickness of a single absorber and the number of folds. Our calculations show that, e.g., CdTe-based ETA solar cells with only 20 nm diffusion lengths can reach 15 % efficiency at absorber thicknesses of 20-30 nm with optimized light-trapping. The same material quality would yield an efficiency of only 10.5 % for a classical single junction solar cell. Our model demonstrates also that tunneling-enhanced recombination represents a major loss-mechanism that severely influences the optimized design.
- O-III.6** 18:00 **COMPARATIVE STUDY OF 3D INORGANIC SOLAR CELLS OBTAINED BY AL-CVD AND SPRAY PYROLYSIS**  
Marian Nanu, Joop Schoonman, and Albert Goossens, Laboratory for Inorganic Chemistry, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands  
The search for low-cost PV solar cells, with a short energy payback time and a high-energy conversion efficiency, calls for innovative combinations of materials and a novel solar cell design. Recently, we reported a new approach towards what is referred to as the 3D solar cell concept [1]. In this solar cell, n- and p-type semiconductors are mixed on a nanometer scale to form a "bulk heterojunction". Atomic-Layer Chemical Vapour Deposition (AL-CVD) is employed for infiltration of (p-type) CuInS<sub>2</sub> inside the pores of nanostructured (n-type) TiO<sub>2</sub>. The results prove the viability of the concept, but industrial application seems to be hindered by the high costs for AL-CVD deposition. Stimulated by these promising results, a new route for low-cost deposition of the CuInS<sub>2</sub> has been developed. Spray pyrolysis offers a cheap alternative to deposit semiconductor thin-films. Also with spray pyrolysis it is possible to infiltrate nanoporous electrodes up to 2mm, if the process conditions are well chosen. The pores of a 2mm nanoporous anatase TiO<sub>2</sub> film (particle size of 50 nm) can be filled (almost) completely with CuInS<sub>2</sub>, deposited by both methods. If AM 1.5 irradiation is applied, the AL-CVD cells show an open-circuit voltage of 0.49 V, a short-circuit current of 18 mA cm<sup>-2</sup>, and a fill factor of 0.44, which add up to an overall energy conversion efficiency of 4%. Almost 3% conversion efficiency is measured for 3D solar cells prepared with spray pyrolysis. These are the best performances of the inorganic 3D solar cells for both deposition routes and are better than polymer-based bulk heterojunctions.  
I. M. Nanu, J. Schoonman, and A. Goossens in press Adv. Mater

## Session IV: Heterojunction properties

Session chairs: A. Etcheberry, Jose Herrero

- O-IV.1** 08:30 -Invited- INTERFACE PROPERTIES OF CHALCOGENIDE BASED SOLAR CELLS  
**Andreas Klein**, Darmstadt University of Technology, Institute of Materials Science, Surface Science Division, Petersenstrasse 23, 64287 Darmstadt, Germany  
 Interfaces of chalcogenide (CdTe and chalcopyrite) based solar cells are investigated using photoelectron spectroscopy with in-situ sample preparation. Experimentally determined reactivities, Schottky barrier heights and valence band offsets with a systematic variation of contact partners are compared with theoretical expectations. The importance of interface induced defects for the charge transport across compound semiconductor / metal contacts and of the contribution of Cu deficient surface layers on the band alignment at chalcopyrite / buffer layer interfaces is discussed.
- O-IV.2** 09:00 -Invited- CHALCOGENIDE SOLAR CELLS: CHOOSING THE BUFFER  
**J.R. Sites** and M. Gloeckler, Physics Department, Colorado State University, Fort Collins CO 80523, USA  
 There are several device-physics considerations in the choice of buffer-layer material for solar cells with CIGS, CdTe, and related absorbers. The choice will vary with the absorber band gap. A straightforward consideration is optical absorption in the buffer, which becomes proportionally more of an issue with higher band-gap absorbers. More subtle is the impact of the conduction-band offset. The details will vary with the thickness, carrier density, and photoconductivity of the buffer layer, as well as with possible band variations within the absorber. The general principles, however, are that a large spike-type offset will severely limit the cell's current and that a cliff-type offset of any size can limit its voltage. At room temperature, there is an offset range of about 0.3 eV where the cell performance is optimal. The match of commonly employed CdS to CIGS with a typical 1.15 eV band gap is near the center of this range. For CdTe and for CIGS with band gap above 1.3 eV, cell voltage with a CdS buffer should be limited, which suggests that a mixed ZnS/ZnO or InS/InO buffer with a band gap a few tenths of an eV above that of CdS may be a better choice. For pure CIS, the spike offset is nearly too large, and respectable performance with CdS relies on the CdS photoconductivity.
- O-IV.3** 09:30 CHARACTERIZATION OF INTERFACE-NATURE AND BAND-ALIGNMENT IN CdS/CIGS BI-LAYER STRUCTURE BY PES/IPES  
**N. Terada**, R.T. Widodo, K. Itoh, K. Fujita, T. Okuda and K. Obara, Kagoshima University, 890-0065 Kagoshima, Japan, S. Niki, K. Sakurai, A. Yamada and S. Ishizuka, AIST, 305-8568 Tsukuba, Japan  
 Depth profiles of electronic structure and composition of CBD-CdS/CIGS bi-layers have been studied by ultraviolet, X-ray photoemission and inverse photoemission spectroscopy. Especially, a dependence of band alignment on Ga content in the CIGS was investigated. An intrinsic feature at an arbitrary depth was successfully exposed by etching with an Ar ion beam with a low ion-energy below 400 eV. After a removable of surface contamination, the CdS layer exhibited a compositional ratio of Se/Cd ~ 0.95 and band gap of 2.4 ~ 2.5 eV where the Fermi level was almost centered. These features were identical all over the CdS layer. The band gap started to shrink when core signals of CIGS got detectable by XPS. For the interface over the CIGS with a Ga substitution ratio  $x$  for In of 28 %, final offsets of valence band maximum VBM and conduction band minimum CBM were respectively about +0.7 eV and -0.2 eV, where both VBM and CBM approached to the Fermi level. On the other hand, the offsets of VBM and CBM of the samples with  $x$  of 45 % were +0.9 ~ +1.0 eV and narrower than -0.1 eV, respectively. For most of the interfaces, a presence of a thin, Cu-depleted region with a wide band gap was observed.
- O-IV.4** 09:45 DIRECT DETERMINATION OF THE BAND ALIGNMENT AT  $i$ -ZnO-CONTAINING INTERFACES IN CU(IN,Ga)(S,SE)<sub>2</sub> THIN FILM SOLAR CELLS  
**G. Storch**, L. Weinhardt, C. Heske, and E. Umbach, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, and S. Visbeck, T.P. Niesen, and F. Karg, Shell Solar, 81739 München, Germany  
 In this contribution an investigation of the band alignment at interfaces involving  $i$ -ZnO in Cu(In,Ga)(S,Se)<sub>2</sub> (CIGSSe) solar cells will be presented. We have used photoelectron spectroscopy (PES) and inverse photoemission (IPES) for a direct determination of both the valence and the conduction band offset. In particular the latter is of large importance for an unimpeded transport of charge carriers (electrons) across the interface. As a first step, we have investigated the  $i$ -ZnO/CdS interface as it is commonly used in the standard cell structure. Secondly, we will present results for the  $i$ -ZnO directly sputtered onto the CIGSSe absorber. Both results will be compared with a previous investigation of the  $i$ -ZnO/CIGSSe interface, in which the  $i$ -ZnO layer was deposited by an Ion Layer Gas Reaction [1]. Particular emphasis will be placed on modifications of the absorber surface induced by the deposition method and a discussion of the derived band offsets in view of the electronic properties of the complete CIGSSe solar cell.  
 [1] L. Weinhardt, M. Bär, H.-J. Muffler, Ch.-H. Fischer, M. C. Lux-Steiner, T. P. Niesen, F. Karg, Th.Gleim, C. Heske, and E. Umbach, Thin Solid Films 431-432, 272 (2003).

- O-IV.5** 10:00 POTENTIAL DISTRIBUTION OF Cu(In,Ga)(S,Se)<sub>2</sub> - SOLAR CELL CROSS-SECTIONS MEASURED BY KELVIN PROBE FORCE MICROSCOPY  
Th. Glatzel, H. Steigert, S. Sadewasser, R. Klenk and M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Dept. Solar Energy, Berlin, Germany  
 Current high efficiency chalcopyrite thin film solar cells have a multilayer structure consisting of an absorber, a buffer and a window layer. Modeling and optimization of the structures have been hampered by the lack of characterization methods to assess the electrical potential and conduction band alignment in actual devices. In this work Kelvin Probe Force Microscopy (KPFM) under ultrahigh vacuum (UHV) conditions is used to directly image the electronic structure of a complete thin film solar cell based on Cu(In,Ga)(S,Se)<sub>2</sub> absorber material. The potential distribution along different solar cells is directly measured by KPFM on polished and UHV-cleaned cross sections. Due to the high energy sensitivity together with a lateral resolution in the nanometer range, detailed information about the various interfaces within the heterostructure is obtained. In combination with simulations of the tip-sample interaction, the work function of the different layers and the built-in voltage of the heterostructure is deduced. In a previous work we have demonstrated that the use of a Zn<sub>1-x</sub>Mg<sub>x</sub>O alloy instead of the i-ZnO layer influences the conduction band offset between chalcopyrite absorber and window layer. This substitution enabled us to improve the solar cell performance from  $\eta = 6.3\%$  for CdS-free solar cell with pure i-ZnO to  $\eta = 12.5\%$ , comparable to that of the reference cells with CdS buffer ( $\eta = 13.2\%$ ). We present KPFM studies of these devices to illustrate the possibilities of our novel characterization method. The studies demonstrate that KPFM is an excellent tool for the characterization of heterostructures on a nanometer length scale. In chalcopyrite solar cells this can lead to a direct correlation between the electronic structure and the solar cell performance.
- O-IV.6** 10:15 INTERFACE ANALYSIS OF ZnO/CIGS<sub>Se</sub> AND (Zn,Mg)O/CIGS<sub>Se</sub> BY SYNCHROTRON-BASED SPECTROSCOPY  
I. Lauermann, A. Grimm, I. Kötschau, Ch.-H. Fischer, S. Sokoll, R. Klenk, Th. Glatzel, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Berlin, Germany; L. Weinhardt, G. Storch, O. Fuchs, C. Heske, Exp. Physik II, Universität Würzburg, Germany, C. Jung, W. Gudat, BESSY, Berlin, Germany; T. P. Niesen, S. Visbeck, F. Karg, Shell Solar GmbH, München, Germany  
 Sputtered (Zn,Mg)O is shown to be a suitable replacement for the CBD-CdS buffer and the i-ZnO layer in Cu(In,Ga)(S,Se)<sub>2</sub> solar cells, resulting in an efficiency of 12.5%, compared to a CdS/i-ZnO reference with 13.2%. At present, no convincing explanation is available why this material, in contrast to sputtered i-ZnO, makes the wet-chemical deposition of a buffer material obsolete. Furthermore, high efficiencies with (Zn,Mg)O are only achieved in combination with Cu(In,Ga)(S,Se)<sub>2</sub> absorbers, while (Zn,Mg)O/CuInS<sub>2</sub> solar cells show a poor performance. The long-term aim of our work is to explain this behavior. As chemical changes at the interface between the absorber and the sputtered oxide could have an impact on the cell performance, synchrotron-based photoelectron spectroscopy (PES) and X-ray emission spectroscopy (XES) were used to examine the interfaces between Cu(In,Ga)(S,Se)<sub>2</sub> and CuInS<sub>2</sub> absorbers and thin sputtered layers of both (Zn,Mg)O and ZnO. In order to avoid contamination, both materials were sputter-deposited in a UHV-compatible chamber directly attached to the analysis system. Deposition of oxide layers of approx. 0.4 nm, 0.6 nm, and 2 nm with subsequent analysis were performed in a step-wise fashion. Changes in the chalcopyrite "surface" composition were observed after deposition of both (Zn,Mg)O and ZnO on Cu(In,Ga)(S,Se)<sub>2</sub> and on CuInS<sub>2</sub>. A detailed analysis of these results together with data from valence band photoemission and O K X-ray emission are presented.

10:30

**BREAK**

Session V: Absorber growth and properties

Session chairs: John Kessler, Heinrich Metzner

- O-V.1** 11:00 -Invited- Na IN Cu(In,Ga)Se<sub>2</sub>  
**A. Rockett**, D. Liao, C. Lei, and I. Robertson. Department of Materials Science and Engineering, University of Illinois, 1304 W. Green St., Urbana IL 61801, USA  
 Na is found to improve the performance of Cu(In,Ga)Se<sub>2</sub> [CIGS] solar cells. However the mechanisms for this are not clear. This paper briefly reviews the literature on the observations to date and adds our recent results studying Na in the grain boundaries of commercial CIGS polycrystalline films by TEM. In addition, data for epitaxial CIGS films grown with and without Na are provided. Literature shows strongly that Na segregates to the surfaces of CIGS grains rather than remaining in the bulk of the crystallites. Although there is data suggesting weak electrical effects of Na, for example the reduction of defect state compensation in CIGS films, it is now clear that the majority of the effect of Na is through grain boundaries or the surface. It has been suggested repeatedly that Na acts through passivation of grain-boundary defects or reduction of the boundary depletion regions either directly or through catalyzing incorporation of O into those boundaries. No direct correlation of O with Na is observed in measurements of device layers and no direct positive correlation of O concentration with device performance is found. A positive correlation of performance with Na concentration is found. The Na concentration does scale somewhat with grain boundary density averaged over large areas of film, suggesting that it may be active there. What is agreed is that modest Na concentrations increase grain size in polycrystals, change preferred orientation, and improve device results. These suggest that it may act through the surface, modifying growth mechanisms or defect organization during growth. TEM evidence shows that strong concentration of Na in the grain boundaries, sufficient to passivate surface defects by itself, is unlikely to occur (although the results are not definitive due to the mobility of Na atoms on surfaces). Certainly, no evidence is found for a clear mechanism for action of Na in the boundaries.

- O-V.2** 11:30 **Cu K-EDGE X-RAY FINE STRUCTURE CHANGES IN CdTe WITH CdCl<sub>2</sub> PROCESSING**  
 Xiangxin Liu and A.D. Compaan, U. of Toledo, Toledo, OH 43606 USA, and Jeff Terry, Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago IL 60616 and Department of Physics, University of Notre Dame, Notre Dame IN 46556, USA  
 We have used the MR-CAT beamline of the Advanced Photon Source at Argonne National Laboratory to study the fine structure in the Cu K-edge x-ray absorption in 2 μm thick polycrystalline films of CdTe on fused silica. 4 nm of evaporated Cu is diffused either before and after vapor CdCl<sub>2</sub> treatments in dry air. Cu absorption is monitored through the Cu K<sub>α</sub> fluorescence using a 13 element Ge detector. The radial distribution function inferred from the absorption fine structure indicates predominantly Cu<sub>2</sub>Te when Cu is diffused into the as-deposited CdTe film but indicates a Cu<sub>x</sub>O environment when Cu is diffused *after* the vapor CdCl<sub>2</sub> treatment. We believe most of the diffused Cu decorates grain boundaries as oxides, consistent with the low doping densities typically observed in CdTe solar cells. The significance for grain boundary passivation will be discussed. *Work supported at UT by NREL and at APS by U.S. DOE-OER.*
- O-V.3** 11:45 **SUBSTRATE INFLUENCE ON Cu(In,Ga)Se<sub>2</sub> FILM TEXTURE**  
T. Schlenker, V. Laptev, H.W. Schock, and J.H. Werner, University of Stuttgart, Institute of Physical Electronics, Pfaffenwaldring 47, 70569 Stuttgart, Germany  
 This study reports on the evolution of Cu(In,Ga)Se<sub>2</sub> film surface orientation during growth and on the substrate influence on the resulting film texture. A thermal evaporation process deposits 0.5 to 1 μm thick Cu-poor Cu(In,Ga)Se<sub>2</sub> layers with constant deposition rates of all elements during growth on Mo single crystals, polycrystalline Mo, and highly oriented pyrolytic graphite. X-ray diffraction measurements allow the determination of the film texture. On highly oriented pyrolytic graphite, on (100)-oriented Mo, and on (111)-oriented Mo surfaces Cu(In,Ga)Se<sub>2</sub> grows with a pure (112) surface orientation, whereas on (110)-oriented Mo single crystals the (220/204) Cu(In,Ga)Se<sub>2</sub> surface orientation dominates. On polycrystalline Mo substrates no significant preferred film orientation for layers up to 1 μm thickness exists. Annealing of Cu(In,Ga)Se<sub>2</sub> films on polycrystalline Mo substrates leads to an increase of the mean grain size and to an evolution of a (112) preferred film orientation. Cu(In,Ga)Se<sub>2</sub> adsorbed on highly oriented pyrolytic graphite substrates experiences negligible substrate interactions. Thus, the Lotgering factor of 1 for the Cu(In,Ga)Se<sub>2</sub> (112) surface orientation proves that this orientation is energetically preferred. Among the investigated single crystalline Mo substrates, only (110)-oriented Mo has an impact on the resulting Cu(In,Ga)Se<sub>2</sub> film texture. This substrate influence and the fact that (112) oriented grains grow at the expense of other orientations reveal why Cu(In,Ga)Se<sub>2</sub> films grow on polycrystalline Mo with no preferred orientation during early stages of growth but result in a (112) texture for later growth stages.
- O-V.4** 12:00 **FORMATION AND CHARACTERISATION OF MoSe<sub>2</sub> IN Cu(In,Ga)Se<sub>2</sub> BASED SOLAR CELLS**  
D. Abou-Ras, G. Kostorz, ETH Zürich, Institute of Applied Physics, 8093 Zürich, Switzerland, D. Bremaud, M. Kälin, F.V. Kurdesau, A.N. Tiwari\*, ETH Zürich, Thin Film Physics Group, Laboratory for Solid State Physics, Technoparkstrasse 1, 8005 Zürich, Switzerland, M. Döbeli, Paul Scherrer Institute, c/o ETH Zürich, Institute for Particle Physics, 8093 Zürich, Switzerland, \*also at: Centre for Renewable Energy Systems and Technology, Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire, LE11 3TU, UK  
 Thin-film solar cells based on Cu(In,Ga)Se<sub>2</sub> (CIGS) in “substrate configuration” have been grown on Mo coated glass substrates. The formation or absence of an intermediate MoSe<sub>2</sub> layer between Mo and CIGS can influence the layer adhesion and photovoltaic properties of the solar cells. However, the formation kinetics and identification of the MoSe<sub>2</sub> in CIGS based solar cells remain unclear.  
 In the present study, the reaction kinetics of MoSe<sub>2</sub> formation were studied by selenising the Mo layers at different temperatures and for different durations. The samples were characterised by means of Rutherford backscattering, X-ray diffraction, electron diffraction, bright-field and high-resolution transmission electron microscopy. It was found that in all samples, a homogeneous MoSe<sub>2</sub> layer formed on top of the Mo layer. The temperature dependence of the formation of MoSe<sub>2</sub> shows an increasing layer thickness with increasing temperature. For a substrate temperature of 450°C, no difference in the MoSe<sub>2</sub> layer thickness of Mo substrates selenised for 10 and 40 min. is visible. This indicates that at substrate temperatures of 450°C, the diffusion process of Se from the sample surface through the formed MoSe<sub>2</sub> is too slow, all adsorbed Se is re-evaporated. The electrical, structural and chemical properties of CIGS-based solar cells with and without intentionally grown MoSe<sub>2</sub> intermediate layer will be reported.
- O-V.5** 12:15 **ELECTROCHEMICALLY PROCESSED CuInS<sub>2</sub> ABSORBER LAYERS**  
T. Wilhelm, B.Berenguier, M.Aggour, M.Kanis and H.J.Lewerenz, Division of Solar Energy, Hahn-Meitner-Institut Berlin, Glienicker Str. 100, 14109 Berlin, Germany  
 Various electrochemical processes for removal of deleterious Cu-S phases on CuInS<sub>2</sub> absorber layers are compared. The processes are developed from combinations of cyclic voltammetry and chronoamperometry in specific electrolytes. First evaluation of conditioning procedures is done in a photoelectrochemical solar cell (PECS) comprising a vanadium (II)/(III) redox electrolyte. Two modification approaches yield promising results: (i) a treatment in redox active electrolyte and (ii) the use of organic complexing agents. Both treatments are based on cathodic activation steps of the Cu-rich CuInS<sub>2</sub> layer and scanning to anodic potentials at which the accumulation condition for the semiconductor surface is reached or exceeded. In the anodic potential regime, successive oxidative corrosion of CuS, Cu<sub>2</sub>S and CuInS<sub>2</sub> occurs. For treatment (i), the decomposition potential of CuInS<sub>2</sub> is shortly exceeded resulting in a PECS with superior performance than KCN etched samples and a conversion efficiency of 8% in a solid state device. Treatment (ii) was designed to alleviate the dissolution of the Cu-S phases by formation of a stable Cu containing complex and to suppress redeposition on the CuInS<sub>2</sub> surface. Therefore, the decomposition potential of CuInS<sub>2</sub> was not exceeded in this case. First results show a PECS efficiency of 1.3%. Photoelectron spectroscopy analysis of the processed samples show that the Cu/In ratio at the surface is considerably more stoichiometric than after KCN etching.

12:30

**LUNCH**

14:00

## POSTER SESSION III

## Characterisation

Session chair: Hans-Werner Schock

## O/PIII.01

PHOTOLUMINESCENCE AND RAMAN SPECTROSCOPY OF POLYCRYSTALLINE AgInTe<sub>2</sub>

A. Jagomägi, J. Krustok, J. Raudoja, I. Oja, M. Grossberg. Department of Materials Science, Tallinn Technical University, Ehitajate tee 5, Tallinn 19086, Estonia

The ternary compound AgInTe<sub>2</sub> belongs to the I-III-VI<sub>2</sub> family of chalcopyrite semiconductors and it can be used in photovoltaic cells or other optoelectronic devices. In spite of its importance very little is known about photoluminescence and Raman properties of AgInTe<sub>2</sub>. Low temperature (10K) photoluminescence spectrum of this compound shows 3 different peaks. The E1 peak at 1.023 eV probably has an excitonic origin, the D1 peak at 0.959 eV has 2 phonon replicas with phonon energy of 25 meV and the possible origin of this peak is a donor-acceptor pair recombination with activation energy  $E_a = 35$  meV. The D2 peak at 0.741 eV is caused by deep defects. The room temperature Raman spectrum of this compound was measured for the first time and reveals 6 peaks. Peak at 122 cm<sup>-1</sup> is evidently due to A1 mode. Very intensive peak is also at 140 cm<sup>-1</sup>. According to IR measurements, this peak can be related to one of the E modes, but at the same time there is no other experimental data confirming this assertion. For that reason it can be also be one of the B1 modes. Other Raman peaks are not so well resolved. It is therefore difficult to make any assignments for these peaks. However, using Raman data of other tellurides we can assume, that the peak at 266 cm<sup>-1</sup> is a combination of E and B2 modes. At the same time the 217 cm<sup>-1</sup> peak is probably related to the longitudinal optical E mode.

## O/PIII.02

## ION BEAM LUMINESCENCE OF CdS THIN FILM FORMED BY SPRAY PYROLYSIS

M. Khanlary, IKIU University, Iran, P. Townsend, Sussex University, U.K., B. Ullrich, Bowling Green University, USA

CdS thin films were produced by spray pyrolysis technique. Three bands located in green, yellow and red region were observed from ion beam luminescence (IBL) spectra of as deposited films. Temperature dependence of the spectra by cooling the sample from 280 to 50K, was investigated. Moreover, the variations of spectra with various species of implanted ions were also studied. The peak position of green band was found to be red-shifted as the temperature decreased. Our suggestion is that, in some temperature a phase transition from hexagonal to cubic structure occurs in CdS thin film. The origin of emissions are discussed.

## O/PIII.03

PIEZOELECTRIC PHOTOTHERMAL INVESTIGATION OF PROTON IRRADIATION INDUCED DEFECTS IN CuInSe<sub>2</sub> EPITAXIAL FILMS

Y. Akaki(a,b), N. Ohryoji(a), A. Fukuyama(a), K. Yoshino(a), S. Kawakita(c), M. Imaizumi(c), S. Niki(d), K. Sakurai(d), S. Ishizuka(d), T. Ohshima(e) and T. Ikari(a), (a)Department of Electrical and Electronic Engineering, Miyazaki University, 1-1 Gakuen-kibanadai, Miyazaki, 889-2192, Japan, (b)Department of Electrical Engineering, Miyakonojo National College of Technology, 473-1 Yoshio, Miyakonojo, Miyazaki, 885-8567, Japan, (c)Office of Research and Development, NASDA Tsukuba Space Center, 2-1-1, Sengen, Ibaraki, 305-8505, Japan, (d)Photonics Research Institute, National Institute of AIST, 1-1-1 Umezono, Tsukuba, Ibaraki, 305-8568, Japan, (e)Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gumma 370-1292, Japan.

CuInSe<sub>2</sub> (CIS) material belonging to chalcopyrite type semiconductors is a promising candidate for future thin-film space solar cells with high conversion efficiency and excellent radiation tolerance. However, the effect of an irradiation on the optical property of CIS films is not yet clear. In this study, a PPT spectrum of the CIS thin films before and after proton irradiation are investigated. The generation and annihilation of defect levels was clearly observed by this method. The CIS epitaxial layers were grown on a semi-insulating GaAs substrate by MBE. Thickness of the thin film CIS sample was 1.0 micro meter and the Cu/In ratio was determined to be 1.0 by means of an electron probe microanalysis. The cells were irradiated with proton energy of 0.38 MeV and the fluence of  $1 \times 10^{14}$  cm<sup>-2</sup>. A PPT spectra before and after proton irradiation were obtained at room temperature. In addition to the direct free exciton transitions observed around 1.02 and 1.23 eV, the signal from the irradiation induce defect level were elucidated. After the curve fitting procedures by decomposition into the Gaussian functions, we concluded that the observed peak at 0.93 and 0.84 eV was due to the intrinsic and irradiation-induced defect. The generation of the In interstitials may results in the degradation of the solar cells.

## O/PIII.04

THE INFLUENCE OF THERMAL ANNEALING IN PRESENCE OF CdCl<sub>2</sub> ON THE ELECTROPHYSICAL PROPERTIES OF THE CdS/CdTe SOLAR CELLS

Petru Gasin(a), Mihail Caraman(b), Sergiu Vatavu(c) (a)Moldova State University, Faculty of Physics (b)Moldova State University, Faculty of Physics, Chair of Physics (c)Moldova State University, Faculty of Physics, Scientific Research Lab "Semiconductor Physics" Moldova State University, Faculty of Physics, 60 A. Mateevici str., MD-2009, Chisinau Moldova

CdS/CdTe solar cells have been manufactured by consecutive depositing CdS and CdTe thin films on glass using closed spaced sublimation. CdS and CdTe thin film's thicknesses vary as follows: 0.7-1.1 μm and 5-10 μm respectively. Ni and SnO<sub>2</sub> were used as ohmic contacts to CdTe and CdS respectively. Short circuit current (at 80 mW/cm<sup>2</sup>) 40-90 mA/cm<sup>2</sup> and OC voltage is 0.1-0.3 V. The fabrication process included annealing in presence of CdCl<sub>2</sub> with temperature up to 450°C. Photovoltaic parameters after heat treatment are: current: up to 24 mA/cm<sup>2</sup>, and OC voltage: 0.8 V. For to determine and predict cell's behavior and the influence of heat treatment on cell's performance, the electrical and optical measurements were performed.

It was established that current flow mechanism is determined by the tunneling processes through the dislocation lines penetrating the space charge region of the heterojunction. The investigation of the energy states in CdS/CdTe solar cells were performed by means of absorption and photoconductivity, quantum efficiency, lifetime vs. temperature and photoconductivity kinetics measurements. From the analysis of the absorption spectra of the CdTe films as a part of the SnO<sub>2</sub>/CdS/CdTe/Ni solar cells, it was established that as a result of heat treatment in CdCl<sub>2</sub> an impurity level localized at ~20 meV from the top of the valence band of CdTe was formed. The high photovoltaic properties of solar cells are determined by the presence of the recombination level with a lifetime equal to 180 ns. The interface structure of the heterojunctions was studied by absorption and luminescence spectra at 78,300 K. The heterojunctions heat treatment leads to the structure defects removal in the semiconductor layers and to the formation of Cd<sub>x</sub>Te<sub>1-x</sub> (x=0,95) solutions layer at the interface.

- O/PIII.05** STRUCTURAL PROPERTIES AND QUALITY OF THE PHOTOEXCITED STATE IN Cu(InGa)Se<sub>2</sub> SOLAR CELL ABSORBERS WITH LATERAL SUBMICRON RESOLUTION  
G.H. Bauer(a), L. Gütay(a), R. Kniese(b), (a)Institute of Physics, Faculty of Mathematics and Natural Sciences, Carl von Ossietzky University, 26111 Oldenburg, Germany, (b)Center for Solar Energy and Hydrogen Research ZSW, 70569 Stuttgart, Germany  
Yields of laterally recorded confocal luminescence of Cu(InGa)Se<sub>2</sub> solar cell absorbers (prepared under conditions of a pilot line production) show considerable variations (factors 2-5) in the length scale of few microns (3-10 μm) which do not directly correlate with structural-topological features (grains) in the micron and sub-micron scale extracted from simultaneously analyzed optical reflection and from afm-scans. Variations in pl-yield get larger with Ga admixture, as well as sizes of lateral patterns rise. Regimes of different luminescence yields additionally show variations of position and of the shape of peaks indicating via different combined densities of states of radiative transitions the remarkable lateral variation in composition of metallurgical phases. We present and discuss these lateral features in 2-D Fourier transforms and in operations in Minkowski space (opening functions) and show the size of scan regimes necessary for ensemble data to be statistically representative.
- O/PIII.06** PHOTOLUMINESCENCE STUDY OF POLYCRYSTALLINE CdS/CdTe THIN FILM SOLAR CELLS  
Jochen Van Gheluwe, Jorg Versluys, Paul Clauws, Dirk Poelman Ghent University, Department of Solid State Sciences, Gent, Belgium  
The CdCl<sub>2</sub> activation treatment is an essential step in the production of high quality CdS/CdTe junctions with good conversion efficiencies, but the mechanisms behind this process are still not fully understood. In this work two types of samples grown by close spaced sublimation (CSS) are investigated. One type had a CdCl<sub>2</sub> activation in vacuum while the other was activated in an air ambient. Low temperature photoluminescence measurements of both the front and the back surface were performed (for back surface PL the back contact was removed by sputtering). The observed PL emission is further analysed by studying the dependence of the PL emission intensity on the incident laser excitation power. In addition the temperature dependence of the emission is examined. Possible explanations are proposed and the results are compared with literature data.
- O/PIII.07** Y LUMINESCENCE IN POLYCRYSTALLINE CdTe FILMS GROWN BY CSVT-TECHNIQUE  
M. Cárdenas-García, J. Aguilar-Hernández, G. Contreras-Puente, Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, Edificio No. 9 U.P.A.L.M., 07738 México D.F., México  
The PL spectrum of CdTe at low temperatures usually shows a luminescent band in the low energy side at 1.470 eV, in epitaxial layers as well as in single crystals. In some samples the 1.470 eV band overlaps with the broad defects band, centered at 1.40 eV. This band was first observed in epitaxial CdTe layers grown by MBE. Several mechanisms have been proposed as the origin of this band: a) bound exciton radiative mechanism, b) recombination of bound excitons to extended states, c) DAP (donor-acceptor pair) transitions, for which the acceptor level is an A-center of the type C2-Cd - ClTe. More recently this luminescent band has been identified as the Y luminescence band arising from excitons bound to dislocations, specifically Te(g) type glide dislocations. In this work we have analyzed CSVT-CdTe polycrystalline films, focusing our attention in the evolution of the defect band, by using selective pair luminescence (SPL). Our results show that the defect band consists of independent structures one of them peaking at 1.470 eV. We carried out the study of this band as a function of both intensity of beam excitation and temperature. The change of the PL intensity as well as the change of the band maximum as a function of temperature allows us to establish that the 1.470 eV luminescent band is actually the so called Y band in CdTe single crystals.
- O/PIII.08** CIGS J-V DISTORTION IN THE ABSENCE OF BLUE PHOTONS  
A.O. Pudov and J.R. Sites, Colorado State Univ., Ft. Collins CO, USA, M.A. Contreras, National Renewable Energy Laboratory, Golden CO, USA, T. Nakada, Aoyama Gakuin Univ., Kanagawa, Japan, H.-W. Schock, Inst. Physikalische Elektronik, Univ. Stuttgart, Germany  
Common window materials used with CIGS absorbers produce conduction-band barriers that may significantly distort the current-voltage curves, especially when short-wavelength photons are excluded from the illumination spectrum. Earlier work documented this effect for CIS absorbers (band gap near 1.0 eV) with CdS windows and referred to it as the "red kink" [1]. With a set of higher band-gap (1.15 eV) CIGS absorbers that were nominally identical, little or no effect is seen with CdS window layers. However, wider band-gap (lower electron affinity) ZnS(O,OH) or InS(O,OH) windows, prepared by chemical-bath deposition, clearly show the J-V red kink, where "red" in each case refers to photons with lower energy than the window band gap. The J-V distortions have turn-on and turn-off time constants on the order of minutes, and they correlate with major variations in apparent quantum efficiency when it is measured with varying intensity and spectral content of bias light. The data to be reported presents a consistent picture of a conduction-band spike that increases with window band gap, but can be reduced through photogeneration in the window material, especially when the net donor concentration in the window is small. [1] I.L. Eisgruber et al, Solar Energy Mat. Solar Cells 53, 367 (1998).
- O/PIII.09** EFFICIENCY LIMITATIONS FOR WIDE BAND GAP CHALCOPYRITE SOLAR CELLS  
M. Gloeckler and J.R. Sites, Colorado State University, Department of Physics, Fort Collins CO 80523, USA  
Wide band gap chalcopyrite solar cells, most prominently Cu(In,Ga)Se<sub>2</sub> with high Ga content, have failed over the past years to achieve high conversion efficiencies. Starting from a simple baseline case of a ZnO/CdS/CIGS solar cell, we use numerical modeling tools to investigate the effects of bulk and interface recombination for a broad range of absorber band gap energies assuming that the Ga/In ratio primarily affects the conduction band. Our model predicts that even very small interface recombination velocities limit the open circuit voltage, if the band offset between buffer and absorber layer is close to zero or negative. This is the case for CdS/CIGS structures with absorber band gaps above 1.3-1.4 eV. Our simulations further predict that surface phases or pinning of the Fermi level at the interface can inhibit interface recombination, which leads to an improvement in cell efficiency. Maximum conversion efficiency for all band gap energies is calculated based on a generic window layer/absorber structure assuming that the band alignment can be arbitrarily chosen. The implication of this work is that although all record CIGS efficiencies have been achieved with CdS buffer layers, CdS may not be the best buffer layer for wide band gap chalcopyrite solar cells. Our results agree very well with the reported record efficiency for CdS/CdTe, CdS/CuGaSe<sub>2</sub>, and CdS/Cu(In,Ga)Se<sub>2</sub> solar cells.

- O/PIII.10** THE INFLUENCE OF IMPURITIES ON GROWTH AND PROPERTIES OF CIGS USING TWO-STEP PROCESSING  
H. Sankaranarayanan, V. Mohanakrishnaswamy, S. Pethe, C.S. Ferekides and D.L. Morel, University of South Florida, Tampa FL USA  
Formation of high electronic quality CIGS requires precise control of the atomic constituents using a multi-step coevaporation process. To approach this level of quality using two-step, all-solid-state processing requires understanding and control of both the kinetics and thermodynamics of film growth. In addition to the usual considerations we find that external factors, especially impurities, have a major influence on film properties. Using Cu/Ga metal layers as precursors it is found that CIGS formation requires Se to be introduced prior to In in the growth sequence. This usually occurs naturally, though uncontrollably, in single growth chambers. We have been able to mitigate this problem by using a separate growth chamber for the precursor layers. Na enters the film from the glass substrate and is known to contribute to improved performance. Our analysis indicates that it plays a strong role in balancing compensation. However, we find that complex defect formation accompanies Na as well, and that details of Mo deposition are critical to effecting proper Na inclusion. The presence of water vapor interferes with these mechanisms, especially during the early phases of growth. To some extent the simultaneous presence of background Se and water vapor in a single chamber environment can be mitigated by adopting judicious deposition procedures. A comprehensive model of film growth and performance will be presented.
- O/PIII.11** TWINNING IN CdHgTe, CdTe AND HgTe  
I.V. Kurilo(a), I.O. Rudyi(a), M.S. Fruginskij(a), I.S. Virt(b), M. Kuzma(c), P. Sagan(c), J. Zawislak(c), (a)Lviv Polytechnic National University, 12 Bandera str., 79646 Lviv, Ukraine, (b)Drohobych State Pedagogical University 24 Franko str., 82100 Drohobych, Ukraine, (c)Institute of Physics, University of Rzeszow, Rejtana 16A, 35-959 Rzeszow, Poland  
CdTe, HgTe and CdHgTe bulk crystals grown from melts and a vapour phase. Epilayers have been obtained by isoVPE and PLD techniques on substrates CdTe, KCl, GaAs and Al<sub>2</sub>O<sub>3</sub>. Selective and ionic etching, optical and interference microscopy, RHEED, SEM and TEM and X-ray to-pographic investigation to investigate extended defects – growth twins and deformation twins were used. The correlation between twins formation and growth conditions of the crystals and layers is established. The sub-strate orientation influence on formation of the twins has been established. Formation of such defects in epilayers probably is connected with layers nucleation processes. Usually it is considered that the twins boundaries are capable to accumulate impurity with the subsequent formation of the inclusions second phase. However our estimations values of strains tensor components around of spherical inclusions executed within the framework of model Mott – Nabarro and also on the basis of the approach of van der Merve with reference to heterointerface shows that of such allocation can be the twinning reason. Deformation twinning is displayed in the diagrams of compression and indenter penetration diagrams as fine jumps of a stresses (serrated yielding). The ways suppression of twinning during lay-ers growth are discussed.
- O/PIII.12** LATTICE DISTORTION AROUND IMPURITY ATOMS AS DOPANTS IN CdTe  
H. Haas, E. Holub-Krappe, H.-E. Mahnke, HMI Berlin GmbH, 14109 Berlin, Germany, V. Koteski, N. Novakovic, VINCA Institute of Nuclear Science, POB 522, 11001 Belgrade, Serbia, P. Fochuk, B. Hahlovsky, University of Chernivtsi, 274012 Chernivtsi, Ukraine  
The incorporation of impurity atoms for doping is often accompanied by lattice distortions and the formation of defect complexes, in some cases drastically influencing electrical and optical properties. We have measured the lattice distortion around As (acceptor), Se (isovalent), and Br (donor, anion sublattice) as well as Ga (donor, cation sublattice) in CdTe with fluorescence detected EXAFS at HASYLAB. The experimental challenge lies in the compromise between a concentration high enough for X-ray absorption and low enough to avoid compensation and clustering. We could experimentally verify the lattice relaxation with a bond length reduced by 8% around the As atom as inferred indirectly from ab-initio calculations of the electric field gradient in comparison with the measured value in a PAC experiment (S. Lany et al., Phys. Rev. B 62, R2259 (2000)). Our calculations of the relaxation were performed with the WIEN97 package using the linearized augmented plane wave method and the FHI96md pseudo-potential program. Using a super-cell approach for As on the Te site in CdTe, we find good convergence with increasing cell size so that the result can be taken as representative for the low doping limit. The extension to the neighbouring elements Se and Br again yields perfect agreement between experiment and model calculation with a sizeable lattice expansion in the case of Br. This result may be taken as evidence for the high tendency of Br to form a Br A-centre (Br plus metal vacancy) in CdTe.
- O/PIII.13** SURFACE STUDY OF CIGS FILMS CLEANED BY PHYSICAL TREATMENTS  
R.T. Widodo, N. Terada, K. Itoh, K. Ohki, T. Okuda and K. Obara, Kagoshima University, 890-0065 Kagoshima, Japan, S. Niki, K. Sakurai, A. Yamada and S. Ishizuka, AIST, 305-8568 Tsukuba, Japan  
To develop intrinsic surface nature of chalcogenide films grown in estranged systems, which is essential to study their electronic structure, two methods have been examined: 1) protection with Se layer deposited just after film growth and 2) Ar ion beam etching. An easy re-evaporation of the Se layer by vacuum annealing at moderate temperature yielded removal of surface contaminations and a surface composition close to nominal one. In-situ photoemission and inverse photoemission spectra showed that valence band maximum and conduction band minimum of CuInSe<sub>2</sub> film annealed at 225 °C, 60 min located 0.58 eV below and 0.52 eV above the Fermi level EF, respectively. These were almost identical to clean CIS bulk. The annealing above 250 °C resulted in Se depletion and rise of EF. For the etching method, a low kinetic energy Ek of irradiating ions was a key to develop intrinsic surface. The etching with Ar ions with Ek > 500 eV resulted in apparent broadening in photoemission spectra. CuGaSe<sub>2</sub> films etched with the beam of Ek=400 eV, current density of 0.08 mA/cm<sup>2</sup>, showed a band gap about 1.65 eV where EF was almost centered. These results reveal that these treatments are effective techniques to obtain intrinsic surfaces of CIGS films.

O/PIII.14

EVOLUTION OF THE DEFECT SYSTEM IN PHOTOEXCITED CADMIUM TELLURIDE

A.B. Smirnov, R.K. Savkina, V. Lashkaryov Institute of Semiconductor Physics of NASU, pr. Nauki 45, 03028 Kiev, Ukraine  
Since a laser technology is extensively applied in semiconductor material processing, the control of the state of such transformation direction – to improvement or to change for the worse – is important. We observed the photosensitivity increasing, modifying electrical properties and dislocation structure of CdTe crystals photoexcited by pulsed ruby laser irradiation ( $\lambda=0.694 \mu\text{m}$ ,  $t=20\text{ns}$  duration) with pre-threshold energy density. However, changes take place not only in the irradiated field of sample, but also outside. Moreover, we determined that the decreasing of the energy of the point defects generation takes place. This phenomena signifies the unpredictability of the laser treatment and requires investigation. The analysis of the laser-induced heating and point defects diffusion have showed these factors cannot be responsible for this so-called "long-range" effect. We suggest it should be connected with propagation of surface elastic waves induced by pulsed laser irradiation. The possible mechanisms of the optical excitation of sound waves in semiconductors which could have resulted in point and extended defect system transformation were analyzed.

O/PIII.15

TEMPERATURE DEPENDENCE OF TIME-RESOLVED PHOTOLUMINESCENCE OF BOUND EXCITONS IN CuInS<sub>2</sub> CRYSTALS

Kazuki Wakita, Kazuhito Nishi, Yoshihiko Ohta and Takashi Onishi, Department of Physics and Electronics, Graduate School of Engineering, Osaka Prefecture University, Japan

The ternary semiconductor CuInS<sub>2</sub> is a promising photovoltaic base material for solar cell because of its optimum band-gap energy of 1.5 eV. Although in recent years, CuInS<sub>2</sub>-thin films of high quality have been achieved, their defect properties are still not well understood. In this paper, we have studied the temperature dependence of time-resolved photoluminescence (PL) of bound excitons on CuInS<sub>2</sub> bulk-crystals grown by the traveling heater method to investigate their relatively shallow defect states. The PL spectra at 10 K display three sharp peaks of bound excitons (Ex1 at 1.531 eV, Ex2 at 1.525 eV and Ex3 at 1.520 eV) and a weak shoulder on the higher side (A free exciton, EA at 1.535 eV) in the band-edge region. The Ex2 and Ex3 decay curves show clearly single-exponential line, with decay-time constants of 2.1 ns and 3.5 ns, respectively, for a good fit to the data. On the other hand, the Ex1 decay curve follows a double-exponential with decay-time constants of 120 and 500 ps, respectively, for fast and slow components. We believe that the values of 500 ps, 2.1 ns, and 3.5 ns correspond to the radiative lifetime, respectively, for the bound excitons of Ex1, Ex2, and Ex3. Furthermore, we have measured the temperature dependence of the emission intensity and the lifetime of bound excitons. From the results, we will also discuss the defect states associated with the bound excitons.

O/PIII.16

PHOTOLUMINESCENCE STUDIES OF Cu(In,Ga)Se<sub>2</sub>

N. Rega, A. Zajogin, S. Siebentritt, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, 14109 Berlin, Germany, M.J. Romero, National Renewable Energy Laboratory, Golden CO 80401, USA

Optimization of the solar cells efficiency requires in particular good knowledge of defect states in the absorber material. In the present work we report on the results of photoluminescence (PL) studies on the Cu(In,Ga)Se<sub>2</sub> layers with varying Ga-content. All samples were epitaxially grown on a GaAs substrate by means of metal-organic chemical vapour deposition (MOCVD) process at slight Cu-excess ([Cu]/[III] ~ 1,1). In order to determine the nature of the observed peaks we have performed our PL experiments over 2 decades of the excitation intensity and over a temperature range of 5 to 70K. In this way we could for the first time identify excitonic luminescence for the [Ga]/[Ga]+[In] ratios <0,3 and >0,85. Exciton binding energies and bandgaps were found to rise with increasing Ga-content and to be in good accordance with the theoretically predicted values. Emissions at lower energies were shown to belong to a donor-acceptor-pair (DAP) transition identical to the DA1 transition in both CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> as well as their phonon replicas. The defect depth was found to increase with increasing Ga-content. The study is supplemented by cathodoluminescence investigations of epitaxial films and by PL measurements of polycrystalline films.

O/PIII.17

PEEM-CHARACTERISATION OF KCN-ETCHED CuInS<sub>2</sub>-SURFACES

K. Müller, Y. Burkov, A. Goryachko, D. Schmeisser, Brandenburgische Technische Universität Cottbus, Angewandte Physik-Sensorik, 03013 Cottbus, P.O. Box 101344, Germany

Photo-emission-electron microscopy (PEEM) is used for studies of KCN-etched CuInS<sub>2</sub> surfaces. CuInS<sub>2</sub> (CIS) is used as polycrystalline absorber layer for thin film solar cells and a characterisation need to be performed in terms of morphological informations, but first of all, of the elemental distribution and of doping inhomogenities at the surface. We demonstrate that the method is capable for such surface studies with high resolution. Excitation with Hg-illumination allows characterisation of doping inhomogenities. The use of synchrotron radiation allows visualisation of inhomogenities at the surface and in between of single grains. In addition, by taking images around the absorption edges of Cu, In or S, we are able to map elemental distributions in high resolution, separated from morphology dependent surface potentials or lateral distributions of work function. With this technique we characterised the effect of an in situ thermal treatment on above mentioned surface properties.

O/PIII.18

STUDY OF Cu-Se AND In-Se BOND-LENGTH DISTRIBUTIONS IN CuInSe<sub>2</sub>, Cu<sub>2</sub>In<sub>4</sub>Se<sub>7</sub> AND CuIn<sub>3</sub>Se<sub>5</sub>

J.M. Merino, M. León, Departamento de Física Aplicada C-XII, Universidad Autónoma de Madrid, 28049 Madrid, Spain, S. Diaz-Moreno, Diamond Light Source, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11, 0QX, U.K., G. Subías, Instituto de Ciencia de Materiales de Aragón, CSIC-Univ. de Zaragoza, 50009 Zaragoza, Spain

The local atomic structure around the Cu and In atoms of CuInSe<sub>2</sub>, Cu<sub>2</sub>In<sub>4</sub>Se<sub>7</sub> and CuIn<sub>3</sub>Se<sub>5</sub> was studied using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at the Cu and In K-edges. Room and low (~30 K) temperature EXAFS measurements were performed at beamline BM29 at the European Synchrotron Radiation Facility (ESRF) and collected data were analysed using the freely available IFEFFIT package. The analysis assumed a chalcopyrite structure for the CuInSe<sub>2</sub> samples and a P-chalcopyrite structure for Cu<sub>2</sub>In<sub>4</sub>Se<sub>7</sub> and CuIn<sub>3</sub>Se<sub>5</sub>. The results show that the In-Se bond length remains constant within the experimental uncertainty for all three compounds, but slight differences are observed in the Cu-Se bond lengths. These decrease with the Cu content in accordance with previous X-ray diffraction results on the same samples. The values obtained for the Debye-Waller factors in the CuInSe<sub>2</sub> samples are lower for the In-Se bond compared to Cu-Se, which is consistent with a higher ionicity in the former bond.

**O/PIII.19****KINETICS OF DONOR ACCEPTOR PAIR RECOMBINATION IN Cu-DEFICIENT CuGaSe<sub>2</sub>**

T. Riemann and J. Christen, Institute of Experimental Physics, Otto-von-Guericke-University, PO Box 4120, 39016 Magdeburg, Germany, M. Dworzak and A. Hoffmann, Institute of Solid State Physics, Technical University Berlin, Hardenbergstr. 36, 10632 Berlin, Germany, S. Siebentritt and I. Beckers, Hahn-Meitner-Institute, Glienicke Str. 100, 14109 Berlin, Germany

CuGaSe<sub>2</sub>, like other chalcopyrites, can accommodate large deviations from stoichiometry by the formation of intrinsic defects. When grown under Cu deficiency defects like Cu vacancies or Ga-Cu antisites are introduced. The low temperature luminescence spectrum is dominated by a strongly asymmetrically broadened (FWHM = 50 meV) emission around 1.61 eV which shifts further to lower energies with increasing Cu deficit. It has been attributed to a donor-acceptor pair transition (DAP) which strongly broadens under the influence of fluctuating potentials caused by the high degree of compensation. The strongly non-exponential decay resulting from the complex DAP recombination mechanism is analyzed using ps-cathodoluminescence (CL) and is quantitatively interpreted by the DAP model of Thomas and Hopfield. An impurity concentration of  $1 \cdot 10^{15} \text{ cm}^{-3}$  and a recombination rate of  $2.5 \cdot 10^8 \text{ s}^{-1}$  corresponding to a minimum radiative lifetime of 4 ns is determined. Spectral-time-resolved CL directly visualizes the strong red-shift of the DAP emission during decay  $E(t) = E_0 - 9.24 \text{ meV} \cdot \ln(t/t_0)$ . The initial CL decay times increase by more than 3 orders of magnitude over the emission band, resulting in time constants well below 3 ns at the high-energy side contrary to more than 10 microseconds at the low-energy tail. This spectral dependence is quantitatively described by a localization model of Gourdon-Lavallard.

**O/PIII.20****LAPLACE-DLTS ANALYSIS OF THE MINORITY CARRIER TRAPS IN THE Cu(In,Ga)Se<sub>2</sub> -BASED SOLAR CELLS**

P. Zabierowski, Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland, U. Rau, Institute of Physical Electronics, University of Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany, M. Bodegard, Angstrom Solar Center, Uppsala University, P.O. Box 534, 75121 Uppsala, Sweden

In the highly efficient CIGS-based devices the Fermi-level is pinned at the CdS/CIGS interface close to the conduction band. In the currently accepted model this is attributed to the continuous distribution of donor-like states located at the CdS/CIGS interface. The activation energy of these states, calculated from DLTS and admittance spectroscopy data, varies from sample to sample and ranges between tenths to hundreds meV. In this work we perform detailed analysis of the Laplace-DLTS data and we show that the position of the corresponding peaks in the DLTS and AS spectra depend not only on energy but also on electrical field (thermally assisted tunnelling effect). The values of the activation energies after correction for the electrical field agree very well with the transition energies predicted by theoretical calculations for InCu<sup>++</sup>, InCu<sup>+</sup>, InCu<sup>+</sup>VCu and VSe<sup>++</sup> defects. Thus we conclude that the minority carrier signal is not only due to continuous distribution of traps at the interface but also to the close-to-interface bulk donor states. This implies however, that the value of the activation energy should not be straightforwardly used for evaluation of the CdS/CIGS conduction band offset. We correlate these results with the deep level profiles deduced from capacitance-voltage and drive level profiling measurements.

**O/PIII.21****TEMPERATURE DEPENDENCE OF THE DIODE IDEALITY FACTOR IN CuInS<sub>2</sub> - ON - Cu- TAPE SOLAR CELLS**

Johan Verschraegen and Marc Burgelman, Gent University, Electronics and Information Systems, Pietersnieuwstraat 41, 9000 Gent, Belgium, Jürgen Penndorf, IST, Im Technologiepark 7, 15236 Frankfurt/Oder, Germany

CuInS<sub>2</sub> on Cu-tape (CISCuT) cells are an interesting thin film solar cell concept because of the use of a flexible Cu-tape as a substrate and potentially low cost production methods. The downside of the seemingly simple manufacturing process is the rather complex and not fully understood cell structure. In this article we will present short circuit current (I<sub>sc</sub>) versus open circuit voltage (V<sub>oc</sub>) measurements that were done for temperatures between 100K and 360K. From these measurements the dark saturation current and the diode ideality factor were calculated. The temperature dependence of these characteristics gives good indications about the dominant current transport mechanisms. We were able to fit the ideality factor very well to a formula derived by F.A. Padovani and R. Stratton [1], for the whole temperature range. The formula was originally derived for tunnelling through a Schottky barrier, but has been used successfully for diodes as well. The dark saturation current could also be fit, but only for temperatures above 240K. Below 240K the dark saturation current shows a kind of hysteresis, it depends on whether the cell is being cooled or heated. We conclude that tunnelling at the junction interface makes up the primary contribution to the current and is thus limiting the open circuit voltage. This work is part of the European CISLINE project (ENK6-CT-2001-00519). [1] F. A. Padovani, R. Stratton, Field and Thermionic-Field Emission in Schottky Barriers, Solid State Electronics, 9, pp. 695-707, 1966

**O/PIII.22****EFFECT OF PROTON IRRADIATION ON CUGASE<sub>2</sub> EPITAXIAL FILMS**

T. Rissom, S. Siebentritt, M. Ch. Lux-Steiner, Hahn-Meitner-Institut Berlin, Glienickestr. 100, 14109 Berlin, Germany

CuGaSe<sub>2</sub> with a band gap of 1.7 eV is considered a promising material for high band gap thin film solar cells. The effect of irradiation caused by protons with an energy of 1 MeV on epitaxial and polycrystalline CuGaSe<sub>2</sub> films is investigated. While in experiments by other groups Cu(In,Ga)Se<sub>2</sub> and CuInSe<sub>2</sub> showed an extraordinary stability against irradiation, i.e. any degradation could be annealed, first experiments on epitaxial CuGaSe<sub>2</sub> hint to a much higher sensitivity to radiation. The epitaxial CuGaSe<sub>2</sub>-films are prepared slightly copper rich by MOCVD on semi-insulating GaAs-Wafers, polycrystalline films are prepared by co-evaporation on glass. They are characterized by temperature dependent Hall-Effect and resistivity measurements in a van-der-Pauw configuration and photoluminescence spectroscopy. Annealing of the damage by elevated temperature or illumination is investigated. The sensitivity of epitaxial and polycrystalline films is compared.

**O/PIII.23****LASER-LIGHT SCATTERING AS AN IN-SITU PROCESS CONTROL FOR PVD DEPOSITION OF Cu(In,Ga)Se<sub>2</sub> THIN FILMS**

A. Neisser, C.A. Kaufmann, R. Klenk, R. Scheer, Hahn-Meitner-Institut Berlin GmbH, Glienickestrasse 100, 14109 Berlin, Germany

Chalcopyrite thin film absorber layers for today's record solar cells are prepared by complex coevaporation schemes. Such schemes can only be successfully implemented if precise monitoring and control of the films composition and stoichiometry is achieved. We have recently introduced in-situ diffuse spectroscopic light scattering as a powerful tool for investigating the growth of polycrystalline Cu(In,Ga)Se<sub>2</sub> thin films. In this contribution we introduce laser light scattering as a simple and reliable process control for the three-stage deposition process. Monitoring the intensity of diffusively scattered laser light during Cu(In,Ga)Se<sub>2</sub> coevaporation allows (i) control of the thickness and the composition ( $[\text{Ga}]/([\text{In}]+[\text{Ga}])$  ratio) of the (In,Ga)Se<sub>2</sub> precursor layer, (ii) identification of the CuSe<sub>2</sub> phase segregation in stage 2 and, (iii) detection of the stoichiometry transition in stage 3. This results in a full in-situ control the entire deposition process. Furthermore changes in the growth process with substrate temperature have been investigated and the results are applied to growth processes on temperature sensitive substrates such as polyimide foils.

- O/PIII.24** NON-EXPONENTIAL CAPACITANCE TRANSIENTS OBSERVED WITH DEEP LEVEL TRANSIENT SPECTROSCOPY ON CuInGaSe<sub>2</sub> SOLAR CELLS  
E. Schlenker(a), V. Mertens(a), M. Köntges(b), R. Reineke-Koch(b), J. Parisi(a), (a)University of Oldenburg, Institute of Physics, Department of Energy and Semiconductor Research, 26111 Oldenburg, Germany, (b)Institute for Solar Energy Research Hameln-Emmerthal (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany  
 As an increase in the open circuit voltage of Cu(In,Ga)Se<sub>2</sub> solar cells (CIGS) is intended, the interest in CIGS devices with gallium to gallium plus indium ratios (GGI) diverging from the standard composition of about 0.28 is rising, too. To understand more about the In-Ga alloy system and the compositional influence on the defects in the materials, we investigate CIGS solar cells of different GGI with majority and minority carrier deep level transient spectroscopy. The obtained capacitance transients show no pure exponential behaviour, although some exponential influence is visible in the  $\Delta C/C \cdot \log(t)$  representation. As usually expected, our data shows a clear dependence on the sample temperature. We found that considering the thermal activation, it is not possible to fit the data with a sum of several exponential or stretched exponential functions. Therefore, the simple picture of several separated defects observed at one temperature has to be modified.
- O/PIII.25** RHEED STUDY OF CdTe AND CdHgTe THIN FILMS GROWN ON Si BY PULSE LASER DEPOSITION  
P. Sagan(a), G. Wisz(a), M. Bester(a), I.O. Rudyj(b), I.V. Kurilo(b) I.E. Lopatynskij(b), I.S. Virt.(c, d), M. Kuzma(a), (a)Institute of Physics, University of Rzeszow, Rejtana 16A, 35-959 Rzeszow, Poland, (b)State University, "Lviv Polytechnic", Bandera 12, 90646 Lviv, Ukraine, (c)Section of Experimental Physics, Pedagogical University, Franco 24, 82-100 Drogobych, Ukraine, (d)Institute of Biotechnology, University of Rzeszow, Rejtana 16A, 35-959 Rzeszow, Poland  
 The solar cells (SC) technology develops into two directions: a) design of new architecture of device as tandem cells, MIS inersion layer, and b) searching new photovoltaic materials as amorphous silicon, copper indium diselenide etc. Now a day very promising system for SC is CdTe/CdS. In the paper we study the properties of patterned Si surfaces as a substrate for CdTe layers. Two kinds of such surfaces were used: pyramid like, and plate like. Such surfaces have particular properties for CdTe growth. The first one has the (111) orientation and second consist of crystallographic planes of high Miller indices. By a proper surface structuring the interface surface/layer can be modify. By pulsed laser deposition method the layers of CdTe as well as Hg<sub>1-x</sub>Cd<sub>x</sub>Te ( $x=0.2$ ) were obtained on the structuring Si surfaces. The third substrate Si with flat structure was used also for comparing of results. Patterns of reflection high-energy electron diffraction (RHEED) were obtained and interpreted for layers of various thickness. Comparing the diffraction patterns obtained from layers deposited on various Si substrates one can conclude that the plate like substrate surface is the best for epitaxy.
- O/PIII.26** COMPENSATING DONORS IN THE Cu(In, Ga)Se<sub>2</sub> ABSORBERS OF SOLAR CELLS  
M. Igalson, Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland and M. Bodegård, Ångström Solar Center, Uppsala University, P.O. Box 534, 751 21 Uppsala, Sweden  
 In this contribution we use DLTS, admittance spectroscopy, and transient photocapacitance TCP for investigation of electron-type traps in the CIGSe devices. We present the evidences that levels revealed in the junction capacitance spectroscopy of CIGSe absorbers obtained by co-evaporation are due to two bulk donor-type centers. We discuss the results obtained for various samples (ZnO/CdS/CIGS, ZnO/ALD-iZnO/CIGS, and also for comparison n-type single crystal CuInSe<sub>2</sub> Schottky junctions) and show that the capacitance measurements at low temperature region reveal bulk electron traps of energies corresponding to theoretical prediction for InCu antisite. Additional proof has been provided by measuring the optical transitions of electrons to these levels induced by sub-band gap illumination (TCP). Other, much deeper level, involved in the persistent phenomena typical for CIGSe devices, is not sensitive to subband-gap illumination, while thermal excitation requires energy higher than 0.8 eV. We estimate the recombination properties of both centers by performing TCP experiment with blue light introducing holes into the bulk of absorber, and provide arguments that deep relaxing donor is a major recombination center in the efficient cells, while shallower one does not contribute significantly to the recombination losses.
- O/PIII.27** DETERMINATION OF THE QUALITY OF CUIN<sub>2</sub>-BASED SOLAR CELLS COMBINING RAMAN AND PHOTOLUMINESCENCE SEPCTROSCOPY  
E. Rudigier, T. Enzenhofer, R. Scheer, Hahn-Meitner Institute, Dep. SE3, Glienicke Str. 100, 14109 Berlin, Germany  
 Raman and Photoluminescence spectroscopy are found to assess the quality of absorber layers in CuIn<sub>2</sub> thin film solar cells. The combination of the Raman linewidth of the A<sub>1</sub>-mode with solar cell data as formed out of those films reveals a direct correlation. For linewidths larger than 3.8 cm<sup>-1</sup> a significant worsening of the solar cell parameters is found. But for linewidths smaller than 3.8 cm<sup>-1</sup> a saturated behavior of the solar cell parameters is observed. This saturation indicates other origins of performance limitation than structural defects to be present in CuIn<sub>2</sub>-based devices. Additionally, the results from Raman analysis as well as the solar cell parameters are compared with Photoluminescence data required from the respective samples. Both a broadening of the Raman linewidth and a worsening of the solar cell parameters correlate with an increase of the intensity of a donor-acceptor transition. Thus, the density of optoelectronic active defects is manifested in structural properties of the films.
- O/PIII.28** MORPHOLOGY AND STRUCTURE OF THIN EPITAXIAL Cu(In,Ga)S<sub>2</sub> FILMS ON Si SUBSTRATES  
Th. Hahn, H. Metzner, U. Reislöhner, J. Cieslak, J. Eberhardt, M. Müller and W. Witthuhn, Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Max-Wien-Platz 1, 07743 Jena, Germany.  
 Thin epitaxial layers of the quaternary chalcopyrite semiconductor Cu(In,Ga)S<sub>2</sub> (CIGS) were grown on sulphur terminated Si substrates of various orientations using molecular beam epitaxy (MBE). Prior to film deposition, the Si substrates were etched and terminated in situ utilizing elemental sulfur from the MBE-source. For the S-terminated Si surfaces, it was found that the unfavourable native surface reconstructions of Si are suppressed and a highly anisotropic etching via the desorption of SiS was observed. The CIGS samples were investigated with special emphasise on the film morphology, the nucleation of the very first monolayers, and the possibility to grow perfectly lattice matched chalcopyrite layers on Si through variation of the In/Ga-ratio. Rutherford backscattering spectroscopy (RBS) and atomic force microscopy (AFM) measurements were carried out to characterize their compositions, thicknesses, homogenities, and film roughnesses. In situ electron diffraction (RHEED) shows metastable CuAu-type ordering for CuInS<sub>2</sub> (CIS), while CuGaS<sub>2</sub> (CGS) crystallizes in the chalcopyrite structure exclusively. Furthermore it was found, that CIGS on Si exhibits three dimensional growth for all Ga-concentrations with strongly enhanced nucleation at step edges, while CGS, despite its large lattice mismatch, yields the smoothest films.

**O/PIII.29**EPITAXIAL CuInS<sub>2</sub> on Si(111) USING DI-TERT-BUTYL-DISULFIDE AS A SULPHUR PRECURSOR

C. Lehmann, W. Calvet, T. Plake and C. Pettenkofer, Hahn-Meitner-Institut, Glienicker Str. 100, 14109 Berlin, Germany

The ternary chalcopyrite semiconductor CuInS<sub>2</sub> with a direct bandgap of 1.53 eV is well suited as absorber for thin film solar cells. In a new approach we realise molecular beam epitaxy (MBE) of CuInS<sub>2</sub> on hydrogen terminated Si(111) using di-tert-butyl disulfide (TBDS) as sulphur precursor in combination with elemental copper and indium sources. The films are analysed in situ with photoelectron spectroscopy (PES) and low energy electron diffraction (LEED). Ex situ, the samples are investigated with x-ray diffraction (XRD) and scanning electron microscopy (SEM). We find that at growth temperatures below 350°C no carbon is incorporated into the deposited film. Furthermore, on the In-rich side of the CuInS<sub>2</sub> preparation we additionally observe metallic In at the surface. However, the valence band structure remains that of a typical CuInS<sub>2</sub> film. During the growth in the Cu-rich regime, an instant segregation of CuS (degenerated p-type semiconductor) occurs, which can be identified by the shifting of the valence band edge towards the Fermi level. In general, successful growth of epitaxial CuInS<sub>2</sub> is only permitted if the substrate is illuminated with ultraviolet (UV) light which can be deduced from 1x1 ordered LEED patterns.

**O/PIII.30**STRUCTURAL PECULIARITIES OF CCSVT-GROWN CuGaSe<sub>2</sub> THIN FILMS

M. Rusu, S.Doka, R. Würz, A. Meeder, P. Schubert-Bischoff, N. Pfänder, E. Strub, J. Röhrich, W. Bohne, Th. Schedel-Niedrig, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Glienicker Str. 100, 14109 Berlin, Germany

CuGaSe<sub>2</sub> (CGSe) thin films with a Ga/Cu ratio in the range of 1.0-1.3 were grown on plain and Mo-coated soda-lime glass substrates by the chemical close-spaced vapour transport (CCSVT) technique. Based on CGSe films with Ga/Cu ~ 1.12, ZnO/CdS/CGSe solar cells were prepared with an efficiency of 8.7% (AM1.5). Therefore, investigation of the structural properties of CCSVT-grown CGSe films is of special interest. The crystallinity and phase composition of the films were checked by means of X-ray diffraction and transmission electron microscopy. The elemental composition was analysed by energy dispersive X-ray technique and X-ray fluorescence spectrometry. Additionally, composition measurements and depth profiling of the elements were performed by elastic recoil detection analysis. It was concluded that the as-grown CGSe films possess high bulk homogeneity with Ga- and Cu-poor, and Se-rich surface. At the rear side, at the CGSe/Mo interface a MoSe<sub>2</sub> interfacial layer (~20-40 nm) is found and also an excess of metallic Ga. The films, grown directly on glass, exhibit similar structure, except the MoSe<sub>2</sub> layer. Photoluminescence was used as a complementary technique to study the evolution of the Ga content at the front and rear sides as function of the Ga/Cu ratio in the film. The behaviour of the intensity ratio of the deep defect luminescence (ascribed to Ga vacancies) to the shallow defect luminescence (known to shift towards lower energies with higher Ga content) supports the CGSe microstructural model.

**O/PIII.31**

## THERMAL CHARACTERIZATION AND DETERMINATION OF RECOMBINATION PARAMETERS IN CdTe FILMS ON GLASS SUBSTRATE BY USING OPEN PHOTOACOUSTIC CELL TECHNIQUE

M.A. Gonzalez-Trujillo(a), A. Cruz-Orea(b), M. de L. Albor-Aguilera(c), F. de L. Castillo-Alvarado(c), (a)Departamento de Ciencias Básicas, Escuela Superior de Computo, IPN, Miguel Othon de Mendizabal s/n, Lindavista, CP 07738 Mexico DF, México, (b)Departamento de Física, Centro de Investigación y Estudios Avanzados del IPN, Av. IPN No. 2508, Col. Sn. Pedro Zacatenco, CP 07360 México DF, México, (c)Departamento de Física, Escuela Superior de Física y Matemáticas, IPN, Edificio 9, Unidad Profesional "Adolfo López Mateos", CP 07738 México DF, México.

CdTe is a semiconductor with a wide variety of applications and perspectives for electronic industry (high efficiency photoelectric cells, infrared radiations detectors, etc.). Some work has been done studying CdTe using photoacoustic techniques to get, for example, the thermal properties for CdTe/Glass system. In this work we study, by using open photoacoustic cell technique, the thermal properties and recombination parameters of CdTe/Glass system with different layer thickness. We obtain thermal diffusivity values for these samples and their superficial recombination velocity. In the case of the obtained recombination velocities these ranged from 137 to 187 cm/seg which are in agree with reported values in the literature for similar samples.

**O/PIII.32**IN-SITU AND IN-DEPTH RESOLVED EX-SITU CHARACTERISATION OF THERMALLY INDUCED RECRYSTALLISATION OF CuInS<sub>2</sub> POLYCRYSTALLINE THIN FILMS FOR SOLAR CELL DEVICES: OBSERVATION OF POLYMORPHIC TRANSFORMATIONS

B. Barcones, A. Pérez-Rodríguez, L. Calvo-Barrio, A. Romano-Rodríguez, J.R. Morante, Universitat de Barcelona, C/Marti Franqués 1, 08028 Barcelona, Spain, E. Rudigier, I. Luck, J. Djordjevic, R. Scheer, Hahn Meitner Institute, Glienicker Strasse 100, 14109 Berlin, Germany

This work reports a quasi real-time microstructural investigation of thermal processes in CuInS<sub>2</sub> polycrystalline films for solar cell devices. The analysis of the Raman spectra measured during the process has allowed to obtain direct experimental evidence on the existence of a thermally induced polymorphic transformation of metastable CuAu ordered domains into the equilibrium chalcopyrite structure. The presence of these domains in the CuInS<sub>2</sub> film has been correlated with a worsening of the efficiency of the solar cell device, which gives interest to the analysis of these transformations and their dependence on the processing parameters. Processed films were obtained by sequential Cu and In sputtering onto Mo coated glass substrates and sulphurised in a graphite box. Samples were subjected to thermal processes involving different temperature slopes and atmospheres (including inert and sulphur). In-situ Raman and XRD measurements have been compared with the ex-situ analysis of the processed layers by in-depth resolved MicroRaman and Auger Electron Nanoprobe. This has allowed to correlate the existence of the polymorphic transformation with the presence of an In rich composition in the back region of the films. This contrasts with the high thermal stability of the CuAu phase in films prepared under both In rich and Cu rich conditions but leading to more uniform chemical in-depth profiles (closer to stoichiometry). In this last case, the existence of CuAu to Chalcopyrite transformation is always related to a sulphurisation process, and the final amount of polymorphic phase in the film is determined by the growth temperature and the Cu to In ratio during sulphurisation.

**O/PIII.33****ON CORRELATION OF CdS AND CdSe VALENCE BAND PARAMETERS**

P.P. Horley, V.V. Gorley, P.M. Gorley, Yuri Fedkovych Chernivtsi National University, 2 Kotsyubynsky Str., 58012 Chernivtsi, Ukraine and J. Gonzalez-Hernandez, Yu.V. Vorobiev, CINVESTAV Unidad Queretaro, Libramiento Norponiente 2000, Fracc. Real de Juriquilla, 76230 Queretaro QRO, Mexico

Cadmium sulfide and selenide are widely used for different solar cell applications as wide-gap window layers. Optimization of photovoltaic devices to increase their performance is impossible without adequate parallel computer modeling of physical processes taking place in illuminated cell. To achieve quantitatively correct calculation data one needs to use the whole set of the material parameters describing device components. Despite both cadmium sulfide and selenide having numerous published experimental and theoretically predicted data including information on energy gaps separating conduction band extremes in the center of Brillouin zone and effective mass tensor components of the carriers, there exists significant disagreement between the values of the latter, published in different sources. The given paper is dedicated to the partial solution of this problem, showing the existence of strong correlation between intermediate energy gaps in valence bands of CdS and CdSe. The values mentioned were determined with higher precision than the present reference data, allowing one to establish strict analytical relation between the components of effective mass tensors of these two semiconductors. Using the conformity criterion obtained, self-congruent effective mass values were determined for holes in both CdS and CdSe.

**O/PIII.34****EFFECT OF CdCl<sub>2</sub> ACTIVATION ON THE IMPURITY DISTRIBUTION IN CdTe/CdS SOLAR CELL STRUCTURES**

M. Emziane(a), K. Durose(a), N. Romeo(b), D.P. Halliday(a) (a)Department of Physics, University of Durham, South Road, Durham, DH1 3LE, U.K., (b)INFN, Department of Physics, University of Parma, Parco Area delle Scienze 7a, 43100 Parma, Italy.

CdTe/CdS/In<sub>2</sub>O<sub>3</sub>/glass solar cell structures were investigated from an impurity distribution viewpoint. This study was carried out using quantitative secondary ion mass spectrometry (SIMS) profiling from the CdTe surface through to the glass substrate. Particular emphasis was made on the potentially electrically active impurities possibly originating from the CdCl<sub>2</sub> processing step, and therefore more likely to affect the CdTe/CdS solar cell devices. Impurities such as Cl, O, Cu, Na, In, Sb, Sn, Si, Zn, Pb and S were systematically depth-profiled before and after CdCl<sub>2</sub> treatment of the structures. It has been shown that some of the impurities like O and Cu were clearly not originating from the CdCl<sub>2</sub> activation process. Other impurities such as Cl, Na and Sb were definitely present in the activated structures due to their presence in the CdCl<sub>2</sub> starting material used in the treatment. Si diffusion from the glass substrate as well as Te and S interdiffusion at the CdTe/CdS interface following the CdCl<sub>2</sub> treatment were also quantitatively highlighted. These structures were also studied by low temperature photoluminescence.

**O/PIII.35****CuGaSe<sub>2</sub> (001) Surface A (1x4) Reconstruction**

Th. Denizou, N. Esser, Institute of Spectrochemistry and Applied Spectroscopy, Albert-Einstein-Str. 9, 12489 Berlin-Adlershof, Germany, S. Siebentritt, R.Hunger and M. Lux-Steiner, Hahn-Meitner-Institut Berlin, Glienickestr. 100, 14109 Berlin, Germany, P. Vogt, Institute of Solid State Physics, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Although chalcopyrites have been used as absorber in thin film solar cells for nearly 30 years not much is known about their surface structure, which might be an important information towards growth and interface optimization. We have studied the chalcopyrite CuGaSe<sub>2</sub> (001) surface preparation by Ar<sup>+</sup> ion bombardment and annealing. The samples were grown by MOCVD on a (001) GaAs substrate on axis with a near-stoichiometric ratio Cu/Ga. The preparation was optimized so that we finally obtained a flat, well-ordered surface. The composition was analyzed with AES and a (1x4) reconstruction of the surface was observed with LEED for the first time. Further investigation were carried out via surface sensitive soft X-Ray Photoelectron Spectroscopy.

**O/PIII.36****PHOTOSENSITIVITY OF HETEROJUNCTIONS MANUFACTURED BY A METHOD OF ELECTROCHEMICAL DEPOSITION**

A.Sh. Abdinov, H.M. Mamedov, H.A. Hasanov, Baku State University, Z. Khalilov st. 23, 370148 Baku, Azerbaijan Republic

The work is devoted to creation of  $p, n-Si/n-Cd_{1-x}Zn_xS$  heterojunctions with  $0 \leq x \leq 0.6$ , by a method of electrochemical deposition and study their electrical, and also photoelectrical properties. The basic attention at investigations was focused to dependence of properties of the investigated heterojunctions on  $Cd_{1-x}Zn_xS$  films composition and regime of thermal annealing (TA) of structure. The process of electrochemical deposition of films from  $CdSO_4 + ZnSO_4 + Na_2S_2O_3$  aqueous solution on  $p-Si$  and  $n-Si$  plates, with resistivity  $\rho_p = 8 \div 20$  Ohm-cm and  $\rho_n = 10 \div 60$  Ohm-cm accordingly, was carried out in a special quartz vessel at 300 K. Electrical potential of deposition and current density through a solution thus varied in  $-(0.4 \div 2.5)$  V и  $(8 \div 45)$  mA/cm<sup>2</sup> accordingly. It's established, that direct branches of the volt-ampere characteristics (VAC) investigated heterojunctions for all considered film compositions at low voltages correspond to exponential, and higher voltages to the linear laws. The calculated values of exponential coefficient on the basis of volt-ampere and volt-capacitance measurements, appreciably differs from experimentally found. It testifies to multistage character of tunneling processes or presence in the spatial charge field of investigated structures of narrow channels of tunneling. The study of VAC shows, that the rectification effect in investigated heterojunctions depends also on temperature and duration of thermal annealing. Is established, that the best rectification ( $k_p = 800 \div 1200$ ) for heterojunctions  $p-Si/n-Cd_{1-x}Zn_xS$  is provided after thermal annealing at  $t = 380^\circ C$  and  $\tau = 8$  minute, and for heterojunctions  $n-Si/n-Cd_{1-x}Zn_xS$  ( $k_n = 500 \div 700$ ) at  $t = 350^\circ C$  and  $\tau = 7$  minute. Short circuit current value and course of photosensitivity spectral dependence curves of the investigated heterojunctions essentially depend on a regime of thermal annealing and  $Cd_{1-x}Zn_xS$  films composition. The photosensitivity spectrum investigated structures, which have not been subjected thermal annealing, covers wavelength region of  $0.5 \div 1.28 \mu m$ , and has maximums at 0.6 and 1.13  $\mu m$ . With increase of temperature up to  $350 \div 380^\circ C$  and increase of annealing duration up to 7-8 minute the value of photosensitivity grows, and its spectrum extends. Thus appreciable shift of a short wavelength maximum to higher energy region also is observed, and in the long wavelength region of  $0.8 \div 1.34 \mu m$  the value of photosensitivity is increased almost in 1.5  $\div$  2 times. Thus at illumination 1500 Lx, short-circuit-current density ( $I_{sc}$ ) and open-circuit-voltage ( $U_{osv}$ ) of heterojunctions  $n-Si/n-Cd_{0.4}Zn_{0.6}S$  reach  $U_{osv} = 0.46$  V and  $I_{sc} = 3.8$  mA/cm<sup>2</sup>, and for heterojunctions  $p-Si/n-Cd_{0.4}Zn_{0.6}S$   $U_{osv} = 0.58$  V and  $I_{sc} = 4.7$  mA/cm<sup>2</sup>.

**O/PIII.37**RELAXATION AND RADIATIVE RECOMBINATION DYNAMICS IN CuGaSe<sub>2</sub>

A. Hoffmann and M. Dworzak, Institute of Solid State Physics, Technical University Berlin, Hardenbergstr. 36, 10632 Berlin, Germany, T. Riemann and J. Christen, Institute of Experimental Physics, Otto-von-Guericke-University, PO Box 4120, 39016 Magdeburg, Germany, S. Siebentritt and I. Beckers, Hahn-Meitner-Institute, Glienicke Str. 100, 14109 Berlin, Germany

CuGaSe<sub>2</sub> is a promising material for the active region of thin-film solar cells. We investigate the emission mechanism of CuGaSe<sub>2</sub> applying cw-photoluminescence (PL) in conjunction with time resolved cathodoluminescence (CL) at helium temperature. When grown under Cu excess near-stoichiometric CuGaSe<sub>2</sub> is formed plus a secondary phase of Cu selenide which accommodates the Cu excess. In material grown under Cu excess the low temperature luminescence spectrum is dominated by two donor-acceptor pair transitions (DAP) at 1.62 and 1.67 eV. Excitonic recombination is also observed at 1.71 eV. The DAP transitions are attributed to a shallow donor at 12meV below the conduction band and two acceptors at 60 and 100 meV above the valence band. Additional lower energy transitions have been attributed to phonon replica of the DAP transition based on the constant energy difference between the up to three peaks and the DAP peak of 33 meV, which corresponds well to the energy of the LO phonon of 34 meV. While the intensity of the excitonic transitions at 1.71 eV instantly decays with the blanking of the exciting electron beam, CL transients of the several DAPs exhibit a characteristic non-exponential behaviour with time constants of tens of nanoseconds. Both DAP transitions are quantitatively analyzed in the DAP model of Thomas and Hopfield. Spectral-time-resolved CL reveals a competition between both DAPs with increasing decay time resulting in slower decay for the DAP involving the deeper acceptor.

15:45

**BREAK**

## Session VI: Characterisation

Session chairs: Gottfried Bauer, Marc Burgelman

**O-VI.1**

16:00

SOLAR CELLS BASED ON CCSVT-GROWN CuGaSe<sub>2</sub> - ABSORBER AND DEVICE PROPERTIES

M. Rusu, S. Wiesner, S. Doka, C.A. Kaufmann, N. Grigorieva\*, Th. Schedel-Niedrig, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Glienicke Str. 100, D-14109 Berlin, Germany, \*Research Institute of Physics, St. Petersburg State University, Ulyanovskaya Str. 1, 198504 St. Petersburg, Russia

ZnO/CdS/CuGaSe<sub>2</sub> solar cells were prepared using CuGaSe<sub>2</sub> (CGSe) polycrystalline thin films deposited by the chemical close-spaced vapour transport (CCSVT) technique. The device photovoltaic properties are investigated with respect to the bulk and surface properties of the CGSe films. The high structural quality of the thin film absorber is shown. The investigation of the optical spectra revealed a red shift of the absorption edge with the increase of the Ga content, as well as an erosion of the distinct structure corresponding to three band-to-band transitions characteristic for CGSe. The CdS/CGSe interface was investigated by means of elastic recoil detection analysis (ERDA). It was found that the CGSe surface composition influences the composition of the CdS buffer prepared by chemical bath deposition (CBD). By adapting the CdS preparation conditions and the [Ga]/[Cu] ratio in the absorber, an efficiency of 8.7% of the solar cells was achieved. The transport mechanism in the dark and under illumination was analysed. For the first time, a thermally activated recombination process in a large temperature region is observed on CGSe-based solar cells. The diode parameters of the best cell at 300 K receive values: ideality factor A = 1.8, saturation current density J<sub>0</sub> = 2.2 x 10<sup>-7</sup> mA/cm<sup>2</sup>, series resistance R<sub>s</sub> = 1.3 W cm<sup>2</sup>, shunt resistance R<sub>sh</sub> = 4.5 kW cm<sup>2</sup>. (The corresponding parameters reported for the best polycrystalline device with an efficiency of 9.5% read A ~ 2.1, J<sub>0</sub> ~ 7 x 10<sup>-7</sup> mA/cm<sup>2</sup>, R<sub>s</sub> ~ 1.4 W cm<sup>2</sup> and R<sub>sh</sub> ~ 1.4 kW cm<sup>2</sup>.)

**O-VI.2**

16:15

## STRUCTURAL TRANSITION DURING DEPOSITION OF CIGS FILMS WITH HIGH GALLIUM CONTENT

K. Sakurai, S. Ishizuka, A. Yamada, K. Matsubara, K. Iwata, P. Fons, T. Kojima, S.Niki, AIST EEL, Tsukuba, 305-8568 Japan, S. Nakamura, Y. Kimura, T. Baba, S. Nakanishi, TUS Elec. Eng., Noda, 278-8510 Japan

Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells have achieved a conversion efficiency of over 19%, the highest among any polycrystalline thin film solar cells. Currently, the best performance is achieved with a Ga composition of x~0.3, where it gives a bandgap of E<sub>g</sub>~1.2eV, lower than the theoretical optimum E<sub>g</sub>~1.3eV (x~0.5). To achieve higher performances, further improvements in the quality of the absorber layers at x > 0.3 are required. We have investigated the structural changes of the CIGS absorbers during the three-stage deposition process, under varied Ga content (x=0.3~1.0), using Spectroscopic Light Scattering (SLS), SIMS, SEM, XRD, EPMA and ICP. The deposition time was about 2 hours for each film. At high Ga contents such as x=1.0 (i.e. CuGaSe<sub>2</sub>), the film structure showed a distinctive two-layered structure at the beginning of stage 2, and abruptly changed to a single layered structure around a specific point, where the SLS profile showed a distinctive inflection. This sudden structural change was done in less than 5 minutes, and was also accompanied by a considerable change in the depth-oriented composition profiles, especially by those of Cu and Na.

**O-VI.3**

16:30

ELECTRONIC TRANSPORT MECHANISMS IN CuGaSe<sub>2</sub>

Susanne Siebentritt, Thorsten Rissom, Martha Lux-Steiner Hahn-Meitner-Institut, Glienicke Str. 100, 14109 Berlin, Germany

The transport and scattering mechanism for majority carriers in CuGaSe<sub>2</sub> is extracted from the temperature dependence of the mobility. The mobility of holes in epitaxial and polycrystalline CuGaSe<sub>2</sub> films has been determined by temperature dependent Hall and conductivity measurements over a wide range of compositions. The results are compared to data from the literature and are modeled according to the various scattering mechanism taking into account improved phonon interaction data and data on the electronic structure. It is shown that acoustical phonon scattering is negligible, while scattering on optical phonons and on charged and neutral defects plays a crucial role around room temperature. At temperatures below 200-250°C hopping conduction becomes dominant. Scattering data and the resulting mobility vs. temperature curves are an important input in solar cell modeling.

O-VI.4 16:45

THE DETERMINATION OF CARRIER MOBILITIES IN CIGS PHOTOVOLTAIC DEVICES USING HIGH FREQUENCY ADMITTANCE MEASUREMENTS

JinWoo Lee and J. David Cohen, Materials Science Institute, University of Oregon, Eugene OR 97403, USA, William N. Shafarman, Institute of Energy Conversion, University of Delaware, Newark DE 19716, USA

Hole mobilities in CIGS are determined through carrier density measurements using the Hall effect, coupled with DC conductivity measurements. This requires the use of co-planar contact sample geometries and insulating substrates. However, mobilities determined in this fashion may not accurately represent the electronic behavior of CIGS incorporated into photovoltaic device structures with sandwich geometry contacts. To obtain carrier mobilities within the CIGS layer in working devices we have developed a new approach using ac admittance measurements utilizing frequencies up to 100MHz. We have been able to clearly identify the dielectric relaxation times in such polycrystalline CIGS devices and, hence, the conductivity within the undepleted portion of the absorber layer itself. The hole carrier densities are then determined using drive-level capacitance profiling (DLCP) at frequencies just below those of the dielectric carrier freeze-out. Such DLCP determined carrier densities are typically quite low: at or below  $1 \times 10^{15} \text{ cm}^{-3}$  for most of the samples studied. Using the above method we have found typical free carrier hole mobilities of  $6 \text{ cm}^2/\text{Vs}$  in polycrystalline CIGS samples with Ga fractions near 30at.%. Such mobilities have been found to exhibit a remarkably small temperature dependence (less than 10%) between 100K and room temperature. In one CIS sample we found a somewhat higher mobility, roughly  $10 \text{ cm}^2/\text{Vs}$  (at 200K). We will discuss the variation of mobilities determined in this fashion for samples of varying grain sizes, and also following the long term exposure of light.

17:00

DISCUSSION II

Rommel Noufi, Lars Stolt, Al Compaan, Shigeru Niki  
Chalcogenide thin film solar cells in 2020

Friday, May 28, 2004

Morning

Session VII: Defects and polycrystallinity

Session chairs: Margret Igalson, J. David Cohen

**O-VII.1** 08:30 -Invited-

ANALYSIS OF CdTe AND CIGS SOLAR CELLS IN RELATION TO MATERIALS ISSUES

**M. Burgelman**, J. Verschraegen, S. Degraeve and P. Nollet, University of Gent, Dept. ELIS, Pietersnieuwstraat 41, 9000 Gent, Belgium

By now, extensive experimental research is available on thin film solar cells based on CdTe and on CIGS, and their electrical and optical behaviour is characterised by a multitude of diverse characterisation techniques. At the same time, numerical simulation programmes have matured and are available to the research community to assist in interpreting these measurements consistently. Once multiple measurements are (more or less) quantitatively described, the numerical simulation can be used to explore the effect of a variation of materials parameter (e.g. the presence or absence of a property, or variation in a range of values) to the final solar cell characteristics. Examples of such analysis for CdTe and CIGS solar cells will be shown. In CdTe cells, much research has been devoted to the activation treatment of the absorber, and to the technology of the back contact. Analysis of ample measurements has evidenced the crucial role of the profile of the (effective) doping density through the device. It will be illustrated in how far reaching this relative simple (but hardly mastered) materials property influences cell characteristics such as roll-over and cross-over of I-V curves, also in dependence on illumination and voltage, conventional and apparent quantum efficiency, and finally fill factor and efficiency. In CIGS cells, the case will be illustrated with the influence of grading of the materials composition (band gap grading), and with the influence of the details of the CIGS electronic surface structure on the I-V curves.

**O-VII.2** 09:00

DEFECT RELATED PHOTOLUMINESCENCE OF EPITAXIAL CuInS<sub>2</sub>

J. Eberhardt, H. Metzner, J. Cieslak, Th. Hahn, U. Reislöhner, A. Dietz, and W. Witthuhn, Institut für Festkörperphysik, Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany, F. Hudert and R. Goldhahn, Institut für Physik, Technische Universität Ilmenau, PF 100565, 98684 Ilmenau, Germany.

Using molecular-beam epitaxy (MBE), CuInS<sub>2</sub> (CIS) films have been grown on 4-inch Si(111) substrates. Composition as well as layer thickness and roughness were determined via Rutherford backscattering (RBS). For a detailed investigation by means of photoluminescence (PL) spectroscopy, samples of different Cu to In ratio were either taken as grown or subjected to post-growth treatments including KCN etching, annealing in air, in-diffusion of Cu, or hydrogen implantation. Chosen samples were processed to solar cells. As typical PL signatures, we observed the following: broad emissions centred at 1.0 and 1.2 eV (signatures #1 and #2, respectively), two PL peaks located at 1.32 and 1.35 eV (#3 and #4), the donor-acceptor (DA) transitions at 1.39 and 1.44 eV (#5 and #6), and a near-band-gap transition at about 1.5 eV (#7). All types of processing reduce emissions #1 and #2. A typical and unique feature of the CIS epitaxial layers is the coexistence of the DA transitions #5 and #6, which occur for either Cu-rich (#5) or In-rich (#6) bulk single-crystalline or polycrystalline CIS material.

**O-VII.3** 09:15

QUASI-FERMI LEVEL SPLITTING AND IDENTIFICATION OF RECOMBINATION LOSSES IN Cu(In,Ga)Se<sub>2</sub> THIN FILMS VERSUS OPTICAL BAND GAP FROM ROOM TEMPERATURE LUMINESCENCE

G.H. Bauer(a), R. Brüggemann(a), S. Tardon(a), S. Vignoli(b), R. Kniese(c), (a)Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany, (b)Lab. PMCN (CNRS UMR), Université Claude Bernard Lyon1, 69622 Villeurbanne Cedex, France, (c)Center for Solar Energy and Hydrogen Research ZSW, 70569 Stuttgart, Germany

Photoluminescence (pl) from Cu(In,Ga)Se<sub>2</sub> films prepared in a pilot line with cell efficiencies of up to 13% has been analyzed for Ga-contents of 0.0-1.0 at AM1-equivalent photon fluxes and 300K. CIGS films were front side CdS-passivated and deposited on glass and on Mo. We translate the pl into the Bose-term of Plancks' generalized law by correcting for spectral absorption and extract the splitting of the quasi-Fermi levels which shows the upper limit for the open circuit voltage of final devices. The spectral absorption of CIGS analyzed by transmission and reflection (integrating sphere) shows for each Ga content non-negligible subgap absorption indicating a substantial combined density of states in the gap at energetics almost independent of Ga-content. At variance with the optical gap the shift of the pl-peak to higher photon energies and the rise of its yield is comparatively weak and accordingly the increase in Fermi level separation is small (32% of the band gap shift for photon energies > 1.4 eV). We discuss our results particularly the departure of the experimental Bose-term from the theoretical one (effective absorption does not equal effective emission) in terms of a two-phase system with different local lifetimes and quasi-Fermi levels of minorities.

**O-VII.4** 09:30 -Invited-

RECENT PROGRESS TOWARD UNDERSTANDING GRAIN BOUNDARIES IN Cu(In,Ga)Se<sub>2</sub>  
**M.J. Romero**, C.-S. Jiang, R. Noufi and M.M. Al-Jassim, National Renewable Energy Laboratory (NREL), 1617 Cole Boulevard, Golden CO 80401-3393, USA

Grain boundaries in Cu(In,Ga)Se<sub>2</sub> (CIGS) are attracting a lot of interest to researchers involved in the progress of solar cells based on these chalcopyrite compounds. The motivation for this effort is their apparent beneficial effects on performance. In addition, better understanding the anomalous behavior observed in Cu(In,Ga)Se<sub>2</sub> can potentially inaugurate the future development of superior electronics and optoelectronics based on the engineering of grain boundaries.

In this contribution, we report on recent studies of CIGS thin films by cathodoluminescence and scanning probe microscopies (SPM), which provide excellent spatial resolution to probe individual boundaries. Among the SPM methods are photon emission spectroscopy based on scanning tunneling microscopy (STM) and scanning Kelvin probe microscopy (SKPM). Cathodoluminescence reveals that grain boundaries are inaccessible for carriers excited at grain interiors and SKPM shows the existence of a hole barrier. The effects of stoichiometry and composition of CIGS, as well as orientation and location of grain boundaries will be presented in detail. Finally, we confront the experimental evidence accumulated over the last years with the theoretical models proposed for such grain boundaries.

**O-VII.5** 10:00 -Invited-

HOW CAN POLYCRYSTALLINE CdTe/CdS OUTPERFORM THEIR SINGLE CRYSTAL ANALOGUES?

**Iris Visoly-Fisher**, Sidney R. Cohen and David Cahen, Weizmann Institute of Science, Rehovot, Israel, Arie Ruzin Dept. of Physical Electronics, Tel Aviv University, Tel Aviv, Israel

Why do certain polycrystalline (PX) solar cells show performance superior to that of corresponding single crystal ones? To understand if cell performance is limited by grain bulk, -surface and/or GBs, we explored combinations of high-resolution mapping of electronic properties of single grain boundaries (GB) and -surfaces in PX p-CdTe/n-CdS solar cells. Combining results from scanning capacitance microscopy (SCM), scanning Kelvin probe microscopy (SKPM), and conductive probe AFM (CP-AFM) and comparing images taken under varying conditions, allowed elimination of topography-related artifacts (especially problematic for the relatively widely used SKPM) and verification of the measured properties.

As expected SCM & SKPM show a hole transport barrier across CdTe GBs, with variation in barrier height between different GBs. BUT, we also find direct evidence (by CP-AFM & SCM) for conduction along these GBs. This means that the regions around the GBs function as extension of the carrier collection volume. This, together with gettering of defects and impurities from the bulk into the GBs, explains the good photovoltaic performance of these PX cells (at the expense of some voltage loss, as is indeed observed). These GB features are induced by the CdCl<sub>2</sub> heat treatment, used for CdTe/ CdS cell manufacture, which is known to improve the cell performance. We will explain the implications of these findings, including differences and similarities with other types of PX cells. We thank USDOE/NREL for partial support (and , within that framework, C.Ferekides and First Solar for solar cells), Veeco for SCM support, S.Richter (TAU) for CP-AFM support and I.Bar-Joseph (WIS) for SCM use.

10:30

**BREAK**

Session chairs: Uwe Rau, Ken Durose

**O-VII.6** 11:00

WHY DO CIGS-BASED SOLAR CELLS HAVE SUPERIOR PERFORMANCE? INSIGHT INTO THE PROPERTIES OF GRAIN BOUNDARIES AND THE SURFACE AS INFLUENCED BY GROWTH DYNAMICS

**R. Noufi**, M.J. Romero, C.-S. Jiang, Y. Yan, J. Abu-shama, and K. Ramanathan, National Renewable Energy Laboratory (NREL), 1617 Cole Blvd., Golden, CO 80401-3393, USA

We first present a model describing the properties of grain boundaries (GBs) and the surface region in CIGS thin films, and then compare the model to grain interiors (GIs). This model is based on consistent results from various scanning probe microscopies, such as the scanning Kelvin probe, micro-cathodoluminescence, scanning tunneling microscopy, and electron microscopy. These tools compare electronic properties of GBs and GIs, as well as 2-dimensional potential distributions on the surface of the film. We also support the model with chemical composition at GBs compared to GIs and show structural differences. The model is based on the existence of a graded Cu-poor defect layer of finite thickness in the surface region and at the GB. The graded Cu deficiency causes an electron-rich (or less p-type) boundary at the surface and around the GB (interface), compared to the GI. The former lowers the valence-band maximum, effectively increasing the bandgap in this region compared to the GI (see refs. below). The net effect is a barrier that repels holes from GBs and the surface region, and a conduit for electrons. The collective results of the model explain the superior performance of the CIGS-based device and may guide 2-dimensional device modeling to predict current-voltage characteristics. [Refs.: Albin et al., *MRS Proc.*, **228**, p.267 (1992); Jaffe et al., *Phys. Rev.* **B27**, 5167 (1983); **B99**, 1882 (1984)].

**O-VIL7** 11:15 -Invited-

EFFICIENCY LIMITS OF CIGS SOLAR CELLS

**J.H. Werner**, Universität Stuttgart, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70563 Stuttgart, Germany

On small areas, solar cells from Cu(In,Ga)Se<sub>2</sub> (CIGS) have reached more than 19 % conversion efficiency; commercial modules with 12 % efficiency are becoming available . Thus, the question arises how high the efficiencies of cells and modules from CIGS may become in future. This contribution discusses how the efficiency of CIGS is limited by i) the radiative lifetime and the finite mobility, ii) the optical properties of CIGS, iii) the present material quality expressed by mobility, diffusion length and doping, iv) electronic inhomogeneity induced by band gap fluctuations and, v) electronic inhomogeneity by charge induced electrostatic fluctuations. It turns out, that world record cells from CIGS are limited by voltage dependent electrostatic charges. The voltage dependent charge is responsible for the ideality factors  $n > 1$  in the current/voltage curve limiting the efficiency of the world best cells to below 20 %. Larger cell efficiencies require a drastic reduction of electrostatic potential fluctuations which are a direct consequence of the polycrystallinity of CIGS.

11:45

DISCUSSION III

David Cahen, Angus Rockett

Are grain boundaries in chalcogenides unique?

12:45

**LUNCH**

Friday, May 28, 2004

Afternoon

14:00

SYMPOSIUM SUMMARY