E-MRS

2014 Spring Meeting Lille, France – May 26th - 30th

SYMPOSIUM A

Thin film chalcogenide photovoltaic materials

Symposium Organizers:

Marika Edoff,Uppsala University

Angstrom Laboratory, Sweden

Alessandro Romeo, University of Verona, Italy

Daniel Abou-Ras, Helmholz Zentrum Berlin, Germany

David Mitzi, IBM T. J. Watson Research Center, New York, USA

Takashi Minemoto, Ritsumeikan University, Shiga, Japan

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PROGRAM VIEW : 2014 Spring
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Symposium : A

Thin film chalcogenide photovoltaic materials

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start at	Subject	Num.
09:00	**OPENING (welcome and various information for the participants)**	
	In situ monitoring : R. Scheer, K. Albe	
09:15	**In-Situ XRD Analysis of the Recrystallization Process in CZTS Nano Particles Synthesized by Hot-Injection** **Authors :** Marco Brandl, Rameez Ahmad, Monica Distaso, Wolfgang Peukert, Rainer Hock **Affiliations :** Chair for Crystallography and Structural Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Staudtstr. 3, 91058 Erlangen, Germany; Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Cauerstr. 4, 91058 Erlangen, Germany **Resume :** Kesterite CZTS is a promising material for thin film solar cell applications. The biggest advantages of this compound lie in the abundancy and non-toxicity of the contained elements. Low temperature hot injection synthesis can provide a economic way to produce CZTS nano particles for application in solution processed solar cells. Powder X-ray diffraction measurements on the as -synthesised particles suggest that the crystal structure is cubic and can be best described as sphalerite-like. This means that the cations in the CZTS are statistically distributed on the cation sites of the crystal lattice rather than well-ordered like in the tetragonal kesterite structure. An in-situ XRD measurement while annealing the particles up to 550° C revealed a recrystallization process that transforms the structure from cubic to tetragonal meaning an ordering of the cations. A systematic study has been performed to link different synthesis conditions to the characteristics of the recrystallization.	A.O1 1
add to my program	**(close full abstract)**	
09:30	**In-situ XRD study of alloyed Cu2ZnSnSe4 – CuInSe2 thin films for solar cells** **Authors :** S. Hartnauer, L. A.M. Wägele, W. Fränzel, R. Scheer **Affiliations :** Martin-Luther-University Halle-Wittenberg, Photovoltaics group **Resume :** We investigate the growth of Cu2ZnSnSe4-CuInSe2 (CZTISe) thin films using a 2-stage (Cu-rich / Cu-free) co-evaporation process under simultaneous application of in-situ angle dispersive XRD and laser light scattering (LLS) systems. Infrared and red LLS is used to determine the thin film growth rate and the stoichiometric point, where the Cu/(Zn+Sn+In) ratio equals unity. We make use of the fact that at elevated substrate temperatures the X-ray diffraction peaks of ZnSe and CZTISe can be distinguished. This is in contrast to XRD measurements at room temperature because the thermal expansion of the CZTISe is significantly larger compared to ZnSe. By varying the contents of indium in CZTISe the lattice constant is changed. Single phase CZTISe is formed in a wide range without any decomposition into separate CZTSe and CISe phases, only at a high In concentration this separation occurs. The formation of ZnSe is significantly inhibited because even with low indium content, we cannot detect any ZnSe with in-situ XRD or Raman-spectroscopy. CZTSe with In also shows different time-resolved PL characteristics. The PL intensity indicates defect states with lifetimes up to microseconds for pure CZTSe layers, whereas this long lifetime is not detected with indium implementation. First solar cells of CZTISe have been prepared and show comparable performance to pure CZTSe.	A.O1 2
add to my program	**(close full abstract)**	

09:45 **Investigation of low temperature Cu(In,Ga)Se_2 multi-step co-evaporation growth on polyimide foil by real-time EDXRD: grain orientation and growth path**
Authors : Dieter Greiner, Roland Mainz, Stephan Brunken, Hengemeh Allaf Navirian, Jakob Lauche, Christian A. Kaufmann, Manuela Klaus, Christof Genzel, Thomas Unold
Affiliations : Helmholtz-Zentrum Berlin f?r Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
Resume : Thin film solar cells with Cu(In,Ga)Se2 (CIGSe) absorbers prepared by co-evaporation reach highest efficiencies even on flexible polymer substrates. The use of flexible polyimide (PI) substrates has advantages for roll-to-roll device fabrication, and PI-based devices are light weight and have a shorter energy pay-back time compared to devices on glass substrates. Commercial PI foils, however, only tolerate temperatures of up to ~420?C, which can lead to a different reaction path during the multi-stage co-evaporation process, a pronounced Ga gradient, and impede the incorporation of copper. To study low temperature CIGSe growth during co-evaporation, we have investigated the formation of crystalline phases and their orientation by real-time energy-dispersive X-ray diffraction (EDXRD) at the synchrotron facility BESSY II using molybdenum-coated PI foils with and without an 8 nm thick NaF precursor layer. A set-up with two detectors provides information about the preferential orientation of the crystalline grains. We see a strong preferential orientation in the In2Se3 layer already in stage 1 if deposition is performed onto the NaF precursor. Apart from the mere presence of a NaF precursor as the decisive factor for oriented growth to occur, the Se flux and Cu-rate have also been identified to impact grain orientation during film growth. Interdependences of the low-temperature growth, sodium supply, Se flux and Cu rate are discussed. A.O1 3

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10:00 **Coffee break**

High-efficiency solar cells and modules : A. Tiwari, M. Paire

10:30 **CIGS PV technology - Current Status and Future Prospects**
Authors : S. Niki1, S. Ishiuka1, Y. Kamikawa1, H. Komaki1, K. Matsubara1, H. Shibata1, A. Yamada1, K. Hara2, A. Masuda2, N. Terada3, T. Sakurai3, K Akimoto3
Affiliations : 1, Research Center for PV Technologies, AIST, Tsukuba Ibaraki, Research Center for PV Technologies, AIST Tosu, Saga, Kagoshima University, Kagoshima, Japan, Tsukuba University, Ibaraki, Japan
Resume : Thin film solar cells based on chalcogenide materials such as CdTe and CIGS have emerged and have been leading thin film solar cell technologies. A few GWs of modules have been produced annually. Chalcogenide solar cells have advantages over other technologies in terms of performance, cost, long term stability, etc. In this presentation, the current status of CIGS solar cell technologies and the improvement in the performance of CIGS solar cells and modules will be first introduced. A significant improvement in solar cell performance has been reported with conversion efficiencies of as high as η=20.8%, though the efficiencies of commercial modules are limited to η=10-13%. The efficiency goal for 2030 is set to be η=30% for small area cells and η=25% for large-size modules, therefore improvement in conversion efficiencies for both cells and modules are required. In order to fill the efficiency gap between small-area cells and commercial modules, the multi-stage evaporation technique has been applied to fabricate the monolithically integrated CIGS submodules. The conversion efficiencies of integrated submodules on 10x10cm2 sodalime glass and flexible ceramics substrates have been improved up to η=16.6% and η=15.9%, respectively. Monolithically-integrated submodules (~2x2 cm2) with efficiencies of as high as η=18.3% have been recently demonstrated, indicating that the CIGS technologies are competitive with respect to the current Si and CdTe technologies in terms of both cost as well as performance. A.O2 1

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11:00 **High efficiency CdTe thin film PV devices grown by MOCVD**
Authors : G. Kartopu*, V. Barrioz, S. D. Hodgson, E. Tedejor, D. Dupin, A.J. Clayton, S.Rugen-Hankey, W.S.M. Brooks, D. A. Lamb and S.J.C. Irvine
Affiliations : Centre for Solar Energy Research (CSER), Glyndŵr University, St Asaph Business Park, St Asaph, LL17 0JD, UK
Resume : CdTe photovoltaic (PV) devices continue to dominate thin film based PV research and manufacturing globally. The current production cost of CdTe PV A.O2 2

modules ($0.68/Wp) coupled with the recently reported world record efficiencies (19.6% for solar cells and 16.1% for modules) are likely to extend this position. Here we report on the relatively high efficiency CdZnS/CdTe PV devices produced using metalorganic chemical vapour deposition (MOCVD) at atmospheric pressure. Optimisation of a post-deposition activation anneal significantly improved the fill factor (FF) and open circuit voltage (Voc) of the devices to around 78% and 788mV, respectively. Additionally, the CdZnS window layer thickness was tuned to improve the short circuit current density (26 mA cm-2) without sacrificing on the FF or Voc. As a result, CdTe solar cells with 16.1% best and 15.4% mean (16 cells) efficiency were obtained, using ITO/glass substrate and evaporated gold back contact of 0.25 cm2. For cells with 2 cm2 area the best efficiency was 13.6%. We also report on the preparation of 5 × 7.5 cm2 CdTe micro-module devices with several series connected 2 cm2 cells, resulting in an initial ~10% efficiency. Low-cost, non-vacuum deposited back contact materials (carbon/silver bilayer via screen printing and/or inkjet printing) were also evaluated on the micro-module devices.

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11:15

Analysis of Cu(In,Ga)Se2 solar cells with high efficiencies up to 20.8 %

Authors : Philip Jackson, Dimitrios Hariskos, Roland Wuerz, Oliver Kiowski, Wolfram Witte, Wolfram Hempel, Axel Eicke, Wiltraud Wischmann, Michael Powalla

Affiliations : Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg (ZSW), Industriestrasse 6, 70565 Stuttgart, Germany

Resume : We report on a new world record efficiency of 20.8 % for Cu(In,Ga) Se2 (CIGS) thin film solar cells. In order to better understand the characteristic features of such high efficiency cells, we analyse them with various methods such as scanning electron microscopy SEM, X-ray fluorescence XRF, X-ray photoelectron spectroscopy XPS, secondary ion / neutral mass spectrometry SIMS / SNMS, and capacitance voltage measurements CV. We describe experimental measures that we have taken to increase the efficiencies significantly, and correlate the experimental settings with the analytical findings. Apart from the analysis of individual cells with very high efficiencies, we also have brought together our data from several thousand CIGS cells with high efficiencies in order to provide for a broad statistical basis for our correlation attempts. One important observation of this investigation is the compositional shift for such high efficiency CIGS solar cells beyond well established boundaries. Our results suggest that we have gained new experimental parameters and new flexibility in traditional parameters. They also suggest that there is a very realistic potential for CIGS solar cell efficiencies to exceed 21 %.

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11:30

Very high efficiency Cu(In,Ga)Se2-based thin-film solar cells grown with a single-stage process

Authors : Erik Wallin (1), Olle Lundberg (1), Ulf Malm (1), Tobias Jarmar (1), Ralf Hunger (2), Marika Edoff (1,3), Lars Stolt (1,2)

Affiliations : 1. Solibro Research AB, Uppsala, Sweden 2. Solibro GmbH, Bitterfeld-Wolfen, Germany 3. Uppsala University, Uppsala, Sweden

Resume : For all reported Cu(In,Ga)Se2-based (CIGS) thin-film solar cells reaching an efficiency of 20% or above, the CIGS layer has been grown with a so called three-stage process or variants thereof (multi-stage). Presented here are results showing that also with a so called single-stage CIGS process, very high efficiencies can be achieved. Single cell efficiencies of 20% (20.1% from internal measurement) for a single cell and 18.7% for a mini-module (aperture area, externally confirmed) are demonstrated. From a production point of view this single-stage process has some advantages compared to a normal three-stage process. Relatively short deposition times (12 minutes) and moderate substrate temperatures (~530ºC) can be used. Also only one evaporation chamber/zone is needed. From material and electrical characterization quite some differences between this single-stage process and the classical three-stage process are observed. The CIGS grains of the material presented here are in the order of 1 µm and with a strong preferred (112) orientation. The Ga/(Ga+In) profile has a strong back-contact grading but without the typical “notch” close to the CIGS surface, normally seen for three-stage CIGS. With these and additional results from electrical and material characterization it is shown that there is a large window of CIGS features and process parameters that can result in very high efficiency CIGS solar cells.

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11:45 **DISCUSSION SESSION: High-efficiency solar cells (M. Edoff, D. Abou-Ras)**

12:15 **Lunch break**

CIGS: Na+K : S. Niki, T. Unold

14:00 **Influence of alkali and metallic impurities in Cu(In,Ga)Se2 thin film solar cells**

Authors : Patrick Reinhard1, Fabian Pianezzi1, Benjamin Bissig1, Debora Keller1,2, Adrian Chirila3, Shiro Nishiwaki1, Rolf Erni2, Stephan Buecheler1, Ayodhya N. Tiwari1

Affiliations : 1 Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland; 2 Electron Microscopy Center, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland

Resume : Thin film solar cells based on the chalcopyrite Cu(In,Ga)Se2 absorber material have recently shown light-to-power conversion efficiencies as high as polycrystalline silicon. A crucial aspect that has al-lowed such progress over the years is the adequate control and addition of impurities throughout the absorber layer during or after growth. Whereas doping with alkali elements such as sodium and potas-sium typically shows a positive impact on the device properties, the presence of metallic impurities (Fe, Cr, Ni) diffusing from the substrate leads to the formation of detrimental defects. The different behaviour of Ni and Cr on the formation of deep defects and therefore electronic properties of the final device is also presented. In this work we discuss the role of these impurities in CIGS absorbers grown by a low-temperature co-evaporation process, and compare it to some extent to high temperature grown CIGS. Recent devel-opments in our group showed that the alkali elements Na and K have to be differentiated. Their addi-tion during or after the absorber growth can lead to significant differences on the absorber surface and bulk properties. Finally, prospects of further efficiency improvements and cost reduction drivers will be presented.

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14:30 **Atom probe tomography investigation of the influence of CIGSe deposition process on Na distribution**

Authors : F. Couzinie-Devy (a,b), E. Cadel (a), N. Barreau (b), L. Arzel (b), P. Pareige (a)

Affiliations : (a) Groupe de Physique des Matériaux (GPM), UMR 6634 CNRS, Avenue de l'Université BP 12, 76801 Saint Etienne de Rouvray, France (b) Institut des Matériaux Jean Rouxel (IMN), UMR 6502 CNRS, 2 rue de la Houssinière BP 32229, 44322 Nantes cedex 3, France

Resume : Atom probe tomography (APT) is the only nano-scale-sensitive analytic tool which combines high elemental detection limits and accurate spatial resolution. In the case of polycrystalline layers, it allows separate investigations of grain boundaries and grains interior. In the present contribution, APT has been used to investigate atomic scale chemistry of polycrystalline Cu(In,Ga)Se2 (CIGSe) thin films grown by either 3-stage process or 2-stage [1]. In the case of the 3-stage process, several samples have been investigated, corresponding to the following process key steps: - (In,Ga)2Se3 at the end of the 1st stage - layers corresponding to [Cu]/[III] ratio of 0.3 and 0.7 (during the 2nd stage) - Cu-rich CIGSe (at the end of the 2nd stage) - completed CIGSe (end of the 3rd stage). From the analysis, 3D atomic volumes have been reconstructed and grains boundaries composition profiles drawn providing information about elements distribution at the GBs and within the grains. Changes in sodium distribution during the 3-stage process growth are highlighted and compared to the CIGSe deposited by the 2-stage process. From these results, the influence of copper-deficient phases on sodium distribution within the CIGSe layer is discussed. [1] J.Kessler, J.Schöldström and L.Stolt, "Rapid Cu(In,Ga)Se2 growth using "End Point Detection", Proc. 28th IEEE PVSC, Anchorage (2000) 509.

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14:45 **How DC-sputtering conditions during the Mo back contact deposition influence the absorber properties in Cu(In,Ga)Se2-based thin film solar cells** A.O3 3

Authors : T. Lepetit (1), D. Mangin (2), E. Gautron (1), M. Tomassini (1), S. Harel (1), L. Arzel (1), N. Barreau (1)

Affiliations : (1) Institut des Mat?riaux Jean Rouxel (IMN), UMR 6502 CNRS 2 rue de la Houssini?re BP 32229, 44322 Nantes cedex 3, France ; (2) Institut Jean Lamour, UMR 7198 CNRS - Universit? de Lorraine Parc de Saurupt, CS 50840, 54011 NANCY cedex, France

Resume : We studied the influence of molybdenum synthesis conditions on the photovoltaic performance of Cu(In,Ga)Se2-based (CIGS) solar cell. DC-sputtered back contact Mo layers were deposited on soda-lime glass (SLG) under different argon pressure conditions. CIGS absorber was then deposited simultaneously on these SLG/Mo, following the 3-stage process. Although these devices have similar photovoltaic performance at room temperature (16% efficiency without MgF2 coating), J(V,T) measurements show that activation energies and thus recombination paths are different. To find a material origin to such differences, SIMS profiles were carried out and revealed different alkaline (Na, K) distributions. Transmission electron microscope was used to investigate the Mo/CIGS interface but no clear difference was found on the MoSe2 interlayer. However, EDS profiling along single grains shows that the 100 nm region below the CIGS/CdS interface is different, depending on the Mo properties. The Ga content x=[Ga]/([Ga] [In]) appears higher in this region with increasing sputtering pressure. These results suggest that alkali supplied through the Mo influence the composition of the CIGS grown during the 3rd stage of the process, which impacts the electronic transport.

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15:00

On the origin of optimum sodium content in low-temperature CIGSe

Authors : S. Puttnins a/b, J. Neerken c, M.S. Hammer c, I.Riedel c, T. Unold d, F. Daume a, A. Rahm a, A.Braun a and M. Grundmann b

Affiliations : a Solarion AG, Pereser Hoehe 1, 04442 Zwenkau, Germany; b Institut für Experimentelle Physik II, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany; c Laboratory for Chalcogenide Photovoltaics, Energy and Semiconductor Research Laboratory, Univ. Oldenburg, 26111 Oldenburg, Germany; d Helmholtz Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin, Germany;

Resume : Sodium is known to play a key role for the optimization of Cu(In,Ga) Se2 (CIGSe) solar cells performance for more than 20 years. However, no conclusive model has been proposed for the origin of optimal sodium content in respect to solar cell efficiency. In this study we varied the sodium content of low-temperature grown CIGSe absorbers. We observed a strong influence of the sodium content on the properties of the bare CIGSe layers and corresponding solar cells. Based on the results obtained from time-resolved photoluminescence measurements, temperature and illumination dependent current-voltage profiling, temperature and voltage dependent quantum efficiency measurements and space charge spectroscopy we will show that high sodium contents cause a simultaneous increase of the net doping concentration and the defect density. While enhanced doping of the CIGSe layer has positive effect on the fill factor and open-circuit voltage, the increased defect concentrations have detrimental effect for the solar cell performance. Thus, the identification of the optimal sodium content is of major importance for the further improvement of the CIGSe absorber deposition process.

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15:15

Effect of potassium fluoride post deposition treatment on chalcopyrite solar cell absorbers

Authors : Paul Pistor, Dieter Greiner, Christian A. Kaufmann, Iver Lauermann, Jakob Lauche, Stephan Brunken, Wolfram Calvet, Alexander Steigert, Mihaela Gorgoi, Frank Hergert, Reiner Klenk, Thomas Unold, Martha-C. Lux-Steiner

Affiliations : Helmholtz-Zentrum Berlin, Bosch Solar CISTech GmbH

Resume : Alkaline metals play a key role for the performance of chalcopyrite solar cells. While the effect of sodium on doping concentration, crystal growth and In-Ga interdiffusion has been well established in the past, new findings have drawn much attention to the influence of adding potassium to the absorber during growth or after the absorber deposition. The current world record device has recently been achieved by Chirila et al. by a combined NaF and KF post deposition treatment (PDT) of Cu(In,Ga)Se2-absorbers prepared by co-evaporation on polyimide foils. Their experiments showed evidence for a severe Cu and small Ga depletion of the absorber surface after the PDT. In this contribution we follow this line and investigate the influence of a KF PDT on solar cell parameters of different chalcopyrite absorbers on glass, especially the effect on open circuit voltage and fill factor. The effect on the doping concentration is investigated by capacitance based spectroscopy. We are able to confirm the Cu depletion at the surface of the absorbers after a PDT with potassium fluoride by XPS with laboratory X-ray sources. In addition, we find

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the KF PDT responsible for changes in the band structure of the chalcopyrite absorbers in the surface near region while the bulk band gap seems to remain unchanged. We are furthermore able to detect changes in the elemental profiles before and after KF PDT with the use of hard X-ray XPS (HIKE/HAXPES @ BESSY II synchrotron).

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15:30 **Potassium and sodium post-deposition treatments of low-temperature evaporated Cu(In,Ga)Se2 thin films for high efficiency solar cells: a comparative study**

Authors : Patrick Reinhard1, Fabian Pianezzi1, Benjamin Bissig1, Debora Keller1,2, Max Döbeli3, Harald Hagendorfer1, Shiro Nishiwaki1, Rolf Erni2, Stephan Buecheler1, Ayodhya N. Tiwari1

Affiliations : 1Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland; 2Electron Microscopy Center, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland; 3Ion Beam Physics, ETH Zürich – Swiss Federal Institute of Technology, Schafmattstrasse 20, CH-8093 Zürich, Switzerland;

Resume : Alkali-doping of Cu(In,Ga)Se2 (CIGS) absorber layers is a key aspect for the processing of high efficiency thin film solar cells. Sodium addition has long been known for its positive effect on electronic properties of the absorber layer, whereas the addition of other alkali metals was believed to be less beneficial. Our group however recently introduced a KF post-deposition treatment (KF PDT) of the absorber layer grown at low temperature, allowing the processing of a 20.4% efficiency flexible device. In contrast to NaF PDT, the KF PDT leads to a significant chemical modification of the surface of the CIGS layer which allows the formation of an improved junction with the CdS buffer layer. Additionally a removal of Na atoms from the bulk of the film is observed when the KF PDT is done after the NaF PDT. In this study, we address in more details the differences between NaF PDT and KF PDT in view of their influence on the absorber surface and bulk composition. CIGS thin films are grown onto polyimide substrates by a low-temperature multistage co-evaporation process and subjected to various combinations of NaF and/or KF PDT. Electron microscopy (SEM, TEM), secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), and various element analysis methods (RBS, ERDA, ICP-MS) are used to carefully compare the effects of both PDTs onto the absorbers microstructure. A.O3 6

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15:45 **Coffee break**

Poster 1: Absorber growth and properties - CIGSSe and CdTe : M. Edoff, V. Bermudez

16:00 **Effects of substrate on CuInGaSe2 thin film solar cells**

Authors : Chae-Woong Kim12, Ki-hwan Kim12, Jin Hyeok Kim2, Chaehwan Jeong1,*

Affiliations : 1 Energy & Applied Optics Division, Solar Cell Research Team, Korea Institute of Industrial Technology (KITECH), Gwangju 500-480, South Korea 2 Department of Material Science and Engineering, Chonnam National University, Gwangju, 500-757, South Korea

Resume : Cu(In1-x,Gax)Se2 (CIGS) thin films with direct band gap and high absorption coefficient are one of the promising absorbing materials for solar cells. CIGS solar cells on flexible substrate offer the advantage to be lightweight and low cost. That can be used for several applications, especially in building (BIPV) and transport (TIPV), where stainless steel is already commercially used but polyimide is not been reported. It might be thermal stability of poly imide films is limited, therefore solar cells on poly imide substrate have processed at substrate temperature below 500°C. In this work, we have developed the flexible CIGS solar cells on the stainless steel and polyimide substrate by 3-stage co-evaporation method. And then compare with each samples. The deposited films are basically characterized by scanning electron microscope (SEM), Raman spectroscopy, X-ray diffraction (XRD), X-ray Fluorescence (XRF), Time-Resolved Photoluminescence (TRPL), Glow Discharge-Optical Emission Spectrometer (GD-OES). And then, to complete the solar cells, a buffer layer of 50nm CdS was deposited by chemical bath deposition (CBD), followed by a double layer (high resistivity/low resistivity) of RF sputtered i-ZnO/Al-ZnO. The Al front contacts were deposited by thermal evaporator. No anti-reflection (AR) A.P1 1 coating was applied. The photovoltaic properties of small area solar cells were characterized with I-V and quantum efficiency measurements.

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16:00

Selenization of printed Cu-In-Se alloy nanopowder layers for fabrication of CuInSe2 thin films solar cells

Authors : Armin E. Zaghi1,3,6, Marie Buffière2,3,6, Guy Brammertz4,5, Nick Lenaers1,3,6, Marc Meuris4,5, Jef Poortmans2,3, Jef Vleugels1

Affiliations : 1-Department of Metallurgy and Materials Engineering (MTM), KU Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium 2-Department of Electrical Engineering (ESAT), KU Leuven, Kasteelpark Arenberg 10, 3001 Heverlee, Belgium 3-imec – partner in Solliance, Kapeldreef 75, 3001 Heverlee, Belgium 4-imec division IMOMEC – partner of Solliance, Wetenschapspark 1, 3590 Diepenbeek, Belgium 5-Institute for Material Research (IMO) Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium 6-SIM vzw, Technologiepark 935 - 9052 Zwijnaarde, Belgium

Resume : One of the promising low cost and non-vacuum approaches for the fabrication of semiconductor CIGS (CuIn1-xGaxSe2) thin film absorbers is the printing of precursor materials followed by a sintering/selenization process. The conditions of the selenization process such as temperature, duration, and selenium vapor pressure have a large effect on the morphological and electronic properties of the final CIGS film. In this study, the effect of the selenization parameters on printed mechanically synthesized CuInSe alloy nanopowder layers was investigated. A 1-2μm thick layer of CuInSe alloy nanopowder was deposited on a Mo coated glass substrate by means of the doctor blade coating technique of a nanopowder based precursor suspension. The selenization process was performed by a home-made rapid thermal processing (RTP) furnace, consisting of a graphite box in a quartz tube filled with argon gas, heated by infrared lamps. The selenization furnace has two RTP heating zones for independent temperature control of the different ends of the graphite box, holding respectively the selenium source and the coated deposit. The temperature of the selenium source was kept constant around 390-400C° during the selenization to provide a constant supply of selenium vapor. Different temperature profiles were applied to the CIS deposits. A two steps selenization process at 250°C for 10min followed by rapid heating to 520°C for 15 min was found to result in better grain growth and sintering of the CuInSe2 layer compared to a single step selenization at 520°C for 20 min. The solar cell fabricated by the two steps selenization had efficiency of 4.8% and a fill factor of 44%, while the device fabricated by single step selenization had efficiency of 2.7% and fill factor of 33%.

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16:00

Gallium diffusion treatment of chalcopyrite absorber layers

Authors : Nick Lenaers [1 2 3], Marie Buffiere [2 3 4], Guy Brammertz [2 5 6], Armin Zaghi [1 2 3], Marc Meuris [2 5 6], Jef Poortmans [2 4], Jef Vleugels [1]

Affiliations : 1. Department of Metallurgy and Materials Engineering – MTM, KU Leuven, Kasteelpark Arenberg 44, BE-3001 Heverlee, Belgium 2. imec – partner in Solliance, vzw, Kapeldreef 75, BE-3001 Heverlee, Belgium 3. SIM vzw, Technologiepark 935, BE-9052 Zwijnaarde, Belgium 4. Department of Electrical Engineering – ESAT, Kasteelpark Arenberg 10, BE-3001 Heverlee, Belgium 5. imec division IMOMEC – partner in Solliance, Wetenschapspark 1, BE-3590 Diepenbeek, Belgium 6. Institute for Materials Research (IMO), Hasselt University, Wetenschapspark 1, BE 3590 Diepenbeek, Belgium

Resume : Copper indium diselenide (CISe) has a band gap of 1.0 eV, which is below the optimal value for solar cells. This band gap can be increased by alloying gallium to form copper indium gallium diselenide (CIGS), with a typical gallium-to-indium ratio of around 0.3. During the conventional co-evaporation process, an optimal efficiency is achieved by controlling the gallium flux to reach a saddle-like depth distribution of gallium. However, when using a non-vacuum process consisting of the selenization of a precursor layer, this distribution is impeded by the tendency of gallium to accrue near the back contact. In this study, the effect of an additional gallium treatment on CIS layers is investigated and compared with the effect of aluminium, which can also be used as a dopant for CIS. Different concentration of gallium and aluminium solutions were prepared and drop-casted on the surface of a co-evaporated CIS layer. Despite their lower solubility, sulphate salts were used instead of nitrates because the latter degraded the layer too much. The layers were treated under inert atmosphere at different temperatures in order to achieve a front-graded doping distribution by diffusion. After removal of the salt residue, the effect of this treatment was assessed by photolumiscence spectroscopy. Solar cells were made from the best absorbers using a CdS buffer layer and an aluminium doped ZnO front contact. These results were related to the doping distribution.

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16:00

Comparing the effects of potassium and sodium co-evaporation during Cu(In,Ga)Se2 growth in a low temperature multi-stage process

Authors : Benjamin Bissig, Fabian Pianezzi, Patrick Reinhard, Shiro Nishiwaki, Stephan Buecheler, Ayodhya N. Tiwari

Affiliations : Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland

Resume : It is well known, that incorporation of typically 0.1 at% of Na into the Cu(In,Ga)Se2 (CIGS) absorber layer is necessary to reach highly efficient solar cells. When CIGS is grown on soda-lime glass Na - and in lower amounts also K - naturally diffuse from the substrate into the CIGS layer. When producing the solar cell with a low temperature process on flexible polyimide substrate the alkaline metals have to be introduced actively. As it was observed previously that K and Na influence the elemental interdiffusion in CIGS, especially for the low temperature process care has to be taken at which deposition stage they are introduced. To investigate the influence of K and Na on the CIGS properties we introduced them during different intervals of the 3rd deposition stage. By means of admittance spectroscopy we com-pare the defect spectra for the cases when either K or Na is present during different time intervals of the deposition. Further we correlate the defect spectra with temperature dependent IV and EQE meas-urements. The influence on material composition is discussed with respect to secondary ion mass spectroscopy (SIMS) measurements.

A.P15

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16:00

4-Amino-1,2,4-Triazole: Playing a key role in the chemical deposition of Cu-In-Ga metal layers for photovoltaic applications

Authors : Ulrich Berner (1)(2), Markus Widenmeyer (1), Patrick Engler (1), Philip Dale (2)

Affiliations : (1) Robert Bosch GmbH, Corporate Sector Research and Advance Engineering, Applied Research Chemistry (CR/ARC), Robert Bosch Platz 1, 70839 Gerlingen-Schillerhöhe, Germany; E-mail: ulrich.berner@de.bosch.com; (2) Université du Luxembourg, Laboratory for Energy Materials, 41, rue du Brill, L-4422 Belvaux, Luxembourg

Resume : Liquid film processing of CIGSe absorber layers has the potential to lower production costs significantly due to the absence of energy expensive vacuum steps, and higher material utilization in comparison to vacuum based approaches. We previously described a new solution based approach via a metallic intermediate with virtually no carbon residues leading to devices with a maximum of 11% power conversion efficiency. The used ink system is based on metal carboxylates in a mixture of a nitrogen containing base and an alcohol. Processing of uniform metallic layers with this ink system is possible up to a temperature of 160°C. Above, the film segregates because of the low melting points and high surface tensions of liquid indium. With 4-amino-1,2,4-triazole (4ATA), we found an additive that can stabilize the metallic layer between 160°C and the arrival of Se from the gas phase at temperatures above 300°C leading to metal selenides. For the stabilization we propose a mechanism based on a complex of Cu^{2+} and 4ATA. The additive itself has four nitrogen atoms that are available as possible coordination sites. Thus 4ATA can bridge between two or more metal cations yielding bi- or multi-nuclear species. We propose that in our ink system, polynuclear clusters are stabilizing the film through a network of bridges. Concerning organic residues, the complex has been shown to decompose completely during the selenization. Elemental analyses of the absorber layer reveal carbon residues ≤0.1%.

A.P16

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16:00

Effect of selenium content of CuInSex alloy nanopowder precursors on recrystallization of printed CIS absorber layers during selenization heat treatment

Authors : Armin E. Zaghi1,3,8, Marie Buffière2,3,8, Jaseok Koo4, Guy Brammertz6,7, Maria Batuk5, Joke Hadermann5, Woo Kyoung Kim4, Marc Meuris6,7, Jef Poortmans2,3, Jef Vleugels1

Affiliations : 1-Department of Metallurgy and Materials Engineering (MTM), KU Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium 2-Department of Electrical Engineering (ESAT), KU Leuven, Kasteelpark Arenberg 10, 3001 Heverlee, Belgium 3-imec – partner in Solliance, Kapeldreef 75, 3001 Heverlee, Belgium 4-School of Chemical Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan-si, Gyeongbuk, 712-749 Korea 5-Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium 6-imec division IMOMEC – partner of Solliance, Wetenschapspark 1, 3590 Diepenbeek, Belgium 7-Institute for Material

A.P17

Research (IMO) Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium 8-SIM vzw, Technologiepark 935 - 9052 Zwijnaarde, Belgium

Resume : Polycrystalline CuInSe2 (CISe) semiconductor is an efficient light absorber material for thin films solar cell technology. Printing is one of the promising low cost and non-vacuum approaches for fabrication of thin film solar cells. This requires preparation of a precursor material with controlled composition and contamination, which can be transformed to a dense polycrystalline CuInSe2 layer via a heat treatment in ambient selenium atmosphere (Selenization). In this study, the effect in the selenium content of high purity mechanically synthesized CuInSex (X: 0.5, 1, 1.5, 2) alloy precursors on the recrystallization of the CuInSe2 phase during the selenization process is investigated. The nanostructure and phase variation of CuInSex nanopowders were investigated by different characterization techniques such as XRD, SEM, TEM and EDX. 1-2 µm thick CuInSex nanopowder layers were coated on Mo-coated glass substrates via doctor blade coating of nanopowder dispersions. The recrystallization process of CuInSex coatings into the CuInSe2 phase during selenization in selenium vapor was investigated via in-situ XRD up to 600˚C. The CuInSex precursors with lower selenium content (X: 0.5, 1) showed a more pronounced phase conversion to CuInSe2 phase compared to the CuInSex precursors with higher selenium content (X: 1.5, 2). Moreover, SEM micrographs after selenization revealed that the CuInSex (X: 0.5, 1) precursor resulted in a denser polycrystalline CuInSe2 semiconductor layer with larger crystals. This could be due to a more intensive atomic interdiffusion within the CuInSex (X: 0.5, 1) precursor system and the formation of intermediate fluxing phases such as CuSe during selenization.

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16:00

Anomalous phenomena related to Na diffusion in Cu(In,Ga)Se2 thin films

Authors : FABIAN WILANGOWSKI1, JENS BASTEK1, ROLAND WUERZ2, J. ALBERT3, NICO STOLWIJK1

Affiliations : 1Universitaet Muenster, Institut für Materialphysik, 48149 Muenster, 2Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg, 70565 Stuttgart, 3Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin

Resume : Na is an important impurity in solar-grade Cu(In,Ga)Se2 (CIGSe) as it improves the light-conversion efficiency in photovoltaic applications. In standard fabrication processes running near 600 °C, Na diffuses from the soda-lime glass substrate through the Mo contact layer into the active zone of the solar-cell structure. However, dedicated Na diffusion experiments are difficult to perform, which has led to a lack of reliable data and to poor knowledge about the diffusion mechanism. We investigated Na diffusion with the radiotracer technique using a Na-22 source deposited at the CIGSe front surface. It is remarkable that the depth profiles resulting after diffusion in a lamp oven and subsequent sectioning by ion-beam sputtering exhibit peculiar shapes. Obviously, the observed behaviour is strongly affected by the absorption of Na in glass substrate and layer interfaces. Our findings point to the simultaneous occurrence of a fast and a slowly moving Na species. It is shown that the diffusivity assessed for the slow Na species is in fair agreement with the redistribution of Na-23 during the diffusion of natural Fe into CIGSe, as deduced from SIMS depth profiling. A.P18

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16:00

Controlled bandgap CuIn1-xGaxS0.1Se0.9 (0.10 ≤ x ≤ 0.65) solar cells from electrodeposited precursors

Authors : João C. Malaquias, Dominik M. Berg, Jan Sendler, William N. Shafarman, Marc Steichen, Phillip J. Dale

Affiliations : University of Luxembourg, Laboratory for Energy Materials ; University of Delaware, Institute of Energy Conversion ; University of Luxembourg, Laboratory for Photovoltaics ; University of Delaware, Institute of Energy Conversion ; University of Luxembourg, Laboratory for Energy Materials ; University of Luxembourg, Laboratory for Energy Materials

Resume : Cu(In,Ga)Se2 is an absorber material for thin film solar cells, with a record efficiency of 20.8 % when grown by co-evaporation methods. Electrodeposition and annealing (EDA) of metal precursors is a low-cost and easily scalable alternative to co-evaporation methods. A hindering factor of EDA is the difficulty of incorporating Ga into the precursor, due to the strong Hydrogen Evolution Reaction in water during the electrodeposition step. In previous work, we countered this issue by depositing from a Deep Eutectic Solvent, accurately controlling the Ga/(Ga+In) (Ga/III) ratio (0.1 ≤ Ga/III ≤ 0.9). Another limitation is the phase segregation during annealing, resulting in a CuGaSe2/CuInSe2 system. To avoid segregation we employed a three-step A.P19 annealing, introducing a limited quantity of sulphur (S/(S+Se) = 0.1) in the absorber's surface. In this work, absorbers and solar cells originating from electrodeposited precursors with 0.10 ≤ Ga/III ≤ 0.65 are characterised. X-ray diffraction results clearly show the CIGS 112 peak shifts to higher angles with increasing Ga content, in agreement with the expected composition values. Additionally, these results show identical incorporation of sulphur in all layers. Photoluminescence and I-V measurements corroborate the XRD results. To the best of our knowledge, it is the first time that controlled incorporation of Ga, over a large Ga/III range, is achieved for EDA processed CIGSSe. A maximum solar cell efficiency of 9.8% was obtained.

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16:00

Formation of dense CIGS layers from hybrid, carbon-free inks

Authors : Ruben Dierick, Pieter Arickx, Boris Capon, Christophe Detavernier, Zeger Hens

Affiliations : Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium, Coating and Contacting of Nanostructures, Ghent University,Krijgslaan 281-S1, B-9000 Ghent, Belgium

Resume : Cost reduction is a strong incentive to replace vacuum-based processing by solution-based processing in the formation of thin film chalcogenide compounds. In the case of $Cu(In,Ga)(S,Se)_2$ (CIGS), research has shown that this approach is catching up in terms of efficiency with conventional methods. In particular, methods involving colloidal nanocrystals as precursors are promising. Here, binary or(qua)ternary colloidal nanocrystals of the CIGS system are synthesized directly in solution, and a range of post-synthetic techniques exists to fine-tune the ink to enhance the deposition and transformation behavior. In this study, we present inks optimized for transformation towards dense CIGS layers with large crystallite sizes. To reduce the risk of contamination of the final layer to a minimum, treatments are discussed to strip off the surface organic ligands, and replace them by carbon-free alternatives. Moreover, using a mixture of nanocrystals and metal complexes, we demonstrate that an optimal morphology of the as-deposited layer is reached due to the surplus of stabilization the complex provides to the nanocrystals during the drying process. To conclude, the selenization and incorporation of these CIGS layers in working solar cells is addressed.

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16:00

Deposition of CISe and CIGSe layers by hybrid approach

Authors : P. Reyes*, T. Painchaud, L. Arzel, N. Barreau and S. Velumani

Affiliations : Department of Electrical Engineering (SEES),CINVESTAV- I.P.N., Av. IPN #2508 Col. San Pedro Zacatenco, Mexico D.F., Mexico ; Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France

Resume : A key problem for the future of the CuIn(Ga)Se2 (CI(G)Se) solar cell technology is the up-scaling of laboratory techniques while maintaining low cost-high conversion efficiency. A new approach of a two-steps hybrid deposition method using low cost/non-vacuum and high efficiency/vacuum techniques has been elected for this work.We studied the CI(G)Se based solar cells prepared by spray pyrolysis(1st stage)and co-evaporation(2ndand3rd stage)deposition techniques.XRD, Raman spectroscopy and EDS shown that In2Se3 and (In,Ga) 2Se3 sprayed films were obtained. Comparisons with co-evaporated precursors show same γ-phase with different preferential orientation and smaller grains for sprayed films. From all the results, it can be concluded that CI(G)Se thin film preparation was achieved from spray pyrolyzed In2Se3 and (In,Ga)2Se3 precursors using the hybrid method with efficiencies of 5% and 6.5% for CISe and CIGSe solar cells, respectively. This denotes the applicability of hybrid approach for photovoltaic devices fabrication. However, structural and morphological comparison of CISe and CIGSe layers shown inhomogeneity in CIGSe, characterized by a bilayer within film(small grains on bottom, large on top).This could be due to the introduction of gallium and oxygen(possibly incorporated during non-vacuum precursor deposition)forming gallium oxides, acting as a barrier for crystal growth. In agreement with this, the experiments were designed in order to identify and overcome this barrier.

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16:00

Fabrication of CuIn(S,Se)2 and Cu2ZnSnS4 Thin Films by Spray Pyrolysis Method and Their Photovoltaic Properties

Authors : Wilman Septina, Shigeru Ikeda, Yoshihito Kawasaki, Nguyen Thi Hiep, Takashi Harada, Michio Matsumura

A.P1 12

Affiliations : Research Center for Solar Energy Chemistry, Osaka University

Resume : Chalcogenide compounds such as Cu(In,Ga)(S,Se)2 and Cu2ZnSn (S,Se)4 have been studied as candidates for low-cost solar cells owing to their high absorption coefficient and suitable band gaps energy in the range of 1.0 eV to 1.5 eV. Moreover, the compounds can be prepared as polycrystalline, which allows flexibility in the fabrication methods. Spray pyrolysis is an attractive method because large-area films with good uniformity can be prepared at low cost. In addition, composition of the films could be controlled effectively by adjusting the concentration of the constituents in the precursor solution. In the present study, selenium-rich CuIn(S,Se)2 thin films were fabricated by selenization of spray deposited CuInS2 precursor film. Inclusion of Na to the precursor film enchanced the crystallinity of the CuIn(S,Se)2 film. The maximum conversion efficiency of the device with such film in the solar cell structure of Mo/CuIn(S,Se)2/CdS/ZnO/ITO/Al was 4.35% (JSC: 30.18 mA cm-2, VOC: 0.36 V, FF: 0.41). Dependences of structural properties of the fabricated films to their photovoltaic performances will be discussed. We also attempted to fabricate Cu2ZnSnS4 by sulfurization of sprayed sulfide precursor. XRD and Raman spectrum of the sulfurized film confirmed that the fabricated film was Cu2ZnSnS4 without any detectable secondary phase. Photoelectrochemical characterization confirmed the p-type characteristic of the film. The preliminary photovoltaic properties also will be presented.

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16:00

Characterization of solution-processed chalcopyrite thin film solar cells

Authors : Ji Eun Kim(1), Yunae Cho(1), Dong-Wook Kim*(1), Se Jin Park(2), Sung Hwan Moon(2), and Byoung Koun Min(2)

Affiliations : (1)Department of Physics, Ewha Womans University, Seoul 120-750, Korea; (2)Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

Resume : Low-cost and printable chalcopyrite thin-film solar cells were fabricated by a precursor solution-based coating method. In-depth characterizations and analyses of the solution-processed chalcopyrite thin film solar cells can provide us valuable information regarding further enhencement of the energy conversion efficiency. In this work, we investigated temperature-dependent photovoltaic and electrical characteristics of Cu(InxGa1−x)S2 (CIGS) and Cu(InxGa1−x)(S1-ySey)2 (CIGSSe) cells, exhibiting energy conversion efficiencies over 8%. The transport and admittance spectra of the two cells showed distinctive features, due to difference in microstructures, band-gap energiers, and dominant trap states. Such differences can influence the collection efficiency of the photo-generated carriers.

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16:00

Doping of the Polycrystalline CdTe-Absorber in CdTe/CdS Solar Cells

Authors : Ch. Heisler, M. Salge, H. Hempel, U. Reislöhner, C. Ronning, W. Wesch

Affiliations : Friedrich-Schiller-Universität Jena, Physikalisch-Astronomische Fakultät, Institut für Festkörperphysik, Max-Wien-Platz 1, 07743 Jena, Germany

Resume : One of the major challenges to enhance the efficiency of CdTe/CdS solar cells is to increase the shallow doping of the CdTe absorber far beyond the typical level of 10^{14}cm^{-3}. While the doping of CdTe single crystals and MBE grown epitaxial layers have been studied in detail in literature, we investigated the doping of polycrystalline CdTe layers as part of a typical CdTe/CdS solar cell in standard superstrate configuration. We introduced additional dopants either during growth by means of our in-situ doping chamber or by subsequent implantation doping and completed the samples to solar cells. The implantations were performed at room temperature after growth as well as after the activation process in $CdCl_2$-atmosphere. The ions' stopping ranges were calculated with SRIM2008 and the ion fluencies of the multiple implantations were adjusted to generate almost homogeneous implantation profiles with concentrations ranging from 10^{15} to 10^{18}cm^{-3}. The doping was primarily characterized by photoluminescence, admittance spectroscopy and CV-profiling. The results and the doping efficiency in polycrystalline CdTe will be discussed with respect to the activation process and the peculiarities of the superstrate technology.

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16:00

Investigation of the effect of potassium on Cu(In,Ga)Se2 solar cells

Authors : Anke Lämmle, Roland Würz, Michael Powalla

Affiliations : Zentrum für Sonnenernergie- und Wasserstoff-Forschung - Baden Württemberg (ZSW-BW)

Resume : Latest results show that potassium (K) has a beneficial effect on CIGS solar cells. To investigate the influence of K on the CIGS layer, Alkali-free Cu(In,Ga)Se2 (CIGS) absorbers were grown on Mo coated alumina substrates. One was doped with potassium (K) by a potassium fluoride (KF) precursor layer and another by a KF post deposition treatment (PDT) after the CIGS growth. A

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third sample was kept untreated as reference. The CIGS composition and the K concentration were observed by secondary neutral mass spectroscopy and secondary ion mass spectroscopy, respectively. We show that K can be successfully incorporated into the CIGS layer by both processes. The CIGS composition of the KF-precursor sample shows a stronger GGI profile. By analysing the samples with scanning electron microscopy we observed smaller CIGS grains for the KF-precursor sample compared to the K-free reference. IV-measurements oft the KF-PDT and the KF-precursor sample show a rel. increase in the efficiency η of 27% and 28%, respectively. The external quantum efficiency measurements of the KF-precursor sample show an increased absorption in the infrared region. Capacitance-Voltage measurements reveal an increase in the net doping concentration of both samples treated with K. We assume that the enhancement is caused by passivation of grain boundaries and donor-like defects, as previously demonstrated for Na.

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16:00

CuInSe2 semiconductor formation by laser annealing

Authors : Helene J. Meadows, David Regesch, Maxime Thevenin, Jan Sendler, Thomas Schuler, Sudhajit Misra, Brian J. Simonds, Mike A. Scarpulla, Viktor Gerliz, Levent Guetay, Phillip J. Dale

Affiliations : Laboratory for Energy Materials, University of Luxembourg, Belvaux, Luxembourg; Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg; Materials Science and Engineering, University of Utah, Salt Lake City, Utah, USA; Electrical and Computer Engineering, University of Utah, Salt Lake City, Utah, USA; Laboratory for Chalcogenide Photovoltaics, University of Oldenburg, Oldenburg, Germany

Resume : A common fabrication method for CuInSe2 (CISe) absorber layers involves 2-stages: precursor deposition followed by annealing. Electrodeposition of precursors offers advantages over vacuum deposition techniques, being at ambient pressure and temperature, and highly resource efficient. A high temperature annealing step is required to form absorber layers suitable for completion into photovoltaic devices. Replacing furnace with laser annealing reduces the duration of this step by 2-3 orders of magnitude. However past work shows it is problematic, yielding defective absorber layers with poor optoelectronic properties. We show how scanning a 1064 nm Nd:YAG laser beam over an electrodeposited CISe precursor promotes reactions, stimulates grain growth and improves optoelectronic properties. For the first time, 1 s dwell time is proved to be sufficient to produce an absorber layer which gave 1.6 % power conversion efficiency in a final solid state device. Finite element modelling indicates that rapid annealing is possible as a result of the high maximum film temperature. However, device efficiency is limited by the inhomogeneity inherent to this precursor type, and the Gaussian laser beam profile. Deviations in the incident flux on the precursor affects the reactions taking place; evidenced by the spatially inhomogeneous Cu-Se plates on the absorber surface and fluctuations in the photoluminescence (PL) yield. Eliminating these variations is expected to improve device performance.

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16:00

Influence of the indium/gallium gradients on the Cu(In,Ga)Se2 devices deposited by the co-evaporation without recrystallization

Authors : Tomasz Drobiazg, Ludovic Arzel, Paweł Zabierowski, Nicolas Barreau

Affiliations : Faculty of Physics, Warsaw University of Technology, Koszykowa 75, PL 00-662 Warsaw, Poland, Institut des Matériaux Jean Rouxel (IMN)—UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière B.P. 32229, 44322 Nantes Cedex 3 France; Institut des Matériaux Jean Rouxel (IMN)—UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière B.P. 32229, 44322 Nantes Cedex 3 France; Faculty of Physics, Warsaw University of Technology, Koszykowa 75, PL 00-662 Warsaw, Poland; Institut des Matériaux Jean Rouxel (IMN)—UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière B.P. 32229, 44322 Nantes Cedex 3 France

Resume : In the laboratory scale, cells based on Cu(In,Ga)Se2 grown by the 3-stage process reach the best performance because of high VOC-JSC combination. One of the reasons for that could be the V-shaped gradient of Ga to In atomic ratio throughout the CIGSe layer, which results from large differences in diffusion coefficients of In and Ga. The location of the lowest Ga-content in the CIGSe (i.e. Ga notch), also corresponds to the Cu-poor to Cu-rich transition during the 2nd stage. Since this transition is associated to the phenomenon of recrystallization, the arising question is whether the high VOC-JSC combination is effectively inherent to the V-shaped gradient or to the recrystallization. In our work we attempt to eliminate the influence of the recrystallization to exclusively study the influence of Ga/In gradients. Our approach was to co-evaporate samples by the one-step process with different

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gradients by the continuous modification of In and Ga fluxes during the deposition and keeping constant that of Cu such that its ratio to group III elements was 0.9. With this method, we could obtain a set of CIGSe layers either free of gradient, with linear gradient (i.e. no notch) or V-shaped gradient with notch at different distance from the CIGSe surface. The cells prepared from these layers have been characterized electrically and the first results indicate that samples with gradients exhibit better JSC and slightly lower VOC than the samples without gradients but optimized band gap.

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16:00 **Cu(In,Ga)(S,Se)2 solar cells from salt solution by non-vacuum processing**

Authors : Erik Ahlswede, Ines Klugius, Thomas Schnabel

Affiliations : Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung ZSW

Resume : There has been an increasing interest in developing Cu(In,Ga)Se2 solar cells from vacuum-free processing routes in order to save equipment and process costs. Typically either inks from nanoparticle precursors or so called true solutions are deposited on Mo coated substrates and selenized in a subsequent step. True solutions offer the advantage of simple ink preparation and use of easily available commercial metal salts, but often have restrictions in cell efficiencies due to undesired residues that are necessary to adjust the viscosity of the ink. In an earlier work based on the approach of Kaelin et al. (efficiency of 6.7 % [1]), we encountered huge carbon-rich bottom layers underneath the active absorber film [2]. In this paper we discuss two different approaches based on metal salts using either dimethylsulfoxide or propanediol as solvents and the influence of thiourea on ink and cell properties: Typically less carbon residues are present and the cell voltage can be increased significantly. Solar cells with efficiencies of up to 7.2 % could be demonstrated by this promising and simple non-vacuum approach. [1] Kaelin et al., Thin Solid Films 460, 486 (2005). [2] Haug et al., Thin Solid Films 519, 7464 (2011).

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16:00 **Oxidation of In2Se3 and (In,Ga)2Se3 precursor layers and its effect on the CISe and CIGSe based solar cells**

Authors : P. Reyes*, T. Painchaud, T. Lepetit, S. Harel, L. Arzel, N. Barreau and S. Velumani

Affiliations : Department of Electrical Engineering (SEES),CINVESTAV- I.P.N., Av. IPN #2508 Col. San Pedro Zacatenco, Mexico D.F., Mexico ; Institut des Matériaux Jean Rouxel (IMN)-UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

Resume : The present study investigates the effects of oxidation on In2Se3 and (In,Ga)2Se3 precursors films and the consequences on the properties of CISe and CIGSe films prepared with these precursors and its respective solar cells.The In2Se3 and (In,Ga)2Se3 films were grown using i)chemical spray pyrolysis (non-vacuum) and ii)co-evaporation (vacuum).Precursors prepared by co-evaporation were thermally oxidized at 300ºC in open-air atmosphere for 1h and 24h.The precursors prepared by spray were not subjected to additional oxidation but the one that is produced during the deposition itself. Both type of precursors prepared by i and ii were used to perform the 2nd and 3rd stage of the so called three-stage co-evaporation process. XPS results show not only the presence of sodium on the oxidized precursors but also a strong relation between the content of sodium and oxygen: the more (less) oxygen, the more (less) sodium. This strongly suggests a catalytic effect between sodium and oxygen on the In2Se3 and (In,Ga)2Se3 surface. The electrical characterizations of the co-evaporated CIGSe solar cells using the oxidized precursors show an important improvement in fill factor from 71% to 74% at 1h oxidation with efficiencies up to ~15% meanwhile no significant improvement in CISe solar cells with oxidized precursor were observed. This suggests that oxygen in the precursor, in right amount, could help to improve the performance of CIGSe devices prepared by three-stage process.

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16:00 **CuInSe2 based solar cells prepared by selenization of chemical bath deposited In2S3/CuxS stacks**

Authors : S. Lugo1, Y. Sanchez2, N. Neuschitzer2, H. Xie2, C. Insignares-Cuello2, V. Izquierdo-Roca2, Y. Peña1, E. Saucedo2

Affiliations : 1. Universidad Autonoma de Nuevo Leon, UANL, Fac. de Ciencias Quimicas, Av. Universidad S/N Ciudad Universitaria San Nicolas de Los Garza Nuevo Leon, C.P. 66451, Mexico. 2. Catalonia Institute for Energy Research (IREC), Jardins de les dones de negre 1, 08930 Sant Adria del Besos-Barcelona, Spain.

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Resume : CuInSe2 (CISe) photovoltaic grade thin films are usually grown by expensive vacuum based methods or chemical routes that require highly toxic precursors. In this work, we present the synthesis of CISe absorbers by a simple chemical bath deposition (CBD) route reporting a champion cell with 2.3% conversion efficiency. In a first step, In2S3/CuxS stack were deposited as precursors by CBD onto Mo-coated soda lime glass substrates, using respectively thioacetamide and N-N'-dimethylthiourea as S source. After, the CISe thin films were synthesized by the In2S3/CuxS precursor's selenization at 450 ºC. Varying the growth time of each precursor layer, we study the impact of the cationic composition in the range 0.80≤Cu/In≤1.24. The obtained films were characterized by X-ray diffraction (XRD), Raman Spectroscopy and Scanning Electron Microscopy (SEM). The tetragonal chalcopyrite structure of CISe was identified by XRD and Raman, confirming that all the S was replaced by Se. SEM images shows a compact and homogeneous film and by cross-section the thickness was estimated around 700 nm. With these absorbers we prepare devices, and the parameters of the champion cell were a Voc of 369 mV, Jsc of 13.698 mA/cm2, FF of 45.7 % and efficiency of 2.3 %. To our knowledge, this is the first working CISe solar cell deposited by CBD. We will discuss the impact of the Cu/In ratio on the optoelectronic parameters of the solar cells, and the future perspective o this cost effective technology.

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16:00 **Study on the role of oxygen during CdTe film growth by CSS and activation of junction in CdTe/CdS solar cells**

Authors : E. Regalado-Pérez, X. Mathew

Affiliations : Instituto de Energías Renovables, Universidad Nacional Autónoma de México

Resume : In this work we report our studies on the influence of oxygen on the properties of CdTe films grown by close spaced sublimation (CSS), and the variation of net hole concentration with the amount of oxygen in the vapor chloride treatment ambient. Motivation of this work was to investigate how the presence of oxygen during film growth influences the interfusion of S and Te across the junction and consequently formation of a ternary alloy at the interface. The CdS and CdTe layers were grown by chemical bath deposition (CBD) and CSS, respectively. The films were characterized extensively for morphological and opto-electronic properties. The grain size showed a very marked dependence on the amount of oxygen in the CSS chamber. The fabricated cells were investigated using J-V, C-V and EQE measurements. Overall, higher efficiencies and greater uniformity of the devices were obtained for samples processed with a higher content of oxygen. It was observed that the amount of oxygen during activation process determines the net hole concentration in CdTe near the back contact, which ultimately seems to saturate around 6×10ˆ15 cm ˆ-3 for the condition of 50% oxygen in the vapor chloride treatment ambient. In general it was observed that the hole concentration reduces by two orders of magnitude from the region near back contact to CdTe/CdS interface. The cross-over of dark and light current in devices annealed in the absence of oxygen is correlated with the diffusion of Cu from the back contact. NA-ND vs. W (depletion width) profile of the junction showed that the impurity concentration in the depletion region is not uniform, displaying a characteristic U-shape. This non-uniformity can be due to factors such as diffusion of Te and S or the presence of other elements such as diffused Cu from back contact. We have observed a relation between the presence of oxygen in treatment chamber with the doping concentration at the back contact region. The results will be discussed along with SIMS data on elements across the film and junction area. Acknowledgements: This work is part of the projects CeMIE-Sol, and SENER-CONACyT 117891.

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add to my program **(close full abstract)**

16:00 **Radiative recombination mechanisms in CdTe thin films**

Authors : S. Vatavu 1,2, S. Bakhshi 1, S. Collins 1, V. Palekis 1, C. Rotaru 2, and C. Ferekides 1

Affiliations : 1 Department of Electrical Engineering, University of South Florida, 4202 East Fowler Ave, Tampa, FL 33620, USA; 2 Faculty of Physics and Engineering, Moldova State University, 60 A. Mateevici str., Chisinau, MD-2009, MOLDOVA.

Resume : The investigation of the defects and their role in cadmium telluride is a key issue in improving the performance of CdTe based thin film solar cells. CdTe thin films have been deposited onto alumina substrates by the Elemental Vapor Transport technique. As-deposited CdTe thin films deposited under a wide range of Cd/Te vapor ratios (0.35 to 2.0) have been investigated by low temperature photoluminescence (PL). Temperature dependent PL experiments have been carried out in 15-130K temperature range by use of a spectrophotometric system based on SPEX500m monochromator. 488, 514.5

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and 632.8 nm lasers have been used for the excitation of luminescence. The PL spectra covers the whole range characteristic for CdTe from 0.8 to 1.6 eV. Depending of the ratio the PL bands exhibit a distinctive behavior. Free and bound exciton annihilation is seen in the 1.598-1.585 eV for all ratios but their contribution to the band is different. 1.547 eV band (1.00 ratio) is not shifting as the Cd/Te vapor ratio varies to its extremities, on the contrary the PL band in the 1.45-1.52 eV region, a complex one, having well evidentiated peculiarities has its peak intensity shifted towards lower energies as the Cd/Te vapor ratio increases up to 2.0 and remains the same as for a ratio of 1.00. This evolution is determined by the contribution to a specific transition of the CdTe native defects. A comparison study of the radiative recombination mechanisms for the EVT films and CdTe single crystals is given.

add to my program **(close full abstract)**

16:00 **Formation of CuInSe2 from CuSe and InSe binary compounds by wet process**

Authors : Hyungmin Lee, Hyunsoo Kim, Dong-seob Jeong, Hyeonwook Park, Chinho Park*

Affiliations : School of Chemical Engineering, Yeungnam University, Republic of Korea

Resume : The chalcopyrite CuInSe2 (CIS) was used as an absorber layer for CuInSe2/CdS hetero-junction solar cell performance. CIS have direct band gap (1.04 eV) and high absorption coefficient (10^5 cm^-1) of the order for photons with energies above 1 eV. In this study, CIS was synthesized from binary compound of CuCl and selenium powder using alcohols as solvent. CIS thin film was prepared by mixing powders of CuSe and InSe binary phase and heat treatment. The binary precursors such as CuSe, InSe and In2Se3 were synthesized using facile chemical route from suitable resources at different stoichiometric ratios. And then, high-quality CIS absorption layer was formed by using three binary compounds. The properties of CIS films were studied and characterized, systemically. The structural property was determined by using X-ray Diffraction, optical property of CIS films was measured by photoluminescence (PL) and UV-Vis, and the surface morphology of the films was recorded by Scanning Electron Microscope. Finally, the composition of CIS films was informed by using Energy Dispersive X-ray Analysis (EDX) technique. This work was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation (No. 20133030011330) and the Human Resources Development Program (No. 20104010100580) Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. A.P1 23

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16:00 **Influence of hollow cathode plasma activation on the growth of Cu(In,Ga)Se2 thin films**

Authors : Roland Wuerz1, Friedrich Kessler1, Henry Morgner2, Stefan Saager2

Affiliations : 1) Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg (ZSW), Stuttgart 2) Fraunhofer-Institut f?r Elektronenstrahl- und Plasmatechnik (FEP), Dresden

Resume : When growing Cu(In,Ga)Se2 (CIGS) absorber layers for CIGS thin-film solar cells on polyimide film, the maximum substrate temperature is limited to 450?C-500?C compared to about 600?C process temperature on glass substrates. Crystallization of CIGS grains thus needs to be optimized e.g. by prolonging the process time. This option may be feasible in the lab but not in industrial application. Plasma activation is another way to enhance the crystallization process during CIGS layer growth at low substrate temperatures. A special hollow cathode arc discharge source has been developed at FEP for CIGS plasma activation [1]. The hollow cathode plasma source was integrated into a roll-to-roll CIGS pilot line at ZSW to improve the CIGS growth process by activation of all evaporated species such as Cu, In, Ga and Se over a web width of 30 cm. The CIGS layers were grown on polyimide film in a low temperature inline multi-stage CIGS process. We observe that the plasma activation modifies the growth behavior of the CIGS layer. The Cu content of the CIGS layer (CGI = [Cu]/([In] [Ga]) increases with increasing plasma intensity, whereas In and Ga contents decrease, the integral GGI = [Ga]/([Ga] [In]) is nearly constant, and the deposition rate increases by about 2 %. With increasing plasma intensity the GGI profile becomes more flat which is an indicator for improved interdiffusion of In and Ga in the presence of a plasma. Hence the performance of CIGS solar cells is directly correlated to the plasma discharge current. The cell efficiency could be increased from 10.0 % to 11.0 % by plasma activation using a medium discharge current of 50 A. A.P1 24

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16:00 **Fabrication of CIGSSe Thin Film Solar Cell by Non-Vacuum Process**

Authors : Jaehong Kim1, Yang Hwi Cho1, Yeokwon Yoon1, Kye Ung Lee1, Kyung Min Ahn1, Yong Min Jung2, Kwang Bok Kim2, Tae Seok Lee1

Affiliations : 1. GS Caltex R&D Center, Daejeon, 350-380, Korea; 2. Kumho Electronic, Inc R&D Center, Gwangju, 546-12, Korea

Resume : Conventional CIGS absorber layers are formed by vacuum deposition processes such as sputtering or co-evaporation, which requires high production cost due to expensive vacuum equipments and high energy & material consumption. Several research groups in US, EU and Korea are working on the development of low cost non-vacuum techniques to substitute the vacuum-based process of CIGS absorber layer formation. In this study the non-vacuum process for CIGSSe absorber layer formation consists of five steps: (1) CIGS precursor synthesis, (2) CIGS ink coating & drying, (3) pre-annealing for carbon residue removal, (4) selenization annealing for CIGSSe recrystallization, and (5) sulfurization annealing for bandgap engineering near absorber layer surface. Among them, appropriate coating method and annealing process are the most important factors to achieve a dense and uniform absorber layer, and eventually high cell efficiency. High precision slot die coater was used to coat a CIGS ink on sub-module sized (30x30 cm2) Mo/SLG substrates. The coating parameters (ex. ink flow rate, die moving speed, etc.) and the drying condition were optimized in order to avoid micro-crack generation on CIGS coating film and to achieve the film thickness uniformity. In addition, the effect of annealing parameters (temperature, time and atmosphere) on carbon residue removal and CIGSSe recrystallizaton rate was investigated. After the process optimization of coating and annealing, the cell efficiency was dramatically increased. A.P1 25

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16:00 **Influences of Precursors, pH, and Annealing Temperature on CIGS Thin Films prepared by Solution-based Deposition Methods**

Authors : Yujie Zhang, Ho Young Jun, Si Ok Ryu*

Affiliations : School of Chemical Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan 712-749, South Korea

Resume : The polycrystalline Cu(In,Ga)Se2 absorber for the thin film solar cells were synthesized on the glass substrates using a modified spray process and a continuous flow reactor process at low temperature conditions. The as-deposited Cu(In,Ga)Se2 thin films were annealed under nitrogen atmospheric condition without additional selenization. In order to investigate the effect of precursors on the physical properties of the film, the Cu(In,Ga)Se2 thin films were prepared by both solution-based processes with varying the precursor of solutions and then they were characterized for morphological, structural, and optical properties. For the effect of pH on the physical properties of the film, the Cu(In,Ga)Se2 thin films were prepared by the solution-based deposition process with varying the pH of solution in the range of 10~11. The properties of the prepared thin films were affected by the experimental conditions such as the precursor, the pH, and the annealing temperature. Based on the XRD measurements, the optimum conditions for annealing and pH to synthesize the CIGS thin films were 200°C and 9.45, respectively. The crystalline structure of the film annealed at 200°C was in good agreement with the tetragonal structure in the reference. In addition to XRD, SEM, UV-vis, and XPS were employed to study the influence of the experimental variables on the physical properties of the films. A.P1 26

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16:00 **A Study of the Chelating Effect in Hybrid Ink Process for CuInSe2 (CIS) Thin Film Solar Cell**

Authors : Ara Cho, SeJin Ahn, Jae Ho Yun, Jihye Gwak, Seung Kyu Ahn, Young-Joo Eo, Jun Sik Cho, Ju Hyung Park, Jin Su Yu, Kihwan Kim, Keeshik Shin, Kyunghoon Yoon

Affiliations : Photovoltaic Laboratory, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon, 305-343, Korea

Resume : We have tried hybrid ink process as a new beneficial concept to form CIGS thin films. Apart from known particle-based and solution-based non-vacuum processes, a chelating agent is used with nanoparticles and ion precursor solution in hybrid ink process. Moreover, the chelating agent used in the hybrid ink has its own viscosity so it can be used as a binder. In this study, we used monoethanolamine (MEA) was used as a chelating agent to bind the In precursor and the Cu-Se nanoparticles, which exhibited better performance than a different alkanolamine, triethanolamine (TEA). MEA easily forms a complex with Cu in the Cu-Se nanoparticles. To observe the effect of chelating agent in the hybrid ink, Cu-rich Cu-Se nanoparticles were washed by MEA to reduce the Cu content in the nanoparticles through the formation of a Cu-MEA complex. As A.P1 27 a result, CuInSe2 thin films were obtained at a fabrication temperature that was 80 °C lower than usual (530 °C). The fabricated devices made at 450 °C with hybrid inks of washed Cu-Se or normally synthesized Cu-Se exhibited conversion efficiencies of 5.04% and 1.04%, respectively, which confirmed that the Cu-MEA complex affected the performance of CIS solar cells that were produced with the hybrid ink process.

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16:00 **A Method to Supply Extra Se by Sputtering For CIGS Absorber Fabrication Without Post Selenization**

Authors : Chia-Hao Hsu, Chih-Huang Lai

Affiliations : National Tsing Hua University

Resume : Sputtering from a single quaternary Cu(In,Ga)Se2 (CIGS) target or multiple binary targets has been proposed to fabricate CIGS absorber. However, a post selenization is usually required in these processes, because sufficient Se supply (which means over stoichiometry) is hard to be realized by sputtering. Increasing Se content by sputtering from a Se target is unpractical due to its low melting point. In this work, we investigate a new method to supply Se for CIGS fabrication by sputtering from an Sb2Se3 target. CIGS absorber was deposited by sputtering from a quaternary CIGS target and an Sb2Se3 target at elevated substrate temperature without post-selenization. Two approaches, cosputtering and sequential sputtering of the targets, were investigated. Sb2Se3 is easily evaporated, forming vapor of SbSe and Se2. Therefore, at the process temperature of CIGS around 500-550℃, high Se flux can be provided by sputtering of the Sb2Se3 target without modification of Cu/III or Ga/In+Ga ratio and with no detectable Sb residue, as examined by XRF. SEM analysis revealed increased grain size with higher Se flux. Although little variation of Se/M ratio were observed, significant increase in photoluminescence intensity were observed when the Se flux was increased. The conversion efficiency was improved by 4% (absolute) by providing higher Se flux. A.P1 28

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16:00 **Effect of CdCl2 vapor phase pretreatment annealing on the properties of CSS CdS and CdTe/CdS thin film solar cells**

Authors : Nicolae Spalatu, Jaan Hiie, Vello Valdna, Malle Krunks, Mihail Caraman, Valdek Mikli, Natalia Maticiuc

Affiliations : Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia; Physics Department, Moldova State University, A. Mateevici str. 60, Chisinau MD 2009, Republic of Moldova

Resume : A comparative study was carried out for three treatment variations: high-temperature anneal in N2 atmosphere, high-temperature anneal followed by CdCl2 vapour phase treatment, and CdCl2 vapour phase treatment, which had two different kinds of CdS window layer: as-deposited CdS and CdCl2 air-annealed CdS. The heat treatment reactor permitted independent control over the CdCl2 source temperature, hence CdCl2 vapor pressure at the CdS and CdTe surfaces. Modeling of the thermal and mass transfer for the reactor geometry shows that at temperature of 420o C in air, the CdCl2 vapor pressure over the CdTe surface is 10 mtorr. CdCl2 air -annealing of CdS window layer promote the recrystallization of the film, resulting in large and closely packed grains and making it resistant to Te diffusion. X -ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy show improved crystallographic properties of the CdTe layer and reduced CdS/CdTe interdiffusion when the CdCl2 air-annealed CdS window layer is used prior to CdTe deposition. The effects of CdCl2 vapor phase pretreatment and post treatment conditions on interdiffusion, grain coalescence and device operation are presented. The CdTe/CdS solar cells fabricated using an anneal at 400oC in N2 atmosphere and CdCl2 air-annealed CdS window layer prior to the CdCl2 vapor phase treatment exhibited improved electrical characteristics, compared to cells fabricated with no preanneal step, yielding an high efficiency. A.P1 29

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16:00 **Breath of CIGS: Introducing a post oxygen atmosphere to reduce effects of Se deficiency in one-step sputtered Cu(In1-xGax)Se2 solar cells**

Authors : Tzu-Ying Lin, Jeff Lin, Wei-hao Ho, Chia-Hao Hsu, Shih-Yuan Wei, Jung-Wei Liao, and Chih-Huang Lai *

Affiliations : Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan A.P1 30

Resume : One-step sputtering process using a quaternary Cu(In1-xGax)Se2 (CIGS) target has been demonstrated a promising approach to fabricate the chalcopyrite CIGS system. However, one of the main issues of this one-step sputtered CIGS layer is the highly deficiency of Se, which could result in Se vacancies acting as the origin of related defects during the electron-hole recombination and then significantly reduces the efficiency. In this work, we successfully reduce the side effect of Se deficiency by introducing an oxygen atmosphere after sputtering the CIGS layer. We first deposited an amorphous NaF layer on top of a Mo-coated subtract, followed by the deposition of the CIGS layer. After deposition, we put the samples in a 1 atom oxygen atmosphere at room temperature for varied time periods. The resulted composition of the CIGS layer was probed using the high resolution hyper probe field emission electron probe microanalysis (FE-EPMA). We find that with increasing the exposure time period of oxygen atmosphere, both contents of oxygen and sodium increases. Since the diffusion rates of both sodium and oxygen at room temperature are relatively low, the increased both contents suggest the promoted diffusion rates of both sodium and oxygen by the large difference between the electron affinity of sodium and that of oxide, behaving like breath of the CIGS layer. The increased content of oxygen then eases the side-effect of Se deficiency. In summary, by introducing a post-oxygen atmosphere at room temperature, we reduce the side effects of deficiency of Se in the one-step sputtered CIGS layer, yielding the enhancement in efficiency over 3%.

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16:00

Selenization of In/Cu-multilayer stacks - An investigation of the phase formation processes

Authors : M. Oertel, C. Ronning

Affiliations : Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Helmholtzweg 3, 07743 Jena

Resume : We present the results of our investigations of the phase reactions during the selenization of thin dc-sputtered In/Cu-multilayer stacks in a high vacuum chamber at temperatures between 260°C and 340°C. This aims to get a defined structure of an In-selenide- and a Cu-selenide-layer as the origin for an interdiffusion to form the $CuInSe_2$-absorber-layer. The chronological evolution of the phases at constant temperatures and the influence of the temperature and the selenium vapour flux on the formation reactions are discussed. The investigations were done by ex-situ analysis of the different selenized samples with X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS). By controlling the starting conditions of the $CuInSe_2$-forming interdiffusion reaction we get high quality absorbers without any gallium, which reach total area efficiencies of 11.8% (13.0% active area) in a $CuInSe_2$-thin-film solar cell.

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16:00

Low Temperature Formation of CuInSe2 Solarcell Absorbers by an All Printed Two Species Nanoparticulate Se + Cu In Precursor

Authors : Stefan A. Möckel1, Tobias Wernicke1, Matthias Arzig1, Philipp Köder1, Marco Brandl2, Rameez Ahmad3, Monica Distaso3, Wolfgang Peukert3, Rainer Hock2, Peter J. Wellmann1

Affiliations : 1) Department of Materials Science, Chair of Materials for Electronics and Energy Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany; 2) Chair for Crystallography and Structural Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Staudtstr. 3, 91058 Erlangen, Germany; 3) Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Cauerstr. 4, 91058 Erlangen, Germany;

Resume : In the last years a lot of research was performed on different printing techniques like deposition either from solution or from nanoparticle dispersions. In the field of nanoparticles one has to distinguish between two types of nanoparticles. One type consists of nanoparticles with well formed chalcopyrite phase, and the other type consists of different precursor phase particles, taking advantage of the effect of recrystallization during annealing. Therefore in the present work an all printed nanoparticulate precursor containing two species of nanoparticles was used. Metallic Cu In nanoparticles were mixed with an excess of elemental Se nanoparticles, dispersed and deposited by doctor blading. In-situ characterization was performed by dynamic scanning calorimetry and in situ x-ray diffraction. In addition termination reactions were carried out and the samples were characterised using Raman, ex situ XRD and scanning electron microscopy. Thereby a complete reaction of Cu In nanoparticles with the elemental selenium nanoparticles was observed below 340°C. The samples for ex situ measurements were annealed up to 550°C in a semi closed graphite box without additional selenium supply. EDX characterization showed a loss of selenium during annealing while the selenium content of the annealed samples still exceeds the stoichiometric composition of the chalcopyrite phase. The data show the high potential of nanoparticulate precursor systems to reduce process temperatures and costs.

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16:00

Activation of CdTe-based thin films with Zinc Chloride

Authors : C. Drost, B. Siepchen, B. Späth, V. Krishnakumar, C. Kraft, T. Modes (2), O. Zywitzki (2)

Affiliations : CTF-Solar GmbH, Manfred von Ardenne Ring 20 F, 01099 Dresden, Germany; (2) Fraunhofer Institute for Electron Beam and Plasma Technology FEP, Winterbergstrasse 28, 01277 Dresden, Germany

Resume : The manufacturing of CdTe-based thin film modules comprises an activation which turned out to be inevitable for a significant enhancement of the solar cell performance. CdCl2 is commonly used as a flux reagent for this activation process. Because of its toxicity, there is high demand for a replacement of CdCl2 with less hazardous chlorine-containing compounds. Recent studies have shown that ZnCl2 may be a suitable substitute. The activation with ZnCl2 is difficult in order to get results comparable to the standard process. We observed pronounced generation of pinholes during the heating of ZnCl2-coated substrates as well as formation of insoluble Zn-based residuals on the samples after activation. The aqueous ZnCl2-containing film is deposited via sponge roller technology on CSS generated CdS/CdTe layers prior to heat treatment with activation parameters comparable to the CdCl2 process. The back contact is generated by NP-etching and deposition of a sputtered standard Au layer. A series of solar cells, which have been activated either with ZnCl2 or CdCl2 for comparison, have been prepared and analyzed. The analysis was performed using IV- and CV measurements, high resolution scanning electron microscopy, high quality cross section preparation by ion polishing, electron beam induced current and quantum efficiency.

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16:00

Fabrication and characterization of homogeneous CIGSSe2 thin films solar cells by multi-step method

Authors : Sung-Min Youn 1, Jin Hyeok Kim 2, Chaehwan Jeong1*

Affiliations : 1. Applied Optic & Energy Research Group, Korea Institute of Industrial Technology, Gwangju 500-480, South Korea 2. Department of Material Science and Engineering, Chonnam National University, Gwangju, 500-757, South Korea

Resume : Cu(In,Ga)(S,Se)2 (CIGSSe2) absorber layer has been an intensive candidate of high quality thin film solar cells. It is one of major methods to use sputter and rapid thermal process(RTP) in which selenization occurs. In this work, metallic precursor(Cu3Ga/In) was deposited onto Mo/soda-lime glass (SLG)by using sputtering system and then multi-step annealing process was used to adjust Ga grading for single phase CIGSSe2 thin films. Multi-step annealing consisted of (1)pre-annealing, (2)selenization by Se vapor, (3)post-annealing in Ar atmosphere and (4)sulfurization by H2S. The 1st and 2nd step but only led grain growth of metallic precursor, but also was attributed to selenization. The 3rd step showed reaction of Ga and CIS layer so that Ga-homogeneous CIGSe2 absorber layer was made. 4th step formed CIGSSe2 to grade energy band gap of surface. And then, to complete the solar cells, a buffer layer of 50nm CdS was deposited by chemical bath deposition (CBD), followed by a double layer (high resistivity/low resistivity) of RF sputtered i-ZnO/Al-ZnO. The Al front contacts were deposited by thermal evaporator. The deposited films are basically characterized by scanning electron microscope (SEM), Raman spectroscopy, X-ray diffraction (XRD).

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16:00

Effects of CuSe precursor layers on the properties of CIGS thin film solar cells fabricated by one-step sputtering

Authors : Tae-Won Kim, Jae-Cheol park, Seung-Hyoun Lee, Seong-Jae Boo, Ho-sung Kim

Affiliations : Applied Optics & Energy R&D Group Korea Institute of Industrial Technology Gwangju, SOUTH KOREA

Resume : We have investigated CIGS solar cells fabricated by one-step sputtering process employing a quaternary Cu(In1-xGax)Se2 single target. In spite of all its advantages like simple control of composition and no selenization process needed, the small grain size (~100nm) of the CIGS layers fabricated by the one-step sputtering is considered to be one of the major obstacles holding back the improvement of the cell efficiency. Meanwhile, CuSe binary system has three kinds of polymorph phases like α-CuSe, β-CuSe, and γ-CuSe depending on temperatures. According to their phase diagram, the CuSe is likely to be separate liquid phase and β-Cu2-xSe around 530 ºC. We have examined the effects of CuSe precursor layers on the properties of CIGS thin film fabricated by one-step sputtering and the cell efficiency. We found, consistent with our expectation, that pre-deposition of CuSe thin film with the thicknesses of

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150~300nm prior to the deposition of CIGS plays a crucible role in the grain growth from ~100 nm to ~1,000 nm. This dramatic improvement in the grain size was accompanied by better cell efficiency. Although further improvement in the cell efficiency is required, we have demonstrated that the CuSe precursor layers to bring positive effects on the properties of CIGS thin film solar cells fabricated by one-step sputtering.

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16:00 **Study the effect of Al Addition to CuInSe2 Absorber on its properties**

Authors : Fianti Fianti, Kyoo Ho Kim

Affiliations : Yeungnam University

Resume : CuInSe2 Chalcopyrite is a candidate absorber for solar cell application promising low cost with less consumed materials than Si. Al was added to CIS forming Cu(In,Al)Se2 (CIAS) for band gap energy increasing for optimum solar light trapping resulting higher electric energy output. Moreover, Cu poor condition is preferential composition condition for p-type conductivity and composition tolerance. This research was carried out to investigate the Al addition to CIS at Cu poor CIAS, [Cu]/[In+Al] ratio = 0.55. The CIAS thin films were prepared by pulsed laser deposition (PLD) at room temperature and selenization in Ar ambient at 500 oC. The charazterization was covered film composition, structure, optical properties, and cross sectional morphology. All films show CIAS single phase and high absorption coefficient. The CIAS diffraction peak, band gap energy, and film grain size alter due to the Al addition. A.P1 36

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16:00 **Solution-processed CuIn(S,Se)2 absorber layers for application in thin film solar cells**

Authors : P. Arnou 1*, C.S. Cooper 2, A.V. Malkov 2, J.W. Bowers 1, J.M. Walls 1

Affiliations : 1 Centre for Renewable Energy Systems Technology (CREST), School of Electronic, Electrical and Systems Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK; 2 Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

Resume : CIGS is a high performance PV material for thin film solar cells. It can be deposited by solution-based techniques; the use of which has the potential to decrease the manufacturing costs for PV. The most successful solution-based technique for CIGS includes hydrazine, which forms soluble precursors that can decompose cleanly. However, it is very toxic and explosive and unsuitable for large scale production. The substitution of hydrazine is challenging, as most chalcogenides are not easily dissolved in common solvents. In this work, CuIn (S,Se)2 thin films were spin coated, using an alternative and relatively non-toxic solvent mixture of a dithiol and a diamine. This solvent mixture can dissolve sulphides and selenides rapidly at room temperature. Metal sulphides or selenides were dissolved in the solvent mixture separately and the solutions were mixed in different ratios. The precursor mixture was spin coated on molybdenum-coated glass. The solution was first coated at a low rotation speed, followed by a faster rotation and the coating was repeated, so as to obtain the required thickness. Between each coating, the film was dried on a ceramic hot plate. Finally, the dried coated sample was annealed in selenium atmosphere in a tube furnace. The annealing was performed with and without the selenium source, at various temperatures, annealing time, ramping rates and flow rates of inert gas. Each process was optimized in order to obtain high quality absorbers for use in solar cells. A.P1 37

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16:00 **Cu(In,Ga)Se2 solar cells prepared by single-step reactive magnetron co-sputtering from metallic targets in an Ar:H2Se atmosphere**

Authors : Jonas Schulte, Karsten Harbauer, Klaus Ellmer

Affiliations : Helmholtz-Zentrum Berlin für Materialien und Energien GmbH Hahn-Meitner-Platz 1, 14109 Berlin

Resume : By simultaneous sputtering from CuGa and In targets in an Ar:H2Se atmosphere single phase Cu(In,Ga)Se2 films can be directly deposited onto heated substrates. Similar to the previous work of the Thornton group in the 1980’s it was found, that for Cu-poor deposition conditions excess indium is re-evaporating for substrate temperatures above a critical value Tcrit, most probably due to the formation of volatile In2Se species. The value of Tcrit is in the range of 400 to 500°C and increases for higher H2Se contents and in the presence of Na during the deposition. By realizing supply rates from the two targets with an In excess, the In re-evaporation effect can be used for a self-adjustment of the film composition to [Cu]/([In]+[Ga]) ≈ 1. This allows the reproducible preparation of Cu(In,Ga)Se2 absorber films, which achieve A.P1 38 reasonable cell efficiencies of about 11% for a wide range of supply ratios from the CuGa and In target. By this method, however, the final film composition is nearly Cu-rich, which limits the open circuit voltage of the cells. By increasing the incorporation of indium by using a higher H2Se content in a final Cu-poor deposition stage, a Cu-poorer composition and higher efficiencies of above 12% could be achieved. Our process is suited for a perspective industrial application, since the well-established large-area high-throughput deposition technology of magnetron sputtering is used not only for contact or window layers but for the active layer itself.

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16:00

CIGSe absorber layers deposition by single target magnetron sputtering

Authors : R.Meunier, S.Fabert, M.Ricci, P.Y. Thoulon, T.Aviles, J.P. Vilcot, A. Lafond, M. Carette, P.Y. Jouan, M.P. Besland

Affiliations : Crosslux S.A / Institut des matériaux Jean Rouxel (IMN); Crosslux S.A / Institut des matériaux Jean Rouxel (IMN); Crosslux S.A; Crosslux S.A ; Institut d'Electronique, Microélectronique et Nanotechnologie (IEMN);Institut d'Electronique, Microélectronique et Nanotechnologie (IEMN); Institut des matériaux Jean Rouxel (IMN); Institut des matériaux Jean Rouxel (IMN); Institut des matériaux Jean Rouxel (IMN); Institut des matériaux Jean Rouxel (IMN);

Resume : In the last decades, the deposition of CIGSe thin films by sputtering has seldom been investigated. Besides, the sputtering of a single quaternary CIGSe target would be a real advantage for industrial development. Indeed, sputtering technique exhibits a good compatibility with industrial up-scaling and limits selenium use with respect to toxicity issues. In 1992, Hernandez et al.1 early published on CIGSe layers deposited by sputtering of a single quaternary CIGSe target. More recently, Frantz et al2 using such so called "one step sputtering" succeeded to obtain a CIGSe solar cell with an efficiency of 8.9%. At IMN laboratory, a dedicated chamber has been home-designed for CIGSe thin films deposition using one step sputtering. CIGSe thin films were deposited on SLG/Mo substrates by radio-frequency magnetron sputtering and then annealed under controlled atmosphere. The evolution of chemical composition, electrical and structural properties versus deposition parameters will be presented. 1. Hernández Rojas, J. L. et al.. Appl. Phys. Lett. 60, 1875–1877 (1992). 2. Frantz, J. A. et al. Thin Solid Films 519, 7763–7765 (2011). Keys Words: CIGSe, Thin films, Magnetron sputtering, One step sputtering

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add to my program **(close full abstract)**

16:00

Low temperature fabrication of 15%-efficient solar cells based on Cu(In,Ga)Se2 films by Pulsed Electron Deposition technique

Authors : Stefano Rampino(1), Matteo Bronzoni(1), Filippo Annoni(1), Francesco Bissoli (1), Marco Calicchio(1), Edmondo Gilioli(1), Enos Gombia(1), Francesco Pattini(1), T. V. Vimalkumar(2) and Massimo Mazzer(1)

Affiliations : (1) IMEM - CNR Parco Area Delle Scienze 37/A 43124 Parma (2) Department of Physics St.Thomas College,Thrissur Kerala,India.

Resume : We describe a novel route to low-cost production of Cu(In,Ga)Se2 (CIGS) solar cells based on Pulsed Electron Deposition (PED) technique: the CIGS absorber layer is deposited in a single step by using a stoichiometric quaternary target, without needing any selenization treatment nor further cation adjustment. Due to the high energy of evaporating atoms in PED technique (10-100 eV), high quality CIGS films can be grown even at low substrate temperature (< 300 °C), allowing the employment of flexible and low-melting substrates, as metal or plastic sheets. The p-type conduction of CIGS can be ranged from 10^14 to 10^17 cm-3 by finely controlling the number and the thickness of NaF layers deposited by PED, prior or during the absorber growth, using a rotating multi-target apparatus. Photovoltaic efficiencies exceeding 15% have been obtained on lab-scale devices, proving that PED is a promising technology for a competitive low-temperature fabrication process of CIGS solar cells.

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16:00

Low-temperature epitaxial growth of Cu(In,Ga)Se2 on Ge by Pulsed Electron Deposition

Authors : Stefano Rampino(1), Matteo Bronzoni(1), Lorenzo Colace(2), Paola Frigeri(1), Enos Gombia(1), Francesco Mezzadri(1), Lucia Nasi(1), Luca Seravalli(1), Francesco Pattini(1), Giovanna Trevisi(1) and Edmondo Gilioli(1)

Affiliations : (1) IMEM - CNR, Parco Area Delle Scienze 37/A -43124 Parma ITALY (2) Department of Engineering - University "Roma Tre", Via Vito Volterra, 62 - 00146 Rome ITALY

A.P1 41

Resume : We report on high quality epitaxial growth of Cu(In,Ga)Se2 (CIGS) thin films on n-type {001}-oriented Ge substrates using the Pulsed Electron

Deposition (PED) technique. Thanks to the high-energy of ablated adatoms (10-100 eV), chalcopyrite CIGS single-crystal films with thickness > 1.5 µm were obtained at a substrate temperature of 350 ?C. Transmission Electron Microscopy and X-Ray Diffraction techniques indicate a (001)CIGS||(001)Ge epitaxy system, with a calculated lattice mismatch of 0.7 %. Twins and stacking faults along the (112) direction have been observed as only structural defects in CIGS film, while no misfit dislocations were found at the CIGS-Ge interface. A main optical band located 220 meV below the bandgap is measured by photoluminescence technique. Current-Voltage and Capacitance-Voltage measurements confirm an intrinsic p-type conductivity of CIGS films, with an apparent free carrier concentration of ≈10^16 cm-3. These characteristics of single-crystal CIGS promise a variety of potential applications as absorber layer in single and multi-junction thin-film solar cells.

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16:00

CdCl2 activation treatment: a comprehensive study by monitoring the annealing temperature

Authors : Bing Lei Xu^, Ivan Rimmaudo^, Andrei Salavei^, Fabio Piccinelli*, Simone Di Mare, Daniele Menossi , Alessio Bosio , Nicola Romeo , and Alessandro Romeo^
Affiliations : ^LAPS-Laboratory for Applied Physics, Department of Computer Science, University of Verona, Ca' Vignal 1, Strada Le Grazie 15, 37134 Verona, Italy, tel.: 39-045 -8027974, e-mail address: alessandro.romeo@univr.it * Department of Biotechnology, University of Verona, Strada Le Grazie 15, 37134 Verona, Italy Physics and Earth Science Department, University of Parma, V.le G.P. Usberti, 7A-43124, Italy

Resume : CdTe thin film solar cells have demonstrated high scalability, high efficiency and low cost fabrication process. One of the key factors for the success of this technology is the transformation of the absorber layer by an activation treatment where chlorine reacts with CdTe in a controlled atmosphere or in air, improving the electrical properties of the absorber, and enhancing the intermixing of the CdS/CdTe layers. With this work we study the activation process by analyzing the CdCl2 treatment made by wet deposition with different annealing temperatures from 310 °C up to 410 °C in air keeping the same CdCl2 concentration in methanol solution. In this way the whole dynamic of the chemical reaction from the minimum activation energy is analyzed. Activated CdTe layers have been analyzed by means of X-ray diffraction spectroscopy and atomic force microscopy: grain size shows a strong dependence on the temperature, the known (111) preferential orientation reduces with temperature increase. A detailed analysis of the formation of intermixed CdS-CdTe layer with temperature will also be reported. Finished devices with efficiencies from 8% for the low temperature annealing up to more than 14% for the high temperature ones, have been thoroughly analyzed by current-voltage, capacitance-voltage and drive level capacitance profiling techniques, showing that carrier concentration is independent with temperature but that a complete different behavior of the defects is reported.

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16:00

The activation of thin film CdTe solar cells using alternative chlorine containing compounds

Authors : B. Maniscalco 1, G. West 2, J.W. Bowers 1, A. Abbas 1, P.M. Kaminski 1, J.M. Walls 1
Affiliations : 1 Centre for Renewable Energy Systems Technology, (CREST), School of Electronic, Electrical and Systems Engineering, Loughborough University, Leicestershire, LE11 3TU, UK 2 Materials Department, Loughborough University, Leicestershire, LE11 3TU, UK

Resume : The re-crystallization of thin film CdTe using CdCl2 is a vital process for obtaining high efficiency devices. However, the precise micro-structural mechanisms are not well understood. In this study, we have used alternative Cl-containing compounds to determine if these can also re-crystallize the CdTe layer and to understand the separate roles of Cd and Cl during the activation. The compounds used were: Tellurium tetrachloride (TeCl4), Cadmium acetate (Cd((CH3CO2)2), Hydrochloric acid (HCl) and Zinc chloride (ZnCl2). TeCl4 was used to assess the role of Cl and the formation of a Te-rich outer layer which may assist the formation of the back contact. (Cd((CH3CO2)2) and HCl were used to distinguish the roles of Cd and Cl. Finally, ZnCl2 was employed as an alternative to CdCl2, since the location of Zn following the treatment can be determined by TEM and EDX. We report on the efficacy of using these alternative Cl-containing compounds to remove the high density of linear defects present in as-deposited CdTe. We also report on an increased conversion efficiency using these compounds confirming the importance of Cl in the process. In all cases, wet treatment was used as process. All the devices were

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completed by depositing a sputtered gold back contact. The device performance was measured using I-V curves, Spectral Response measurements. Material and structural analysis was performed using X-ray electron spectroscopy, Scanning Electron Microscopy, Transmission Electron Microscopy.

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16:00 **Effects of deposition parameters on the composition of Cu(In,Ga)Se2 thin films deposited by magnetron pulsed DC sputtering**

Authors : Thomas AVILES, Jean-Pierre VILCOT

Affiliations : Institut d'Electronique, de Microélectronique et de Nanotechnologie UMR CNRS 8520

Resume : Industrial Cu(In,Ga)Se2 (CIGS) thin films formation process generally require two steps : 1) Cu-In-Ga precursors deposition 2) crystallization under selenium atmosphere (H2Se). Unfortunately, hydrogen selenide is very hazardous, being the most toxic selenium compound. Nevertheless, recent works have shown that it is possible to obtain good quality CIGS absorbers by sputtering in an inert atmosphere without additional selenium supply. From an industrial point of view, it is interesting to simplify CIGS formation process and to avoid the use of H2Se. This work shows the effect of deposition parameters on the composition of CIGS thin films deposited by a simple method: magnetron pulsed DC sputtering from a single quaternary target in an inert atmosphere without additional selenium. This straightforward method doesn't allow a direct tuning of the films composition but a good control of the composition is important to achieve good quality absorbers. For example, good photovoltaic properties can be obtained only if the composition is slightly Cu-deficient and Se -rich. The evolution of CIGS thin film composition is studied when working pressure, gas flow, power, substrate temperature, type of substrate, pulse frequency and duration are modified and these evolutions are interpreted. Taking into account industrial application, the possibilities of adapting the CIGS target composition is discussed. A.P1 44

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16:00 **Compensation of In loss during selenization of CuGa/In by external supply of In2Se vapor**

Authors : Junhyun Park, Kyeongchan Moon, Woo Kyoung Kim

Affiliations : School of Chemical Engineering, Yeungnam University

Resume : It is well known that In element can be lost during the Cu(InGa)Se2 (CIGS) formation by selenization of CuGa/In precursor or the post-deposition annealing of pre-fabricated CIGS absorber at elevated temperature. In this study, the reaction pathways of In-Se binary system was investigated by high-temperature XRD. Then, based on the reaction pathways of binary In-Se, the method for external supply of InxSe vapor during rapid thermal annealing(RTA) of CuGa/In/Se precursors is suggested. The results showed that as-deposited crystalline In phase melted at around 150 deg.C, and was transformed to In4Se3 at around 220 deg.C. At 300 deg.C and higher temperature, high-temperature stable gamma-In2Se3 formed. The amorphous In2Se, which is known to be most volatile In-Se binary compound, is expected to form from In (l) + Se(l) at around 220 deg.C or higher, and from decomposition of In4Se3 at around 300 deg.C. The CuGa/In/Se precursors were selenized in an RTA system composed of a quartz tube reactor with a diameter of 62 mm, sample tray and infrared heater. It was confirmed that In was lost during RTA evidenced by reduction in Cu/III ratio, e.g., 0.89 (precursor) to 0.95 (CIGS). Quartz/Se/In sample tray cover was employed to supply InxSe vapor externally during RTA of CuGa/In/Se precursors. To form volatile In2Se phase, prior to RTA, pre-annealing between 220 and 350 deg.C was performed. A.P1 45

add to my program **(close full abstract)**

16:00 **Laser Treatment as Surface Modification Technique for CdTe Solar Cells**

Authors : V. Palekis1, B. J. Simonds2, V. Evani1, M. Khan1, P. Bane1, M. A. Scarpulla2, and C. Ferekides1

Affiliations : 1 Department of Electrical Engineering, University of South Florida, Tampa, FL, 33620, USA; 2 Materials Science and Engineering, University of Utah, Salt Lake City, UT, 84112, USA.

Resume : The formation of stable, low resistance and non-rectifying contact to p-CdTe is a significant challenge in the fabrication of highly efficient solar cells. Surface preparation techniques including wet etches are typically used to produce a p+ surface through the formation of a Te-rich layer, followed by the deposition of a metallic contacting material. In this study laser annealing treatment is investigated in order to replace wet treatments for modifying the CdTe surface prior to contact formation. The laser anneals were carried out using a KrF excimer laser at 248nm with a 25ns pulse. X-Ray diffraction (XRD) A.P1 46 and scanning electron microscopy (SEM) were used to study morphological changes on CdTe films laser treated under different incident laser fluences. CdTe surface melting point was observed near 80mJ/cm2 energy density. Current–voltage and spectral response measurements were used to analyze CdS/CdTe solar cells treated with laser annealing. Both open circuit voltage (Voc) and field factor (FF) were improved for laser treated samples versus samples with no laser treatment. Increasing the number of laser pulses resulted in elimintation of the roll-over observed in the J-V characteristics of cells with non-ohmic contacts. The best cell fabricated to-date using all dry laser-based processing resulted in efficiency greater than 13%.

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16:00

Rapid synthesis of CuInSe2 from sputter-deposited bilayer In2Se3/Cu2Se precursors

Authors : Jaseok Koo(a), Kyeongchan Moon(a), Saleh Alhammadi(a), Chae-Woong Kim (b), Chaehwan Jeong(b), Woo Kyoung Kim(a)

Affiliations : (a) School of Chemical Engineering, Yeungnam University; (b) Applied Optics and Energy Research Group, Korean Institute of Industrial Technology

Resume : It has been suggested that Cu(InGa)Se2 can be rapidly formed from binary selenide bilayer (InGa)2Se3/CuSe diffusion couples, even at low temperature. However, vacuum co-evaporation method may not be commercially preferred for the preparation of (InGa)2Se3/CuSe precursors primarily due to its poor compositional uniformity in large area. In this study, bilayer In2Se3/Cu2Se precursors were deposited by sputtering In2Se3 and Cu2Se composite targets sequentially. It was found that as-deposited In2Se3 is amorphous and stoichiometric, while as-deposited Cu2Se is crystalline phase with a slight loss of Se during sputtering process. To form CuInSe2, the bilayer precursors were processed in a rapid thermal annealing (RTA) system with a Se ambient. To simulate NREL 3-stage process which is known to produce large-grain and high-quality CuInSe2(CIS) absorber, pre-selenization of In2Se3/Cu2Se was optimized and performed to form In2Se3/CuSe(or CuSe2). Then, subsequent RTA process was designed to form the intermediate phase of In2Se3/CIS/CuSe(+liq.) following liquid-assisted grain growth. This RTA with pre-selenization produced the large grain of CIS. By using this precursors, furthermore, the reaction time and temperature could be reduced to 5 min and 450 deg.C.

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16:00

Elaboration of efficient CIGS solar cells by one-step electrodeposition of oxide precursor films

Authors : Tarik SIDALI, Aurélien DUCHATELET, Elisabeth CHASSAING, Daniel LINCOT

Affiliations : EDF/IRDEP (Institute of Research and Development on Photovoltaic Energy), 6 quai Watier, 78401 Chatou Cedex, France

Resume : A new way to prepare metallic precursors for CIGS solar cells has been recently introduced by our group leading to efficiency above 12%. It consists in the electrodeposition of Cu-In-Ga mixed oxides followed by thermal reduction. The aim of this communication is to present basic materials elaboration studies for a better understanding and optimization of the process. The deposition of Cu-In-Ga oxide layers is carried out in nitrate acidic aqueous solutions. The composition is controlled by the concentration of Cu(II), In(III) and Ga(III) in solution and the applied potential. In and Ga oxide deposition starts at -0.8 V/MSE well before that of the metallic counterpart avoiding parasitic hydrogen production. The process is thus highly robust. We will focus on the study of the nucleation mechanism on Mo substrates. We show that it starts with 3D nucleation of metallic copper, a key point of the process. Copper then catalyses the precipitation of In and Ga oxides. The resulting film is governed by the interplay between these steps. The reducing heat treatment under hydrogen leads to the formation of various phases In, Cu2(In,Ga) or Cu9 (In,Ga)11. GD-OES analyses show that composition gradients are present. After selenization full composition range of CIGS is achievable with the presence of gallium profiles, giving efficient devices. Cells with 11-12% efficiency are routinely obtained, with 12.4% record efficiency and avenues exist for further improvements.

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16:00

Cu(InGa)Se2 formation from bilayer (InGa)2Se3/CuSe precursors by following NREL 3-stage process

Authors : Kyeongchan Moon, Junhyun Park, Saleh Alhammadi, Woo Kyoung Kim

Affiliations : School of Chemical Engineering, Yeungnam University

Resume : NREL 3-stage process is believed to follow optimum reaction path to high-quality Cu(InGa)Se2 (CIGS) formation, evidenced by maintained record

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efficiency. One drawback might be a relatively long reaction time. So, in this study, we propose the rapid reaction path starting from fast diffusion couples of (InGa)2Se3/CuSe, while maintaining NREL 3-stage process. Bilayer precursors were prepared by vacuum co-evaporation with different CuSe thickness, i.e., different Cu/III ratios (0.5, 0.7, 0.9, 1 and 1.5). The reaction pathways was confirmed by in-situ high-temperature XRD, showing (InGa)2Se3/CuSe to (InGa)2Se3/CuSe2 at 220 deg.C, and then peritectic decomposition of CuSe2 to CuSe liq. at 330 deg.C, which will enhance liquid-assisted grain growth. Bilayer precursors were heat-treated in either rapid thermal annealing reactor or vacuum evaporator with a Se overpressure environment. The results showe d that CIGS formation was completed within 3 min, with a fairly large and dense grain. Further detailed results of film and device characterization will be presented.

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16:00 **Study of step-graded Na-doping methods and different annealing time on the electrical properties of Cu(In,Ga)Se2-based solar cells grown by Pulsed Electron Deposition technique** A.P1 50

Authors : A. Kingma, F. Annoni, M. Bronzoni, F. Bissoli, M. Calicchio, E. Gilioli, E. Gombia, F. Pattini, S. Rampino

Affiliations : IMEM-CNR, Institute of Materials for Electronics and Magnetism, Parco Area delle Scienze 37/A, 43124 - Parma (Italy)

Resume : In order to improve the Cu(In,Ga)Se2 (CIGS)-based solar cells performances, we report a novel route for sodium incorporation in the absorber layer and a study on the effects of different annealing times. The Na-precursor and the absorber are both grown with Pulsed Electron Deposition (PED) technique, which allows single-stage deposition of stoichiometric CIGS films at low temperature (<300°C). However, this procedure does not seem optimal for a homogeneous Na diffusion into the absorber, a feature required to obtain high efficiency especially over large areas. In our work, the PED features are exploited to create different multilayer NaF/CIGS structures simulating the Na diffusion, in order to maximize the device efficiency. In this way it is possible to control the Na content and to generate an optimal Na-grading in the CIGS absorber. Another way to promote the Na diffusion is to vary the annealing time. Different samples, prepared by using 30 nm precursor film of NaF deposited on the Mo back contact, were annealed in argon atmosphere at 4.5x10-3 at 300 °C for 0, 20, 40 and 80 min, respectively. CV, IV and Voc versus temperature measurements and SIMS analysis are used to evaluate the electrical properties (charge carrier density, depletion layer width, cell parameters) and the Na distribution. As results, both the multilayered structures and the annealing time improve the efficiency and homogeneity of the cells, thus they are suitable to reach high efficiency over large areas.

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16:00 **Photoluminescence Studies of EVT deposited CdTe Thin Films** A.P1 51

Authors : S. Collins 1, S. Vatavu 1, 2, S. Bakhshi 1, V. Palekis 1, M. Khan 1, V. Evani 1, C. Ferekides 1

Affiliations : 1 Department of Electrical Engineering, University of South Florida, 4202 East Fowler Ave, Tampa, FL 33620, USA; 2 Faculty of Physics and Engineering, Moldova State University, 60 A. Mateevici str., Chisinau, MD-2009, MOLDOVA.

Resume : Low temperature investigation of the photoluminescence spectra gives a possibility to trace the modification of the energetic diagram of native defects in CdTe, the latter being directly related to deposition technology. The Elemental Vapor Transport (EVT) Method allows control of the vapor composition which influences properties and stoichiometry of the deposited films. The main process parameter varied during this study was the Cd/Te vapor ratio. Films deposited at Cd/Te ratios ranging from 0.35 to 2.00 were deposited and subsequently characterized using PL measurements in the temperature range of 15-130K at 514.5 nm excitation. Distinct PL bands were identified in the various spectra: 1.367 eV, 1.477 eV, 1.486 eV, 1.547 eV, 1.585 eV and 1.598 eV. As the Cd/Te ratio increased to 2.00 the intensity of the PL bands with peak energy at 1.367 eV, 1.477 eV, 1.486 eV 1.585 eV increased. The increase of Cd/Te ratio results in complete quenching of the 1.547 eV band presumably due to elimination or reduction in the concentration of cadmium vacancies. Furthermore, the decrease of Cd/Te ratio in the film, from 1.00 to 0.35, reveals the fact that 1.367 eV, 1.477 eV, 1.486 eV and 1.547 bands have their peak intensity reaching a maximum value for Cd/Te=0.46. The 1.585 eV band has maximum intensity at Cd/Te ratio=0.6. The temperature and intensity dependence of the PL bands is being analyzed and results on activation energies and transition types are being determined.

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16:00

Importance of green density of nanoparticle precursor film in microstructural development and photovoltaic properties of CuInSe2 thin films

Authors : Yoonjung Hwang, Byung-Seok Lee, Ye Seul Lim, and Doh-Kwon Lee
Affiliations : Photo-electronic Hybrids Research Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Korea; Department of Nanomaterials Science and Engineering, University of Science and Technology, Daejeon 305-350, Korea

Resume : There is tremendous interest in using nanocrystals to fabricate CIGS (or CIGS-related) PV devices. To date, efficiencies have been relatively low, and thus a lot of research is being made at the moment to figure out how to increase it. In this regards, the main concern of this article is to elucidate the origin of low open-circuit voltage (VOC) and fill factor (FF) that are typically observed in the solution-processed CIGS PV devices and to provide a simple way to improve them, which has been overlooked in the literature so far. We found that the improvement in green density of Cũ In nanoparticle films by cold-isostatic pressing (CIP) results in a dramatic enhancement of PV performance of low-bandgap CISe solar cells. An almost 3-fold increase in the average efficiency was achieved from 3.0 to 8.2% with the highest value of 9.02%. In addition, by means of the diode analysis and VOC̃ T measurement, we found that the remarkable enhancement of VOC, FF, and efficiency was essentially attributed to the suppressed interface recombination. Accordingly, a comprehensive discussion was dedicated to addressing the significance of related parameters, i.e., reverse saturation current and diode ideality factor as determinants of the magnitude of recombination current and its predominant mechanism. According to our findings, the defect-chemical modification of CIGS/CdS junction in a way to reduce the interfacial recombination will further increase the efficiency.

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	Ultra-thin absorbers and high-efficient CdTe modules : O. Lundberg, T. Dalibor	
08:45	**Highly Reflective Rear Surface Passivation Design for Ultra-Thin Cu(In,Ga)Se2 Solar Cells** **Authors :** Bart Vermang, Viktor Fjällström, Timo Wätjen, Fredrik Rostvall, Marika Edoff, Ratan Kotipalli, Frederic Henry, Denis Flandre, Rickard Gunnarsson, Iris Pilch, Ulf Helmersson **Affiliations :** Bart Vermang; Viktor Fjällström; Timo Wätjen; Fredrik Rostvall; Marika Edoff: Ångström Solar Center, Uppsala University, P.O. Box 534, 75121 Uppsala, Sweden Ratan Kotipalli; Frederic Henry; Denis Flandre: ICTEAM, Université Catholique de Louvain, Place du Levant 3, 1348 Louvain-la-Neuve, Belgium Rickard Gunnarsson; Iris Pilch; Ulf Helmersson: Plasma & Coatings Physics, Linköping University, IFM, 58183 Linköping, Sweden **Resume :** Reducing absorber layer thickness below 500 nm in regular CIGS solar cells decreases cell efficiency considerably: both short circuit current and open circuit voltage are reduced, respectively due to incomplete absorption and high Mo/CIGS rear interface recombination. In this work, an innovative rear cell design is developed to avoid both effects: a highly reflective rear surface passivation layer with nano-sized local point contacts is used to enhance rear internal reflection (Rb) and decrease rear surface recombination velocity (Sb) significantly, as compared to a standard Mo/CIGS rear interface. Two methods are demonstrated. (1) (MgF2/)Al2O3 (> 50 nm) passivation stacks combined with nanosphere-shaped precipitates formed in chemical bath deposition of CdS to generate point openings, where Rb is increased substantially by Al2O3 thickness tuning and/or the MgF2 bottom layer refractive index. And (2) Al2O3 passivation layers (≤ 10 nm) combined with Mo nanoparticles (formed by a plasma process) as point contacts, where absorption is boosted by plasmonic light trapping. In both cases, Sb is reduced significantly at the Al2O3/CIGS rear interface (down to 100 cm/s, see [1]). Among all, current-voltage, quantum efficiency, electron-beam-induced current and transmission electron microscopy measurements will be presented, accompanied by optical and electrical simulations. [1] B. Vermang, Sol. Energ. Mat. Sol. Cells 117 (2013) 505-511 and IEEE J. Photovolt. 4 (2014) 486-492	A.O4 1
add to my program	(close full abstract)	
09:00	**Backwall superstrate configuration for ultrathin Cu(In,Ga)Se2 solar cells** **Authors :** J. K. Larsen, H. Simchi, P. Xin, K. Kim, W. N. Shafarman **Affiliations :** Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark, Delaware 19716, USA, current address: Uppsala University, Engineering Sciences, Solid State Electronics, Box 534, SE-751 21, Uppsala Sweden; Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark, Delaware 19716, USA;Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark, Delaware 19716, USA;Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark, Delaware 19716, USA;Institute of Energy Conversion, University of Delaware, 451 Wyoming Road, Newark, Delaware 19716, USA **Resume :** One approach to lower material costs and increase manufacting throughput of Cu(In,Ga)Se2 based solar cells is to reduce the absorber thickness. In this work a novel backwall superstrate device structure (glass/ITO/MoO3/Cu(In,Ga)Se2/CdS/i-ZnO/Ag) is developed. This structure is tailored to enhance the performance of devices with ultrathin aborber layers, due to deposition of a silver reflector after all other device processing and the	A.O4 2

possibility to apply textured substrates. The backwall structure utilizes a recently developed MoO3 transparent back contact to allow illumination from the back. Device parameters are investigated as a function of absorber thickness, and it is found that devices with the backwall configuration outperform substrate devices in the absorber thickness range dCIGS = 0.1-0.5 ?m. The advantage of the backwall configuration is mainly through superior JSC. Quantum efficiency measurements indicate that this improvement can be ascribed to the silver front reflector and elimination of parasitic absorption in CdS. The highest efficiency obtained with the backwall configuration is 9.7% for a device with an absorber thickness of only 0.3 ?m compared to 3.6% for the comparable substrate device. These results clearly demonstrates the potential of the backwall structure for utilization of ultrathin absorber layers.

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09:15 **Superior stability of ultra thin CdTe solar cells with simple Cu/Au back contact**

Authors : Ivan Rimmaudo, Andrei Salavei, Bing Lei Xu, Simone Di Mare, and Alessandro Romeo

Affiliations : Laboratory for Applied Physics, Department of Computer Science, University of Verona, Strada Le Grazie 15, 37134 Verona, Italy, alessandro.romeo@univr.it, ph: 390458027974, fax 390458027929

Resume : Due to its high scalability and low production cost, CdTe solar cells have shown a very strong potential for massive energy production, however tellurium scarcity is a limitation for this technology. We have already demonstrated efficiencies above 11% for devices with 1.5 micron thick CdTe. Moreover a different electrical operation has been shown, considering that the depletion region takes a very large part of the device. In this work, many CdTe solar cells, made with different absorber thickness, were prepared for different accelerated lifetime tests, showing different reactions to the aging and in particular a remarkable stability as CdTe thickness reduces with a standard Cu/Au back contact. Among solar cells with absorbers from 0.7 to 6 microns thickness, with efficiencies ranging from 8 to 14%, the thin absorber devices show negligible reduction of efficiency under dark and open circuit (Voc) conditions for more than 9000 hours, whereas in the same conditions, for standard devices, the efficiency reduces up to 20% in less than 1000 hours. The solar cells have been also tested in accelerated lifetime conditions, one sun illumination and 85°C, in both short circuit (Jsc) and open circuit, showi ng different behaviors in stability as the CdTe thickness changes: Statistics of several tens of cells also with different amount of copper in the back contact and analysis of the electrical parameters will address the key points to this phenomenon, important for module production. A.O4 3

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09:30 **Progress towards practical CdTe solar modules with 17 % efficiency**

Authors : Markus Gloeckler

Affiliations : First Solar Inc.

Resume : CdTe has enjoyed the strongest commercial success of all thin-film solar cell technologies despite its historical moderate conversion efficiency. CdTe's excellent manufacturability attributes, including extremely high deposition rates, ease of uniform large area processing, and forgiving process tolerances have been instrumental in establishing capable manufacturing at a strong cost-performance ratio. The highest reported CdTe research cell efficiency has increased by more than absolute 3% over the last 2.5 years and at the time of this writing stands at 19.6%, as compared to the S-Q limit of nearly 33%. Device performance improvements over the past 20 years have been dominated by Jsc and FF increases. Voc has been largely stagnant around 850mV and only recently been taken above 880mV in very high efficiency devices (>19%) and above 915mV in a polycrystalline CdTe high-voltage device. Recent research indicates that Voc at these levels is strongly correlated to minority carrier lifetime, which it is believed can be improved through techniques currently in development. If successful, Voc of 925mV with modest improvements in Jsc and FF should enable a 22% CdTe cell in the near-term without assuming any radical change to materials or device architecture. Based on this visible trajectory for research cell performance and CdTe's relatively narrow gap between research cell and large area efficiency, module performance can be expected to reach 17% in the coming few years. Such conversion efficiencies will put CdTe field performance significantly ahead of commodity crystalline Si module technologies at real operating temperatures which can average 50C to 60C on a power-weighted basis in typical dessert conditions. A.O4 4

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10:00 **coffee break**

CdTe: doping + interfaces : W. Jaegermann, M. Gloeckler

10:30

Band alignment at the buried CdS/SnO2:F interface in CdTe thin-film solar cells

Authors : D. A. Hanks 1, P. S. Kobyakov 2, S. G. Rosenberg 1, J. H. Alsmeier 3, M. Blum 1, R.G. Wilks 3, L. Weinhardt 1,4,5, M. B?r 1,3,6, W. Sampath 2, C. Heske 1,4,5,7

Affiliations : 1Dept. of Chemistry, University of Nevada, Las Vegas (UNLV), Las Vegas, NV 89154-4003, USA; 2Next Generation Photovoltaics Center, Colorado State University (CSU), Fort Collins, CO 80523, USA; 3Solar Energy Research, Helmholtz-Zentrum Berlin f?r Materialien und Energie GmbH (HZB), 14109 Berlin, Germany; 4ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany; 5Institute for Photon Science and Synchrotron Radiation (IPS), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany; 6Institut f?r Physik und Chemie, Brandenburgische Technische Universit?t Cottbus-Senftenberg, 03046 Cottbus, Germany; 7Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

Resume : CdTe/CdS-based thin-film solar cells are established candidates for cost-effective devices yielding high efficiencies. To further improve performance, a fundamental understanding of the chemical and electronic structure throughout the CdCl2-treated CdTe/CdS/SnO2:F/glass layer stack is necessary. Significant diffusion processes occur during manufacturing, particularly induced by the post-deposition CdCl2 treatment. Thus, most interfaces in the device are not fully formed until after these treatments, presenting a challenge to standard surface-science characterization of step-wise material deposition. In this study, we probe the buried CdS/SnO2:F interface using a combination of surface-sensitive characterization and reproducible cleaving in an inert environment. We have characterized the chemical structure of both surfaces exposed after the lift-off with XPS, and find that they can mainly be identified as SnO2 on the ?glass side? and CdS on the ?lift-off side.? Furthermore, a significant presence of Cl was detected on both sides of the interface, indicative of interdiffusion processes induced by the CdCl2-treatment. The position of the conduction band minimum and valence band maximum with respect to the Fermi energy of both surfaces were directly measured with IPES and UPS, respectively. We will provide an in-depth chemical and electronic structure analysis of the buried CdS/SnO2:F interface and discuss the effects of diffusion on the derived electronic structure.

A.O5 1

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10:45

Luminescent, structural and chemical properties of defects in MBE- and CSS-grown CdTe films for solar cell applications

Authors : Mowafak Al-Jassim, John Moseley, Harvey Guthrey, Zhiwei Wang, Helio Moutinho, Wyatt Metzger and Yanfa Yan

Affiliations : National Renewable Energy Laboratory, Golden, Colorado 80401, USA.

Resume : CdTe solar cells are the leading thin film solar cell technology. However, despite their near ideal bandgap, the cell efficiency is far less than the theoretical limit, and considerably less than efficiencies reported in other systems with similar bandgaps, such as GaAs. The purpose of this study is to investigate the loss mechanisms in commercial CdTe cells by comparing them with model systems. We combined scanning electron microscopy (SEM)-based cryogenic cathodoluminescence (CL) spectrum imaging and electron backscatter diffraction (EBSD) in order to map the spatial distribution of various atomic-level defects in CdTe films as a function of deposition and film processing. Two different deposition techniques were used. Lattice-matched, epitaxial CdTe films were deposited on single crystal as well as polycrystalline CdTe substrates by molecular beam epitaxy (MBE). For comparison purposes, polycrystalline CdTe films were deposited using our standard close-spaced sublimation (CSS) method on glass-based substrates. Correlations between the CSL relationship, defect structure, and radiative recombination intensity at grain boundaries and intra-grain regions are then made and discussed in the context of film deposition conditions and post-deposition processing history. Further, the effect of the CdCl2 passivating treatment was investigated. The distribution of Cl on grain boundaries and intra-grain dislocations was studied by time of flight SIMS (TOF-SIMS) imaging and high resolution STEM-EELS. These results were correlated with the recombination behavior of these defects as revealed by CL.

A.O5 2

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11:00 **Copper(I) oxide (Cu2O) back contact for a pin CdTe solar cell**

Authors : J. Türck, P. Conner, S. Siol, A. Klein, W. Jaegermann

Affiliations : Technische Universität Darmstadt, Materials and Earth Sciences, Surface Science

Resume : Due to the weak dopability of CdTe, the pin-structure should be an ideal solar cell configuration for CdTe solar cells. Cu2O is a possible material to be used as back contact in a CdTe pin solar cell. Cu2O is an intrinsically p-doped semiconductor with a band gap of 2.1 eV and a high work function of 5.2 eV, and should work as electron reflector. CdTe and CdS Layers for the solar cells have been prepared by Closed Space Sublimation on commercial SnO2:F substrates (Pilkington TEC C15B) in superstrate configuration. Before depositing Cu2O the solar cells have been activated and cleaned to remove the oxidation products. The Cu2O back contact was prepared by reactive RF magnetron sputter deposition. As secondary back contact Au was used. The energy band alignment between CdTe and Cu2O was experimentally determined by in-situ X-ray Photoelectron Spectroscopy, carried out at the DAISY-SOL (DArmstadt Integrated SYstem for Solar cell research), revealing a very small valence band offset. A conversion efficiency of 13% was achieved for solar cells with Cu2O back contacts including several post deposition annealing step. The impact of Cu2O layer thickness and deposition temperature was investigated. A.O5 3

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11:15 **TEM and XPS studies of CdS/CdTe interface: comparison of CdS films deposited by CBD and CSS techniques**

Authors : Han Jun-feng1, 2*, V. Krishnakumar2, Hermann-Josef Schimper2, Wolfram Jaegermann2, M.P. Besland1

Affiliations : 1, Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France 2, Institute of Materials Science, Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany

Resume : CdS layers were deposited by close space sublimation (CSS) and chemical bath deposition (CBD) methods. CdTe layer had been grown by CSS on the two CdS layer types. Further, CdS/CdTe interfaces were investigated by HRTEM and XPS. TEM observations of cross sections showed large grain sizes in the range of 50-70 nm for CSS CdS layer. The interface between CSS CdS and CdTe appeared clear and sharp, like an abrupt hetero-junction. Besides, CBD CdS layer had very small grain sizes in the range of 5-10 nm. The interface between CBD CdS and CdTe was not as clear as CSS CdS. XPS analysis on Cd 3d and S 2p core levels were performed in both cases while growing the CdTe layer. In the case of CSS CdS layer, a sudden shift to lower binding energies was observed in relation with the CdTe layer coverage. Whereas, Cd 3d and S 2p core levels binding energies were gradually shifted with CdTe coverage for CBD CdS layer. In addition, XPS depth profile analyses indicated that a higher diffusion might occur at the CBD CdS/CdTe interface. Finally, CdTe solar cells based on CSS CdS layers exhibited higher efficiencies than those based on CBD CdS layers. The relationships between the solar cell performances and properties of CdS/CdTe interfaces will be discussed on the basis of HRTEM and XPS analyses. A.O5 4

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11:30 **The physics of CdTe p-type doping with Cu**

Authors : J. Perrenoud, C. Gretener, L. Kranz, S. Buecheler, and A.N. Tiwari

Affiliations : Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Thin Films and Photovoltaics, ?berlandstrasse 129, 8600 D?bendorf, Switzerland

Resume : In this work it is shown by analytical and numerical calculation that the deep Cu on Cd acceptor de-fect is indeed capable of explaining the CdTe p-type doping despite it`s position deep insight the bandgap ~300meV above the valance band. We show how the deep acceptor is fully ionized at room temperature using analytical formula and the software SCPAS and discuss the appropriate physical treatment of such deep acceptor levels. Surprisingly the hole concentration in CdTe at room temperature is not limited by partial ionization but by Cu solubility. This will be shown by temperature dependent measurements and quenching experiments. The theoretical findings are validated by experimental data including temperature dependent Hall Effect and transmission line method measurements, and scanning kelvin probe measurements on CdTe layers and substrate configuration CdTe solar cells with precisely controlled Cu doping. By solving the basic semiconductor equations using SCAPS we will elaborate the consequences of the acceptor depth on CdTe solar cells, the impact on Voc, FF and Jsc. A.O5 5 add to my program (close full abstract)

11:45 **DISCUSSION SESSION: Contacts and further functional intermediate layers for CdTe solar cells (A. Romeo)**

12:15 **Lunch break**

Industry : D. Lincot, M. Powalla

14:00 **Challenges for the industrial development of electrodeposited Cu(In,Ga)(S,Se)2 based photovoltaic modules**

Authors : V. Bermudez1, S. J. Ferrer1, P. P. Grand1, V. Izquierdo-Roca2, C. Insignares2, A. Fairbrother2, A. Perez-Rodrigues23

Affiliations : 1NEXCIS, Rousset, France, 2IREC, Barcelona, Spain, 3IN2UB Barcelona, Spain

Resume : Cu(In,Ga)(S,Se)2 (CIGS) has held during the last decades the title of “promising technology” to achieve high efficiency photovoltaic modules at low cost. CIGS has demonstrated its capabilities at the laboratory scale with a record efficiency of 20.8% [1] in small cells, overtaking the highest efficiency of multicrystalline Si cells. However, the industry has not reached maturity mainly due to the large gap between record small cell and commercial module efficiencies. One of the main advantages of electrodeposited stack metal layers for precursor formation to form CIGS is the high homogeneity and tight control of thickness and morphology of the precursors. Moreover, as the deposition is done under non-vacuum conditions the quality control process monitoring of the electrodeposited layers can be done in-line and in-situ under real-time conditions. This is achieved with non-contact techniques which have been developed for this application. This fact provides a clear advantage to perfectly asses the quality of precursors arriving at the step of thermal treatment under the chalcogen species. The most important challenges in terms of material, deposition process, characterization, and final fabrication of photovoltaic modules are strongly dependent on the precursor formation kinetics and its final quality, as well as the thermal conditions the stack layers face before absorber formation.

A.O6 1

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14:30 **Impact of Gallium on variations of the composition in Cu(In,Ga)Se2 thin film solar cells grown on flexible polyimide substrate**

Authors : Stefan Ribbe1,2, Andreas Rahm1, Alexander Braun1, Frank Bertram2, Jürgen Christen2

Affiliations : 1Solarion AG, Pereser Höhe 1, 04442 Zwenkau, Germany 2Institute for Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany

Resume : The most important key parameter in CIGS absorber layer used for thin film solar cells on flexible substrate seems to be the gallium. Its concentration affects the grain size as well as band gap of the absorber material. The vertical distribution of the gallium has a high influence on the charge carrier collection as well as the open circuit voltage. Especially the efficiency of the solar cell is strongly influenced. CIGS absorber layers were grown by a 3-stage co-evaporation process in which gallium just as indium and selenium is deposited in the first and the last step. In order to investigate the impact of the gallium content with respect to the efficiency of the thin film solar cells the gallium supply in the 3-stage process was varied in the first and in the last stage so that the integral GGI (Ga/(In+Ga) ratio) also differs. By means of I-V measurements under standard test conditions the highest efficiency was found for a GGI at around of 0.22. Microscopic inhomogeneities were investigated by highly spatially resolved Cathodoluminescence spectroscopy (CL) at low temperature (5 K) showing lateral fluctuations of the composition and vertically running changes of the gallium content. The change of gallium content leads to a change of the characteristic of the gallium gradient. The resulting gradient is visualized by the vertical shift of the CL peak wavelength on the cross section of the samples.

A.O6 2

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14:45 **Cu(In, Ga) Se2 solar cells on flexible substrate fabricated by an innovative roll to roll hybrid sputtering an evaporation process**

Authors : S. Binetti , A. Le Donne, P. Garattini, M. Raluca, S. Marchionna, A.

A.O6 3

Gasparotto^1, M. Meschia and M. Acciarri
Affiliations : Milano-Bicocca Solar Energy Research Center (MIB-SOLAR) and Dept. of Materials Science, University of Milano-Bicocca, via Cozzi 53, Milano (Italy) ; 1^ Physical Dept. and University of Padova , Via Marzolo 8, Padova (Italy)

Resume : Nowadays there are two main approaches to produce CIGS solar cells: sputtering followed by selenization evaporation and coevaporation process. High efficiency solar cells are obtained by the sequential three-stage co-evaporation process. On the other hand sputtering system is more suitable for an industrial application but the efficiencies are systematically lower. In our laboratory we have developed a new hybrid sputtering and evaporation system to obtain a scalable process combining the advantages of both techniques. The cylindrical geometry of the deposition chamber can be exploited for a roll to roll process on different large substrates (soda lime glass, flexible stainless steel or polyimide films). In this system the metal precursors are sputtered on cylindrical transfer tools then the deposited material is evaporated on the substrate in a Se atmosphere by local heating means. The sputtering deposition and successive evaporation continue until the desired thickness and composition of the film are obtained. We have systematically investigated the absorber layers and the solar cells grown on flexible substrates by a number of techniques including SIMS spectrometry, Raman and PL spectroscopy, X ray diffraction, Scanning Electron Microscopy, external quantum efficiency and I/V. The results reveal good performances (□ around 12 %) of the cells grown at T=450°C on polyimide film, high deposition rates and good control of Ga grading and Na content, for further optimization.

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15:00

Characterizing Efficiency Losses in Printed CZTSSe Solar Cells

Authors : Kaushik Roy Choudhury, Yanyan Cao, Jonathan V. Caspar, Qijie Guo, Lynda K. Johnson, Irina Malajovich, Wei Wu
Affiliations : DuPont Central Research and Development, Experimental Station, Wilmington, DE 19880

Resume : Interest and research activity in Cu2ZnSn(S,Se)4 (CZTSSe) as an earth-abundant sustainable material system for use in thin-film photovoltaics has been increasing rapidly in recent years, culminating in recently reported device efficiencies exceeding 12%. However, the critical device parameters (Jsc and Voc) of even the champion devices are still far below their physical limit. The key to more significant improvements in device performance (reduction of the deficits in Jsc and Voc, and enhancement of device fill factor) lies in the better understanding of junction characteristics as well as carrier collection and recombination mechanisms. In this paper we report on detailed characterization of high-efficiency (~9%) printed CZTSSe solar cells derived using binary and ternary nanoparticle precursors. We employ a variety of methods including variable temperature current-voltage measurements, voltage and light-bias dependent quantum efficiency measurements, admittance spectroscopy and deep level capacitance profiling (DLCP) to identify the sources of efficiency losses in these devices. Time-resolved terahertz spectroscopy was used to measure carrier lifetimes and to determine recombination mechanisms in the CZTSSe thin-films. The connection between these loss mechanisms and device microstructure will be discussed. We also report on and discuss novel solution-based processing of the charge-separating p-n junction leading to unprecedented changes in the device physics of these cells.

A.O6 4

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15:15

New materials and processes for thin film CIS solar modules with increased efficiencies and reduced cost

Authors : T. Dalibor, J. Palm, S. Jost, R. Lechner, S. Pohlner, R. Dietmüller, A. Heiss, H. Vogt, F. Karg
Affiliations : AVANCIS GmbH, Munich, Germany

Resume : The PV module price erosion requires the CIS-based thin film module technology to steadily achieve cost and efficiency optimizations. We demonstrate various significant changes to the conventional CIS layer stack ZnO:Al/i-ZnO/CdS/CIGSSe/Mo/SiN/glass. The cost and performance optimization of the new material systems and the processes involved resulted in the fabrication of 30x30cm² R&D champion modules with aperture efficiencies above 16.5% (in-house measurement). The new layer stack comprises a dry PVD-deposited InxSy-based buffer layer without toxic waste water. The commonly used Mo back electrode is substituted by a modified low cost back electrode deposited on a special float glass with higher strain point. We reduced the cell width after optimization of the magnetron sputtered ZnO:Al window layer. Application of ps P1 and P2 laser patterning processes allowed for a

A.O6 5

further reduction of dead area. Thorough characterization of the individual layers supported the optimization of the overall performance of the device: PL decay time, XRF, SIMS, Raman and VIS/IR spectroscopy, resistivity and hall measurements. For the evaluation of the final device we apply spectral response and electroluminescence besides the STC I-V characterization from which we extract primary and secondary solar parameters.

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15:30 **coffee break**

Poster 2: Absorber growth and properties - CZTSSe : David Mitzi + Susanne Siebentritt

16:00 **Synthesis and characterization of Cu2ZnGeSe4 thin films for photovoltaic applications**

Authors : M. Buffière1,2, H. El Anzeery1,2,5,6, G. Brammertz3,4, M. Meuris3,4, J. Poortmans1,2

Affiliations : 1 Department of Electrical Engineering (ESAT), KU Leuven, Kasteelpark Arenberg 10, 3001 Heverlee, Belgium; 2 imec- partner in Solliance, Kapeldreef 75, 3001 Leuven, Belgium; 3 imec division IMOMEC - partner in Solliance, Wetenschapspark 1, 3590 Diepenbeek, Belgium; 4 Institute for Material Research (IMO) Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium; 5 KACST-Intel Consortium Center of Excellence in Nano-manufacturing Applications (CENA), Riyadh, KSA; 6 Microelectronics System Design Department, Nile University, Cairo, Egypt;

Resume : Wide band gap materials are very promising absorbers for thin film solar cells. So far, the most studied absorbers for such application are: CuGaSe2, CuInS2 and CuZnSnS4. Cu2ZnGe(S,Se)4 (CZGSSe) can be also considered as a potential alternative for thin film devices since, theoretically, it exhibits a wide bandgap of about 1.5 eV. In this work, CZGSe thin films were deposited on Mo-coated SLG substrates by sequential deposition of sputtered Cu, Zn and e-beam evaporated Ge from elemental targets followed by selenization at high temperature using H2Se gaz. We report on the effect of the initial composition of the precursor and the impact of the stack order of the metallic layers on the physical properties of the absorber. The CZGSe thin films were characterized by means of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and optical transmission analysis. A preliminary study has shown that polycrystalline CZGSe thin films can be obtained for an annealing temperature above 400 oC. The best homogeneity and morphology of CZGSe thin films were obtained for metal stacked layers with the following order: (Mo/)Cu/Zn/Ge. This can be explained by the difference in mechanical stress induced by the deposition techniques between the Ge and the Cu/Zn layers, as well as the formation of secondary phases during the selenization process. We show that by adjusting the thicknesses of the Cu, Zn and Ge stacked layers, the final composition of the CZGSe absorber can be controlled and the formation of secondary phases such as ZnSe can be prevented. This synthesis process allows synthesizing CZGSe absorber with an optical band gap up to 1.45 eV.

A.P2 1

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16:00 **Fabrication of CZTSSe Solar Cells from Solution Processing of Nanocrystals**

Authors : Joel van Embden, Anthony Chesman, Enrico Della Gaspera, Noel Duffy, Jacek Jasieniak

Affiliations : CSIRO Materials Science and Engineering Bayview Ave, Clayton, VIC 3168 Australia

Resume : Solution processable solar cells prepared from low-cost and earth abundant elements are emerging as a valuable alternative compared to conventional devices deposited via vacuum-based processing. Here we discuss the advantages of utilizing compositionally and structurally tuned colloidal nanocrystals (NCs) as building blocks of such devices. Our recent efforts in developing scalable methods for synthesizing kesterite Cu2ZnSnS4 (CZTS) NCs, enable the deposition of CZTS thin films using a variety of solution-based methods, such as printing and spraying. The NCs surface chemistry is optimized using short chain volatile ligands, enabling them to be dispersed in a variety of non-toxic polar solvents and permitting the development of fully tailored inks compositions. The as-deposited nanocrystalline films possess poor electronic properties, arising from the large number of grain boundaries and from the presence of the organic ligands. Chemical and thermal treatment steps are applied in order to modify the surface chemistry, incorporate Se into the lattice

A.P2 2

and induce large scale grain growth, resulting in a highly photoactive p-type layer. The n-type cadmium sulfide layer is also deposited from solution using an aqueous bath method. Working devices with efficiency up to 7.6% are prepared. Every processing factor is discussed in detail, highlighting the significant challenges that need to be overcome in order to fabricate working CZTSSe thin film solar cells from nanocrystals.

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16:00 **Raman scattering study of the A-modes in kesterite $Cu_2ZnSnSe_4$ polycrystalline thin films**

Authors : Chia-Wen Chang, Yu-Yun Wang, Ho-Min Chen, Hung-Ru Hsu, Shih-Hsiung Wu, Tung-Po Hsieh, Chung-Shin Wu

Affiliations : Green Energy and Environment Research Laboratories, Industrial Technology Research Institute (ITRI)

Resume : In this work, hydrazine-hydrate solution-based methods have been successfully employed to fabricate Cu_2ZnSnS_4 (CZTS) nano-particle. CZTS precursor thin films on Mo-coated glass substrates were grown by the doctor-blade coating technique. The CZTS thin films were selenized at temperatures of 550oC with Se vapor in quartz tube furnace. Microstructure investigation and A-modes speculation of $Cu_2ZnSnSe_4$ (CZTSe) thin films have been systematically studied with the increase of selenization ramping rate and temperature. Selenization was performed at temperatures of 550 oC with the ramping rate in the range 5 °C/min to 30 °C/min. The Raman peaks at 170 cm-1 and 192−194 cm-1 are found to have asymmetry signals. The Raman signal at 170 cm-1 is found to be composed of two gaussian fitting peaks at 168 cm-1 and 172 cm-1 are related with $MoSe_2$ and CZTSe signals, respectively. The deconvolution of A-mode at 191-195 cm-1 Raman signal into two Gaussian peaks. The A-modes are decomposed of two symmetry gaussian peaks at A’-mode 191 cm-1 (FWHM 10 cm -1) and A-mode 194 cm-1 (FWHM 5 cm-1). The area ratio of gaussian peaks A/A’ increases with decreasing ramping rate. We attribute that broaden A’ Raman peak is probably originated from disordered-phase in matrix as well as A sharpen 194 cm-1 peak is kesterite ordered-phase in polycrystalline $Cu_2ZnSnSe_4$ grains. A.P2 3

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16:00 **Study of structural and optoelectronic properties of $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ (x = 0 to 1) alloy compounds**

Authors : M. Grossberg, K. Timmo, T. Raadik, E. Kärber, V. Mikli

Affiliations : Department of Materials Science, Tallinn University of Technology, Estonia

Resume : The I2-II-IV-VI4 (I=Cu,Ag; II=Zn,Cd; IV=Si,Ge,Sn; VI=S,Se) series of quaternary chalcogenide semiconductors have drawn wide interest for their application as solar-cell absorbers. In this study we investigate the optoelectronic and structural properties of $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ (CZTGeSe) alloy compounds with x varying from 0 to 1 with a step of 0.1. Radiative recombination processes in CZTGeSe polycrystals were studied by using low-temperature photoluminescence (PL) spectroscopy. A continuous shift from 0.96 eV to 1.33 eV of the PL band position with increasing Ge concentration was detected. Recombination mechanisms responsible for the PL emission are discussed. The crystal structure and the lattice parameters of the CZTGeSe polycrystals were determined by using X-ray Diffraction (XRD) analysis. A linear decrease of the lattice parameter from a = 0.569 nm to a = 0.561 nm with increasing Ge concentration was detected. Raman spectroscopy analysis revealed unimodal behavior of the dominating A1 Raman mode that showed linear shift from 196 cm-1 to 205 cm-1 with increasing Ge concentration. A.P2 4

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16:00 **Preparation of $Cu_2ZnSnSe_4$ Thin Films through Selenization of Muti-layer Precursors in Selenium Atmosphere for Solar Cell Application**

Authors : Wei-Chao Chen1, 2, 3, Hsien-Wen Li4, Jih Shang Hwang4, Kuei-Hsien Chen2*, Li-Chyong Chen3

Affiliations : 1 Engineering and System Science, National Tsing Hua University 2 Institute of Atomic and Molecular Science, Academia Sinica 3 Center for Condensed Matter Science, National Taiwan University 4 Institute of Optoelectronic Science, National Taiwan Ocean University A.P2 5

Resume : Here, we performed a 4-step selenization process and discussed the corresponding reaction mechanism that involves binary and ternary compounds as intermediates. At the beginning stage, we deposited the metal precursors using Cu–Zn and Sn targets by RF magnetron sputtering process. Then, the reaction of Se vapour with samples at a series of varying temperatures was studied. By precisely controlling the nucleation temperatures from 150 oC to 500 oC during the 4-step selenization, the homogeneity and crystal quality of

CZTSe can be improved, and the binary phase can be totally ruled out. At the first stage using 150 oC in vacuum, the stack alloy contains elemental Sn as well as bronze (Cu6Sn5) and brass (Cu5Zn8). Then, the phase formation began with the emergence of ZnSe, CuSe, and Cu-Sn-Se between 250 oC and 360 oC in Se atmosphere. Raman spectroscopy definitively showed the CZTSe phase emerging around 360 oC, although the presence of Cu–Sn–Se phases could not be totally ruled out. Finally, stoichiometric and less impurity CZTSe thin film formed at the optimum annealing conditions of 500 oC for 10 min. Noting that lower or higher temperature lead to insufficient crystallization or undesirable phase segregation. Finally, the device performance demonstrated an open circuit voltage and short circuit current of CZTSe solar cell close to 310 mV and 35.63 mA/cm2, yielding an overall efficiency of 4.75 %.

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16:00 **Defect study of solution-processed Cu2ZnSn(Sx,Se1-x)4 thin film absorbers using photoluminescence and modulated surface photovoltage spectroscopy** A.P26

Authors : Xianzhong Lin1, Thomas Dittrich1, Sergui Levcenco1, Jaison Kavalakkatt1, Martha Ch. Lux-Steiner1,2, and Ahmed Ennaoui1

Affiliations : 1 Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany 2 Freie Universität Berlin, Berlin, Germany

Resume : Recently we have developed a novel synthesis and formulation of copper-zinc-tin-sulfur nanoparticle inks relying on binary and ternary chalcogenide nanoparticles (ZnS, SnS and Cu3SnS4) as precursors. The CZTSSe thin films were formed by annealing the spin coated Cu-Zn-Sn-S nanoparticle precursor thin films under Se-containing atmosphere. The chemical composition of the resulting absorber layers can be tuned by varying the ratios of the nanoparticle precursors in the inks. In this contribution, we report on the study of the defect states of Cu2ZnSn(Sx,Se1-x)4 (CZTSSe) thin films by combination of photoluminescence (PL) and surface photovoltage (SPV) spectroscopy. Prior to the PL and SPV measurements, the morphology and phase purity of the absorber layers were investigated with scanning electron microscopy and X-ray diffraction. The Raman spectroscopy was utilized to further confirm the structural properties. PL measurements revealed donor-acceptor pairs transition as evidenced by a blue shift of PL peak by less than 15 eV/decade with increasing excitation power. Regarding to temperature dependent PL measurements, we found that a-two activation energy model gave the best fit for the Arrhenius plot. Additionally, temperature dependent SPV further confirmed the defect states. A deeper defect with activation energy of approximate 300 meV was found. The relationship and the assignment of these defect states will be discussed in details. Solar cell formation is completed by chemical bath deposition of CdS buffer layer followed by sputtered i-ZnO/ZnO: Al bi-layers. Using pre-optimized conditions, we achieved 3% efficient solar cells.

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16:00 **Morphology study of CZTS formed at diverse annealing conditions using different precursor routes** A.P27

Authors : Verena Kaltenhauser(a), Christine Buchmaier(a), Thomas Rath(a), Stefan M?ller(b), Ferdinand Hofer(c), Roland Resel(d), Gregor Trimmel(a)

Affiliations : (a) Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria (b) Institute of Anorganic Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria (c) Institute for Electron Microscopy and Fine Structure Research, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria (d) Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Resume : Kesterite-type Cu2ZnSnS4 (CZTS) is a very promising absorber material for low cost and high efficiency thin film photovoltaic modules due to its direct band gap of 1.5 eV and due to its high absorption coefficient. Especially direct solution coating approaches for depositing kesterite absorbers are very interesting since they offer all the requirements essential for a low-cost roll-to-roll PV technology. In this contribution we investigated different annealing conditions of the precursor layers in order to obtain high purity CZTS with large crystallite size. Therefore, different precursor routes, such as metal salts with thiourea or thioacetamide as sulfur source and DMSO as solvent were applied. In another approach, metal xanthates were used as precursors. This route offers the advantages that no chlorides are present in the precursor layer, no additional sulfur source is necessary and the precursor compounds decompose at temperatures below 200 ?C. We compared different heating rates, annealing times, temperatures and atmospheres. The main focus was set on differences in roughness, crystallinity, chemical composition, purity and morphology of the prepared CZTS thin films. Moreover, based on these results, first solar cells were fabricated. We used surface profilometry, X-ray diffraction, Raman spectroscopy and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX) for the characterization of the thin films.

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16:00 **Local work function of Cu2ZnSn(S,Se)4 (η> 9.1%) thin-films with respect to ZnS thickness in precursor by two-step sputtering** A.P2 8

Authors : Gee Yeong Kim1, Ju Ri Kim1 William Jo1,*, Dae-Ho Son2, Kee-Jeong Yang2, Dae-Hwan Kim2, and Jin-Kyu Kang2

Affiliations : 1Department of Physics, EwhaWomans University, Seoul, 120-750, Korea; 2Daegu Gyeongbuk Institute of Science and Technology, Daegu, 711-873, Korea

Resume : Cu2ZnSnSSe4 (CZTSSe) and its related compounds are the most promising absorber materials for thin films solar cells because of their abundance, low toxicity, good optical absorption. The CZTSSe thin-films were grown by stacked sputtering and co-sputtering with different ZnS thickness and subsequent selenization process in a furnace (DGIST made the CZTSSe thin-film solar cells). For this study, thickness of ZnS layer in precursor of CZTSSe thin-films influence composition ratio and photovoltaic properties were exhibited. It also confirmed that there are significant different with conversion efficiency and device performances depending on ZnS thickness. Kelvin probe force microscopy was used to explore the local electrical properties of the CZTSSe thin-films. The work function of CZTSSe thin-film indicates around 4.7 eV. Depending on ZnS thickness, work function distribution of CZTSSe thin-film present different. The surface work function provides clues to understand the effects ZnS layer between CZTSSe thin-film solar cells. With respect to Zn composition, higher work function phase is identified compare with CZTSSe (Φ = 4.7 to 4.8 eV). It could be attributed by the formation of secondary phases at CZTSSe surfaces. From the local electrical characterization, we can identify the effects of ZnS thickness in CZTSse thin-film solar cells. Consequently, the Zn composition in CZTSSe thin-film solar cell is essential of consideration to improving cell efficiency.

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16:00 **Optical spectroscopy studies of Cu2ZnSnSe4Thin Films** A.P2 9

Authors : M.V.Yakushev1,2; I. Forbes3; A.V.Mudryi1,4; M. Grossberg5; J.Krustok5; N. S. Beattie3; M. Moynihan2; and R.W. Martin1

Affiliations : 1Department of Physics, SUPA, University of Strathclyde, Glasgow, G4 0NG, UK; 2Academy of Science of Russia and URFU, Ekaterinburg, Russia; 3Northumbria Photovoltaics Applications Centre, Northumbria University, Newcastle upon Tyne, UK; 4Scientific-Practical Material Research Centre of the National Academy of Science of Belarus, Minsk, Belarus; 5Tallinn University of Technology, Tallinn, Estonia.

Resume : Cu2ZnSnSe4 (CZTSe), containing cheap and earth abundant elements, has a great potential for wide scale PV due to its direct band gap, possibility of p-type doping and high absorption coefficient. However, very little experimental evidence has been reported on the nature of its intrinsic defects. Improving the structural quality of CZTSe provides an opportunity to clarify the defect nature and electronic properties using optical spectroscopy. Thin films of CZTSe were synthesised by selenisation of magnetron sputtered metal precursor layers deposited on soda-lime glass. The X-ray diffraction and Raman spectra demonstrate single phase material. Photoluminescence (PL) spectroscopy is used to study the defect nature in a number of films of different structural quality. In lower quality films PL spectra show a broad low intensity band at 0.98 eV, which doesn’t shift with changing excitation power. In high quality material the band becomes narrower and two phonon replicae are resolved. Increasing excitation power shifts the band towards higher energies, suggesting that the mechanism is donor-acceptor pair (DAP) recombination. We propose a recombination model involving two pairs of donors and acceptors, which is supported by the Arrhenius quenching analysis and evolution of the DAP line spectral position with temperature. The band gap is determined from absorption spectra and observed to shift from 1.05 eV at 4.2 K to 1.01 eV at room temperature.

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16:00 **Formation and characterization of Cu2ZnSiSe4 high band gap absorber for thin film solar cells** A.P2 10

Authors : Hossam ElAnzeery, Marie Buffière, Ounsi ElDaif, Souhaib Oueslati, Khaled Ben Messaoud, Guy Brammertz , Rafik Guindi, Marc Meuris and Jef Poortmans

Affiliations : KACST-Intel Consortium Center of Excellence in Nano-manufacturing Applications (CENA), Riyadh, KSA; Microelectronics System Design department, Nile University, Cairo, Egypt; imec – partner in Solliance, Kapeldreef 75, 3001 Leuven,

Belgium; Department of Electrical Engineering, KU Leuven, Kasteelpark Arenberg 10, 3001 Heverlee, Belgium; Department of Physics, Faculty of Sciences of Tunis, El Manar, Tunisia; Institute for Material Research (IMO) Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium; imec division IMOMEC – partner in Solliance, Wetenschapspark 1, 3590 Diepenbeek, Belgium

Resume : Cu2ZnSiSe4 (CZSiSe) is a promising potential alternative material to obtain a high band gap absorber for multi-junction thin film solar cell devices. Theoretically, CZSiSe can reach bandgap of up to 1.7eV, however not many work have been reported on the fabrication and characterization of this absorber material. In this work, CZSiSe absorber is fabricated using a multistep process sequence. In the first step, Cu and Si are sequentially deposited using evaporation techniques on molybdenum coated soda lime glass substrate. The sample is then annealed to form copper silicide. This is followed by sputter deposition of Zn. Finally, the sample is selenized using H2Se gas at high temperature to form Cu2ZnSiSe4. The composition of the CZSiSe absorber was controlled through the optimization of the thicknesses of Cu, Si and Zn stacked layers with the annealing temperature. X-ray Diffraction (XRD) was used to show the formation of copper silicide peaks at annealing temperature as low as 200 degrees. Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), Photoluminescence Spectroscopy (PL) and optical measurement analysis were also used to characterize CZSiSe absorber material. An analysis of the electronic and physical properties of the studied CZSiSe absorber will be reported and discussed. Finally, we will show tests on n-type CdS/p-type CZSiSe based solar cells in order to assess the potential of this material as an absorber in thin film photovoltaic device

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16:00

Selenization of solution-deposited CZTS precursors under controlled Se overpressure in evacuated glass ampules

Authors : Stefan G. Haaß, Carolin M. Sutter, Yaroslav E. Romanyuk, Ayodhya N. Tiwari
Affiliations : Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Thin Films and Photovoltaics, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

Resume : One of the most critical steps in the synthesis of solution-deposited Cu2ZnSn(S,Se)4 absorber layers is the inevitable annealing at high temperatures in order to obtain the polycrystalline semiconductor material. At this point the loss of Sn as a result of decomposition and evaporation of SnS has to be prevented by controlling the overpressure of these volatile phases. In this work the annealing process was performed in evacuated glass ampules thus offering the possibility to tailor exactly the Se partial pressure. Two series of annealings under different conditions were investigated: with an increasing amount of Se and with different precursor compositions. For the first series, XRD and XRF measurements show increased incorporation of Se with increasing amount of Se put into the ampules. The second series uses precursors with different metal ratios starting from copper poor to copper rich compositions (0.75 ≤ Cu/(Zn Sn) ≤ 1.11). SEM and EDX measurements reveal segregation of copper rich phases on top of the initial layer in the Cu-rich regime. All samples were processed to complete devices and IV-measurements were performed for electrical characterization. Device efficiencies up to 5.2% were obtained for copper poor and zinc rich precursor compositions and a comparably high amount of Selenium provided during the annealing process.

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16:00

Influence of defects on photoluminescence from Cu2ZnSnS4 thin films

Authors : J. P. Teixeira (1), R. A. Sousa (1), J. P. Leitão (1), M. G. Sousa (1), A. F. da Cunha (1), P. A. Fernandes (1,2), P. M. P. Salomé (3)
Affiliations : (1) Departamento de Física and I3N, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal; (2) Departamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal; (3) International Iberian Nanotechnology Laboratory, Laboratory for Nanostructured Solar Cells, Av. Mestre José Veiga, 4715-330 Braga, Portugal;

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Resume : New solar cell absorber materials like Cu2ZnSnS4 (CZTS), are nowadays object of intense study in order to improve the power conversion efficiency of the devices. For that same purpose, in this work we prepared CZTS thin films and evaluated the influence of the sulfurization conditions (temperature, duration and evaporated sulphur mass) on their physical properties. The precursor structures were prepared with of eight periods each consisting on layers of the binaries (CuS, SnS2) and of elemental Zn. This approach allows a better control of the film’s composition in depth. Scanning

electron microscopy revealed higher grain size for samples sulfurized at higher temperature and with more sulphur mass. The structural analysis, performed by X-ray diffraction and Raman spectroscopy, has shown that the dominant phase in all samples was the CZTS. The photoluminescence analysis of the samples with higher grain size and higher cell conversion efficiency showed that the dominant band corresponds to radiative recombination of electrons localized in tails of the conduction band and holes localized in acceptor energy levels. This type of transition is observed in CZTS for the first time. It was estimated an ionization energy for the acceptor levels of 284±8meV and a depth of 22±1meV for the electrons energy levels in the tail of the conduction band. The non-radiative de-excitation mechanisms were assigned to two channels, one involving a discrete energy level and another involving a band.

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16:00 **The influence of SnS powder during annealing process on S/(S+Se) ratio and open circuit voltage in CZTSSe thin film solar cells**

Authors : Chung-hao Cai , Shih-Yuan Wei , Chih-Huang Lai

Affiliations : Department of Materials Science and Engineering , National Tsing Hua University , Taiwan R.O.C

Resume : Cu2ZnSn(S,Se)4 (CZTSSe) absorbers are produced by two-step process by means of selenization of stacked precursors. The stacked precursors are prepared from Cu,ZnS,SnS2 targets by Ion Beam Sputtering deposition (IBSD) onto Mo-coated glass substrates with the stacking order :SLG/Mo/ZnS/SnS2/Cu .The stacked precursors are annealed at 550°C in a graphite box with Se and SnS powder. The effects of the amount of tin sulfide during selenization on the structure and morphology, as well as the electrical properties of the CZTSSe absorbers have been investigated. SEM studies reveal that the grain sizes decreased as the amount of tin sulfide increased. Raman spectroscopy studies show CZTSe peak intensity decreased and CZTS peak intensity increased as the amount of tin sulfide increased. EDX and ICP studies demonstrate that S/Se+S ratio which ranging from 0 to 0.5 can also be preciously controlled by tuning selenization condition. Device characteristics show that open circuit voltage increased obviously and short circuit current density almost kept the same when the amount of tin sulfide increased. The best cell performance can be achieved under the certain amount of SnS powder and the conversion efficiency is 7.2% with Voc=410mV , Jsc=30.61mA/cm2 and FF=0.58. A.P2 13

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16:00 **Pulsed laser deposition of thin films of CZTS: Fluence and substrate temperature dependence**

Authors : Andrea Cazzaniga, Rebecca B. Ettlinger, Stela Canulescu, Jørgen Schou, Nini Pryds

Affiliations : DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde; Denmark, DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark; DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark; DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark; DTU Energy Conversion, Technical University of Denmark, DK-4000 Roskilde, Denmark

Resume : Thin films of Cu2ZnSnS4 (CZTS) have been produced with Pulsed Laser Deposition (PLD) using a KrF excimer laser operating at a wavelength of 248 nm. Pulsed laser deposition is one of the most promising techniques for achieving high quality films of complex stoichiometry. By this process all elements from the CZTS target are arriving simultaneously at the substrate, but if the target material includes volatile species, e.g. S or Sn atoms, the films may lose a considerable amount of these elements during the deposition. In this study we will investigate the loss of volatile elements during the transfer process as well as the crystalline quality of the thin CZTS films as a function of the laser energy (fluence range 1-3 J/cm2) and substrate temperature (up to 250 Co). Further loss of S and Sn during the post-deposition annealing will also be investigated. Compositional analysis is done with energy dispersive x-ray spectroscopy (EDX), the crystalline quality is investigated with Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analysis. The band gap is evaluated with UV-visible spectroscopy. By this technique the use of the toxic and explosive hydrogen sulfide gas during deposition is avoided. A.P2 14

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16:00 **Reactively sputtered films in the Cu2S-ZnS-SnSx system: from metastability to equilibrium**

Authors : Y. Ren, J. J. Scragg, T. Ericson, T. Kubart, C. Platzer-Björkman

Affiliations : Ångström Solar Center, Solid State Electronics, Uppsala University, Box 534, SE-75121 Uppsala, Sweden A.P2 15

Resume : Cu_2ZnSnS_4 (CZTS) is a promising PV absorber containing only abundant elements. Using a two stage process, low temperature reactive co-sputtering followed by heat treatment, we have achieved a 7.9% efficient solar cell. Because the sputtered precursors contain non-equilibrium phases with unusual crystal structures, it is crucial to understand their nature and their conversion into CZTS (and secondary phases) during heat treatment. We report composition and phase analysis of reactively sputtered binary and ternary sulfides in the Cu_2S-ZnS-SnS_x system before and after annealing. In the as deposited films, Raman spectroscopy with 532 and 325 nm excitation reveals expected phases for the binaries (CuS, ZnS and SnS_2) and the ternary (Cu_2SnS_3), and unique metastable phases for the Cu-Zn-S and Zn-Sn-S precursors. Upon annealing, the non-equilibrium phases disappear, accompanied by additional chemical changes. Excess S content in the films is removed, and in the Sn-S and Zn-Sn-S films, further S loss from decomposition of SnS_x ($x>1$) generates SnS. Due to the presence of background SnS vapor, CZTS is generated from the Cu-Zn-S precursor. In the end, the correlation between composition and equilibrium phases of the annealed films in the phase diagram is established. This gives us useful insight allowing better control of annealing conditions.

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16:00 **Compositionally tunable structure and optical properties of $Cu_{1.85}Cd_xZn_{1-x}SnS_4$** A.P2 16

Authors : M.Pilvet, M.Kauk-Kuusik, M.Altosaar, M.Grossberg, J.Krustok, K.Timmo, A. Mere, V. Mikli, M. Danilson

Affiliations : Department of Materials Science, Tallinn University of Technology

Resume : This work reports the analysis of structural and optical properties of $Cu_{1.85}Cd_xZn_{1-x}SnS_4$ (0

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16:00 **Preparation of $Cu_2ZnSn(S,Se)_4$ solar cells using a chemical bath deposition route** A.P2 17

Authors : Chao Gao1, Thomas Schnabel2, Tobias Abzieher2, Mario Lang1, Christoph Krämmer1, Erik Ahlswede2, Michael Powalla2,3, Heinz Kalt1, and Michael Hetterich1

Affiliations : 1 Institute of Applied Physics, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; 2 Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), 70565 Stuttgart, Germany; 3 Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

Resume : Here we report a low-cost aqueous solution method to fabricate $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells. For the preparation, first SnS, CuS, and ZnS precursor layers are successively deposited on a molybdenum-coated soda-lime glass substrate using chemical bath deposition. Tin(II) chloride, ammonium citrate and sodium thiosulfate are used for the deposition of SnS, copper(II) chloride, triethylamine and thiourea for CuS, and zinc acetate, sodium citrate and thiourea for ZnS, respectively. An ammonia solution is used to adjust the pH value and water serves as solvent. Crystalline CZTSSe is then obtained via a closed-space selenization reaction in a graphite box. Solar cells additionally comprise a chemical-bath-deposited CdS buffer layer and a sputtered transparent ZnO top contact. Scanning electron microscopy (SEM) pictures prove the good crystallization of the CZTSSe layers. X-ray diffraction and Raman measurements are consistent with the assumption of kesterite being the dominant phase in the selenized films. By optimizing the parameters, CZTSSe solar cells with efficiencies above 4.4% can be achieved. In contrast to other fabrication methods for CZTSSe solar cells, the presented approach does not use organic solvents and the preparation process is relatively simple (the precursor films are deposited on the substrate directly, so no additional film formation process is needed). These advantages suggest our method to be promising for the fabrication of kesterite solar cells.

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16:00 **Preparation of $Cu_2ZnSnSe_4$ solar cells using a co-evaporation route** A.P2 18

Authors : Chao Gao1, Thomas Schnabel2, Tobias Abzieher2, Mario Lang1, Christoph Krämmer1, Michael Powalla2,3, Heinz Kalt1, and Michael Hetterich1

Affiliations : 1 Institute of Applied Physics, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; 2 Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), 70565 Stuttgart, Germany; 3 Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

Resume : $Cu_2ZnSnSe_4$ (CZTSe) is a promising absorber material for thin-film solar cells utilizing non-toxic earth-abundant constituents. While co-evaporation at high temperatures is the most successful fabrication technique for the related $Cu(In,Ga)(S,Se)_2$ system, this route is more problematic for CZTSe. The reasons include that the single phase range of CZTSe is narrower than for CIGS, and part of the involved chemical species are very volatile at high temperatures. Therefore, a fabrication route based on the deposition of precursors at low temperatures followed by high-temperature selenization seems to be more attractive. By this method, the materials loss can also be controlled in a low level compare to the high-temperature co-evaporation route. In this contribution, Cu2ZnSnSe4 thin films have been prepared on molybdenum coated soda-lime glass substrates by co-evaporation of high-purity (6N) Cu, Zn, Sn, and Se at low substrate temperature (~100 °C) in a molecular-beam epitaxy system (MBE), followed by high-temperature selenization in a graphite box using a tube furnace. Solar cells additionally comprise a chemical-bath-deposited CdS buffer layer and a sputtered transparent ZnO top contact. X-ray diffraction and Raman measurements are consistent with the assumption that mainly kesterite Cu2ZnSnSe4 has formed. The parameters influencing the CZTSe layer properties are investigated. Their optimization results in CZTSe solar cells with efficiencies above 4.6%.

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16:00 Cu2-Zn-IV-VI4 (IV=Ge,Sn; VI=S,Se) quaternary chalcogenide: structural and optoelectronic characterization

Authors : Eduard Garcia-Llamas(a), Raquel Caballero(a), Ivan V. Bodnar(b), Ivan A. Victorov(b), Susan Schorr (c), Máximo León(a) and José Manuel Merino(a)

Affiliations : (a) Photovoltaic Materials Group, Facultad de Ciencias, Universidad Autónoma de Madrid (UAM), 28049 Madrid, Spain (b) Institute of Physics of Solids and Semiconductors, Academy of Sciences of Belarus, 17 P. Brovka Str., 220072, Minsk, Belarus (c) Free University Berlin, Institute of Geological Sciences, Malteserstr. 74-100, Berlin, Germany

Resume : The Cu2-Zn-IV-VI4 (IV=Ge,Sn; VI=S,Se) series of quaternary chalcogenide semiconductors have drawn a wide interest for their application as solar-cell absorbers. Cu2ZnSn(S,Se)4 are abundant and environmentally friendly thin film absorbers with 12.6%[1] record efficiency. It has been shown that the sulphide and selenide quaternary Sn-compounds crystalize in kesterite structure, both showing a certain disorder between the Cu and Zn sites[2,3]. However, their Ge-analogs appear to occur both in stannite or wurtzite-derived structure[4]. Here, different bulk samples of Cu2Zn(SnXGe1-X)Se4 and Cu2Zn (SnXGe1-X)S4 (x = [0.0,1.0]) solid solutions have been grown by Bridgman and chemical vapour transport. The aim of the work is a description of the structural properties of such pentenary solid solutions, with emphasis on the distribution of the isoelectronic cations Cu+, Zn2+ and Ge+ by means of neutron and X-ray diffraction. Besides ellipsometry and Hall effect will be used to understand the relationship between structural and optoelectronic properties. The success of the CIGSe devices is mainly based on the absorber band-gap engineering, and this factor could be the key for the efficiency improvement of CZTGeS solar cells. [1] Wang, et al. Adv. Energy Mater.(2013) [2]Siebentritt et al. Prog. Photovolt.: Res.Appl. 20, 512-9(2012) [3]Schorr. Sol. En. Mater. Sol.Cells 95,1482-8(2011) [4]Chen et al. Phys.Rev. B 82, 195203(2010) [5]Nakamura et al. Jpn.J.Appl.Phys.49,121203(2010)

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16:00 A study on the importance of ligands towards the CZTS particle system for thin film solar cells

Authors : Stijn Flamee; Kim De Nolf; Dirk Van Genechten; Phillip Dale; Jose Martins; Zeger Hens

Affiliations : Ghent University, Umicore, University of Luxembourg

Resume : CZTS is a promising earth abundant material for thin film solar cells. Opposite from CIGS and CdTe, best conversion efficiencies have been obtained using wet chemical deposition methods. This approach makes use of inks, which can be composed of molecular precursors or precursor particles. For particle-based inks, dispersion stability is a key issue. A stable ink is needed for the deposition of crack-free precursor films, yet the additives from the ink remain in this film and may influence its transformation behavior. Here, we report on the influence of oleylamine, thiols and sulfide anions, 3 of the most often used stabilizing agents on CZTS nanocrystals, and their influence on layer deposition and transformation behavior upon sulfurization. In the case of oleylamine-stabilized nanocrystals, we find a clear relation between high ligand density and Newtonian flow behavior of the dispersions and the formation of crack-free films. With thiols, these problems are circumvented since they serve as both stabilizing agent and solvent. However, the presence of organic molecules as stabilizing agents leads to a bilayered structure upon sulfurization, with big CZTS crystallites on the top side, and a carbon rich small crystallite zone on the

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bottom side. Sulfide anion ligands allow carbon free layers to be deposited. The resulting absorber layers are single layers, but with no observable grain growth. It appears that the presence of carbon ligands helps drive grain growth.

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16:00

Optical and microstructural characterization of CZTS thin films with different composition

Authors : C. Malerba, M. Valentini, C. L. Azanza Ricardo, P. Scardi, A. Mittiga

Affiliations : C. Malerba, C. L. Azanza Ricardo, P. Scardi: University of Trento – DICAM, via Mesiano 77, 38123 Trento, Italy; M.Valentini: Sapienza - University of Roma – Department of Physics, p.le Aldo Moro 5, 00156 Rome, Italy; A. Mittiga: ENEA Casaccia Research Center, via Anguillarese 301, 00123 Rome, Italy

Resume : Cu2ZnSnS4 (CZTS) is a quaternary semiconductor which attracted much attention in the recent years as environmental friendly and very promising absorbing material for photovoltaic applications. The best efficiencies of CZTS-based solar cells are obtained using a Zn-rich and Cu-poor composition, but the influence of stoichiometry on CZTS optical and microstructural properties has not yet thoroughly investigated. In this study, CZTS (kesterite) thin films with different compositions were prepared by sulfurization of precursors co-sputtered from CuS, SnS and ZnS targets. XRD, Raman Spectroscopy, EDX and SEM were used for microstructural, compositional and morphological characterization. XRD data were analyzed using Rietveld approach in order to estimate the amount of possible spurious phases as well as the Sn-site occupancy in the CZTS phase. The optical properties were investigated by spectrophotometric measurements and Photoluminescence Spectroscopy. Preliminary results show a dependence of the optical and microstructural properties on the tin content pointing to an improvement of the morphology and to an increase of the energy gap as the tin content increases. All the materials were also used as absorber layer in solar cells. Up to now the best material gave a device with a conversion efficiency of 5.7%.

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16:00

Evolution of the structure and the properties of copper sulfide films as a function of the deposition pressure and the annealing temperature

Authors : A. Didelot, P. Miska, J.F. Pierson

Affiliations : Institut Jean Lamour, UMR CNRS Université de Lorraine, Nancy, France

Resume : Cu2ZnSnS4 coatings are widely studied for their use as absorber layer into photovoltaic devices. A small deviation from this stoichiometry may induce the formation of binary and/or ternary phases. Since the occurrence of such phase lowers the conversion efficiency of the cells, a detailed study of the properties of these binary and ternary phases is required. This communication aims to bring relevant information about the effect of the chemical composition of copper sulfide films on their structural, optical and electrical properties. The films were deposited on silicon and glass substrates by magnetron sputtering of a CuS target. The total pressure in the deposition chamber was adjusted from 0.3 to 2 Pa. As-deposited films are poorly crystallized as confirmed by XRD. An annealing treatment in air at 200°C allows improving the crystallization. An oxidation of the samples is evidenced when the annealing temperature reaches 300°C. However, no significant change is observed by Raman spectrometry after such annealing treatments. The increase of the deposition pressure induces a small variation of the film composition that does not influence the structure. The film morphology is strongly influenced by the increase of the total pressure. Optical properties of the films have been studied by UV-visible spectrophotometry. A maximum of transmittance is observed in the visible range. Finally using Hall effect measurements, the metallic character of copper sulfide films is evidenced.

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16:00

Synthesis and Characterization Cu2ZnSnS4 (CZTS) Thin Film Prepared from (Cu,Zn,Sn)-Ethanolamine Complex Compound

Authors : Ersan Y. Muslih, Kyoo Ho Kim

Affiliations : Cu2ZnSnS4 (CZTS) thin film for solar cell appllication

Resume : Cu2ZnSnS4 (CZTS) thin film was synthesized from Cu-Zn-Sn precursor which is prepared from (Cu,Zn,Sn)-ethanolamine complex compound solution using drop coating technique. The CZT precursor shows CuxZny and CuxSny binary compound films without ZnxSny binary or metal oxide compound as residue from metal-ethanolamine after drying process. The CZTS thin film was successfully formed with composition as copper near stoichiometric and zinc rich with chemical compositions ratio [Cu]/([Zn]+[Sn]) = 0.99, [Zn]/[Sn] = 1.45, and [S]/[metal] = 1.03 after sulfurization process at 550 oC for 120 minutes under Ar + H2S (5%) atmosphere. Optical properties of CZTS thin film

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were direct band gap of 1.52 eV with absorption coefficient more than 105 cm-1 and electrical properties exhibited by p-type semiconductor with mobility and resistivity of 7.64 cm2 /Vs, 3.78 Ωcm respectively.

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16:00 **Detection of selenium residues in CZTSSe via Raman spectroscopy**

Authors : Mungunshagai Gansukh1, Dahyun Nam1, Dae-Ho Son2, Dae-Hwan Kim3, Kee-Jeong Yang2,3, Jin-Kyu Kang 2,3, Hyeonsik Cheong1

Affiliations : 1Department of Physics, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul, 121-742, Republic of Korea; 2Advanced Convergence Technology Center, Daegu Gyeongbuk Institute of Science & Technology, 223 Sang-ri, Hyeonpung-myeon, Dalseong-gun, Daegu 711-873, Republic of Korea; 3Energy Research Division, Daegu Gyeongbuk Institute of Science & Technology, 223 Sang-ri, Hyeonpung-myeon, Dalseong-gun, Daegu 711-873, Republic of Korea

Resume : The record efficiency of Cu2ZnSn(S,Se)4 (CZTSSe) solar cells is currently 12.6%. But it is much lower compared to similar thin film chalcogenide solar cells based on Cu(In,Ga)Se2 (CIGS) with a maximum efficiency 20.8%. One of the possible reasons is that single-phase CZTSSe without secondary phases is difficult to make. Raman spectroscopy is a useful tool for detecting secondary phases in CZTSSe. Most studies on identifying secondary phases in CZTSSe samples using Raman spectroscopy are conducted by using green lasers (514.5 nm and 532 nm), but many secondary phases are not effectively identified. Each secondary phase has an optimal wavelength because of the resonance Raman condition. The Raman signal of selenium measured by green laser is weak and its main peak (236cm-1) can be confused with the CZTSe peak at 233 cm-1. Using the laser wavelength dependence of the Raman intensity we were able to distinguish selenium in the CZTSSe layer. In this study we investigated CZTSSe cells (maximum efficiency 7.3%) made by sputtering followed by selenization. Macro and micro Raman measurement were performed using 3 different wavelengths (441.6 nm, 514.4 nm, and 632.8 nm). Micro Raman mappings were compared with AFM to show that selenium particles were present. Selenium particles that have a size of ~0.3 μm were randomly spread over the samples. There is a high possibility that selenium particles decrease the efficiencies. We suggest that CZTSSe samples made by selenization method should be checked to see whether there are selenium residues.

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16:00 **Non-toxic sol-gel spin coating approach for low cost, earth-abundant photovoltaic absorber: Cu2ZnSn(SxSe(1-x))4, for solar-cell applications**

Authors : Venkatesh Tunuguntla1,2,3, Wei-Chao Chen1,2,4, Pei Hsuan Shih1,5, Kuei-Hsien Chen1, Li-Chyong Chen2

Affiliations : 1Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan; 2Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan; 3Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan; 4 Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan; 5Institute of Optoelectronic Sciences, Nation Taiwan Ocean University, Keelung, Taiwan;

Resume : Polycrystalline inorganic thin film photovoltaic absorbers like, CIGS and CdTe are often dealing with high production costs because of the scarcity of elements and toxic-waste disposal issues, which leads to a quest to the non-toxic and earth abundant alternatives. Besides their non-toxicity and earth-abundance, high absorption coefficient (*104) and a band gap of 1.5 eV (can be tuned 1~ 1.5 eV with varying Se to S ratio), optimal for single-junction solar-cells, make Cu2ZnSnS4 (CZTS) and Cu2ZnSnSe4 (CZTSe) are the promising candidates for low cost solar-cells. In contrast to vacuum-based deposition techniques, the solution-based CZTS deposition techniques become attractive routes due to their high yield and cost-effectiveness, which can be extended for mass-production very easily. Herein, this report presents a simple spin coating process for the preparation of CZTS films using a non-toxic solvent. This process has advantages in terms of the non-toxicity of the solvent, solubility of precursors, annealing time (in H2S ambience) and quality of the final film. In our process, we prepared a viscous coating solution by simple room-temperature sonication, which involves dissolution of organo- metallic precursors (metal-ion sources) and sulphide precursor (sulphide-ion source) in a heterocyclic based solvent in nitrogen-filled glove box and kept for sonication about an hour. The as-obtained clear solution was then spin coated on the molybdenum substrates for 6 layers, with subFor photovoltaic applications, the as-annealed CZTS or CZTSSe films on Mo/SLG substrates were used to fabricate the solar-cell with the Ag/ITO/ZnO/CdS/CZTSSe/Mo/SLG structure, in which CdS was deposited by chemical bath deposition technique, while i-ZnO and ITO were deposited by RF and DC sputtering respectively, and finally the front contact Ag

A.P2 25

was deposited by thermal evaporator. The improved crystalline quality and larger crystallite size of our CZTS or CZTSSe photovoltaic absorbers have been evidenced from the enhanced solar-cell performances, which could yield the efficiencies of 5% and above.

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16:00 **The influence of Ag incorporation on crystallinity, band gap, morphology and device characteristics in CZTSSe solar cells**

Authors : Shih-Yuan Wei, Chung-Hao Cai, Chih-Huang Lai

Affiliations : Department of Materials science and engineering, National Tsing Hua Unirvirsity, R.O.C.

Resume : Ag doped CIGS thin solar cells have been discussed for years. The previous studies have shown the possibilities to enhance the grain growth, which is very helpful to decrease the fabrication temperature. This benefit might help the development of kesterite CZTS based solar cells, which is unstable at high temperature during fabrication. However, there are less studies focus on the Ag doped CZTS solar cells. In this work, (Ag,Cu)2ZnSn(S,Se)4 (ACZTSSe) thin films were fabricated by the two step process with the stacking type precursor layers. The precursor layers were deposited by the ion beam sputtering system (IBS) with the stacking order of Mo/ZnS/SnS2/(Ag,Cu) and followed by the annealing process using a graphite box under both S and Se atmosphere to form the ACZTSSe thin film. The ACZTSSe absorption layer were deposited over a composition range 0 < Ag/(Ag+Cu) < 1. The crystallinity and band gap are measured by the x-ray diffraction, Raman spectroscopy and UV-Vis spectroscopy. Influence of Ag doping on the morphology was analyzed by the second electron second electron microscopy (SEM). We also finished the device fabrication, and the best efficiency is 5.6 % in this experiment. A.P2 26

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16:00 **Galvanostatically-electrodeposited Cu-Zn-Sn multilayers as precursors for crystallising kesterite Cu2ZnSnS4 thin films**

Authors : Rachmat Adhi Wibowo1, Raad Hamid2, Theodoros Dimopoulos1

Affiliations : 1) AIT Austrian Institute of Technology, Energy Department, Photovoltaic Systems, Giefinggasse 2, 1210 Vienna, Austria 2) AIT Austrian Institute of Technology, Mobility Department, Electric Drive Technologies, Giefinggasse 2, 1210 Vienna, Austria

Resume : Stacked Cu-Zn-Sn layers on Mo-coated glass substrates were prepared by galvanostatic electrodeposition as precursors for crystallizing kesterite Cu2ZnSnS4 films. Due to the nature of the MoOx passivating layer on the Mo surface, initial trials were particularly addressed to deposit strong adhesive precursors by firstly depositing Cu layers on Mo-coated substrates from acidic as well as alkaline solutions. It was found that the acidic Cu electrolytes was less ideal for Cu deposition on Mo-coated glass substrates since it led to the low Cu deposit coverage inhomogeneity in addition to extremely poor adhesive Cu deposits. In contrast, utilizing an alkaline Cu solution yielded homogeneous coverage Cu deposits having strong adhesive to Mo-coated glass substrates which was essential for subsequent acidic Zn or Sn galvanostatic electrodepositions. The crystallization of kesterite Cu2ZnSnS4 from metallic stacked Cu/Zn/Sn and Cu/Sn/Zn precursors was investigated as well. The crystallization was completed using a two-stage process namely sulfurization of precursors in a tube furnace under sulfur vapor at 550 ?C. On a basis of complementary structural and chemical compositional analysis, the interdiffusion of elemental phases occurred in the as-deposited stacked precursors as revealed by the presence of binary Cu-Zn and Cu-Sn intermetallic phases. Sulfurisation of precursors seems to crystallise Cu-Zn-Sn precursor films into films exhibiting predominant kesterite phase. This contribution demonstrates that the established metals gavanostatic electrodeposition technique has a technological potential for preparing kesterite precursors. A.P2 27

add to my program **(close full abstract)**

16:00 **Solid State Chemistry Investigations on Cu2ZnSnS4 derivatives for photovoltaic applications**

Authors : L. Choubrac (1), A. Lafond (1), C. Guillot-Deudon (1), M. Paris (1), X. Rocquefelte (1), P. Fertey (2) and S. Jobic (1)

Affiliations : (1) Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France (2) Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin - BP 48, GIF-sur-YVETTE CEDEX, 91192, France A.P2 28

Resume : Although kesterite-based thin-film solar cells efficiencies gradually increase, many material issues are still under investigation. In particular, a full understanding of the cationic ordering in Cu2ZnSnS4 and its derivatives (so called CZTS) is probably needed to improve the performances of such devices. The present study deals with the solid state chemistry investigations of compounds with compositions close to Cu2ZnSnQ4 (Q=S and/or Se) on powder samples. From EDX and microprobe chemical analyses the stability domains of these compounds in the pseudo ternary Cu2Q-ZnQ-SnQ2 diagrams were determined. It is worth noticing that the selenide compounds appear to be much more flexible than the sulfide ones since larger shifts from the 2:1:1:4 stoichiometry are observed (towards Cu-poor Zn-rich compositions). For sulfide compounds the influence of the synthesis conditions (especially the cooling rate at the end of the thermal sequence) on the Cu/Zn disorder in the kesterite structure was investigated by NMR spectroscopy. In the case of the quenched sample, the broadening of the NMR peaks (119Sn and 67Zn spectra) is consistent with a high level of Cu/Zn disorder. Such a disorder has been confirmed by resonant X-ray diffraction on the corresponding single crystal. The same NMR investigation was done on Cu-poor samples and demonstrates that the level of disorder depends not only on the cooling rate but also on the nature of the substitution process which occurs.

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16:00

Effect of thermal annealing on the structural, morphological and optical properties of PLD grown Cu2ZnSnS4 thin films

Authors : G. Teterina1, V. Nevolin1,2, I. Sipaylo1, A. Zenkevich1,3

Affiliations : 1 NRNU “Moscow Engineering Physics Institute”, 115409, Moscow, Russia 2 P.N. Lebedev Physical Institute of the Russian Academy of Science, 119991, Moscow, Russia 3 Russian Research Center “Kurchatov Institute”, 123182, Moscow, Russia

Resume : Earth abundant and environmental friendly material of Cu2ZnSnS4 (CZTS) has recently attracted much attention as a highly promising absorbing material for the low-priced thin film solar cells. However, the effect of the processing parameters on the fundamental CZTS material properties is still under investigation. Recently we have reported about successful growth of CZTS thin films by reactive Pulsed Laser Deposition (PLD) from Cu and alloyed Zn-Sn metallic targets in H2S atmosphere at room temperature [1]. In this work we investigate the effect of thermal annealing on the structural, morphological and optical properties of CZTS films grown by this procedure. The composition of as-grown and post annealed (N2, p ~ 100 kPa, T = 200-400°C in the increment of 50°C) films was analyzed by Rutherford backscattering spectrometry. X-ray diffraction and Raman spectroscopy were used to investigate the effect of thermal annealing on the structural properties. The evolution of CZTS band gap upon thermal annealing was evaluated by the optical spectrometry. Morphological properties were characterized by optical and scanning electron microscopy. The effect of the annealing parameters on the electrical properties of CZTS layers is also investigated. [1] G.D. Surgina, A.V. Zenkevich, I.P. Sipaylo, V.N. Nevolin, W. Drube, P.E. Teterin, M.N. Minnekaev, Reactive pulsed laser deposition of Cu2ZnSnS4 thin films in H2S, Thin Solid Films 535, pp. 44-47 (2013)

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16:00

Effect of Annealing Atmosphere on the Structural and Optical Properties of Cu2ZnSnS4 (CZTS) Thin Films Deposited by Vacuum Evaporation Method

Authors : R. Touati*, M. Ben Rabeh, M.Kanzari

Affiliations : Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs-ENIT BP 37, le Belvédère 1002-Tunis, Tunisie ; Laboratoire de Photovoltaïques et Matériaux Semi-conducteurs-ENIT-IPEITunis Montfleury-Université de Tunis.

Resume : The influence of post deposition annealing in nitrogen and sulfur atmosphere on the structural and optical properties of Cu2ZnSnS4 (CZTS) thin films was investigated. The samples were deposited by thermal evaporation under vacuum method at different glass substrate temperatures ranging from room temperature to 220°C. Post annealing using sulfur vapor was performed in a quartz tube furnace at 150°C during 5 min so as to optimize the kesterite Cu2ZnSnS4 phase. Structural characterization was carried out by using X-Ray diffraction and Raman Scattering whereas optical characterization was performed by recording transmittance and reflectance of the samples in the spectral range 300 nm - 1800 nm. The X-Ray diffraction spectra indicated that polycrystalline CZTS films were successfully obtained after annealing and the samples exhibit (112) preferred plan orientation. Hence, crystallinity was enhanced with substrate temperature as well as with post deposition annealing due to the diffusion of sulfur in the film during the annealing process. Optical study reveals that after annealing the absorption coefficients is found to be higher than 105 cm-1 whereas the direct band gap energy varies in the range of 1.4-1.6 eV. Furthermore, we found that CZTS thin films exhibit P-type conductivity with post deposition annealing.

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16:00 **Fabrication of Cu2Zn(Sn,Ge)Se4 thin-film solar cells by printing and high-pressure sintering process**

Authors : M. Morihama, T. Maeda, T. Wada

Affiliations : Department of Materials Chemistry, Ryukoku University

Resume : Cu2ZnSnS4 (CZTS) is well known as a rare-metal-free photovoltaic material. We studied CuIn1-xGaxSe2 (CIGS) and CZTS solar cells using a printing and high-pressure sintering (PHS) process [1,2]. We also investigated the crystal structure and optical properties of a Cu2Zn(Sn1-xGex)Se4 (CZTGSe) solid solution [3]. The band gap energy linearly increased from 0.99 eV for Cu2ZnSnSe4 (CZTSe) (x = 0.0) to 1.35 eV for Cu2ZnGeSe4 (CZGSe) (x = 1.0). In this study, we fabricated Cu2Zn(Sn,Ge)(S,Se)4 (CZTGSSe) films by the PHS process and fabricated CZTGSSe solar cells.

We synthesized CZTGSe powders with a chemical composition of Cu1.9Zn1.25 (Sn1-xGex)Se4.5 by planetary ball milling and heating at 300 °C for 30 min in an N2 gas atmosphere. Particulate precursor ink was prepared by mixing the CZTGSe powder with an organic solvent with the planetary ball milling. The CZTGSe film was fabricated by PHS and post-annealing with Se and Sn powders in a 5% H2S/N2 gas atmosphere. Some Se in CZTGSe was substituted by S during the post-annealing in an H2S gas atmosphere. We fabricated CZTGSSe solar cells with the device structure of Ag/ITO/i-ZnO/CdS/CZTGSSe/Mo/SLG. The CZTGSSe solar cell with x = 0.2 showed an efficiency (Eff) of 3.1% (Voc = 355 mV, Jsc = 19.8 mA/cm^2 and FF = 43.8%). A.P2 31

[1]T. Wada et al., Phys. Stat. Sol. A 203, 2593 (2006).
[2]F. Gao et al., Mater. Res. Soc. Symp. Proc. 1538, p 21 (2013).
[3]M. Morihama et al., Jpn. J. Appl. Phys., accepted.

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16:00 **Effect of selenization conditions on the growth and properties of Cu2ZnSn(S,Se)4 thin films**

Authors : S. Ranjbar (a), M. R. Rajesh Menon (a), M. G. Sousa (a), P. A. Fernandes (a,b), A. F. da Cunha (a)

Affiliations : (a) I3N- Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal; (b) Departamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal

Resume : Copper Zinc Tin Sulfide (CZTS) continues to be in the limelight as absorber material for thin film solar cells due to its cost effectiveness and potential for high conversion efficiencies. Opto-electronic properties of this material can be tuned to achieve better efficiencies by controlled incorporation of selenium. In this paper we report the growth of Cu2ZnSn(S,Se)4 (CZTSSe) using a hybrid process involving the sequential evaporation of Zn and sputtering of the sulfide precursors of Cu and Sn, followed by a selenization step. Two approaches for selenization were followed, one using a tubular furnace and the other using a Rapid Thermal Processor (RTP). The effect of annealing time, heating rate and temperature on the properties of the films were investigated. Structural analyses were done using XRD and Raman spectroscopy. SEM and EDS were employed to investigate the morphology and composition of the films, and UV-Vis-NIR spectroscopy was used to estimate the band gap. Structural analyses were indicative of the formation of CZTSSe. However, the results also suggest the possible decomposition of the absorber material at longer annealing times and higher temperatures. XRD and Raman analysis along with EDS suggests that the films annealed in the tubular furnace is selenium rich whereas the RTP annealed samples have higher sulfur content. The band gaps of the films were estimated for different annealing conditions and correlated to the amount of sulfur and selenium in the films. A.P2 32

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16:00 **Optical functions and crystal structure of epitaxial and polycrystalline CZTSe**

Authors : L. Gütay (1), Ö. Erdogan (1), C. Stroth (1), I. Riedel (1), R. Djemour (2), M. Mousel (2), A. Redinger (2), S. Siebentritt (2)

Affiliations : (1) Laboratory for Chalcogenide Photovoltaics, University of Oldenburg, Oldenburg, Germany; (2) Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg

Resume : In recent years the question about the polymorphic structure of CZTSe absorber films has become a matter of debate. Still there is no method available to clearly identify the present polymorph in a thin absorber film, e.g. kesterite and stannite. This is considered a critical issue as CZTSe is expected to show significant differences in its characteristics, e.g. optical band gap, depending on its polymorphic structure. In this work we investigate the crystal structure of epitaxial CZTSe films by polarized Raman measurements. The A.P2 33 results allow for a distinction between the possible polymorphs kesterite and stannite which are expected to show substantially different Raman results depending on the polarization configuration in the Raman system. Our results indicate the presence of the kesterite as the main structure in the analyzed films. The epitaxial films are furthermore analyzed by ellipsometry, allowing for the extraction of the dielectric functions of the films. Hence, the resulting optical functions and constants can be assigned to the polymorph of the CZTSe material class, which was found by the Raman analysis. Further, we show ellipsometry results for polycrystalline CZTSe films with different composition. The results are discussed in terms of optical constants and band structure and are compared to the epitaxial reference results.

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16:00

Effects of structural and microstructural properties on optoelectronic characteristics of Cu2ZnSnSe4 thin film solar cells

Authors : M. Dimitrievska (1), S. Lopez (1), G. Gurieva (2), X. Fontané (1), R. Günder (2), V. Izquerdo-Roca (1), E. Saucedo (1), S. Schorr (2 3), A. Perez-Rodrigez (1 4)

Affiliations : (1) Catalonia Institute for Energy Research (IREC), Jardin de les Dones de Negre 1, 08930, Sant Adrià de Besòs, Spain; (2) Helmholtz Centre Berlin for Materials and Energy, Department Crystallography, Hahn-Meitner-Platz 1, 14109 Berlin, Germany; (3) Freie Universität Berlin, Institute of Geological Sciences, Malteserstr. 74-100, 12249 Berlin, Germany; (4) IN2UB, Departament d'Electrònica, Universitat de Barcelona, C. Martí i Franquès 1, 08028 Barcelona, Spain

Resume : In this study we report the effects of different structural and microstructural properties on optoelectronic characteristics of CZTSe thin films synthesized by DC-magnetron sputtering deposition and annealed in a Se containing atmosphere. CZTSe samples with different properties were obtained by varying the cationic ratios, Cu/(Zn+Sn) and Zn/Sn, in ranges of 0.55-0.85 and 1.19-1.66 respectively. A complete phase analysis was done by Raman spectroscopy using excitations from NIR to UV. The crystalline quality of absorbers was investigated in terms of the phonon confinement model (PCM) applied to the Raman spectra. An increase in open-circuit voltage (Voc), correlated with an increase in efficiency, was observed with increasing correlation length obtained from PCM. The structural characterization of the thin films was carried out by grazing incidence X-ray diffraction and a subsequent Le Bail analysis. The obtained lattice parameters a and c proved to be constant for all Zn/Sn ratios, but showed a slight increase with the increasing Cu/(Zn+Sn) ratio. A decrease in strain and domain size calculated using the Williamson-Hall method was observed for samples with higher efficiencies. A gradual decrease in domain size and strain from surface to the back of film was observed and is in accordance with results obtained from scanning electron microscopy. We will discuss the potential impact of the structural and microstructural properties on the performance of the CZTSe based solar cells.

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16:00

Cu2SnS3 thin films grown by co-sputtering and post-annealing

Authors : Romain Bodeux and Sebastien Delbos

Affiliations : EDF R&D, Institute of Research and Development on Photovoltaic Energy (IRDEP), 6 quai Watier, 78401 Chatou, France

Resume : Over the last years, thin films of Cu2SnS3 (CTS) have attracted interest due to these potential photovoltaic applications and solar cells with 2.1 % of efficiency were achieved [1]. CTS is a p-type semiconductor and its absorption coefficient is greater than 10^4 cm-1. The band gap of tetragonal CTS is 1.35 e V while 0.96 eV is for cubic one [2]. In this study, Precursors were deposited on Mo/glass and glass substrates using RF magnetron co-sputtering from Cu2-xS, ZnS and SnxSy targets at room temperature. Precursors with various compositions were achieved and were subsequently annealed in a rapid thermal annealing. The structural characterization showed that CTS is crystallized. The tetragonal structure and cubic structure were correlated with the deposition and annealing conditions. Solar cells based on CTS were synthesized. Cross section scanning electron microscopy of devices showed that the CTS layer exhibits large grains and the CZTS/CdS interface is well defined. However, the solar cells result in low efficiency < 1%. The low efficiency was related to unidentified parasitic phases, which were stabilized during the annealing [3]. [1] D. Tiwari et al., Solar Energy Materials & Solar Cells 113 (2013) 165. [2] P.A. Fernandes et al., Journal of Physics D 43(2010) 215403. [3] S. Fiechter et al., Journal of Physics and Chemistry of Solids 64 (2003) 1859.

A.P2 35

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16:00

Influence of sodium and H2S annealing on CZTS solar cells sputtered from a quaternary compound target

Authors : Patrice Bras, Jan Sterner, Charlotte Platzer-Björkman

Affiliations : Midsummer AB, SE-17543 Järfälla, Sweden/Solid State Electronics, Uppsala University, Box 534, 75121 Uppsala, Sweden.; Midsummer AB, SE-17543 Järfälla, Sweden; Solid State Electronics, Uppsala University, Box 534, 75121 Uppsala, Sweden.

Resume : With a theoretical efficiency around 30% and an optimized band gap for sunlight absorption, Cu2ZnSnS4 is a promising, earth-abundant, material for new generation thin film solar cells. Sputtering CZTS from a quaternary compound target is a quick and potentially industrial-scaled process that has not been investigated deeply yet. We propose a new approach based on an in-line vacuum system for the complete device. CZTS is sputtered from a compound target on a NaF pre-sputtered stainless steel substrate, and then annealed in high-pressure H2S atmosphere. A 1µm thick absorber is obtained within 7 minutes sputtering. Top layers are then deposited, without vacuum breaking. The effects of NaF layer thickness as well as sputtering temperature on CZTS crystallinity have been investigated. It has been observed that large kesterite grains are obtained with the thickest NaF layer combined with CZTS sputtering temperatures above 450°C. Corresponding solar cells showed a well-behaved pn junction but exhibiting a low photocurrent. One reason for the low photocurrent could be decomposition of CZTS at the back contact due to low sulfur pressure during high temperature processing. To investigate this, high pressure H2S annealing of absorber layers sputtered at both low and high temperature was also studied. SEM, XRD analysis and green and UV Raman have been used in order to characterize the samples.

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16:00

Epitaxial Cu2ZnSnSe4 layers by annealing of Sn/Cu/ZnSe(001) precursors on GaAs(001)

Authors : C. Krämmer, J. Sachs, L. Pfaffmann, M. Lang, C. Gao, D. Gerthsen, H. Kalt, M. Powalla, M. Hetterich

Affiliations : Institute of Applied Physics, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; Institute of Applied Physics, KIT; Laboratory for Electron Microscopy, KIT; Institute of Applied Physics, KIT; Institute of Applied Physics, KIT; Laboratory for Electron Microscopy, KIT; Institute of Applied Physics, KIT; Light Technology Institute, KIT and Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), 70565 Stuttgart, Germany; Institute of Applied Physics, KIT;

Resume : Monocrystalline or strongly textured kesterite Cu2ZnSnSe4 (CZTSe) films are highly desirable in order to investigate their basic physical properties. Furthermore, the influence of grain boundaries on the performance of CZTSe solar cells can be studied through a comparison between cells comprising a standard polycrystalline or quasi-monocrystalline absorber. We report on the fabrication of epitaxial CZTSe films by molecular-beam epitaxial growth of ZnSe (001) on GaAs(001) followed by subsequent deposition of Cu and Sn. The precursor stacks are then selenized in a tube furnace. Due to structural similarity between the zincblende and the kesterite crystal structure this procedure should result in nearly monocrystalline or at least strongly textured CZTSe films. Raman spectroscopy confirms the presence of the kesterite phase. X-ray diffraction (XRD) not only shows the presence of the CZTSe(002) and (006) reflections but also a strong enhancement relative to the typically dominant CZTSe(112) reflection in polycrystalline films. This suggests a preferential grain orientation within the CZTSe layer. Further X-ray analysis and electron microscopy show that the films exhibit monocrystalline areas of several microns size with inclusions of smaller grains with a different crystal orientation or composition. Electron backscattering diffraction (EBSD) measurements confirm the conservation of the crystal orientation of the cubic GaAs substrate during growth throughout the whole CZTSe film.

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16:00

Crystallization behavior of Cu2ZnSn(Sx ,Se1-x)4 absorbers processed from sputtered Cu2ZnSnS4 precursors under different selenization conditions

Authors : Solange Temgoua; Romain Bodeux;Negar Naghavi and Sebastien Delbos

Affiliations : IRDEP(Institute of Research and Development on Photovoltaic Energy, (EDF/CNRS/Chimie-paristech, UMR7174) 6 Quai Watier, 78401, Chatou, France.

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Resume : The bandgap of Cu2ZnSn(S,Se)4 can be tuned between 1.0 eV (pure selenide compound) and 1.5 eV (pure sulfide compound) by varying the S/Se ratio. In this study, we compare the variation of crystallization behavior of Cu2ZnSn(SxSe1-x)4 as a function of annealing conditions. First Cu-Zn-Sn-S precursors are deposited on glass/Mo substrate by a cosputtering of Cu, ZnS, and SnS. The crystallization behavior of these precursors during selenization is then studied at different temperatures between 400 and 600?C in order to have a better understanding of annealing on the mechanisms of formation of CZTSSe and secondary phases. The structures of these layers are investigated by XRD and Raman spectroscopy. The results indicate k?sterite phases containing both S and Se. The impact of the annealing conditions on solar cells properties will be presented.

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16:00

Controlling metal ratios and electronic properties in DMSO solution-processed Cu2ZnSn(SSe)4 solar cells.

Authors : M.Werner, C. M. Sutter-Fella, Y. E. Romanyuk, A. N. Tiwari

Affiliations : Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

Resume : Solution based processed kesterite absorbers are a facile and low-cost preparation route with a record efficiency of 12.6% [1]. These record cells target a Cu-poor and Zn-rich stoichiometry (Cu/Zn+Sn=0.8, Zn/Sn=1.1) assuming a great control over the film composition. While the hydrazine slurry route has certain safety hazards, metal salt dissolved in dimethyl sulfoxide (DMSO) offers a safer route. Draw-backs of this solution processing remain poor crystallinity and the control over the metal ratios after annealing. Here we modify the precursor by varying systematically the metal salt concentration, adding a sodium doping in the solution, and changing the thickness of spin-coated precursor. We observe an improvement in carrier collection and device efficiency when adding NaCl to the precursor solution and reducing the selenized layer thickness to ca. 1.5 um thus promoting the crystallization of the complete layer. It was found that Zn/Sn stabilizes to Zn/Sn~1.0-1.1 after selenization in an open reactor independent of the Sn salt concentration. Using optimized conditions solar cell efficiencies >6% achieved and even higher efficiencies are envisaged when using a closed reactor design. [1] Wang, W., Winkler, M. T., Gunawan, O., Gokmen, T., Todorov, T. K., Zhu, Y. and Mitzi, D. B. (2013), Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency. Adv. Energy Mater. doi: 10.1002/aenm.201301465

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16:00

Preparation and characterization of CZTSe thin films by rapid thermal selenization

Authors : Bae-Heng Tseng, Yun-Feng Chen, Cian-Huei Gao, Ge-Wei Yeh

Affiliations : Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

Resume : Cu2ZnSnSe4 (CZTSe) is a material derived from the Cu-III-Se compound by replacing the group III elements with low cost and abundant elements, i.e. Zn and Sn. Recent research indicated that CZTSe-related compounds have high potential for photovoltaic applications with decent device performance. It has been known that the preparation of single-phase CZTSe thin film is difficult and the processes are time-consuming. In this work, we successfully developed a rapid thermal processing technique to synthesize CZTSe films in two minutes. The selenization process was done by annealing the stacked elemental precursors with a heating rate of 20oC/sec and kept at 500oC for 1 min. This process has the advantages of high throughput and low cost. With a proper adjustment of the film composition, a single-phase CZTSe film was successfully prepared and verified by XRD, Raman spectrometry, composition analysis, spectrophotometry, and Hall measurements. The formation mechanisms of the selenized films are also investigated by terminating the process at different temperatures. We found that the CuSe phase formed first at 100oC and trace of ZnSe and SnSe were detected at 300oC and 350oC, respectively. The CZTSe phase started to form at 350oC and became dominant at 400oC. For the improvement in the grain structure, a 30nm -thick Sb interlayer was incorporated into the stacked elemental precursors for subsequent selenization. A highly compact structure with large grains was obtained. The films were also prepared on Mo-coated glass substrates and had no adhesion problem. So far, the energy conversion efficiency of our CZTSe solar cells is 6.2%.

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add to my program **(close full abstract)**

16:00

Structural and microstructural characterisation of Cu2ZnSn(S1-xSex)4 thin films

Authors : G. Gurieva1, M. Dimitrievska2, R. Günder1, H. Xie2, V. Izquierdo-Roca2, A. Pérez-Rodríguez 2,3, E. Saucedo2, S. Schorr1,4

Affiliations : 1 Helmholtz Centre Berlin for Materials and Energy, Department

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Crystallography, Hahn-Meitner-Platz 1, 14109 Berlin, Germany 2 Catalonia Institute for Energy Research (IREC), Jardin de les Dones de Negre 1, 08930, Sant Adrià del Besòs, Spain. 3 IN2UB, Departament d´Electrònica, Universitat de Barcelona, C. Martí Franquès 1, 08028 Barcelona, Spain 4 Freie Universität Berlin, Institute of Geological Sciences, Malteserstr. 74-100, 12249 Berlin, Germany

Resume : Cu2ZnSnX4, where X = S or Se have the suitable optical band-gap energy of 1.0 –1.5eV, which match the preferred range of solar irradiation and large optical absorption coefficient of 104 cm-1, contain only abundant elements, which makes these materials promising candidates for engineering on their base of different high-efficient and low-cost photovoltaic devices Cu/Sn/Cu/Zn metallic multi-stacks were deposited onto Mo coated soda lime glass by DC magnetron sputtering and annealed under S+Se+Sn atmosphere. The absence of secondary phases at the surface was confirmed by Raman spectroscopy. The structural characterization of the thin films was carried out by grazing incidence X-ray diffraction (GIXRD) and a subsequent Rietveld analysis of the diffraction data using the FullProf suite [2]. The kesterite structure was used as starting model for the refinement procedure. The dependence of lattice parameters a and c on S/S+Se ratio is in good agreement with Vergard's law. Microstructural analysis consisted in separation of strain and size effects for CZTSSe thin films, based on Williamson-Hall method [3]. The dependance of domain size and strain on the ratio of S/S+Se will be presented. [1] M.T. Winkler, W. Wang, O. Gunawan , Energy and Envir. Science. (2014) [2] Juan Rodriguez-Carvajal and Thierry Roisnel, www.ill.eu/sites/fullprof/ [3] G. K. Williamson, W. H. Hall, Acta Metall. 1, (1953), 22-31.

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16:00

CZTS inks prepared by microwave assisted method for inkjet and spray deposition

Authors : Thibaut Martini 1.3, Alain Ricaud1, Caroline Chubileau2, Olivier Poncelet2, Konstantin Tarasov2, Céline Martin3, Anne Blayo3

Affiliations : 1Screen-Solar La Petite Maison ZEN - 390 Route de la Traverse 73 000 MONTAGNOLE; 2 CEA LITEN / SEN / LSIN, 17 rue des martyrs, 38054 Grenoble Cedex 9; 3Laboratoire de Génie des Procédés Papetiers. UMR CNRS 5518, 461 rue de la Papeterie, CS 10065, 38402, Saint-Martin d'Hères Cedex

Resume : Non-vacuum deposition of Cu2ZnSnS4 (CZTS) thin films represents a great opportunity for producing low-cost, earth abundant and non-toxic absorber layers for solar cells. The present work describes a wet deposition of CZTS colloids by spray and inkjet techniques. A microwave assisted hydrothermal method has been used for obtaining CZTS nanoparticles. The study presents the use of different precursor salts and stabilizing agent and revealed their major influence on phase purity, chemical composition and crystallinity. The choice of suitable reactants has been made to decrease the residual carbonaceous contamination and to reduce its temperature of thermal decomposition. Printing techniques used in the present study require severe control of the rheological properties as well as chemical and colloidal stability of the ink used for deposition. Only a narrow group of solvents have been identified to be suitable for ink formulation and preparation of uniform and crack-free films with desirable thicknesses. The colloidal inks have been coated by spray and inkjet deposition on Mo/glass substrates and thus obtained films were further annealed in sulfur atmosphere. The resulted CZTS films of 1.5-2 µm thickness have been characterized by SEM/EDX, XRD, Raman spectroscopy as well as by optical and electrical methods. They demonstrated the kesterite phase to have a good crystallinity and desired chemical composition with no secondary phases.

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16:00

Epitaxial Cu2ZnSnSe4

Authors : Alex Redinger 1, Jan Sendler 1, R. Djemour 1, David Regesch 1, Heiko Groiss 2, Dagmar Gerthsen 2 and Susanne Siebentritt 1

Affiliations : [1] University of Luxembourg, Laboratory for Photovoltaics, 41 rue du Brill, Luxembourg; [2] Karlsruhe Institute of Technology, Laboratory for Microscopy, Engesserstr. 7, Karlsruhe, Germany

Resume : Epitaxial Cu2ZnSnSe4 (CZTSe) thin films have been grown via high temperature coevaporation on GaAs(001). Electron backscattering diffraction confirms that epitaxy is achieved in a wide compositional range. However, as we will show, different secondary phases are always present in the epitaxial layer. We present a detailed compositional study and the occurrence of secondary phases as a function of composition via Raman spectroscopy and photoluminescence. The main secondary phases are Cu2SnSe3 and ZnSe which grow epitaxially on top of the CZTSe. This is a direct consequence of the similar

A.P2 43

lattice constants of CZTSe, ZnSe and Cu2SnSe3. In addition, conventional scanning transmission electron microscopy measurements are used to study the occurrence of secondary phases in the epitaxial layers, the quality of the epitaxy and the GaAs/CZTSe interface. The photoluminescence and Raman measurements on the epitaxial samples will be compared to polycrystalline absorbers grown on molybdenum glass substrates. Finally, we present the first epitaxial CZTSe solar cells with a maximum power conversion efficiency of 2.2% an open-circuit voltage of 223 mV and a current density of 16mA/cm2.

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16:00 **Growth of Cu2ZnSnS4 Thin Films by Metal Xanthate Precursors** A.P2 45

Authors : Akiko MOCHIHARA1, 2, Kenji YOSHINO1, 2, *, Minobu KAWANO3, Yuhei OGOMI2, 3, Shyam S. PANDEY2, 3, Qing SHEN2, 4, Taro TOYODA2, 4 and Shuzi HAYASE2, 3

Affiliations : 1Department of Electrical and Electronic Engineering, Miyazaki University, 1-1 Gakuen Kibanadai-nishi, Miyazaki 889-2192, Japan 2CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan. 3Department of Engineering Science, Faculty of Informatics and Engineering, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan. 4Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu 808-0196, Japan

Resume : In recent years, the Cu2ZnSnS4 (CZTS) and Cu2ZnSnSe4 (CZTSe) compound semiconductors are potential alternative materials to CuInGaSe2 (CIGS) for thin film photovoltaic absorber layers. This is because all of the elements in CZTS and CZTSe are abundant in the earth, and the bandgap energy is controlled by the ratio of S and Se. Therefore, environmental concerns are eliminated with these materials, paving the way for gigawatt scale mass production of solar cells. Despite their brief history in solar cell technology, CZTS, CZTSe, and Cu2ZnSn(S,Se)4 (CZTSSe) solar cell devices are rapidly advancing in the solar cell markets. For example, CZTSSe solar cells fabricated at IBM have achieved an efficiency of 11.1% using a hydrazine solution process [1]. Shin et al. have reported CZTS thin-film solar cell with an efficiency of 8.4% using a vacuum based thermal evaporation process [2]. Repins et al. have reported CZTSe solar cells with an efficiency of 9.2% using co-evaporation process [3]. In this work, CZTS thin film on glass substrate is grown by dipping-coat from Cu-, Zn- and Sn-xanthate solution as precursor materials. The samples are annealed under nitrogen atmosphere. X-ray diffraction (XRD), electron probe microanalysis (EPMA), scanning electron microanalysis (SEM), thermoprobe analysis and the four-point probe method are carried out. The XRD spectra indicate that a peak of CZTS (112) starts to observe at 150 °C. This temperature is lowest in non-vacuum process of CZTS film. The all samples indicate chalcopyrite structure and polycrystalline as evidenced by the XRD spectra. A value of full width at half maximum of (112) peak increases with increasing temperature. This indicates that an grain size increases with increasing annealing temperature. The samples are non-uniform composition such as Cu-poor and Zn-rich at low temperature and become S-poor with increasing temperature. Sulfur evaporates because vapor pressure of sulfur is high. The all samples are p-type conductivity by thermo prove analysis because Cu vacancy (VCu) defects is dominant in the samples from EPMA results. The resistivity increases with the increasing annealing temperature. It is assumed that this reason is due to decreasing carrier concentration. Donor type defects such as (Vs) increases with increasing the annealing temperature. [1] T. K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, and D. B. Mitzi, Adv. Energy Mater. 3, 34 (2013). [2] B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, and S. Guha, Prog. Photovol: Res. Appl. 21, 72 (2013). [3] I. Repins, C. Beall, N. Vora, C. DeHart, D. Kuciauskas, P. Dippo, B. To, J. Mann, W. C. Hsu, A. Goodrich, and R. Noufi, Sol. Energy Mater. Sol. Cells 101, 154 (2012).

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16:00 **Preparation and characterization of CZTS Thin films by electrodeposition technique** A.P2 46

Authors : T. S. Tlemçani1, F. Cherkaoui El Moursli2, F. Hajji2, E.B. Benameur1, I. Chaki1, A. Belayachi1and M. Abd-Lefdil1D. Muller3, K. Bouras3, and A. Slaoui3

Affiliations : 1University of Mohammed V-Agdal, Materials Physics Laboratory, P. B. 1014, Rabat, Morocco. 2Equipe Batteries Lithium et Dépôts Electrolytiques, Université Mohammed V-Agdal, Rabat, Morocco. 3ICube UMR 7357, 23 rue du Loess - BP 20 CR - 67037 Strasbourg- France.

Resume : Cu2ZnSn(SexS1-x)4 (CZTS) is a promising absorber material with a high absorption coefficient (>104 cm-1) and a desirable band gap (~1.5 eV). Recently, a new conversion efficiency rating of 12.6% for 0.42cm² CZTS solar

cell, was reached [1]. CZTS layers were deposited using a single step electrodeposition process, the thermal annealing was varied from 450 to 550°C The obviated layers were characterized by different tools. Using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Raman scattering, the morphology, the structure as well as the composition of the electrodeposited films are determined. Keywords: Cu2ZnSnS4, thin film, electrodeposition, annealing, characterization. [1]. W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, D. B. Mitzi, “Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency”, Adv. Ener. Mater, Article first published online: 27 NOV 2013, DOI: 10.1002/aenm.201301465.

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16:00

Optical properties and secondary phase identification in PLD-grown Cu2ZnSnS4 for thin-film photovoltaics

Authors : Andrea Crovetto (1), Andrea Cazzaniga (2), Rebecca B. Ettlinger (2), Jørgen Schou (2), Ole Hansen (1,3)

Affiliations : (1) DTU Nanotech, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark; (2) DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark; (3) CINF, Center for Individual Nanoparticle Functionality, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Resume : One major hurdle to production of Cu2ZnSnS4 (CZTS) thin films for photovoltaic applications is the narrow phase diagram region in which CZTS is expected as a single phase at most temperatures of interest. Unwanted secondary phases such as ZnS, CuxSnSx+1 and SnxSy are thus likely to be included in CZTS films independently of the chosen deposition technique. Identification by standard X-ray diffraction (XRD) of some of those phases is challenging since their diffraction peaks overlap with CZTS peaks. In this study we employ Raman spectroscopy to determine which secondary phases are incorporated in CZTS films grown by pulsed laser deposition (PLD) for a range of laser energies and substrate temperatures. Film properties, such as absorption coefficient, refraction index and thickness are extracted from ellipsometry measurements. The same set of properties is evaluated for chemical-bath-deposited CdS due to its important use as a buffer layer in chalcogenide solar cells. The validity of the optical model used to derive optical constants by ellipsometry is discussed in relation to results from direct measurement methods such as UV-visible spectroscopy, Scanning Electron Microscopy (SEM) and profiling. Identification of secondary phases in CZTS films under different PLD process parameters and their effect on optical constants is an important factor in optimizing the deposition process for production of high-efficiency CZTS solar cells.

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16:00

Electronic transport properties of Cu2ZnSn(S1−xSex)4 thin films obtained from Lift-off process

Authors : A. Darga, F. Sorin, C. Longeaud, Yury Berdnikov, Elin Sondergard, J.P. Kleider, J. Alvarez, A. Jaffre

Affiliations : Sorbonne Universités, UPMC Univ Paris 06, UMR 8507, Laboratoire de Génie Electrique de Paris, F-91190 Gif sur Yvette, France; Institute of Materials, Laboratory of Photonic materials and fiber devices, Ecole Polytechnique Fédérale de lausanne, Switzerland; CNRS, UMR 8507, Laboratoire de Génie Electrique de Paris, F-91190 Gif sur Yvette, France; Surface du Verre et Interfaces, UMR 125 CNRS/Saint-Gobain 39 Quai Lucien Lefranc, 93303 Aubervilliers Cedex, France

Resume : In this work the electronic transport properties of Cu2ZnSn (S1−xSex)4 (CZTSSe) thin film materials have been investigated by photocurrent based techniques. We have used SSPC (Steady State Photocurrent) and MPC (Modulated PhotoCurrent) techniques which are well-known techniques that have been intensively used to investigate on variety of thin films including CIGS. These techniques require a sample deposited on an insulating substrate and fitted with coplanar ohmic electrodes. As for CIGS, CZTSSe is generally deposited on a glass substrate coated with molybdenum, a configuration which is not suitable for SSPC and MPC measurements. Thus, we have developed a mechanical lift-off process in order to detach the CZTSSe layer from its molybdenum substrate and transfer it to an insulating glass substrate. The quality of the lift-off process and the CZTSSe structure were investigated by Scanning Electron Microscopy and confocal Raman microscopy, respectively. MPC measurements reveal an exponential band tail with characteristic energies in the range 20-30 meV, depending on the sample. In addition, the photon flux dependence of the SSPC measured at room temperature shows a sub-linear behavior which is consistent with the presence

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of a band tail like defects distribution. To further interpret our results, the values of the characteristic energies will be compared to those determined by others techniques such as photocapacitance and admittance spectroscopy.

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16:00

Application of TAGUCHI’s design of experiments for the preparation of Cu2ZnSnS4 (CZTS) absorber by Spray Pyrolysis.

Authors : Y.ARBA1, H.TCHOGNIA1, B. HARTITI1, A. RIDAH1, P.THEVENIN2

Affiliations : 1- MAC&PM Laboratory, ANEPMAER Group, Department of Physics, FSTM, University Hassan II Mohammédia-casablanca, Mohammedia, Morocco 2- LMOPS Laboratory, Université of Lorraine, Metz, France

Resume : Copper zinc tin sulfide (Cu2ZnSnS4, CZTS) has attracted significant attention in over recent years as a next generation of absorber materials in thin film solar cells due to the high natural abundance of all constituents, tunable direct band gap energy and large absorption coefficient. The present study deals with the application of the Taguchi method for the optimization of spray pyrolysis process for the synthesis of CZTS. The Coating experiments were conducted by the parametric study of the fractional factorial design (L27) of the Taguchi method in order to optimize spray process parameters. The Taguchi design evaluated the effects of seven spray process parameters namely the ratios Cu/(Zn+Sn), Zn/Sn and S/Metal, solution rate, air-compression, time of deposition, substrate temperatures on surface roughness, gap energy, structural properties and material ratio. The influence of process parameters on the as-sprayed films is discussed. The Taguchi analysis employed in the present investigation leads to optimize process parameters for the most optimal coatings conditions. Keywords: Spray pyrolysis, Taguchi method, Design of experiment, Cu2ZnSnS4, Solar cell, absorber, Characterization.

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16:00

Cu2ZnSnS4 thin films derived from metal oxide nanoparticles

Authors : K.Tarasov (1), A.Lafond (2), C.Guillot-Deudon (2), T.Martini (1,3)

Affiliations : (1) CEA-DRT (LITEN/DTNM/SEN/LSIN) 17 rue des Martyrs, 38054 Grenoble, FRANCE; (2) Faculté des sciences de Nantes, Institut des matériaux Jean Rouxel, 2 rue de la Houssinière BP 32229, 44322 Nantes, FRANCE (3) Screen-Solar, 390 Route de la Traverse (La Petite Maison ZEN) 73000 Montagnole, FRANCE;

Resume : A novel non-vacuum preparation method of Cu2ZnSnS4 thin films is described. It has been shown that well crystallized kesterite thin films can be prepared using stoechiometric mixtures of oxide nanoparticles of copper, zinc and tin. Metal oxide nanoparticles deposited from alcohol solutions by spin-coating on glass or Mo/glass substrates were subsequently annealed at 400-550°C in a sulfur containing atmosphere (S° or H2S). As shown by SEM-EDX, XRD-Rietveld and RAMAN spectroscopy, the mixed oxides can be completely converted into the kesterite phase as low as at 400°C. An increase in annealing temperature allows also to improve the crystallinity and to lower the porosity of the obtained films. The studied method is a promising approach for a low-cost fabrication of absorber layers in solar cells.

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16:00

Nanocrystals capped with Metal Chalcogenide Complex without ligand exchange process: A simple way to prepare soluble precursor for Cu2ZnSn(S,Se)4

Authors : Jeff Lin,Tzu-Ying Lin,Shih-Yuan Wei, Chia-Hao Hsu, Wei-Hao Ho, Jung-Wei Liao,Chih-Huang Lai*

Affiliations : National Tsing Hua University Department of Materials Science and Engineering

Resume : Nanocrystals capped with metal chalcogenide complex (MCC) could be an approach to hydrazine process which provides carbon free and well mixed precursor layer with binary metal sulfides for Cu2ZnSn(S,Se)4 photovoltaic device. However,it needs complicate synthesis process including ligand exchange as reported. Here we demonstrate a simple way to synthesis soluble Cu2S and ZnS nanocrystals capped with MCC Sn2S64- without ligand exchange process between organic ligands and MCC. Nanocrystals is synthesised by directly mixing metal ions with excess S2- presented in MCC solution at room temperature in ambient atmosphere. Nanocrystals formed immediately, then capped with MCC to prevent aggregation. In this study, We found that dispersion depends on the ratio of nanocrystals to MCC. The well dispersed case did not precipitate even after centrifugation, and particle size could be tunable by controlling the concentration of reaction solution. Precursor film was deposited by repeatedly spin coating and baking.Carbon free and single phase Cu2ZnSn(S,Se)4 thin film could be obtained after fast annealing process under Se atmosphere.

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16:00

The Influence of Precursor Cu/Sn ratio and Two-Stage Processing Conditions on the Microstructure of Cu2ZnSnSe4 and Cu2SnSe3

Authors : J. A. Marquez, N. Pearsall, I. Forbes

Affiliations : NPAC, Faculty of Engineering and Environment, University of Northumbria, Ellison Place, Newcastle upon Tyne, United Kingdom, NE1 8ST.

Resume : Cu2ZnSnSe4 (CZTSe) and Cu2SnSe3 (CTSe) thin films have been produced using the two-stage process via the conversion of Cu-Zn-Sn multilayer precursors capped with thermally evaporated Selenium. Precursors with Cu/Sn ratios from 1.9 to 2.3 were converted using the same process conditions. In addition, Cu-Zn-Sn precursors with Cu/(Zn+Sn) ratio of 0.9 and a Cu/Sn ratio of 2, and binary Cu-Sn precursors, were converted at temperatures between 380 °C and 550 °C. X-ray diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) analyses indicated self-regulation of the Cu/Sn ratio and the formation of CTSe. Formation of this phase is consistent with reports on the formation path and the reaction with ZnSe to form CZTSe. The XRD analysis of the CZTSe layers was performed using the PowderCell 2.4 software. A Pseudo-Voigt function was used for fitting the peaks profile. The analysis yielded values for lattice parameters, a and c, a trend that increased to a maximum for Cu/Sn ratio of 1.9.The Williamson and Hall method was used to evaluate the strain and domain size in the CZTSe and CTSe. The dependence of the domain size on the conversion temperature and Cu/Sn will be presented.

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16:00

High Vapour Pressure Selenization and Grain Growth Mechanisms of Sulfide-CZTS Precursors

Authors : Justus Just(1,2), Steffen Kretzschmar(1), Roland Mainz(1), Claudia Coughlan (3;4), Kevin Ryan(3;4), Thomas Unold(1)

Affiliations : 1: Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany; 2: Bergische Universität Wuppertal, Gaußstraße 20, 42109 Wuppertal, Germany; 3: Materials and Surface Science Institute and Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland; 4: 4SFI-Strategic Research Cluster in Solar Energy Research, University of Limerick, Limerick, Ireland

Resume : Due to the instability of CZTS,Se in terms of decomposition and Sn loss at high temperatures, most of the existing approaches to grow high-quality CZTS,Se absorbers consist of a subsequent annealing, sulfurization or selenization step after the deposition of a CZTS precursor. To prevent this decomposition, a high chalcogen partial pressure has to be applied during the crystallization process. Herein we report about fundamental growth mechanisms and properties of CZTS,Se absorber layers, produced by selenization of various different precursors at high selenium partial pressures. We compare growth mechanisms of PVD deposited precursors, nanoparticles and nanorods by applying different temperature and selenium partial pressure profiles. Additionally the role of Na during grain growth is investigated in detail. Grain growth mechanisms are found to be substantially different for different types of precursors: The formation of CZTS,Se grains from nanoparticle precursors is dominated by the interdiffusion of cations and the existence of an unsintered layer, while grain growth of PVD precursors is dominated by nucleation of grains and stress and thus is much more depending on the elemental composition of the precursor. Cu-rich precursors tend to form large grains (~10 µm) under various selenization conditions while the grain growth in case of Cu-poor precursors is much more specifically depending on the parameters of selenization and the supply of Na.

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16:00

Crystallization of Cu2ZnSnS4 (CZTS) Absorber Layer Prepared by Sulfurization of Metal-Ethanolamine Complex Compound

Authors : Kyoo Ho Kim*,Ersan Y. Muslih

Affiliations : School of Material Science and Engineering, Nano and Thin Film Laboratory, Yeungnam University

Resume : Cu2ZnSnS4 (CZTS) thin films were synthesized from CuxZny and CuxSny (Cu5Zn8 and Cu5Sn6) binary compound films that were prepared from a (Cu,Zn,Sn)-ethanolamine complex compound solution using the drop coating technique. The crystallization of Cu2ZnSnS4 after sulfurization at elevated temperatures under an Ar + H2S (5%) atmosphere was examined. Binary metal sulfides (CuS, ZnS, SnS) and ternary metal sulfides (CusSnS3) formed at 250 °C to 350 °C. Cu2ZnSnS4 was formed at 450 °C to 550 °C. At 450 °C, Cu2ZnSnS4 was formed in the presence of secondary phases. The secondary

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phase disappeared with increasing temperature with a single phase at 550 °C. The composition ratio were near stoichiometric copper and zinc rich with the ratio, [Cu]/([Zn]+[Sn]) = 0.99, [Zn]/[Sn] = 1.45, and [S]/[metal] = 1.03. The CZTS thin film showed a direct band gap of 1.52 eV with an absorption coefficient of more than 105 cm-1 and p-type semiconductivity with a mobility and resistivity of 7.64 cm2 /Vs and 3.78 Ωcm respectively.

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16:15 **GaN bulk crystals – status and challenges**

Authors : Izabella Grzegory

Affiliations : Institute of High Pressure Physics PAS Unipress Warsaw, Poland

Resume : GaN crystals of high structural quality are very much required for expanding applications in full color light sources and high power -high frequency electronics. However due to its extreme melting conditions GaN cannot be grown from stoichiometric GaN liquid. New melting data coming from very high pressure (up to 10.0GPa) and temperature (up to 3400K) experiments will be discussed in the context of theoretical simulations of GaN melting. GaN bulk crystals of high quality are therefore grown at pressures much lower than the one expected for melting. Sophisticated approaches (A-DEEP, VAS) based on HVPE on foreign substrates have been developed for obtaining free standing GaN wafers with quality and size sufficient for laser applications. The HVPE is at present, the only method supplying GaN substrates for industry. Its main advantage is high growth rate exceeding 100 □m/h. Real bulk GaN crystals of very high quality are grown by ammonothermal method at moderate pressures of 0.1-0.3GPa and low temperatures of about 400-600oC. Development of this technology is limited by discouragingly low grow rate of about 1 □m/h. This can be improved by increasing both pressure and temperature of the process. Higher rate of about 20 □m/h can be also achieved in Na-flux system where pressures lower than 100MPa and temperature of about 850oC are used. The existing methods and their current state will be discussed. A new approach to GaN bulk crystallization based on growth by HVPE on Ammono-GaN seeds will be also presented. It will be shown that thick (d>2mm) GaN crystals with quality as good as the quality of the seeds can be grown with a rate exceeding 200 □m/h. These studies are crucial for establishing physical limitations of real bulk GaN crystallization process by HVPE.

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16:45 **Chemistry of Ammonothermal Nitride Crystal Growth**

Authors : Shiyu Zhang, Theresia M. M. Richter, Jan Hertrampf, Nicolas S. U. Alt, Eberhard Schlücker, Rainer Niewa

Affiliations : Shiyu Zhang; Theresia M. M. Richter; Jan Hertrampf; Rainer Niewa, Universität Stuttgart, Institut für Anorganische Chemie, Pfaffenwaldring 55, 70569 Stuttgart, Germany Nicolas S. U. Alt; Eberhard Schlücker, Friedrich-Alexander-Universität Erlangen-Nürnberg, Lehrstuhl für Prozessmaschinen und Anlagentechnik, Cauerstr. 4, 91058 Erlangen, Germany

Resume : The ammonothermal process typically employs basic (mostly alkali metals or their amides) or acidid mineralizers (typically ammonium halides) in supercritical ammonia and was proven to be capable of growing a broad variety of nitrides like AlN crystals and free standing GaN wafers as well as further interesting materials [1]. However, the growth mechanism with respect to intermediate species involved was only scarcely elucidated, although the chemical processes during dissolution of the feedstock material, mass transport and crystallization of product crystals are of utmost importance. We report on synthesis and characterization of a number of solid compounds likely to represent intermediates in the ammonothermal growth of GaN. In ammono-basic as well as ammono-acidic media we find different solid gallium compounds to be formed, depending on the chemical nature of the mineralizer as well as the pressure and temperature conditions[2, 3]. These compounds may give rise to identification of the transport active species of GaN crystal growth in supercritical ammonia. The impact on growth kinetics on different crystal faces and the solubility of GaN in ammonia will be discussed. References: [1] Richter, T. M. M.; Niewa, R. Inorganics submitted. [2] Zhang, S.; Hintze, F.; Schnick, W.; Niewa, R. Eur. J. Inorg. Chem. 2013, 5387. [3] Zhang, S.; Alt, N.S.A.; Schlücker, E.; Niewa, R. J. Cryst. Growth submitted.

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17:15 **Charge transfer contribution to adsorption energy– consequences to crystal growth of semiconductors from the vapor**

Authors : Stanislaw Krukowski, Pawel Kempisty, Pawel Strąk, Konrad Sakowski1

Affiliations : Institute of High Pressure Physics, Polish Academy of Sciences, Sokołowska

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29/37, 01-142 Warsaw, Poland and Interdisciplinary Centre for Materials Modeling, Warsaw University, Pawińskiego 5a, 02-106 Warsaw, Poland

Resume : Adsorption of several molecular species, pertinent for crystal growth of the semiconductors at the polar surfaces of GaN, SiC and ZnO were investigated by DFT calculations. The investigated cases include adsorption of ammonia and hydrogen at polar GaN(0001) surface, hydrogen, silicon and carbon at SiC(0001) surface and zinc and oxygen at ZnO(0001) surface. The results of DFT calculations confirm recently obtained predictions that charge transfer between surface and the bulk of semiconductor may affect the adsorption energy. The process may change the adsorption energy, depending on the availability of empty states at the surface and pinning of Fermi level at the surface. In case of the nonpinned Fermi level, the adsorption energy depends on the doping in the bulk. Crystal growth from the vapor is reviewed showing that the adsorption of growing species leads to the increase of the adsorbate to the point where Fermi level is unpinned. Thus majority of the growth processes occurs at this condition, so that the adsorption depends on the doping in the bulk. This mechanism explains the dependence of the growth and doping on the Fermi level in the bulk. These predictions is verified by thermodynamic analysis of the growth of GaN, SiC and ZnO with application of DFT data.

add to my program **(close full abstract)**

17:30 **Multiphonon Processes in cubic and hexagonal GaN and ZnO**

Authors : H.W. Kunert 1, A.G. J. Machatine 1, M. Govender 1,2, B. Mwakikunga 2

Affiliations : 1 Department of Physics, University of Pretoria, South Africa, 2 National Centre for Nano-structured Materials, CSIR, P. O. Box 395, Pretoria, 0001, South Africa

Resume : Using group theoretical techniques we have determined the selection rules for multiphonon processes for first- , second- and higher order multiphonon processes in GaN and ZnO of cubic and hexagonal symmetry. The selection rules for optical transitions induced by electrical dipole and Raman scattering processes are determined. Our experimental Raman spectra confirm the selection rules for allowed modes for combinations and overtones. These results are used to obtain the phonon density of states that influence the thermodynamical and structural properties such as thermal conductivity, expansion coefficients and many others.

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add to my program **(close full abstract)**

18:00 **Development of single crystalline magnetoelastic materials for energy conversion applications**

Authors : Thomas A. Lograsso

Affiliations : Division of Materials Science and Engineering, Ames Laboratory, Ames IA 50011

Resume : Fe-X (X = Ga, Ge, Si, Al, Mo) magnetostrictive alloys offer an extraordinary combination of magnetoelasticity and mechanical properties and are rare-earth-free and environmentally green. These materials can be formed using conventional deformation processing such as wire drawing and rolling, machined and welded, offering a robust alternative to piezoelectrics. As actuators, their high magnetic permeability, low hysteresis and low magnetic saturation fields are attractive for device applications where energy conversion from magnetic to mechanical is desired. More recently, design concepts and applications based on the reverse principle conversion of mechanical vibration energy into magnetoelastic energy are taking advantage of Fe-X alloys excellent mechanical properties to operate in both tensile and compressive modes. Since the first publication of magnetostriction data on the Fe-Ga single crystals [1], we have focused in quantifying and controlling processing-structure-property relationships in the alloys. We experimentally clarified the phase dependence of the magnetostrictive behavior over a wide compositional range in the Fe-Ga alloy system. There are four magnetostriction-composition regimes (Fig. 1) [2, 3]. In regime I of disordered single phase A2 (BCC) and regime III of well ordered single phase D03, the tetragonal magnetostriction constant, (3/2) λ100 increases with Ga content. In regime II, where an A2 + D03 phase mixture exists, and in regime IV, where D03 + secondary phases are present, (3/2) □ 100 decreases with Ga content. The secondary phases small in size and D03 phase do not influence the distribution of the magnetic domains in the alloys, unless the secondary phases at higher Ga content are pronounced and large in size [4]. The relation between magnetic domains and the underlying microstructure is consistent with magnetic force microscopy results and reveals that many reported maze domains structure seen in Fe-Ga alloys results from surface damage during metallographic preparation and are not related to the D03 precipitates. In regime III, water-quenched alloys may contain a phase

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mixture of A2, B2, and D03, but this phase mixture shows higher (3/2) □100 than the pure D03 obtained through slow cooling. Many efforts have been made to model the magnetostrictive behaviors of the Fe-Ga alloys to answer the origin of the magnetostriction enhancement caused by Ga addition to body-centered cubic (bcc) □-Fe and to predict elements leading to further enhancements. The magnetoelastic behavior within a single phase region, such as the □-Fe solid solution, has yet to be adequately explained by any proposed model. For (3/2) □100, Clark et al. suggested that Ga-Ga pairs oriented along [100] directions within the bcc lattice to be the origin [6]. However, this hypothesis is in contrast to a recent EXAFS (extended x-ray absorption fine structure) study [7] in which the magnetostrictive atomic strain was found to be from Fe-Ga pairs, despite the presence of Ga-Ga pairs in the second coordination shell around Ga. Wu et al. [8] proposed an intrinsic model based on electronic spin-orbit coupling interactions. The model initially predicted wrong sign of D03 Fe-Ga [8] and was improved to yield computed (3/2) □100 fitting perfectly with experimental values [9]. However, this model is limited only to certain discrete structural models which do not accurately account for a non-random solid solution, as evident from structural studies of the A2 phase. In addition, there is an argument that the computed results based on this model do not occur in realistic disordered alloys [10]. On the other hand, an extrinsic model proposed by Khachaturyan and Viehland [11] states the rearrangement under a magnetic field of structural domain variants within discrete heterogeneities is largely the source of the enhanced magnetostriction. The domain variants are formed during a series of displacive phase transformations from D03 nanosized phases via Bain strain. However, this hypothesis lacks convincing support from the majority of Fe-Ga experimental results reported in literature event though it seems to be supported by some reports. While there is growing evidence spin-orbit coupling is source of the enhanced coupling in Fe-X alloys, the theoretical concepts necessary to account for solid solutions alloys do not fully account for the observed behavior of the alloys. Using a band filling argument, Wu [9] has predicted that a reduction in electron density at the Fermi level Ef could lead to enhanced magnetoelasticity. Our current experimental set provides some verification to this hypothesis in that increasing the electron valence concentration has resulted in decrease in magnetoelastic coupling factors (Al > Si and Ga > Ge) for the A2 disordered solid solution. To provide a positive experimental validation, elemental additions with a valence of 2 or less are needed. Only Be and Zn have sufficient solubility to test the hypothesis. Given safety concerns related to working with beryllium, zinc is the only viable option to test this prediction. The challenge will be controlling zinc evaporative losses to minimize gradients through the crystal during the growth processes. We have grown bcc Fe-Ga-Zn single crystals under elevated pressure in elevated pressure (15 Bar) Bridgman furnace to overcome the high vapor pressure problem of Zn. Single crystalline measurements of the magnetostrictive strains and elastic constants measurements have been made, allowing for a direct comparison of the magnetoelastic coupling factors between other Fe-X alloys and between the theoretical predictions. References 1. A. E. Clark, J. B. Restorff, M. Wun-Fogle, T. A. Lograsso, and D. L. Schlagel, IEEE Trans. Magn. 36, 3238 (2000). 2. Q. Xing, Y. Du, R. J. McQueeney, and T. A. Lograsso, Acta Mater. 56, 4536 (2008). 3. Q. Xing and T. A. Lograsso, Scripta Mater. 65, 359 (2011). 4. Q. Xing and T. A. Lograsso, Appl. Phys. Lett. 93, 182501 (2008). 5. C. Mudivarthi, S.-M. Na, R. Schaefer, M. Laver, M. Wuttig, and A. B. Flatau, J. Magn. Magn. Mater. 322, 2023 (2010). 6. A. E. Clark, M. Wun-Fogle, J. B. Restorff, T. A. Lograsso, and J. R. Cullen, IEEE Trans. Magn. 37, 2678 (2001). 7. M. P. Ruffoni, S. Pascarelli, R. Grössinger, R. Sato Turtelli, C. Bornio-Nunes, and R. F. Pettifer, Phys. Rev. Lett. 101, 147202 (2008). 8. R. Wu R, Z. Yang, and J. Hong, J. Phys.: Condens. Matter. 15 S587 (2003). 9. Y. N. Zhang, J. X. Cao, and R. Q. Wu, Appl. Phys. Lett. 96, 062508 (2010). 10. T. Khmelevska, S. Khmeleskyi, and P. Mohn, J. Appl. Phys. 103, 073911 (2008). 11. A. G. Khachaturyan and D. Viehland, Metall. Mater. Trans. A 38A, 2308 (2007); ibid 2317 (2007). 12. S. Bhattacharyya, J. R. Jinschek, A. Kachaturyan, H. Cao, J. F. Li, and D. Viehland, Phys. Rev. B 77, 104107 (2008).

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European Materials Research Society

PROGRAM VIEW : 2014 Spring

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Thin film chalcogenide photovoltaic materials

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start at	Subject	Num.
	CZTSSe: growth : C. Platzer-Björkman	
08:30	**High temperature coevaporation of Cu2ZnSnSe4** **Authors :** Alex Redinger, Rabie Djemour, Jan Sendler, Thomas Paul Weiss, Marina Mousel and Susanne Siebentritt **Affiliations :** University of Luxembourg, Laboratory for Photovoltaics, 41 rue du Brill, Luxembourg **Resume :** We present a high temperature coevaporation process to make efficient Cu2ZnSnSe4 (CZTSe) thin film solar cells. CZTSe decomposition at high temperatures is suppressed through a Sn and SnSe evaporation source. Selenium is supplied through a valved cracker source to maximize the Se reactivity. The process consists of three stages. A short first stage at 420°C ensures a high SnSe supersaturation and minimizes large amounts of ZnSe at the back. It is followed by a second stage at 470°C where the final Cu/Zn ratio is fixed. In the third stage Sn, SnSe and Se are supplied in excess to improve the crystal quality. The composition of the absorber can be controlled by the Cu and Zn flux solely while Sn and Se are incorporated in the film in a self-limiting way. Solar cell efficiencies as high as 7.2% have been achieved so far. We present a detailed compositional study and the influence of each stage on solar cell performance is described. The optical properties of the absorbers are analyzed via photoluminescence (PL) and Transmission/Reflection measurements. Both methods indicate that several materials with different bandgaps are present in the absorber. We observe a broad absorption spectrum and multiple transitions in PL. We therefore attribute the broadening of the low energy slope in the quantum efficiency to secondary phases in the absorber. The results achieved via this coevaporation process are compared with a precursor and annealing process with maximum efficiencies of 7.5%.	A.O7 1
add to my program	(close full abstract)	
08:45	**The formation mechanism of secondary phases in Cu2ZnSnSe4 absorber layer** **Authors :** H. Yoo, R. A. Wibowo, G. Manoharan, A. Verger, R. Lechner, J. Palm, S. Jost, R. Hock **Affiliations :** Chair for Crystallography and Structural Physics, Friedrich-Alexander University Erlangen-Nürnberg, Staudtstraße 3, D-91058, Erlangen, Germany; Saint-Gobain Recherche, 39, Quai Lucien Lefranc, 93303 Aubervilliers Cedex, France; AVANCIS GmbH & Co. KG, Otto-Hahn-Ring 6, D-81739 München, Germany **Resume :** Secondary phase formation in a Cu2ZnSn(S, Se)4 (CZTSSe) based p-type layer for photovoltaic applications is one of the major problems which must be overcome to improve solar cell efficiency. To better understand the crystallization mechanism of secondary phases in the material system Cu-Zn-Sn-Se, we investigated the selenization of binary metallic layers as a function of temperature. The sputtered thin film precursors comprise Cu-Zn, Cu-Sn, and Zn-Sn with different sequence. A total six precursors were studied by time-resolved X-ray diffraction while temperature increased from 30 °C to 550 °C. Selenium had been always deposited on top of the metallic precursors in a separate thermal evaporation step. The observed reaction sequences were shown different results depending on the metals which are in first contact with selenium. From these experimental results, the mutual affinities of metals are determined, and a way of reducing the ZnSe crystallization is presented. Preferable precursor composed of ternary metallic layers with Se is also suggested in conclusion with respect to a stacking order of the metals.	A.O7 2

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08:45 **Growth of large size diamond single crystals by plasma assisted chemical vapour deposition**

Authors : Alexandre Tallaire

Affiliations : LSPM-CNRS, Université Paris 13

Resume : The synthesis of large-size diamond single crystals still remains an important challenge particularly with respect to the outstanding properties of this material. In the field of power electronics, the wide band-gap, high thermal conductivity, high carrier mobilities and good chemical stability of diamond are all assets to fabricate devices able to operate at very high voltage and current and under harsh environments. The plasma assisted chemical vapour deposition technique (PACVD) has witnessed tremendous progresses over the last decade. Diamond growth rates can now reach up to several tens of micrometers per hour while the crystalline quality of the material produced is starting to be compatible with electronic applications [1]. The past few years have thus seen the introduction of thick CVD diamond material into the market although its availability remains fairly limited. Nevertheless diamond has yet not been adopted as a semiconductor material for active electronic applications. In fact the available area is usually limited to a few mm² which complicates the processing steps of the material. Point and extended defects are also difficult to control especially to the high level of purity required by electronic applications. Finally the problems of uniform p-type doping over thick layers and the poor activity of n-type doping need to be solved if efficient junctions are to be realised. In this presentation the growth of single crystal diamond by PACVD will be detailed particularly in the light of the remaining challenges. The use of such synthetic material into high-end applications will also be evaluated. [1] A. Tallaire, J. Achard, F. Silva, O. Brinza, A. Gicquel, Growth of large size diamond single crystals by plasma assisted chemical vapour deposition: Recent achievements and remaining challenges. Comptes Rendus Physique, 14 (2013) 169-184.

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09:00 **Electrodeposited Cu2ZnSnS4 thin film solar cell with an efficiency of 8%**

Authors : Feng Jiang, Shigeru Ikeda, Takashi Harada, Michio Matsumura

Affiliations : Research Center for Solar Energy Chemistry, Osaka University

Resume : High quality Cu2ZnSnS4 (CZTS) thin films with the compact and uniform surface morphology were successfully fabricated by electrochemical depositions of Cu, Sn, and Zn metal precursor layers followed by sulfurization in a sulfur atmosphere. Cu poor and Zn rich element ratios were observed in these CZTS films, and the thickness of the obtained CZTS films are about 1um. Despite of some small holes were observed at the interface of CZTS/Mo, a best CZTS thin film solar cells with maximum active-area efficiency of 8% were successfully fabricated. It was also proved that the electrodeposition as a low cost and manufacturable method for preparation of high photovoltaic performance CZTS thin film solar cells is feasible.

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09:15 **Soft thermal processing of Cu2ZnSnSe4/CdS hetero-junction for solar cell efficiency improvement**

Authors : Y. Sanchez1, M. Neuschitzer1, S. Lopez-Marino1, V. Izquierdo-Roca1, L. Calvo -Barrio2,4, O. Vigil-Galan3, A. Perez-Rodriguez1,4, E. Saucedo1

Affiliations : 1. Catalonia Institute for Energy Research (IREC), Jardins de les dones de negre 1, 08930 Sant Adria del Besos-Barcelona, Spain 2. Centres Cientifics i Tecnologics de la Universitat de Barcelona (CCiTUB). LLuis Sole i Sabaris 1-3, 08028 Barcelona, Spain. 3. Escuela Superior de Fisica y Matematicas-Instituto Politecnico Nacional (IPN), 07738 Mexico DF, Mexico. 4. Departament de Electronica (IN2UB), Universitat de Barcelona, Marti i Franques 1, 08028 Barcelona, Spain.

Resume : Cu2ZnSnSe4 (CZTSe) is a potential replacement for the already commercialized Cu(InGa)Se2 (CIGS) thin film photovoltaic absorber. Nevertheless, it exhibits much lower photoelectric conversion efficiency (9.7%) than CIGS (20.9%). To further improve the record efficiency of CZTSe, optimization of the CZTSe/buffer hetero-junction is also of paramount importance to achieve a good device performance. Up to now few reports can be found about the CdS growth conditions and their effects on the optoelectronic properties of the CZTSe based devices. This work reports on the effects of annealing treatment under air of CZTSe/CdS hetero-junction after the CdS chemical bath deposition and the impact on the electro-optical properties of the devices. Parameters such as annealing temperature and time were investigated. A complete characterization of CdS layers grown onto glass substrate will be presented using X-ray diffraction, Raman spectroscopy and scanning electron

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microscopy. An increase from 2.2% for the non-thermally treated junction, to 6.1% efficiency for the annealed one was achieved. Further optimization of the processes allows us to obtain a champion cell with 7.3% efficiency. Additionally, the CZTSe/CdS hetero-junction properties were investigated combining external quantum efficiency measured under different conditions (bias voltage, white bias light, monochromatic bias light) and X-ray photoelectron spectroscopy, showing remarkable differences before and after annealing.

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09:15 **GaN on Si – a hype or the bright future**

Authors : Marianne Germain

Affiliations : EpiGaN nv, Kempische Steenweg 293, 3500 Hasselt, Belgium

Resume : tbd

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09:30 **Effects of deposition termination on CZTSe device characteristics**

Authors : I.L. Repins,1 J.V. Li,1 A. Kanevce,1 C. Perkins,1 K.X. Steirer,1 J. Pankow,1 G. Teeter,1 M. Bär,2,3,4 J.H. Alsmeier,2 L. Weinhardt,4,5,6 D.A. Hanks,2,4 R.G. Wilks,2 C. Heske,4,5,6 D. Kuciauskas,1 C. Beall,1 C. Dehart, 1 J. Carapella, 1 B. Bob, 7 J.S. Park, 1 S.H. Wei1

Affiliations : 1 National Renewable Energy Laboratory, Golden, CO 80401, USA ; 2 Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; 3 Institut für Physik und Chemie, Brandenburgische Technische Universität Cottbus-Senftenberg, Cottbus, Germany; 4 Department of Chemistry, University of Nevada, Las Vegas, Las Vegas, NV, USA; 5 Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; 6 ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; 7 Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095, USA;

Resume : Kesterite devices have made rapid progress, with champion efficiencies reaching 12.6% [1], compared to 6.7% just 6 years ago. [2] However, improvement to near 20% is needed to achieve cost goals associated with TW-scale production. [3,4] Furthermore, even champion devices exhibit voltages that are well below those expected from the measured bulk lifetimes, from 2 to 16 ns. [5,6] Thus, in this work we examine sensitivities to the device performance that originate from the region very near the surface, which may not be characterized by optical or electrical techniques that penetrate further into the film. We use co-evaporated CZTSe to demonstrate the critical importance of the deposition termination (i.e. the fluxes comprising the top ~500Å of the film) on device efficiency. We have explored three different types of deposition termination: 1) The deposition is terminated with ~500Å of ZnSe, applied as the sample is cooling over the temperature range from 510 to 430 oC. This variation produces the best device efficiencies (η= 9.8%, Voc=380 mV, f=68.9% Jsc=37.6 mA/cm2), [7] the highest reported efficiency for a CZTSe device without alloying for band gap expansion. 2) The sample receives no extra ZnSe at the end of the deposition. Efficiencies are greatly reduced (e.g. η= 2.3%, Voc=266 mV, f=50.4% Jsc=16.9 mA/cm2), and open-circuit voltage as a function of temperature indicates a large contribution from surface recombination. 3) The deposition is terminated with ~500 angstroms of ZnSe, applied as the sample is cooling over the temperature range from 300 to 275 oC. This variation produces devices with voltages comparable to or better than the best process, but fill factors and short-circuit currents are greatly reduced by an inflection in the current-voltage curves, as has been described for blocking front barriers in CIGS devices. [8] We present measurement of device and film properties for each of these process variations. Analysis of the ZnSe termination suggests that it reduces surface recombination both through altering the position of the Fermi level at the surface, and through creating a lower recombination velocity surface. The latter deduction matches with theoretical predictions of benign Cu-depleted surfaces. When ZnSe is deposited at high temperatures, there is a few percent diffusion of Cu and Sn into the ZnSe, which reduces the band gap (also consistent with theory), and prevents the ZnSe from acting as a harmful current-blocking barrier. 1. W. Wang , M.T. Winkler , O. Gunawan , T. Gokmen , T.K. Todorov, Y. Zhu , D.B. Mitzi "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency," Adv. Energy Mater. 2013, DOI: 10.1002/aenm.201301465. 2. H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. Motohiro, "Enhanced Conversion Efficiencies of Cu2ZnSnS4-Based Thin Film Solar Cells by Using Preferential Etching Technique," Applied Physics Express 1 (2008) 041201. 3. R. Wendt. (2011). "How to achieve the SunShot goal of $0.50/watt at the module level using compound semiconductors? Industrial perspective," presented at the

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09:45 **High temperature epitaxial growth of graphene and SiC**

Authors : Mikael Syväjärvi

Affiliations : Linköping University and Graphensic AB, Sweden

Resume : Silicon carbide has been thoroughly studied in various crystal growth processes. The common method for SiC epitaxial growth is based on chemical vapor deposition that is typically carried out at 1500-1600 degrees for research in transistor applications. There are benefits in high temperature growth while also challenges appear. Interestingly, we have explored a high temperature sublimation epitaxy approach at 1800-1900 degrees for growth of fluorescent silicon for white LED layers with potential in general lighting. SiC doped with certain elements act as a monolithic rare earth metal free light converter and produces a pure white light. We have also initiated growth of cubic SiC, which doped with boron fits nicely in to the model of intermediate bandgap solar cell theory. The quality of cubic SiC has been an obstacle in use of this polytype. We have shown that the cubic SiC can reach similar quality as produced in commercial hexagonal polytypes. This may open a new research area in SiC, in particular for studies of the photovoltaic properties. In addition, graphene is an emerging material. Our high temperature epitaxial graphene process carried out at 2000 degrees, which is more than 300 degrees higher than in other methods, has shown an outstanding quality. Potentially, it could be a contact material on photovoltaic cubic SiC. We describe the challenges with high temperature crystal growth of fluorescent and photovoltaic SiC, as well as graphene on SiC. A.O7 8

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10:00 **coffee break**

CZTSSe: interface + electrical analyses : D. Mitzi, A. Redinger

10:30 **Observations of an order-disorder transition in Cu2ZnSnS4 thin films**

Authors : Jonathan J. S. Scragg (a), Charlotte Platzer-Björkman (a), Mukesh Kumar (b), Clas Persson (c), Léo Choubrac (d), Jan Sendler (e), Susanne Siebentritt (e)

Affiliations : (a) Ångström Solar Center, Solid State Electronics, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden (b) Environmental Remediation Materials Unit, National Institute for Materials Science, Ibaraki 305-0044, Japan (c) Department of Physics, University of Oslo, NO-0316 Oslo, Norway and Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden (d) Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS 2, rue de la Houssinière, BP 32229, 44322 Nantes cedex 03, France, (e) Université du Luxembourg, Laboratoire Photovoltaïque, 41, rue du Brill, L-4422 Belvaux, Luxembourg

Resume : We report on a fundamental property of Cu2ZnSnS4 (CZTS), which is being investigated for sustainable thin film PV. Cu and Zn cations can be interchanged in the crystal structure of CZTS, giving rise to several structural polymorphs as well as intermediate disordered structures. We have used Raman spectroscopy on thin films and powder reference samples to identify an order-disorder transition (ODT), during which the ground state kesterite (KS) structure converts to disordered kesterite (dis-KS), at about 260°C. We explore this phenomenon further using multi-wavelength Raman and Photoluminescence (PL) spectra to obtain a better estimate of the transition temperature and the rate of change of cation ordering. PL spectra recorded during an interrupted ODT reveal multiple peaks in the range 1.24 to 1.52 eV. The relative intensity of these peaks changes during the ODT, indicating that they may arise from A.O8 1 kesterite domains with different levels of ordering. We compare our experimental results with first-principles density-functional analysis of the disorder formation energy and energy gap as functions of Cu/Zn disorder. Our results suggest that most thin-film CZTS used for PV devices consists largely of dis-KS, while formation of ordered KS requires extended heat treatment below 260°C. We discuss possible ramifications of disorder for device function, in terms of defects and fluctuating potentials, that may impact the open circuit voltage.

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10:45

Atomic scale insights into Cu2ZnSnSe4 thin-film solar cells by Atom Probe Tomography

Authors : Torsten Schwarz 1, Pyuck-Pa Choi 1, Oana Cojocaru-Mirédin 1, Marina Mousel 2, Alex Redinger 2, Susanne Siebentritt 2, Silvana Botti 3, and Dierk Raabe 1

Affiliations : 1 Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237, Düsseldorf, Germany; 2 Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg; 3 LPMCN, CNRS, Université Lyon 1, Villeurbanne, France

Resume : The fabrication of CZTSSe solar cells is often impeded by the formation of secondary phases (Zn(S,Se), Sn(S,Se), Cu2-x(S,Se), Cu2Sn(S,Se) 3, etc), which are formed if growth conditions are outside the narrow homogeneity range of the CZTSSe phase. With conventional characterization methods it is often difficult or even impossible to detect them due to their structural similarity with CZTSSe. Moreover, secondary phase particles may only be a few nanometers in size and thus hardly be detectable. Here, we apply Atom probe tomography and TEM to investigate two different CZTSe absorbers: Cu-rich and Cu-poor precursors were prepared by co-evaporation at 320 °C. Both precursors were etched in KCN and annealed at 500 °C. Absorbers made from Cu-rich precursors yield ~ 6 % efficiency, whereas Cu-poor precursors lead to absorbers with ~ 5 % efficiency. Both precursors exhibit a heterogeneous microstructure and a ZnSe network. Cu-rich precursors also contain Cu2-xSe particles and a novel Cu2Zn6SnSe9 phase, which was confirmed as a stable phase by DFT. We detect a complex, nanosized network of CZTSe and ZnSe for the final absorbers. Some of the ZnSe domains contain nano-precipitates having a Cu- and Sn-rich composition, which cannot be assigned to any known equilibrium phase. Furthermore, TEM investigations reveal a larger grain size for the absorbers with 6 % efficiency. Moreover, we detect Na and K at CZTSe grain boundaries and CZTSe/ZnSe phase boundaries.

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10:45

Development of SiC crystal growth in the past, present and future

Authors : Shin-ichi NISHIZAWA

Affiliations : National Institute of Advanced Industrial Science and Technology

Resume : Since the first reported manmade SiC crystal growth process, Achesson method, SiC crystal growth technology has more than one hundred years history. Achesson method is still used as the process for making abrasive powders. After Achesson method, Lely method was reported. The plate like SiC single crystal can be grown, and SiC has started a new history as an electronics material. Then the modified Lely method has opened door of the seeded crystal growth technologies for SiC. Today, large SiC single crystal is produced by this modified Lely method, and SiC shows the great potential as the post Si semiconductor material. During the last decades, SiC crystal growth process has studied from both quality and quantity points of view. About the quality, hollow core (micro pipe) density reduction was the big issue, and it is almost solved today. Then, more detail about the dislocations such as screw, edge, and the others, are discussed from both crystal growth mechanism and device impact points. About the quantity, 6ich in diameter SiC wafer is already reported. The shape of SiC grown crystal can be controlled by modified the thermal and design of crucible. In order to use SiC as the post Si-semiconductor materials, it is necessary to improve the crystal growth process from the industrial points of view, such as more high growth rate, more high stable polytype control. Some of these trials will be discussed during the symposium.

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11:00

Physical and Electrical characterization of high-performance Cu2ZnSnSe4 based thin film solar cells

Authors : S. Oueslati, G. Brammertz, M. Buffière, H. ElAnzeery, O.Touayar, C. Köble, M. Meuris, J. Poortmans.

Affiliations : KACST-Intel Consortium Center of Excellence in Nano-manufacturing Applications (CENA), Riyadh, KSA; imec division IMOMEC - partner in Solliance, Wetenschapspark 1, 3590 Diepenbeek, Belgium ; Institute for Material Research (IMO) Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium ; imec-partner in

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Solliance, Kapeldreef 75, 3001 Leuven, Belgium ;Department of Electrical Engineering, KU Leuven, Kasteelpark Arenberg 10, 3001 Heverlee, Belgium ; Department of Physics, Faculty of Sciences of Tunis, El Maner, Tunisia ;Microelectronics System Design Department, Nile University, Cairo, Egypt ;National Institute of Applied Sciences and Technology, INSAT, Tunisia; Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany.

Resume : We report the properties of Cu2ZnSnSe4 (CZTSe) solar cells using absorber layer fabricated by selenization of sequential DC-sputtered Cu, Zn and CuSn multilayers followed by annealing at temperature of 460oC for 15 minutes in H2Se Gas. Solar cells are fabricated using standard process flow for chalcopyrite solar cells, i.e. n-type CdS chemical bath deposited buffer layer followed by sputtered intrinsic ZnO and Al-doped ZnO multilayer. MgF2 antireflection coating (ARC) is added in order to reduce reflection losses. The structural characterization of the absorber using SEM-EDX, XRD and Raman spectroscopy showed the formation of high quality CZTSe polycrystalline layer. A maximum efficiency of 10.4% under AM1.5G was measured on a 0.52cm2 solar cell with a short circuit current density of 39.7mA/cm2, an open circuit voltage of 394mV and a fill factor of 66.4%. The comparison of the electrical performance of the solar cell before and after ARC confirmed the enhancement in the collection current when using the MgF2 layer, hence, better electrical parameters were measured. We perform characterization using photoluminescence spectroscopy, external quantum efficiency, JV and admittance versus temperature measurements in order to derive information about possible causes for the low Voc values observed. The main defects derived from these measurements are strong potential fluctuations in the absorber layer with 35meV depth and potential barrier of the order of 182meV in the structure.

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11:15

Phase and Defect Quantization in CZTS Films using Resonant Diffraction

Authors : K.H. Stone, M.I. Ahmad, V.L. Pool, B. Shyam, S. Christensen, I. Repins M.F. Toney

Affiliations : SSRL, Materials Science Division, SLAC National Accelerator Laboratory, Menlo Park, CA; Chemical and Material Science, National Renewable Energy Laboratory, Golden, CO

Resume : The interest in Cu2ZnSn(S,Se)4 (CZTS) for photovoltaic (PV) applications is motivated by the similarities to the promising material Cu(In,Ga)Se2 (CIGS) while being comprised of non-toxic and earth abundant elements. Competition between the kesterite (necessary for PV applications) and the stannite phase of CZTS, as well as a number of binary and ternary competing phases affects the power conversion efficiencies of CZTS devices. However, the structural similarities of many of these phases make their identification through standard x-ray diffraction challenging. Furthermore, the strong possibility of point defects on the Zn and Cu sublattices leads to a significant reduction in solar cell efficiency. The tunable energy x-rays available at synchrotron sources provide a site and element specific probe to investigate such disorder. We have used resonant X-ray diffraction to quantitatively determine the crystallographic phases and level of CuZn, ZnCu, VCu, and VZn point defects present in thin films of polycrystalline CZTS as a function of growth condition. Our goal is to understand and characterize the structural differences and defect levels of films grown under different conditions. By comparing with device efficiencies for these films, we can identify those structural features with the greatest effect on PV performance and the growth conditions to effectively control them.

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11:30

Photoluminescence and DLTS investigation of reactively sputtered Cu2ZnSnS4 thin film solar cells

Authors : L. Van Puyvelde (1), J. Lauwaert (1), P. F. Smet (1), D. Poelman (1), R. Van Deun (2), T. Ericson (3), J. J. Scragg (3), C. Platzer-Björkman (3), S. Khelifi (4), H. Vrielinck (1)

Affiliations : (1) Department of Solid State Sciences, Ghent University, Gent, Belgium (2) L3 – Luminescent Lanthanide Lab, Department of Inorganic and Physical chemistry, Ghent University, Gent, Belgium (3) Ångström Solar Center, Solid State Electronics, Uppsala University, Uppsala, Sweden (4) Department of Electronics and Information Systems, Ghent University, Gent, Belgium

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Resume : Cu2ZnSnS4 (CZTS), which is non-toxic and consists of earth abundant elements, is a promising absorber for thin film solar cells. To obtain higher efficiencies, a better understanding of the defect structures in this material is necessary. In this context, deep level transient spectroscopy (DLTS) and photoluminescence (PL) measurements have been performed on three reactivily sputtered CZTS thin film solar cells. The cells differ in annealing procedure and buffer layer thickness. The defect spectroscopy results are completed with SEM, EDX and EQE measurements. In PL emission measurements the dependence on the excitation wavelength, temperature (5-100 K) and excitation power is investigated. PL excitation measurements (10-120 K) are performed to determine the onset of the absorption. Despite the differences between the cells, three similar broad PL signals appear in all spectra. Current-DLTS measurements with varying pulse heights were applied. A DLTS peak, with a time constant independent of the applied bias pulse height, appears below 200K. This peak can possibly be attributed to resistivity freeze out in the neutral region. At higher temperature an onset of a broad peak can be found.

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11:45 **Impact of Annealing Treatment Before Buffer Layer Deposition on Cu2ZnSn (S,Se)4 Solar Cell**

Authors : Daisuke Hironiwa1, Noriyuki Sakai2, Takuya Katou2, Hiroki Sugimoto2, Ryo Takai3, Jakapan Chantana3 and Takashi Minemoto3

Affiliations : 1Ritsumeikan Global Innovation Research Organization, Ritsumeikan University 2Energy Solution Business Center, Showa Shell Sekiyu K.K 3Department of Electrical and Electronic Engineering, Ritsumeikan University

Resume : Cu(In,Ga)Se2 (CIGSe) is one of the most promising materials for high efficiency thin-film solar cells with the efficiency of over 20 %. In constant, the reported best efficiency of Cu2ZnSn(S,Se)4 (CZTSSe) solar cells so far is 12.6% which is lower than that of CIGSe. In order to improve the solar cell performance, we fabricated CZTSSe solar cells with annealing treatment. The CZTSSe absorbers were produced by annealing of metallic precursors. First, metallic precursors were deposited on Mo / soda-lime glass substrates. The CZTSSe absorbers were produced by conducting sulfurization and selenization of the precursors. The CZTSSe solar cells with annealing treatment at 100, 150, 200, 250 and 300 oC, and a keeping time of 30 min in N2 atmosphere were prepared. Based on the result of Current density - Voltage measurements, an annealing treatment at temperature of 200 oC was most effective. The efficiency of solar cell increased from 5.5 % (no annealing) to 8.8 % (with annealing) by adopting the optimum annealing treatment due to improvement of all solar cell parameters (Short-current density, Open-circuit voltage (Voc), Fill factor). With the annealing treatments, the spectra of external quantum efficiency were significantly increased as compared with that without annealing treatment. Photoluminescence (PL) spectra of CZTSSe layers without buffer layer were measured in order to investigate the defect acting as recombination centers. The peak intensity was significantly increased after annealing treatment. It was suggested that non-radiative recombination should be decreased by annealing treatment. The PL intensity presented a linear relation with all the solar cell parameters, especially Voc. A.O8 7

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12:00 **DISCUSSION SESSION: CZTSSe solar cells - limited by bulk or interface(s)? (D. Mitzi/T. Minemoto)**

12:30 **Lunch break**

Poster 3: buffers/contacts, structural studies and modeling, growth control, and nanostructuring : Takashi Minemoto + Tobias Töndahl

14:00 **Transmission Electron Microscopy Studies on Cu2ZnSnS4 Solar Cell Absorber Material**

Authors : Nessrin Kattan, Bo Hou, David J. Ferm?n, David Cherns

Affiliations : University of Bristol

Resume : Copper zinc tin sulphide (CZTS) has been attracted a lot of attention over the last two decades. Its importance lies in their availability and safety to the environment in additional to its low cost. In this work, CZTS was synthesized by the hot injection method. Transmission electron microscopy (TEM) was applied to confirm CZTS phase by investigating the crystal structure of as-prepared material, before and after annealing to 550?C. The material was analysed using selected area (SAED) and convergent beam electron diffraction (CBED) techniques. A polycrystalline material was formed in the pre-annealing stage. The post-annealed material consist of more uniform crystalline particles A.P3 1 with an average size ~ 53?13 nm. SAED and CBED patterns from the annealed material showed a double cubic tetragonal unit cell due to the presence of super lattice reflections in electron diffraction patterns that consistent with Kesterite or stannite phase. As a result of annealing process, X-ray diffraction and TEM results showed growth of CZTS nanocrystals along (112) plane. Furthermore, the defect structure was investigated by bright and dark field images taken in 2-beam diffraction conditions. In the post annealed stage, the material showed a low density of lamellar twins and dislocations at {112} planes. The crystal structure of these defects was investigated using high resolution (TEM) lattice images showed changing of stacking sequence from cubic basic structure to hexagonal (wurtzite) structure occurred at twining boundaries.

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14:00

Raman Peak Position of Cu(In,Ga)Se2 Film for Predication of Ga/(In+Ga) Content near Its Surface and Open-Circuit Voltage

Authors : Jakapan Chantana[a],Daisuke Hironiwa[a],Taichi Watanabe[b],Seiki Teraji [b],Kazunori Kawamura[b],Takashi Minemoto[a]

Affiliations : [a]Department of Electrical and Electronic Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan [b]Environment & Energy Research Center, Nitto Denko Corporation, 2-8 Yamadaoka, Suita, Osaka 565-0871, Japan

Resume : Cu(InGa)Se2 (CIGS) films on rigid soda-lime glass (SLG) and flexible stainless steel (SUS) substrates are deposited by so-called “multi-layer precursor method” [1]. CIGS films with several Ga/(In+Ga), Ga/III, profiles, investigated by dynamic-secondary ion mass spectroscopy (D-SIMS), are fabricated. CIGS films are destroyed after D-SIMS. However, in case of Raman measurement, not only does it take less than 2 minutes to measure one CIGS sample, but also CIGS film is not damaged after the measurement. An estimated penetration depth of Raman scattering light into CIGS is about 100 nm from its surface. Raman measurement is thereby utilized for investigation of CIGS near its surface. It is reported that open-circuit voltage (VOC) of CIGS solar cell is well correlated to average Ga/III content near its absorber surface (200 nm from CIGS surface), inducing local band gap near the surface [1]. The correlation between average Ga/III near CIGS surface and the Raman peak position of CIGS films is thus investigated. It is demonstrated that Raman peak position is linearly increased with the increase in the average Ga/III near CIGS surface. Consequently, a quantitative estimation of the average Ga/III near CIGS surface can be predicted, when Raman peak position of CIGS film is known. Additionally, the relationship between VOC and Raman peak position can be observed. Ultimately, the Raman peak position, linearly corresponding to average Ga/III near CIGS surface, could be utilized as an indicator of VOC of CIGS solar cells, before cell fabrication, which is a fast and non-destructive method. [1] J. Chantana et al., J. Appl. Phys. 114 (2013) 084501.

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14:00

Spray deposition of Ag nano-dots for absorption enhancement of extremely thin ILGAR® absorber layers

Authors : Y. Liu, Y.P. Fu, T. Dittrich, R. Sáez-Araoz, M. Schmid, M.C. Lux-Steiner, C.-H. Fischer

Affiliations : Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

Resume : Plasmonic enhancement of absorption is a tool for further reduction of the thickness of absorbers. Spray chemical vapor deposition of mono-disperse Ag nano-dots was developed on Mo substrates. Particle size (5-70 nm) and density can be controlled by the reaction parameters (temperature, precursor concentration and time). In2S3 layers were deposited by ILGAR® (ion layer gas reaction), see the review: C.-H. Fischer, et al. Solar Energy Materials & Solar Cells 95 (2011) 1518. Ag deposition on these substrates resulted in the formation of AgInS2 followed by deposition of Ag nano-dots on top. The morphology (SEM), crystal phase (XRD), composition (EDX) and electronic (surface photovoltage spectroscopy) as well as optical properties (UV-Vis) of the In2S3/Ag layers were studied. Related layer systems will be incorporated into solar cells with extremely thin absorbers.

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14:00

Second generation of PV structures based on zinc oxide films grown by atomic layer deposition

Authors : R. Pietruszka1, G. Luka1, B. S. Witkowski1, M. Godlewski1,2

Affiliations : 1Institute of Physics, Polish Academy of Sciences, Warsaw, Poland 2 Department of Mathematics and Natural Sciences College of Science, Cardinal Stefan Wyszynski University, Warsaw, Poland

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Resume : Second generation of the solar cells is based on thin films of e.g. cadmium telluride (CdTe), material with a direct optical band gap of 1.45 eV and a high optical absorption coefficient. This generation of photovoltaic (PV) devices is commercialized and has chances to compete with PV devices based on silicon. In this work we describe the properties of single-crystalline CdTe-based solar cells that contain zinc oxide (ZnO) or cadmium sulphide (CdS) films as an n-type partner to p-type CdTe. In first type of deposited by us structures we verify if zinc oxide can replace commonly used cadmium sulphide. In the second we tested use possibility of deposition CdS films by Atomic Layer Deposition (ALD) method. In both cases structures were covered with TCO films based on ZnO layer doped with Al. In addition to structures mentioned above, we also investigated another possibility of using ZnO-based films in PV devices. We deposited low resistivity ZnO films by the ALD as ohmic contacts to p-type CdTe, CdZnTe and ZnTe. As a metal contact gold, palladium and copper prepared by various deposition method were applied. Present study confirms that high conductivity ZnO films can be used as a low resistivity ohmic contact and transparent electrode (TE) to p-type tellurides, especially to ZnTe. This work was partially supported by the Innovative Economy grant (POIG.01.01.02-00-108/09, the National Centre for Research and Development grant (PBS1/A5/27/2012).

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14:00 **Cu(InGa)Se2 thin film solar cell with an inset of rare-earth doped ZnO conversion layer**

Authors : Hyeonwook Park(a), Hyungmin Lee(a), Matteo Balestrieri(b), Guy Shmerber (b), Gerald Ferblantier(c), S. Colis(b), Aziz Dinia(b), Abdelilah Slaoui(c), Chinho Park(a), Jae Hak Jung(a) and Woo Kyoung Kim(a)(*)

Affiliations : (a) School of Chemical Engineering, Yeungnam University, Republic of Korea ; (b) Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg, CNRS UMR 7504, France ; (c) ICube, Université de Strasbourg-CNRS, France

Resume : Recent achievement of over 20 % cell efficiency (AM1.5, 0.5 cm x cm) in high-performance Cu(InGa)Se2 (CIGS)-based thin film solar cells is very promising. Typically, CIGS cell has a structure of SLG/Mo/CIGS/CdS/i-ZnO/ZnO:Al, and its current can be limited by several optical and collection losses, i.e., shading from front grid, reflection from ZnO, absorption in ZnO and CdS layers, and incomplete generation and collection in CIGS absorber. In this paper, rare-earth doped ZnO (ZnO:RE) layer was employed to replace i-ZnO in the conventional CIGS cell structure for the potential use as a down-shifting or down-converting layer. Firstly, pure and RE (Yb, Nd and Pr)-doped ZnO films were deposited onto Si wafer, quartz and glass substrate by magnetron sputtering system starting from a Zn target covered with small pieces of RE, and then characterized by several techniques including XRD, Raman, SEM, TEM, RBS, UV-VIS, PL etc. For examples, the PL measurements revealed that the main emission peaks of Yb and Nd were detected in the near infrared region, while the primary emission peaks of Pr appeared in the visible light region. Then, ZnO:RE layer was inserted into CIGS cell to form SLG/Mo/CIGS/CdS/ZnO:RE/ZnO:Al structure, where CIGS was prepared by 2-step sputter-selenization process and CdS was deposited by standard chemical bath deposition. Device performance of CIGS cell with RE-doped ZnO layer was characterized by QE and I-V measurements. A.P35

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14:00 **Improvement of CdTe Solar Cell Performance by Using O-doped CdS Window Layer**

Authors : Hui Li, Xiangxin Liu, Junfeng Han, Marie-paule Besland

Affiliations : The Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, Chiness Academy of Sciences; Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS;

Resume : We report a simple and effective strategy for improving performances of CdTe solar cells by radio-frequency magnetron sputtering technique. This strategy only involves oxygen dope into CdS. The transmittance and band gap of oxygen-doped CdS is higher than that of CdS without intentional dopant, and therefore the optical loss due to CdS absorption is greatly reduced. The conversation efficiency of CdTe solar cell is 12.48% with oxygen-doped CdS as window layer grown on commercial soda-lime TEC15 glass without high resistive transparent layer, while the conversation efficiency of CdTe solar cell is only 11.20% with CdS as window layer fabricated at the same condition. It is not only the Jsc increases owing to less optical absorption of oxygen-doped CdS, but also the Voc and FF are improved. We are going to present our ongoing high A.P36 resolution electron transmission microscopy work for better understanding on the interface and grain morphology of such devices.

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14:00 **Photothermal and photoluminescence spectra of Cu(InGa)Se2 with CdS and ZnS buffer layers -- Effect of buffer layer formation on the absorption edges**

Authors : T. Hamada1), H. Hisamatsu1), N. Naghavi2), J. F. Guillemoles2), D. Lincot2), K. Sakai1), A. Fukuyama1), and T. Ikari1)

Affiliations : 1) DEEAP, University of Miyazaki, 1-1 Gakuen Kibanadai-nishi, Miyazaki, 889-2192, Japan 2 IRDEP - UMR 7174 EDF/CNRS/CHIMIE-PARISTECH, 6 quai Watier, 78401 Chatou Cedex, France

Resume : Recently developed CIGS thin film solar cell has ZnO/CdS/CIGS/Mo/SLG structure and the CdS buffer layer plays an important role for device performance. However, effect of such buffer layer on PV cell characteristics is not still clear. Especially, absorption spectrum of the cell is very hard to observe due to the presence of opaque Mo back contact. We have developed the photothermal (PPT) methodology for solving this problem by using a transparent transducer LiNbO3 for a detector and could observe the absorption spectra of the CIGS film samples by measuring the nonradiative transitions of photo excited carriers. We, then, investigate the effect of buffer layer on the absorption edge comparing with the photoluminescence (PL) measurements. Different buffer layer of CdS and ZnS were grown by chemical bath deposition technique. The Ga/(Ga+In) ratio was determined to be 0.3 by an XPS measurement. PL spectra showed dominant peak around 1.05 eV at 4 K and no difference was found for three samples. However, we found the absorption edge of 1.12 eV estimated from the square root plot for the absorption spectra shifted to the lower energy side about 0.04 eV by buffer layer deposition at room temperature. The observed red-shift indicates the band tailing conflicting to our knowledge that the presence of the buffer layer improves the interface conditions and reduces the nonradiative transition. Temperature variations of the PL and PPT spectra are carrying out for making clear the results. A.P3 7

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14:00 **Fabrication of vertical Cu2ZnSnS4/Mo/Si nanocylinder arrays**

Authors : Chonge Wang, Akihito Kondo , Takuya Yamaguchi, Shukichi Tanaka, Yukihiro Tominari,Yasuhiro Hara, Tomohiro Shimizu, Shoso Shingubara

Affiliations : Department of Mechanical Engineering, Kansai University, Japan

Resume : Vertically aligned CZTS (Cu2ZnSnS4)/Mo/Si nanocylinder arrays were formed using Si nanowire arrays on Si substrate as a template, and their optical properties were investigated. Prior to CZTS and Mo deposition, hexagonally-ordered Si nanowire arrays were prepared by metal-assisted etching of Si (100) using patterned Au catalyst. The diameter, length and inter-wire distance of the prepared Si nanowire arrays were 200, 500, 1000 nm, respectively. On the prepared Si nanowire arrays, Mo layer and CZTS layer was sequentially deposited. Then, the CZTS/Mo/Si nanocylinder arrays were formed. The nanocylinder array structures generally works as unti-reflection and light trapping structure. For this reasons, it is expects that an improvement of efficiency of PV cell using CZTS as light absorber. We confirmed an enhancement of light absorbance of the CZTS nanocylinder arrays compared with CZTS film prepared on Mo coated flat Si substrate. The detailed optical properties, such as light incident angle dependence and wire-diameter dependence, will be present. A.P3 8

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14:00 **Adaptation of the surface-near Ga content in co-evaporated CIGS for CdS versus ZnS-based buffer layers**

Authors : Torben Klinkert, Thibaud Hildebrandt, Marie Jubault, Frédérique Donsanti, Jean-François Guillemoles, Negar Naghavi

Affiliations : 1 EDF R&D, Institute of Research and Development on Photovoltaic Energy (IRDEP), Chatou, France 2 CNRS, IRDEP, UMR 7174, 78401 Chatou, France 3 Chimie ParisTech, IRDEP, 75005 Paris, France

Resume : In this work, we show that in order to optimize the efficiency of Cu (In1-x,Gax)Se2 (CIGS) solar cells with Cd-free ZnS-based buffer layers, the Ga concentration in the CIGS absorber layer towards the heterointerface has to be adapted. We varied the In and Ga deposition rates in the last stage of our 3-stage co-evaporation process leading to different compositional ratios of $0.15 \leq x \leq 0.6$ in the top 400 nm of the absorber layer. All absorber layers were then completed with both CdS and ZnS buffer layers by chemical bath deposition. While cells with our standard grading of $x \approx 0.4$ in the front region result in a best performance of 15 % with a CdS buffer, similar efficiencies with a ZnS A.P3 9 buffer layer are only obtained when the Ga content near the heterointerface is reduced down to x ≈ 0.25. Interestingly, the maximum efficiency for the CdS buffer layer coincides with the maximum Voc and FF. For the ZnS buffer layer this is not the case: the Voc increases steadily for higher Ga ratios while the FF is fairly constant for 0.25 < x <0.5 and decreases drastically for more extreme values. Material and diode properties are extracted from chemical, structural and opto-electronic characterization and the results are explained on the basis of the electronic band structure and its alignment at the CIGS/buffer interface. The results illustrate the importance of the absorber layer adaptation for different buffer layers and are an important step on the way to Cd-free buffer layers.

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14:00

Indium Oxysulfide films by Atomic Layer Deposition (ALD) as buffer layers in CIGS solar cells

Authors : Cathy Bugot, Nathanaëlle Schneider, Daniel Lincot, Frédérique Donsanti

Affiliations : Institut de Recherche et Développement sur l'Energie Photovoltaïque (IRDEP), UMR 7174 (EDF-CNRS-Chimie Praistech)

Resume : Cu(In,Ga)Se2 solar cells achieve conversion efficiencies up to 20.8% using cadmium sulfide (CdS) as buffer layer. However, because of its toxicity and its low optical band gap (2.4 eV) which limits the light conversion of CIGS in the UV range of solar spectrum, alternative materials have been developed. In2S3 is a suitable material as Cd-free buffer layer and achieved high efficiency (16.4%). The aim of this study is to increase the flexibility for high efficiency by alloying In2S3 with oxygen for band gap and interfacial energetic engineering. Atomic Layer Deposition (ALD) of In2(S,O)3 is investigated using indium acetylacetonate (In(acac)3), hydrogen sulfide (H2S) and either H2O or O2 plasma as oxygen precursors. The films were fabricated by inserting In2O3 growth cycles during In2S3 deposition process. By using water as precursor, the films have properties similar to those of pure In2S3 and no oxygen was inserted. Oxygen insertion was successfully achieved using O2 plasma at T=160°C, due to exchange reactions between S and O atoms. By increasing the number of In2O3 growth cycles during In2S3 deposition, the optical band gap could be tuned from 2.1 eV for pure In2S3 to 3.3 eV for In2(S,O)3. In2(O,S)3 films with different thicknesses and compositions were explored as buffer layer in CIGS based solar cell. The films properties and the optoelectronic performance will be presented.

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14:00

Optimization of parameters for deposition of ZnO films by Sol Gel using Taguchi method

Authors : Youssef Ammaih ,Abderrazak Lfakir , Bouchaib Hartiti Abderraouf Ridah ,Philippe Thevenin,Meryane Siadat

Affiliations : 1) MAC & PM Laboratory, ANEPMAER group, Faculty of Science and Technique, University Hassan II Mohammedia, Mohammedia, Morocco: AMMAIH Youssef ; Bouchaib Hartiti ; Abderrazak Lfakir; Abderraouf Ridah 2) LMOPS Laboratory, Supelec, University of Lorraine, Metz, France: Philippe Thevenin 3) Laboratoire LCOMS, Université de Lorraine, France : Meryane Siadat

Resume : Zinc oxide (ZnO) is a binary material, semiconductor with a wide direct bandgap (3.37 eV). With their good optoelectronic properties, thin films can be used for several applications in solar cells, gas sensors, piezoelectric sensors, waveguides etc. The ZnO thin films can be prepared by several techniques such as: spray pyrolysis, thermal evaporation, reactive sputtering, sol-gel etc. In this work, we used the Taguchi method of design of experiments to optimize the quality of ZnO thin films by studying the influence of parameters of conditions (concentration, pre-annealing and annealing temperatures) on their structural, morphological and optical properties. The XRD spectra show that ZnO films deposited with different deposition conditions are highly textured and have a preferred orientation along the (002) direction, which confirms the wurtzite structure of ZnO. The Transmittance of our films varies between 70 and 90% and the values of the optical gaps are between 3.10 and 3.25 eV as a function of the deposition parameters. The thin film annealed at 550 ° C for 2 h with a concentration of 0.75 mol / l showed the better quality regarding the properties in general The Taguchi methodology is a rewarding method since it allows not only to reduce the resources involved in all phases of development of ZnO thin films, but also to determine the most influent parameters on their overall properties. With these optimal deposition conditions, the ZnO layers can be doped with Al, In, F to improve their electrical properties

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14:00

COPPER VARIATION IN CU(IN,GA)SE2 SOLAR CELLS WITH INDIUM SULPHIDE BUFFER LAYER

Authors : S. Spiering1, S. Paetel1, F. Kessler1, M. Igalson2, H. AbdelMaksoud2
Affiliations : 1Zentrum f?r Sonnenenergie- und Wasserstoff-Forschung Baden-W?rttemberg, Industriestrasse 6, 70565 Stuttgart, Germany;2 Warsaw University of Technology, Faculty of Physics, Koszykowa 75, 00-662 Warszawa

Resume : In the manufacturing of Cu(In,Ga)Se2 (CIGS) thin film solar cells the application of a buffer layer on top of the absorber is essential to obtain high efficiency devices. Regarding CIGS co-evaporation by roll-to-roll method a vacuum deposition process for the buffer is preferable to conventionally cadmium sulphide buffer deposited by a chemical bath deposition. Promising results were achieved for the deposition of indium sulphide buffer by different vacuum techniques. Currently this material is investigated at ZSW by thermal in-line evaporation with efficiencies >16 % for devices on glass. The solar device performance is very sensitive to the conditions at the absorber-buffer heterojunction. In view of optimization we investigated the influence of Cu content in the absorber on the current-voltage characteristics. For standard solar cells with CdS buffer layer typically 22 23 at.% Cu is found in the CIGS layer. In this work the copper content was varied between 19?23 at.%. An improvement of the cell performance by enhanced VOC was observed for a reduction of Cu to ~21 at.% when thermally evaporated indium sulphide was applied as buffer layer. Influence of stoichiometry deviations on transport mechanism and secondary barriers in the device was studied using detailed dark and light current-voltage analysis and admittance spectroscopy. Conclusions point towards the importance of intrinsic defects distribution in the absorber for the potential characteristics in the cell.

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14:00

In-situ monitoring of CuInSe2 thin films growth by light scattering

Authors : Yoann ROBIN, Matthieu MORET, Sandra RUFFENACH, Roger-Louis AULOMBARD, Olivier BRIOT
Affiliations : Université Montpellier 2, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France ; CNRS, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France ; CNRS, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France ; Université Montpellier 2, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France ; CNRS, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France ;

Resume : Light scattering spectroscopy, mainly developed for CuInxGa(1-x)Se2 thin films growth, has been proven to be an efficient in-situ monitoring tool. It consists of illuminating the substrate surface using a white light and collecting the diffused light with a spectrometer. The on-line information allows monitoring the point of stoichiometry of the grown layer. In this work, we propose an alternative approach of this method, replacing the spectrometer by a standard webcam. This system allows to precisely choose the analyzed area on the substrate surface, which may be the whole sample surface or just a specific zone. We have grown CuInSe2 (CIS) thin films by co-evaporation under vacuum using a MBE equipment. We have simultaneously performed CIS growth on both Mo-coated and bare glass substrates within the same growth run, while, on purpose, the scattered light was collected from the Mo-coated substrate. The CIS thin films were characterized by X-ray diffraction, atomic force microscopy, Hall effect measurements, absorption spectroscopy and energy dispersive spectroscopy for composition. By interrupting the CIS growth at different stages of the growth process, we observe the reproducibility of the collected scattered light spectra exhibiting the same features. These features are correlated to the Cu-rich/In-rich transitions around the points of stoichiometry. The influence of parameters as the In/Cu ratio and the growth temperature on the scattered light signal has been investigated.

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14:00

Impact of degradation on optical and electrical properties of sputtered aluminun doped zinc oxide

Authors : L. Arzel (a), M. Theelen (b,c) , E. Leornard (a) , N. Barreau (a)
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Resume : Aluminum doped zinc oxide (ZnO:Al) is used as transparent conductive oxide for Cu(In,Ga)Se2 (CIGSe) solar cells and modules. Degradation of ZnO:Al layer is a key parameter in the stability of these devices. In this work, we investigated the influence damp heat exposition on physical,

optical and electrical properties of ZnO:Al thin films deposited by RF sputtering on borosilicate glass. We studied physical properties by Raman spectroscopy before and after degradation. We performed reflection (R) and transmission (T) measurements on spectrophotometer before and after degradation. This allows to extract electrical parameter such as carrier concentration, mobility, conductivity, by an optical method. The spectra R/T were fitted through the calculation of the thin film optical constant n and k. The free carrier contribution is described by using the standard and the extended Drude model. The latter gives the best fit. We compare carrier concentration, mobility, conductivity before and after degradation in order to discriminate the influence of the grain and the the grain boundaries on the losses in the electrical transport during degradation.

add to my program **(close full abstract)**

14:00 **Composition-dependent nanostructure of Cu(In,Ga)Se_2 powders and thin films**

Authors : C. S. Schnohr[1], H. Kämmer[1], T. Steinbach[1], M. Gnauck[1], C. A. Kaufmann[2], C. Stephan[2], S. Schorr[2,3]

Affiliations : [1]Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany; [3]Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74-100, 12249 Berlin, Germany

Resume : Both the Ga gradient and the Cu content strongly influence the electrical properties and thus the conversion efficiency of Cu(In,Ga)Se2 thin film solar cells. However, the material composition also affects the atomic arrangements on the nanometer scale which deviate significantly from the average long-range crystallographic structure [1,2]. The anion displacement, in particular, depends sensitively on the kind of neighboring cations [1] and has a significant influence on the material bandgap [2,3]. We have therefore used extended X-ray absorption fine structure spectroscopy to compare the atomic-scale structural parameters of Cu(In,Ga)Se2 powders and polycrystalline thin films with varying composition. No difference in the two sample types is observed for the average Cu-Se, Ga-Se and In-Se bond lengths which are nearly independent of both the Ga and the Cu content. This demonstrates the strong tendency towards bond length conservation typical for tetrahedrally coordinated semiconductors. In contrast, the bond length variation is significantly smaller in the thin films than in the powders, particularly for Cu-poor material. This difference in the nanostructure is proposed to originate from differences in the preparation conditions, most prominently from the different history of Cu composition.

[1] C.S. Schnohr et al., Phys. Rev. B. 85, 245204 (2012).
[2] S. Eckner et al., Appl. Phys. Lett. 103, 081905 (2013).
[3] J. Vidal et al., Phys. Rev. Lett. 104, 056401 (2010).

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14:00 **Cu-(Sb,Bi)-(S,Se) based absorber materials for thin-film solar cells: first-principles description**

Authors : Mukesh Kumar<1,2>, Clas Persson <2,3>

Affiliations : <1> Environmental Remediation Materials Unit, National Institute for Materials Science, Ibaraki 305-0044, Japan <2> Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden <3> Department of Physics, University of Oslo, NO-0316 Oslo, Norway

Resume : In order to meet the increasing demand for energy, earth abundant and low-cost materials fabrication are utmost criteria for photovoltaic (PV) technologies. Very recently, I-V-VI ternary system (I= Cu: V = Sb, Bi; VI = S, Se), which contain inexpensive and earth abundant elements, has been suggested as an alternative material for PV thin-film technologies [1]. Therefore in this study, employing first-principles modeling within the density function theory, we analyze the electronic and optical properties of I-V-VI system. As per different stoichiometries, there are three sets of compounds, namely Cu(Sb,Bi)(S,Se)2, Cu3(Sb,Bi)(S,Se)3, and Cu3(Sb,Bi)(S,Se)4 in I-V-VI ternary system. Cu(Sb,Bi)(S,Se)2 and Cu3(Sb,Bi)(S,Se)3 compounds crystallize in orthorhombic structure, whereas Cu3(Sb,Bi)(S,Se)4 has a base-centred tetragonal structure. Our calculations show that the fundamental band gap energies of these compounds are in the region of 0.4–2.1 eV, which is suitable for PV solar cells applications. Furthermore, the flat energy dispersion of conduction band implies a large optical absorption, and the calculations reveal that the absorption coefficient of these compounds are stronger than other Cu-S based materials like CuInSe2 and Cu2ZnSnS4 [2]. Thereby, I-V-VI ternary system has the potential to be a suitable absorber material in thin-film PV technologies. [1] L.

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Yu et al., Adv. Energy Mater. 3, 43 (2013). [2] M. Kumar et al., Appl. Phys. Lett. 102, 062109 (2013).

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14:00 **Effects of pH and Annealing Temperature on ZnS(O,OH) Thin Films deposited by Solution-based CFM Method for Solar Cells** A.P3 17

Authors : Ho Young Jun , Seon Young Park, Si Ok Ryu*

Affiliations : School of Chemical Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan 712-749, South Korea

Resume : Of the II-VI type binary compounds, zinc sulfide (ZnS) having a wide energy band gap is one of the most attractive semiconductor materials. ZnS is an important semiconductor material with a wide energy band gap (Eg > 3.7eV). It can be used for the fabrication of optoelectronic devices. In special, ZnS became an important material for a buffer layer in thin film hetero-junction solar cells because it does not have any environmental issue unlike CdS, which is used for a buffer layer of the thin film solar cells. It was reported that some amount of ZnO and Zn(OH)2 as the impurities, which are denoted in ZnS (O,OH), are required to be present in the ZnS thin films for fabricating the efficient photovoltaic devices. In this study, ZnS(O,OH) thin films were synthesized by a continuous flow microreactor (CFM) process designed by a modification of CBD process, and then the influences of the pH and annealing temperature on the properties of ZnS(O,OH) thin films were investigated. The ZnS(O,OH) thin films were prepared on several different pHs of zinc precursors. Control of pH was carried out using ammonium hydroxide. The mixing ratios of zinc sulfate heptahydrate and ammonium hydroxide were varied in terms of the pH of the prepared solution. The deposited ZnS(O,OH) thin films were annealed at 300℃~600℃. The films were characterized by XRD, SEM, EDX, XPS, and UV-vis spectroscopy. Their transmittance and the estimated optical band gaps are over 70% in the visible region and 2.9eV~3.7eV, respectively. Based on the XRD and EDX, it was confirmed that the CFM process enables us to carry out the band gap engineering of ZnS(O,OH) by varying the S/O ratio.

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14:00 **Understanding the effect of sputtering process during i-ZnO deposition on cell efficiency of CIGS solar cells** A.P3 18

Authors : 1,2K.-N. Lee, 1Eun-A Ok, 1,2Yu-Seung Son,1 Jong-Keuk Park, 1Won-Mok Kim, 1Young-Joon Baik, 1Doh-Kwon Lee, 2Donghwan Kim, 1Jeung-hyun Jeong

Affiliations : 1Korea Institute of Science and Technology, Seoul 136-791, Korea; 2Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea

Resume : Sputtered intrinsic ZnO (i-ZnO) layer is essential to high-efficiency CIGS solar cells. However, its role in enhancing the efficiency has not been fully revealed, especially with respect of sputtering process conditions. In this work, its sputtering conditions were varied to have different O2 concentrations in sputtering gas (0%, 2%) and different sputtering powers (50, 100, 150 W). An incorporation of O2 increased substantially the efficiency from 15% to 17%. Open-circuit voltage, short-circuit current density, and FF were all improved in companion with the reduction of series resistance. Increase of the sputtering power also tends to improve the efficiency with a similar trend to the case of oxygen incorporation, but its effect is limited. CV profiling and admittance spectroscopy revealed that the oxygen incorporation increased the carrier density and reduced the defect energy from 120 meV to 35 meV, suggesting that it could modify the defect quality of CIGS surface. Electroluminescence (EL) spectroscopy proved that such changes occurred within CIGS layer, by showing the incorporated oxygen reduced the red-shift degree in EL peak (CIGS bandgap) with decreasing temperature. EBIC analysis showed that the carrier diffusion length in the quasi-neutral region of CIGS layer was significantly increased. In summary, the oxygen incorporation influenced through CdS directly CIGS bulk as well as surface. Such an oxygen effect seems related to higher Na doping level in O2 2% sample which is much higher near the interface of CdS/CIGS.

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14:00 **Zinc Tin Oxide (ZTO) thin films deposited via r.f. sputtering as alternative buffer layer for Cu(In,Ga)Se2 solar cells** A.P3 19

Authors : R.A. Mereu*, A. Le Donne, P. Garattini, S. Binetti, M. Acciarri*

Affiliations : Dept. of Materials Science and Solar Energy Research Center (MIB-SOLAR), University of Milano Bicocca, Via Cozzi 55, 20125 Milan, Italy * Corresponding author. Tel.: +390264485134. E-mail address: raluca.mereu@unimib.it; maurizio.acciarri@unimib.it

Resume : Despite long and extensive research effort the interest in transparent and conducting oxide (TCO) layers has not ceased. Lately, zinc tin oxide (ZTO) thin films were evaluated also as new buffer layer for chalcogenide-based PV. In this work, ZTO thin films have been deposited both on soda lime glass and silicon substrates by r.f. sputtering. The influence of sputtering conditions (mainly the sputtering power and film thickness) on the optical properties of the formed layers was investigated. The average transmittance of the ZTO thin films in the visible range resulted as higher as 90%. EDX measurements were performed on the ZTO samples in order to determine the stoichiometry of the Zn and Sn metals in the films. The roughness of the films was as well studied. The effectiveness of this alternative buffer layer in Cu(In,Ga)Se2 solar cells was investigated and promising results in terms of efficiency have been obtained. Since ZTO buffer layers allowed more or less a half of the efficiency reached using CBD-CdS further optimizations of the ZTO buffer layers are currently in progress. Acknowledgments: This work was partially supported by the European Commission through the project SolarDesign (contract no. FP7-NMP-2012-SME-6), by the executive programme of scientific and technological cooperation between Italy and Egypt through the Joint Research Project PGR00116 and by MIUR and Regione Lombardia through the R&D project no. 30208644.

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14:00 **Application of transparent p-type conductive BaCuSeF films to the back contacts of CdS/CdTe solar cells**

Authors : K. Yamamoto 1, H. Sakakima 1, R. Hayashi 2, Y. Ogawa 2, and T. Okamoto 2, T. Wada 1

Affiliations : 1 Department of Materials Chemistry Ryukoku University; 2 Ksarazu National College of Technology

Resume : Transparent p-type conductive materials are indispensable for optoelectronic applications such as polycrystalline tandem-type solar cells. BaCuSeF films have a wide band gap of 2.95eV and demonstrate p-type conductivity[1,2]. BaCuSeF films showed considerably high transmittance of T>50% in the visible light region and high electrical conductivity of σ>1S/cm. Good quality BaCuSeF films could be prepared at a substrate temperature of 200 ^{o}C by pulsed laser deposition and could be applied to the back contact of CdS/CdTe solar cells[3,4]. The solar cell showed large Voc~800mV, but small Jsc~6mA/cm2, resulting in an efficiency of η~2.8%. In order to avoid a reaction at the interface between CdTe and BaCuSeF layers, a thin Li-doped NiO film was inserted at the interface by rf-magnetron sputtering. The obtained solar cell with a NiO:Li buffer layer showed Jsc=9.2mA/cm2 and η=3.2%.

In this study, we improve the performance of the CdS/CdTe solar cells with BaCuSeF back contact. We attempted to modify the CdTe surface before deposition of BaCuSeF layer by etching in various solutions, such as HCl, NH3, and Br aqueous solutions. Etching in the Br aqueous solution considerably improved the performance of the CdS/CdTe solar cells.

[1]H. Yanagi et al., J. Appl. Phys. 100 083705(2006).
[2]M. Yoshikawa et al., Jpn. J. Appl. Phys. 51, 10NC40(2012).
[3]T. Okamoto et al., J. Cryst. Growth, 214-215, 1148(2000).
[4]K. Yamamoto et al., Jpn. J. Appl. Phys., in press.

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14:00 **First-principles study of the electronic structure of CuSbS2 and related photovoltaic semiconductors**

Authors : T. MAEDA, T. WADA

Affiliations : Department of Materials Chemistry, Ryukoku University

Resume : Recently, Ikeda et al. reported a CuSbS2 (CAS) solar cell with a conversion efficiency of 3.1% [1]. CAS is expected to be a promising photovoltaic compound because it has an optimal band gap of 1.52 eV and high absorption coefficient of >10^{4} cm^{-1}. CAS and CuSbSe2 (CASe) have a wurtzite-based chalcostibite structure, which is different from zinc-blend-based chalcopyrite and kesterite structures. In order to clarify the features of CAS and CASe, it is necessary to study their electronic structures. In this study, CAS and CASe's band structures and density of states were calculated with the HSE06 hybrid functional and compared with that of chalcopyrite CuInSe2.

In the band structure, the valence band maximum of CAS is located at the Γ-point and the conduction band minimum is located at the R-point. However, the second lowest conduction band is located at the Γ-point and the energy level at the Γ-point is nearly equal to the R-point. Therefore, CAS has an indirect band gap (Γ-R) of 1.16 eV and direct band gap (Γ-Γ) of 1.25 eV. The partial density of states of CAS (CASe) shows the character of Cu 3d and S 3p (Se 4p) at the top of the valence bands and Sb 5p and S 3p (Se 4p) at the bottom of the

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conduction bands. In the conduction band, CAS and CASe have a p-orbital character (Sb 5p) that differs from the s-orbital character (In 5s) of CuInSe2.
[1] W. Septina, S. Ikeda, Y. Iga, T. Harada, and M. Matsumura, Thin Solid Films 550 (2014) 700.

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14:00 **Ohmic back contact with Copper Sulfide (Cu2S) for CdTe solar cells**

Authors : J. Türck, S. Siol, A. Klein, W. Jaegermann

Affiliations : Technische Universität Darmstadt, Materials and Earth Sciences, Surface Science

Resume : One of the big challenges in the fabrication of a CdTe solar cell is the back contact to p-CdTe. A direct CdTe/metal contact leads to large barrier heights for holes. The formation of a tunnel junction is also impeded, due to the difficulties in doping CdTe p-type. The usual back contact applied to CdTe solar cells are either a thin Te layer, formed by etching as a primary contact, which has a lower valence band offset, followed by a secondary metal contact, or a Cu containing back contact. We prepared a back contact with Cu2S as primary contact. Due to band alignment studies for CdTe/Cu2S contact a small valence band offset is expected. Direct interface studies with X-ray Photoelectron Spectroscopy have revealed, however, a strongly reactive interface. Cu2S was evaporated on a CdTe layer after activation and cleaning step to remove oxidation products. CdTe solar cells have been prepared on commercial SnO2:F substrates (Pilkington TEC C15B) in the superstrate configuration. The CdTe and CdS layers were deposited by Closed Space Sublimation. The performance of solar cell with the Cu2S back contact was studied in comparison with an NP-etched and a direct Au back contact by IV and EQE measurements. After several heating steps over 12% efficiency was reached with the Cu2S Back contact, which was significantly higher than the ones obtained for the other back contacts.

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14:00 **Inversed Cu2ZnSn(S,Se)4/CdS/ZnO Nanorods Thin Film Solar Cells**

Authors : Li-Wen Hsueh, Yu-Tung Yin and Liang-Yih Chen*

Affiliations : Department of Chemical Engineering, National Taiwan University of Science and Technology

Resume : Recently, the copper zinc tin sulfide selenide (Cu2ZnSn(S,Se)4, CZTSSe) material have been greatly regarded as the absorption layer of thin film type solar cell, because the materials own the tunable band gap (1.0 ~1.5 eV), large absorption coefficient (>104 cm-1), low toxicity and great amount on the earth. In addition, the ZnO nanorods (ZnO NRs) with high electron mobility (200 cm2/V s at T=300K) can be a path to transport the carrier rapidly to increase the charge separation. It can also be regarded as light scattering to increase the light capture to provide high electron-hole pairs. In this work, a inversed CZTSSe thin film solar cells were fabricated by solution process. At first, the ZnO NRs were synthesized on the transparent conductive metal oxide (TCO) glass substrates by hydrothermal process. Then the surfaces were decorated by cadmium sulfide (CdS) by successive ion layer adsorption and reaction (SILAR). The absorption layer, CZTS was coated through an ethanolic solution containing Cu-Zn-Sn-S via microwave irradiation method with 50~100 W. Following a selenization process was carried in a horizontal furnace and the treatment temperature was set at 540 oC. Finally, Mo thin film was coated as contact electrode by RF sputtering. The morphologies, microstructures optical properties and electrical characterization were analyzed by Raman, XRD, SEM, TEM, UV-visible and J-V measurement, respectively

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add to my program **(close full abstract)**

14:00 **Fabrication of efficient compound solar cell back contacts by a new developed deposition process**

Authors : M. Winkler 1), C. Gretener 2), L. Kranz 2), J. D. König 1), J. Perrenoud 2), S. Buecheler 2), A. N. Tiwari 2), K. Bartholomé 1)

Affiliations : 1) Fraunhofer Institute for Physical Measurement Techniques IPM, Thermoelectric Systems, Heidenhofstraße 8, D-79110 Freiburg, Germany, markus.winkler@ipm.fraunhofer.de, Phone: +49 / 761 8857 611, Fax: +49 / 761 8857 224 2) Empa - Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Thin Films and Photovoltaics, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland,

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Resume : As severe Schottky barrier formation occurs when CdTe is contacted directly to a metal, an interlayer is needed to provide good contact. Due to its strong p-type character, narrowing the Schottky barrier and therefore allowing holes to tunnel through, Sb2Te3 is a promising material. Furthermore, the use of such a Cu-free back contact material might enhance the stability of the solar cell. However, the typical fabrication of Sb2Te3 by co-deposition on a hot substrate can be challenging due to Te re-evaporation, significantly complicating stoichiometry and property control. In contrast to this commonly used method, our process presented in this work is based on a newly developed deposition technique, circumventing the mentioned problems and obtaining high quality back contacts. We discuss this deposition process and the obtained properties of single Sb2Te3 films in detail. We also present performance studies on superstrate-based CdTe solar cells with such Sb2Te3 back contacts. High quality single-phase Sb2Te3 with large grain sizes, carrier mobilities > 400 cm²/Vs and large Seebeck coefficients was obtained. Changing deposition parameters allows to precisely adjust carrier concentration, demonstrating the flexibility of the method. An efficiency of 11.7% was achieved with an Sb2Te3/Cu/Mo back contact and with an Sb2Te3/Cu/Au contact in a first experimental series with significant potential for further optimization.

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14:00

On the metastable properties of GaCu-related defect and defect complexes in wide bandgap chalopirytes from first principles

Authors : Marek Maciaszek (1), Xavier Rocquefelte (2), Pawel Zabierowski (1)

Affiliations : 1 - Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland; 2 - Institut des Materiaux Jean Rouxel, Universite de Nantes, 2 rue de la Houssiniere, Nantes, 44322, BP 32229, Cedex 3, France

Resume : Efficiency of CIGS-based electronic devices depends significantly on point defects. Among them, IIICu (group III element on copper) antisites are one of the most important because of its very low formation energy and strong coupling with lattice. Recent theoretical calculations predict that they are compensating donors and exhibit metastable character. In particular, defects related to IIICu are thought to be important close to the junction. However, these papers do not give an estimation of the corresponding energy barriers which are the most important parameters from the experimental point of view. In this contribution we focus on GaCu defects (in complexes with VCu) performing ab-initio calculations in LDA and LDA+U approximation. We calculate configuration coordinate diagrams for GaCu and GaCu in complex with one or two VCu. We found that in the case of point defect GaCu, the energy barrier for the relaxation of the DX state by a hole capture is low (~0,15 eV) while the relaxation to the DX state by an electron capture can be spontaneous. In case of complexes combining GaCu and VCu, energies of transition to DX state shift up. In effect, the barriers for a hole capture are smaller (comparing to isolated GaCu) whereas there appears the barrier for electron capture. These findings are very important as the energy barriers can be measured directly and can be used for an experimental verification of theoretical model of IIICu.

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14:00

Defect characteristics and the influence of sodium in Cu(In,Ga)Se2

Authors : Christiane Stephan, Christian A. Kaufmann, Dieter Greiner

Affiliations : Helmholtz-Zentrum Berlin für Materialien und Energie

Resume : Solar cells with a Cu(In,Ga)Se2 (CIGSe) absorber layer are in general fabricated supplying alkali elements (mainly Na) by diffusion from the glass substrate during growth, by evaporation of NaF prior or after thin film deposition. For solar cell devices the final composition of such a CIGSe thin film is Cu-deficient to avoid shunts from Cu2Se. The interplay between composition, sodium content, growth condition and the final performance of such photovoltaic devices is still not entirely understood but of an essential interest for a further enhancement of the efficiency of chalcopyrite - type solar cells. We were now asking structural questions concerning the role of sodium in CIGSe absorber material. Therefore the influence of sodium addition was investigated by neutron powder diffraction and subsequent Rietveld analysis using two different types of samples: powder material, with a well-defined chemical composition, and thin films produced by a multi-stage co-evaporation process. Both types of samples were consisting of the ternary compounds CuInSe2 and CuGaSe2. The resulting structural parameters such as cation site occupancies show differences compared to off stoichiometric Cu(In,Ga)Se2 samples without sodium studied, previously. The structural results will be discussed in terms of the effect on phase relations and on the quality of the resulting solar cell absorber material when providing sodium during material preparation.

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14:00

Spatially resolved X-ray fluorescence on Cu(In,Ga)Se$_2$ cross sections

Authors : Ph. Schöppe[1], A. Kusch[1], M. Oertel[1], C. S. Schnohr[1], A. Johannes[1], S. Eckner[1], M. Burghammer[2], U. Reislöhner[1], C. Ronning[1]

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Affiliations : [1] Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany; [2] European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France

Resume : Compositional and structural properties of the absorber significantly affect the efficiency of Cu(In,Ga)Se_2 solar cells. The integral composition is commonly determined using X-ray fluorescence (XRF). However, the absorber is typically inhomogeneous and thus there is a particular interest in collecting information from defined spatial regions in the nanometer range. Hence, XRF mapping with an X-ray beam diameter of approximately 200 to 300 nm was used to investigate cross section of Cu(In,Ga)Se_2 solar cells. In order to implement this improved spatial resolution in the measurement, thin lamellas were prepared using a focused ion beam. A thin lamella offers the opportunity to collect information even from a single grain. Best results were obtained using a lamella thickness of about 250 nm. This enabled us to determine quantitatively the depth dependent composition of the absorber, particularly the Ga gradient, and its spatial distribution in high resolution.

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14:00 **The structural properties of CdS deposited by Chemical Bath Deposition and Pulsed DC Magnetron Sputtering**

Authors : F Lisco, J W Bowers, G Claudio, P.M Kaminski, J M Walls

Affiliations : Centre for Renewable Energy Systems Technology, (CREST), School of Electronic, Electrical and Systems Engineering, Loughborough University, Leicestershire, LE11 3TU, UK

Resume : In this paper, we report on the use of pulsed dc magnetron sputtering and compare the stoichiometry and optical and structural properties of the thin film CdS layers with those obtained using conventional Chemical Bath Deposition (CBD). This study allows us to compare the advantages and disadvantages of the new pulsed DC magnetron sputtering process. In both cases we have deposited the CdS on flourine doped tin oxide (FTO) coated glass substrates. The FTO was TEC10 and TEC 15 supplied by NSG Pilkington. The CdS thin film microstructure, composition and morphology was examined using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Electron Back Scattering Diffraction (EBSD), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Spectrosopic Ellipsometry (SE). The deposition rate for CdS obtained using pulsed DC magnetron sputtering was 2.7nm/sec using a power of only 500W. The rate increases linearly with power. The deposition rate using CBD is comparatively slow. For example, a 50nm thick film of CdS required 30 minutes and a thickness of 150nm needs about one hour. The new pulsed dc sputtering process produced stochiometric CdS thin films which are crystalline with hexagonal columnar grains. The films are also highly uniform with an optical band gap of 2.3 eV. The use of an argon/oxygen plasma pre-treatment on the substrate results in pinhole and void free thin films A.P3 28

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14:00 **Thickness dependent investigation of wedged Cu(In,Ga)Se2 films prepared by physical vapor deposition (PVD) using hard x-ray photoelectron spectroscopy (HAXPES)**

Authors : W. Calvet1, B. Ümsür1, A. Steigert1, B. Höpfner1, I. Lauermann1, K. Prietzel1, C. Kaufmann1, T. Unold1 and M. Lux-Steiner1,2

Affiliations : 1 Helmholtz-Zentrum-Berlin, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany 2 Freie Universität Berlin, Department of Physics, Arnimallee 14, D-14195 Berlin, Germany

Resume : Often, big variations in the performance of Cu(In,Ga)Se2 (CIGSe) based thin film solar cells are observed although preparation conditions are unchanged. Unfortunately, this phenomenon complicates research in this field in terms of reliability and consistency. In a new approach we are trying to vary the film thickness of a CIGSe absorber on the same sample in order to keep the deposition conditions constant except for the local growth rate and in order get access to the back contact region by reducing the film thickness close to zero. Our plan is to study thickness dependent properties of the thin film by local probing techniques. We have investigated dedicated CIGSe absorbers which were deposited by co-evaporation of Cu, In, Ga, and Se using a modified three stage process. Prior to the growth the molybdenum-coated glass substrate was covered by a specially bended shroud made from tantalum (Ta) leading to a wedged absorber structure with a dilatation of about 2 mm where the film thickness varies from 0 to 2 µm. In this region of interest the thickness dependency of morphology, concentration ratios and electronic properties was studied with secondary electron microscopy (SEM), x-ray fluorescence (XRF) A.P3 29 and hard x-ray photoelectron spectroscopy (HAXPES) probing the CIGSe sample along the thickness gradient. The evidence of the thickness gradient itself was proven with SEM measurements in cross section geometry. By using XRF it was found that with decreasing film thickness the Cu concentration drops down significantly. This finding was also verified by HAXPES measurements. Furthermore an enrichment of Ga towards the Mo back contact was found using the same technique. Besides these results the formation of a molybdenum selenide (MoSe) phase was observed on the fully covered part of the Mo coated substrate indicating a high mobility of Se on Mo under the given temperature conditions of the modified three stage deposition process.

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14:00

Sprayed ZnO Films for CuInGaSe2 Solar Cells

Authors : Kenji YOSHINOa, *, Akiko IDEa, Akiko MOCHIHARAa, Shigeru IKEDAb, Takashi MINEMOTOc

Affiliations : a Department of Applied Physics and Electronic Engineering, University of Miyazaki, 1-1 Gakuen Kibanadai-nishi, 889-2192 Miyazaki, Japan bResearch Center for Solar Energy Chemistry, Osaka University, 1-1 Yamadaoka Suita Osaka, 565-0871, Japan cDepartment of Electrical and Electronic Engineering, Ritsumeikan University, 1-1-1 Nojihigashi Kusatsu Shiga 525-8577, Japan

Resume : Low cost processes are very important problem for solar cell devices. The spray method is one of non-vacuum processes and is respected as low cost method. In our previous works, high quality transparency ZnO films were successfully grown at 100 °C by a conventional atmospheric spray pyrolysis using diethylzinc (DEZ) based solution [1]. The DEZ was diluted with diisopropyl ether to control its reactivity to air and water (supplied by Tosoh Finechem Corporation, JAPAN). Moreover, the growth of Ga-doped ZnO (GZO) /glass films was carried out by spray pyrolysis at 150 °C [2]. The samples had an average optical transmittance of more than 80% and were strongly a-axis orientated. The sheet resistivity of 30 Ω/sq. could be obtained. In this work, the GZO films were successfully grown on ZnO/CdS/CIGS/Mo/glass by spray pyrolysis using DEZ based solution. After covering clean SLG substrates with back electrodes of Mo films by sputtering, CIGS films were deposited using physical vapor deposition. Buffer layers of CdS films were prepared by chemical vapor deposition. Buffer layers of ZnO films (≈ 20 nm) were also prepared by RF sputtering method [3]. The efficiency of the obtained device was 10.3%. The short-circuit current density (Jsc) of 34.3 mA/cm2, open circuit voltage (Voc) of 0.50 V and fill factor (FF) of 0.60 are obtained. [1] K. Yoshino, Y. Takemoto, M. Oshima, K. Toyota, K. Inaba, K. Haga, and K. Tokudome, Jpn. J. Appl. Phys. 50, 040207 (2011). [2] Y. Takemoto, M. Oshima, K. Yoshino, K. Toyota, K. Inaba, K. Haga, and K. Tokudome, 50, 08801 (2011). [3] T. Minemoto, Y. Hashimoto, W. S.-Kolahi, T. Satoh, T. Negami, H. Takakura, Y. Hamakawa Solar Energy and Solar Cell Materials, 75, 121 (2003).

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14:00

Electrochemically-deposited ZnO and Al-doped ZnO transparent layers with variable conductivity for use in thin film photovoltaics

Authors : Michael Richter[1],[2]; Stefan Edinger[1]; Rachmat Adhi Wibowo[1]; Raad Hamid[3]; Johann Summhammer[2]; Theodoros Dimopoulos[1]

Affiliations : [1] AIT Austrian Institute of Technology, Energy Department, Photovoltaic Systems, Giefinggasse 2, 1210, Vienna, Austria [2] Atominstitut of the Austrian Universities, Stadionallee 2, 1020, Vienna, Austria [3] AIT Austrian Institute of Technology, Mobility Department, Electric Drive Technologies, Giefinggasse 2, 1210, Vienna, Austria

Resume : Solution-processed materials for photovoltaics (PV) are intensively investigated, as they demand low capital investment and enable roll-to-roll, high throughput production. ZnO and Al-doped ZnO (AZO) layers are widely employed as buffer and transparent electrode, respectively, in chalcogenide solar cells and other types of thin film PV. The development, therefore, of solution-processed ZnO layers with competitive optoelectronic properties to vacuum-processed, is a matter of great importance for the PV market. We present a systematic investigation on the potentiostatic, electrochemical deposition of ZnO and AZO layers from aqueous solutions of Zn(NO3)2 and Al (NO3)3 precursors, using conductive glass as working electrode, a platinized Ti mesh as counter electrode and a Ag/AgCl reference. The layers' crystal structure, morphology, optical and electrical properties were studied as a function of: (a) the type of conductive substrate (AZO, ITO, AZO/Au/AZO), (b) the applied potential (-0.7 to -1.5 V), (c) the molar concentration of the precursors(0.03-0.1 M), (d) the pH of the solution (3-6), (e) the temperature (70-90oC) and (f) the post-deposition annealing (150-300oC). The incorporation

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of Al-doping dramatically alters the growth properties, but optimum deposition conditions could be obtained for both ZnO and AZO layers, with high optical transparency and resistivity reaching the lower 10-3 Ωcm regime in the case of optimally doped AZO films.

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14:00

Study and optimization of a low power plasma reactor for synthesis of doped and undoped Zinc oxide as the window layer in CIGS solar cells

Authors : Alexandre MA (1,2,3), Frédérique DONSANTI (2), Frédéric ROUSSEAU (1), Daniel MORVAN (1)

Affiliations : (1) Institut de Recherche de Chimie Paris (IRCP), Equipe 2PM (Procédés, Plasmas, Microsystèmes) – UMR 8247, Chimie ParisTech-CNRS – 11 Rue Pierre et Marie Curie, 75005 Paris, France; (2) Institut de Recherche et Développement sur l’Energie Photovoltaïque (IRDEP) –UMR 7174, EDF-CNRS-Chimie ParisTech – 6 Quai Watier, 78401 Chatou, France; (3) Agence de l’Environnement et de la Maîtrise de l’Énergie (ADEME)– 20 avenue du Grésillé, BP 90406, 49004 Angers Cedex 01, France

Resume : Nowadays the researches about the CIGS solar cells have much improved. In order to decrease the production cost, we are studying how to elaborate low cost intrinsic and doped (Al, B) Zinc oxide layers. The low power plasma reactor is an original process which allows to realize ZnO controlled thickness films from an aqueous precursor solution in a cold plasma only, and to reach high growth rates. The quality of deposits (purity, crystallinity, grains size…) depends widely on the special interactions in the reactor between the droplets and the plasma. The parameters of the reactor (gases composition, pressure, power, temperature…) are studied and controlled. The doping depends on the concentration of precursors in the solution. The last optimizations allow to obtain high growth rates of 0.6 nm/s to 1 nm/s. The XRD results show a right crystallinity (würtzite structure). According to the transmittance measures, the films present a good transparency and the calculated optical gap values range between 3,2 and 3,3 eV. This deposition technique using plasma is fast, flexible, low power consumption and easily adaptable. In order to confirm the efficiency of the process, CIGS solar cells with a ZnO window layer realized by the low power plasma reactor will be designed and then their performances will be studied.

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14:00

Numerical Reactive Diffusion Modeling of SEL-RTP Chalcopyrite Absorber Layer Formation

Authors : André Zweschke[1], Peter J. Wellmann[1]

Affiliations : 1) Department of Materials Science and Engineering, Chair of Materials for Electronics and Energy Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

Resume : The diffusion processes during chalcopyrite (CuInSe2) layer formation by rapid thermal processing of stacked elemental layers (SEL-RTP) are still not completely understood. The phase diagram and fundamental underlying reactions are well known. For diffusion constants and kinetic reaction coefficients at least a basic data set is available. Hardly any knowledge is available on the evolution of the microstructure that significantly determines the layer properties in solar cell applications. Computer simulation provides a valuable tool to address the microscopic phase formation process and supplement and clarify the experimental investigations. We present a one dimensional kinetic model, implemented with MATLAB, which describes the diffusive reaction kinetics for layers of partial miscible systems. The chalcopyrite absorber is represented by a cellular automata defined on a domain divided into regular cubic cells. For each cell it stores the concentration and the phase or in case of a phase boundary two phases. Multi-phase and multi-component diffusion is solved by the finite volume method and the boundaries move depending on the thereby calculated mass fluxes across them. The implemented phase competition model, respecting growth speed in dependence of layer thickness governs the sequence of phase formation. Applying the model to elemental layers of Cu, In and Se the initially formed phases are binary compounds. CuInSe2 is observed after sufficient intermixing of the elements.

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14:00

Dependence on morphology of electrical properties and optical anisotropy in nanostructured CuIn5S8 thin films

Authors : F. Chaffar Akkari, A. Sinaoui, S. Chenot, B. Gallas, M. Kanzari

Affiliations : Laboratoire de Photovoltaique et Materiaux Semiconducteur, ecole nationale d'ingenieurs de Tunis, Tunisia CNRS, UMR 7588, INSP, F-75005, Paris, France Sorbonne Universites, UPMC Univ Paris 06, UMR 7588, INSP, F-75005, Paris, France

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Resume : When the flux of evaporated atoms arrives at the growing surface of a thin film at a fixed glancing angle θ, measured from the substrate normal, with stationary substrate, nanorods tilted toward the incident deposition direction are produced. This nanostructuration is due to the shadowing effect and the technique is referred to as GLancing Angle Deposition (GLAD). As a result, additional anisotropic electrical and optical properties are obtained as compared to the case of homogeneous thin films. In this work we investigate the properties of nanostructured thin films obtained by thermal evaporation onto glass and Si substrates of a CuIn5S8 powder. During deposition, the substrates were maintained at room temperature. Different types of nanorods were obtained depending on the growth conditions. At fixed glancing angle nanorods were observed [1]. When a continuous azimuthal substrate rotational at a speed of 0.033 rev.s-1 was added, vertical nanorods were formed. They broadened anisotropically during subsequent growth with a stationary substrate. X-ray diffraction spectra indicated that all the deposited CuIn5S8 films were amorphous. We will present the evolution of the resistivity, as measured using the four-point probe method, for the films containing normal and tilted nanorods. The refractive index, absorption coefficient, optical band gap, Urbach energy and birefringence, will be determined from optical transmittance, reflectance and ellipsometric measurements. [1] A. Sinaoui, N. Khemiri, F. C. Akkari, B. Gallas and M. Kanzari, Eur. Phys. J. Appl. Phys. (2013) 64, 20301

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14:00

Atomic scale investigation of the p-n Junction in CIGS based solar cells: correlation between cell efficiency and impurities.

Authors : A. Koprek*, O. Cojocaru-Mirédin*, C. Freysoldt*, R. Wuerz,** and D. Raabe*

Affiliations : * Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany.; ** Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Industriestrasse 6, 70565 Stuttgart, Germany.

Resume : Cu(In,Ga)Se2 (CIGS) is one of the most promising solar cell in thin-film technology. Although these cells have already exceeded the 20% limit, it is still far below the theoretical limit of ~30%. Further increase of the efficiency is challenging mainly due to the limited knowledge about the processes responsible for losses in energy conversion. Recent studies indicate that the electrical character of impurities, which originate from diffusion across the p-n junction, strongly affects the electrical properties of the absorber and buffer layer. This work presents an atom probe tomography (APT) investigation of the CdS/CIGS interface of CIGS solar cells annealed at different temperatures. APT reveals with sub-nm-resolution Cd and S diffusion over a long distance into the absorber after annealing the sample at 300°C. This is contrasted with a not annealed sample investigated previously. Without annealing, Cd-enriched and Cu,Ga-depleted zones (1 nm) at the CIGS surface were observed. The Cd2+ ions were considered to occupy Cu rather than Ga sites as they have similar ionic radii. Such CdCu+ donors could change the p-n junction properties as it was suggested by “Buried homojunction” and “Type inversion of the CIGS surface region” models. Furthermore, in order to better understand the incorporation of the impurities (such as CdCu, CdGa, but also S-related defects) and their role in cell performance, DFT calculations are done to determine their electrical character and stability.

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14:00

Spatial characterization of CIGS solar cells inhomogeneities

Authors : L. Lombez; G. El Hajje; A. Delamarre; D. Ory; M. Paire; J-F. Guillemoles

Affiliations : Institute of Research and Development on Photovoltaic Energy, 6 quai Watier,78401 Chatou, France

Resume : Spatial characterization methods allow a precise understanding of the solar cells mechanisms since fluctuations of local properties influence global parameters of PV devices. New analysis methods are presented, allowing a better understanding of physical mechanisms. We record spectrally resolved photoluminescence (PL) and electroluminescence (EL) images, with a spatial resolution below 2 ?m, in order to investigate the cells properties. Maps of the quasi-Fermi level splitting (qFls) are obtained from spectrally resolved images of CIGS PL fluxes. Good agreements are found between mean values and open-circuits voltages. However, we demonstrate that the qFls spatial fluctuations cannot be related to locally varying voltages as it was previously assumed. Comparison with EL images allows distinguishing variations of carrier lifetime properties and collection efficiencies. Local measurements of Time Resolved Photoluminescence decays confirm these spatial variations of cells quality. Moreover, the depth variations of the QFls is shown to be of importance in the understanding of the luminescence experiment. In addition to classical PL and

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EL maps, the electric bias variations of luminescence maps are explained by these depth variations using numerical simulations. This result is a key point towards a mapping of transport properties in CIGS cells. Minority carrier diffusion lengths fluctuations are also imaged using a spectrally resolved Light Beam Induced Current method.

add to my program **(close full abstract)**

14:00 **Electrical characterization of CdS films, annealed in reducing, neutral and oxidizing ambients of H2, N2, and air**

Authors : Aleksandr Graf, Natalia Maticiuc, Aleksei Gavrilov, Jaan Hiie

Affiliations : Tallinn University of Technology

Resume : The CBD CdS has highly textured structure with columnar grains perpendicular to the substrate. Application of CBD CdS in the CdS/CdTe structures, subjected to thermal annealing, is problematic since the vertical capillary surfaces (grain boundaries) between the columnar CdS grains perform fast diffusion channels leading to the emergence of short circuits between the absorber and front contact. This idea is supported by low open circuit voltages for CBD CdS in superstrate CdS/CdTe solar cells. It was assumed that the grain boundaries contain residual hydroxy-oxide type compounds and form electrical barriers between columnar grains in the lateral direction of the CdS layer and that the electrical methods should be indicative about the behavior of grain boundaries in the annealing process. The CdS thin films were deposited on glass slides by chemical bath deposition in the presence of 1% chloride as a dopant and a flux and annealed in hydrogen, nitrogen and air ambient at 250 and 400 ° C for 1 h. The annealed layers were characterized by temperature dependence of DC conductivity, Hall mobility and impedance spectroscopy in a wide temperature range 50 - 400 K. It has been found that electrical transport in the annealed layers occurs mainly by tunneling of electrons. Annealing in H2 ambient effectively removes residual phases and enhances formation of electrical barriers. Annealing in air decreases the density of barriers by creation of favorable conditions for sintering of grains. A.P3 37

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14:00 **Reactive sputtering process control for one-step industrial CIGS absorber deposition**

Authors : Ivan Fernandez-Martinez 1, Victor Bellido-Gonzalez, Fernando Briones 1,3, Benoit Daniel 2, Joseph Brindley 2, Ambiorn Wennberg 1, Dermot Monaghan 2.

Affiliations : 1. Nano4Energy SL Spain ; 2. Gencoa Ltd, ; 3. IMM-CSIC, Spain

Resume : Reactive magnetron sputtering, using medium frequency power supplies and reactive feedback control, are now a key tool for large throughput and high productivity coating lines. This development has made it possible to significantly reduce price in many applications, such as antireflective coatings and mobile display devices. The main reason for that price reduction is the increase in deposition rates and high degree of uniformity control achieved. Most processes require reactive gases, such as oxygen or nitrogen, which are relatively easy to implement via fast mass flow controllers. However certain industrial processes require injection and control of species that are not as easy to be delivered in a vapour phase. There are different ways to inject S or Se into the deposition system. Some of them involve evaporation methods where the flow of any of those elements is very difficult to control. In this paper we demonstrate a one-step reactive sputtering process for the absorber deposition, with a precise process control, that would significantly reduce the cost of the CIGS absorber production process and increase reproducibility. It allows an all-vacuum sputtering deposition process of the entire CIGS cell stack, compatible with large-scale manufacturing. For that purpose, a plasma emission monitoring (PEM) based feedback control is implemented in the reactive sputtering process in order to achieve a direct and precise control of the chalcogen (Selenium and Sulphur) species present in the plasma. Two planar magnetrons are used for sputtering of the metal part (mainly Cu-based alloys or Zn) while a valved linear effusion cell is used for the evaporation of Se and S. As changes occur in the plasma environment, the PEM sensor monitors the variations in the signal intensity. This provides an input to the process controller that automatically actuates the linear effusion cell to adjust the chalcogen evaporation rate. The balance of metal and chalcogen atoms is maintained at the optimum level for obtaining high deposition rate and control of the film stoichiometry, which is crucial for obtaining high efficiency devices. A.P3 38

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14:00 **Reference-free quantification of in-depth matrix gradients in chalcopyrite solar cell absorbers** A.P3 39

Authors : C. Streeck 1, B. Pollakowski 1, C. Herzog 2, J. Lubeck 1, M. Gerlach 1, P.

Hönicke 1, R. Unterumsberger 1, S. Brunken 3, C. A. Kaufmann 3, A.Weber 3, B. Beckhoff 1, B. Kanngießer 2, H.-W. Schock 3 und R. Mainz 3
Affiliations : 1 Physikalisch-Technische Bundesanstalt, Abbestr.2-12, 10587 Berlin, Germany 2 Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany 3 Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
Resume : To correlate the device functionality with the respective material properties, both the absolute composition and the in-depth gradient in Cu(In,Ga)Se2 thin films need to be reliably determined. Common depth profiling methods rely on reference materials for comparison and are mostly destructive. Appropriate reference materials for graded Cu(In,Ga)Se2 solar cell absorbers are not available. To address this analytical challenge, synchrotron-radiation based Grazing Incidence X-Ray Fluorescence analysis (GIXRF) with calibrated instrumentation in conjunction with the fundamental parameter approach for quantification is used. The variation of the angle of incidence over a broad range provides quantitative access to the elemental in-depth distribution in the nano- and micrometer range. This GIXRF-methodology can be used for the quantification of elemental depth gradients in Cu(In,Ga)Se2 thin film solar cell absorber layers, in particular for the determination of different In to Ga gradients [1]. This methodology can substantially contribute to the qualification of upcoming solar cell production processes, e.g. for calibration samples for in-line monitoring methods. [1] Streeck et al., Appl. Phys. Lett. 103, 113904 (2013)

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14:00 **Influence of CdS, ZnSnO and Zn(O,S) buffer layers on the metastable behavior of CIGS solar cells**
Authors : Sabrina Novalin, Tobias Törndahl, Adam Hultqvist, Uwe Zimmermann, Johan Lindahl, Marika Edoff, Marcus Rennhofer, Johann Summhammer
Affiliations : Austrian Institute of Technology; Ångström Solar Center, Uppsala University; Ångström Solar Center, Uppsala University; Ångström Solar Center, Uppsala University; Ångström Solar Center, Uppsala University; Ångström Solar Center, Uppsala University; Austrian Institute of Technology; Vienna University of Technology
Resume : Metastable behavior in Cu(In,Ga)Se2 solar cells was investigated for cells only differing in their buffer layer material. The cells included reference samples with CdS buffer layers as well as samples with the alternative cadmium-free buffer layers ZnSnO and Zn(O,S). For analyzing the metastable effects electrical cell characteristics were derived from current-voltage (I-V) measurements. The I-V curves were measured while the cells were exposed to either blue, red or white light (light soaking) at room temperature. Significant variations in cell behavior could be found for cells with different buffer layer materials. While the CdS buffer layer samples were rather unaffected by the light exposure, the cells with alternative buffer layer materials showed both temporary improvements as well as degradations of electrical parameters depending on the wavelength range of the light during exposure. A.P3 40

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14:00 **Characterization of RTP-SEL Kesterite Thin Films by spatially resolved Cathodoluminescence**
Authors : Ulrike Künecke, Christina Hetzner, Stefan Möckel, Peter Wellmann
Affiliations : Materials Department 6, University of Erlangen-Nürnberg, Martensstr. 7, D-91058 Erlangen, Germany.
Resume : We report on the microstructure analysis of kesterite (CZTSe) layers from RTP-SEL (rapid thermal processing of sequential elemental layers) by spatially resolved CL (cathodoluminescence) in a SEM (scanning electron microscopy). In addition EDX (energy dispersive x-ray fluorescence), XRD (x-ray diffraction) and Raman spectroscopy were carried out for validation of the findings. Kesterite thin film samples were prepared on glass by DC sputtering of the Mo back side electrode and the absorber layer components Cu, Zn, Sn. The chalcogen Se was thermally evaporated on top. To study secondary phase formation, the layer sequence of Cu, Zn, Sn was varied in four ways. Rapid thermal annealing was carried out for all samples at ca. 550°C for 5 min in a quasi-closed graphite box. CL spectra exhibit broad emission lines between 0.8 eV and 2 eV with a superposition of distinct narrow lines, e.g. at ca. 1 eV corresponding to the energy gap of CZTSe. The broad emission is attributed to secondary phases, defects and disorder in the kesterite lattice. Strong indication for secondary phases was found due to emission around 1.35 eV and 2.0 eV. XRD and Raman spectroscopy clearly identified secondary phases, however, it was not yet possible to precisely attribute and relate this finding to the CL data. Nevertheless, the spatially resolved CL data allow the precise determination of A.P3 41

the layer homogeneity which is believed to be a key issue for the optimization of the layer formation technology.

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14:00

Comparative study about AZO thin films deposited by Pulsed Electron Deposition and RF-sputtering as TCO for solar cells based on CIGS deposited by PED

Authors : F. Pattini, F. Annoni, M. Bronzoni, F. Bissoli, J. P. Garcia, E. Gilioli, S. Rampino

Affiliations : IMEM-CNR, Institute of Materials for Electronics and Magnetism, Parco Area delle Scienze 37/A, 43124 - Parma (Italy)

Resume : In this study, a comparison between Al:ZnO TCO for CIGS-based solar cells grown by Pulsed Electron Deposition (PED) and RF-magnetron sputtering (RFMS) has been performed. By means of PED technique, polycrystalline [002] mono-oriented thin films with low electrical resistivity and high optical transparency can be obtained from room temperature to 300 °C. The electrical resistivity of these films can be widely varied depending on the growth temperature with a minimum of 3.5x10-4 Ωcm at 150°C and an average transmittance over 90% in the VIS-NIR range. The optimized AZO film were successfully applied on CIGS-based solar cell obtaining an efficiency value of 15.2% This result clearly shows that the PED is a suitable technique for the growth of ZnO-based thin film in particular for devices/applications where low deposition temperature is required. On the other hand, an optimized AZO thin film front contact for CIGS-based solar cells was fabricated via RFMS. The parameters of the technique were tweaked to obtain highly conductive and transparent AZO thin films. The optimized, 890 nm thick AZO film was found to reach a resistivity value of 6.7x10-4 Ωcm and an average transmittance of 86% in the 400-1100 nm wavelength range.

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14:00

Ab initio thermodynamics for CZTS formation and annealing

Authors : Adam J. Jackson, Jarvist M. Frost, Aron Walsh

Affiliations : Centre for Sustainable Chemical Technologies and Department of Chemistry, University of Bath

Resume : Kesterite Cu2ZnSnS4 (CZTS) is a promising candidate for terawatt-scale renewable energy generation, due to the abundance and low cost of its constituent elements.[1] Currently, while experimental work is fragmented across a wide range of precursors and conditions, the majority of thin films share a critical sulfur annealing step. A theoretical screening approach allows like-for-like comparison in the search for a robust, scalable approach for roll-to-roll industrial production. Thermodynamic potentials are calculated for fundamental phases in the annealing system through systematic ab initio calculations. Energies are computed using density functional theory with the PBEsol generalised gradient approximation (GGA), and vibrations are modelled within the harmonic approximation. The FHI-aims quantum chemistry code is used, scaling across thousands of processors for large supercells. A local, numerically tabulated basis set allows periodic crystal structures and isolated gas molecules to be treated equally. Atomic disorder on the Cu and Zn lattice sites is also considered. Free energy functions are formed with respect to both temperature and pressure, allowing the study of arbitrary reactions between the studied species. This leads to insights into the equilibrium between CZTS and competing elemental, binary and vapour phases. [1] Wadia, C., Alivisatos, A. P., & Kammen, D. M. (2009). Environ. Sci. Technol., 43(6), 2072?7.

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14:00

In-situ optical emission spectroscopy for a better control of hybrid sputtering/evaporation Cu(In,Ga)Se2 deposition process

Authors : J. Posada(1), M. Jubault(1), A. Bousquet(2), E. Tomasella(2), D. Lincot(1)

Affiliations : 1 - Institut de Recherche et Développement sur l’Energie Photovoltaïque (IRDEP - EDF R&D - UMR CNRS 7174) 6 Quai Watier, 78401 Chatou, France; 2 - Institut de Chimie de Clermont - Ferrand (ICCF - UMR CNRS 6296 – Université Blaise Pascal)

Resume : Reactive sputtering deposition technique is suitable for large area, thus offering the possibility for more competitive industrial scale-up. In this work, we develop a hybrid one-step co-sputtering/evaporation Cu(InGa)Se2 deposition process, where Cu, In and Ga are sputtered simultaneously with the thermal evaporation of selenium, thus avoiding H2Se use. A parametric study has been performed by varying pressures and power values. With in-situ optical emission spectroscopy (OES), we analyzed the different species present in the reaction chamber and controlled the selenium evaporation temperature. A precise regulation of the Se flux allowed an accurate control of the film composition. We also pointed out the influence of the Se flux on CIGS films roughness and growth rates. OES has allowed us to determine the Se flux threshold so as to avoid targets poisoning. We measured film composition and

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thickness of the samples with X-ray fluorescence. Different phases formed during the process were identified by Raman spectroscopy and X-ray diffraction. Morphology and nucleation were studied by scanning electron microscopy (SEM). The optoelectronic cell properties showed promising efficiency of 10.3% for an absorber with composition ratios of [Cu/In+Ga] = 0.81 and [Ga/In+Ga] = 0.54.

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14:00 **Controlled in-situ sulfur incorporation with different Cu(In,Ga)Se2 absorber pre-treatments for graded Cu(In,Ga)(S,Se)2 solar cell applications**

Authors : Björn J. Müller (1,3), Markus Mock (2,3), Christian Zimmermann (3,4), Veronika Haug (3), Siegmund Zweigart (3), Ulrich Herr (1)
Affiliations : (1) Department of Micro- and Nanomaterials, University of Ulm, D-89081, Germany; (2) Technical University of Darmstadt, D-64289, Germany; (3) Corporate Research, Robert Bosch GmbH, D-70839 Gerlingen, Germany; (4) Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany

Resume : Cu(In,Ga)(S,Se)2 is a promising candidate for highly efficient solar cells due to its tunable band gap for an optimal adjustment on the solar spectrum. One way to adjust the band gap without losing too much in photocurrent consists of a functional front surface grading by incorporating sulfur from the top. An in-situ XRD tool is used as the method of choice to analyze the diffusion processes with three line detectors (Meteor 3D) with almost 1 s in time resolution. The diffusion rate of sulfur can be controlled by the selenization temperature of Cu(In,Ga)Se2 thin films estimating the presence of binary selenides. If the thin film consists of an increasing amount of binary selenides (grain boundaries) the incorporation of sulfur is faster, like an accelerated diffusion process. The time dependent 2θ angle shift has been used to calculate the change in average lattice constant of the irradiated volume of the Cu(In,Ga)(S,Se)2 thin film. At certain Cu(In,Ga)Se2 pre-treatments the 2θ position of the 220/204-reflection follow, under sulfur supply, a diffusion related process ~ t^(1/2) which can be described by Fick's equations. Additionally the sulfur partial pressure is the controlling parameter for the degree and speed of sulfurization. Furthermore the results are confirmed by ex-situ depth resolved methods. Electronically this leads to solar cells with a higher Voc and an almost constant Jsc which altogether opens up the way for optimization of solar cell performance. A.P3 45

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14:00 **Efficient Thermal and Chemical Treatments on CdS Growth to Improve Solar Cells Efficiency**

Authors : J.M. Flores Marquez1, M.L. Albor Aguilera1, Y. Matsumoto Kuwabara2, M.A. Gonzalez Trujillo3
Affiliations : 1ESFM-IPN, Depto. Fisica, U.P.A.L.M., Zacatenco, Mexico D.F. 07738, Mexico; 2CINVESTAV-SEES-IPN, Av. IPN 2508, Zacatenco, Mexico D.F. 07360, Mexico; 3ESCOM – IPN, Formacion Basica, U.P.A.L.M., Zacatenco, Mexico D.F., 07738, Mexico.

Resume : CdS with its large band gap and chemical stability is an n-type semiconductor used as a window layer in many types of solar cells. CdS bi-layers were deposited on SnO2:F by using chemical bath deposition technique (CBD). SnO2:F substrates were treated with HCl (0.1M), Ar and O2 at 500°C and CdS thin films were thermal annealed on CdCl2, Ar and air atmospheres at 400°C. Optical and morphological measurements reveal that HCl treatment is good for CdS growth due to the defects levels are reduced and the grain size is increased respectively. CdS thin films obtained were applied on CdTe solar cells; the photovoltaic efficiency was increased from 4% to 11%. A.P3 46

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Thin film chalcogenide photovoltaic materials

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start at	Subject	Num.
	Novel materials and devices : N. Barreau	
08:45	**Thermal Evaporation of Tin Sulfide for Solar Cell Applications with Potential for Industrial Scale-Up** **Authors :** V. Steinmann [1], H.H. Park [2], R. Jaramillo [1], K. Hartman [1], L. Sun [2], R.E. Brandt [1], R. Chakraborty [1], R.G. Gordon [2], T. Buonassisi [1] **Affiliations :** [1] Massachusetts Institute of Technology, Cambridge, MA 02139, USA [2] Harvard University, Cambridge, MA 02138, USA **Resume :** Tin monosulfide (SnS) has attracted considerable interest as a photovoltaic absorber material due to its potential for large-scale, cost-effective and environmentally friendly power generation. During recent years, thin-film solar cells based on SnS have shown substantial progress [1, 2]. Nevertheless, the latest published SnS-based champion cell still reveals a rather poor efficiency of 2.04% [2], far below the theoretical maximum. We present thin-film SnS solar cells based on thermal evaporation (TE), following the previously developed substrate device stack (Mo/SnS/Zn(O,S)/ZnO/ITO/Ag) [2]. Upon device optimization, our best performing SnS-based solar cells yield new TE SnS record power conversion efficiencies up to 4%. We further demonstrate the potential of SnS based PV for industrial scale-up by demonstrating SnS evaporation rates up to 50 ?/s. While fast deposition results in smaller SnS grains in the as-grown condition, post-deposition annealing increases material quality and minimizes performance losses typically associated with fast deposition rates. In closing, we demonstrate high performing thin-film solar cells based on SnS as the absorber. High-rate physical vapor deposition coupled to post-deposition annealing enables high-throughput processing with a path to industrial scale-up. [1] Ramakrishna Reddy, K., et al., Sol. Energy Mater. Sol. Cells 90, 3041?3046 (2006). [2] Sinsermsuksakul, P. et al., Appl. Phys. Lett. 102, 053901 (2013).	A.O9 1
add to my program	**(close full abstract)**	
09:00	**Cu(In,Ga)Se2 mesa diodes for the study of edge recombination** **Authors :** Myriam Paire (1), Cyril Jean (1), Laurent Lombez (1), Stéphane Collin (2), Jean-Luc Pelouard (2), Jean-François Guillemoles (1), Daniel Lincot (1) **Affiliations :** (1) - Institute of research and development on photovoltaic energy, 6 quai Watier, 78401 Chatou, France (2) - Laboratoire de photonique et de nanostructures, Route de Nozay, 91460 Marcoussis, France **Resume :** The concentrating approach was applied on Cu(In,Ga)Se2 to develop photovoltaic devices with increased efficiency using less rare materials. To withstand the operating conditions, CIGS devices are miniaturized [1,2]. Compared to previous generations of microcells, with only window layer structuration, new microcells with a mesa design are fabricated. These microcells are created by etching ZnO, CdS and CIGS layers. The crucial issue addressed in this study is the electrical behaviour of the device edges, to determine if small microcells do not suffer from excessive recombination. We analyse the influence of different etching techniques on the edge recombination signal. It is found that bromine etch result in well passivated surfaces, and devices as small as 50x50 µm do not experience edge recombination efficiency limitations. This behaviour is remarkable compared to that of microcells made of crystalline materials [3]. For devices where the edges are deteriorated by a chemical post-treatment, a quasi-shunting signal coming from the edges is seen. We tested these microcells under concentrated illumination and important	A.O9 2

Voc and efficiency gains are seen. CIGS mesa diodes are appropriate for a use under concentration, leading to significant gains in terms of efficiency and material usage compared to standard thin films. [1] Paire, Energy Environ. Sci. 4, 4972–4977 (2011) [2] Paire, Appl. Phys. Letters 98, 264102 (2011) [3] Algora, Proc. Of 4th IEEE PVSC, 741-744 (200

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09:15 **Improved Solar Cells with Tin Monosulfide Absorber**

Authors : P. Sinsermsuksakul, L. Sun, S. Woon Lee, H. H. Park, S. Bok Kim, C. Yang and R. G. Gordon

Affiliations : Harvard University, Cambridge, Massachusetts

Resume : Theoretically tin monosulfide, SnS, has the material properties and Earth-abundant composition required to make vast quantities of solar cells with 26% efficiency. However, only 2% efficiency has been achieved in actual cells up to now. Several mechanisms reduce the efficiency of thin-film solar cells. These mechanisms were systematically investigated and minimized in solar cells based on p-type SnS absorber layers combined with n-type zinc oxysulfide, Zn (O,S) layers made by vapor deposition. Strategies were devised for increasing the cell efficiency by reducing the rate of recombination of the photo-excited electrons and holes. Recombination at grain boundaries was reduced by annealing the SnS films in a H2S atmosphere to form larger grains with fewer grain boundaries. Recombination near the p-SnS/n-Zn(O,S) junction was reduced by inserting a few monolayers of tin dioxide between these layers. Recombination at the p-n junction was also reduced by adjusting the conduction band offset by tuning the O/S ratio of the Zn(O,S), and by reducing its free electron concentration with nitrogen doping. The cells with all these improvements were found to have an energy conversion efficiency over 4.4%, which is more than twice as large as the highest efficiency obtained previously using SnS absorber layers. Although this efficiency is not yet high enough for practical use, further improvements can now be envisioned to bring the efficiency much closer to the theoretical maximum.

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09:45 **coffee break**

Joint session with Symp. H - Metrology in solar cells and highlights of EMRP projects : Burkhard Beckhoff, Daniel Abou-Ras

10:15 **Diffusion of buffer-layer and substrate impurities in solar-grade CIGSe and epitaxial CISe layers**

Authors : N. Stolwijk1, J. Bastek1, R. Wuerz2, S. Sadewasser3

Affiliations : 1Universitaet Muenster, Institut fuer Materialphysik, 48149 Muenster, 2Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg, 70565 Stuttgart, 3International Iberian Nanotechnology Laboratory, 4715-330 Braga, Portugal

Resume : We investigate the diffusion properties of several technologically relevant impurities in polycrystalline Cu(In,Ga)Se2 (CIGSe) structures using depth profiling of radiotracers and stable isotopes upon isothermal heat treatments. For comparison, similar experiments are carried out in single-crystal CuInSe2 (CISe) layers epitaxially-grown on GaAs wafers. Pertinent results are obtained for the buffer-layer elements Cd [1] and Zn [2] as well as for the substrate elements Fe [3] and Na. Diffusion coefficients and activation energies are deduced in the temperature range from 200 ?C to 400 ?C from front-side penetration profiles of the radioisotopes Cd-109, Fe-59, Zn-65. The results for Fe and Zn are confirmed by the diffusion of the natural elements using in-depth SIMS analysis. Information on concentration levels and near-surface solubilities is obtained as well. Several anomalous features may relate to the presence of grain boundaries or grown-in defects. Zn-65 profiles in CIGSe exhibit double-hump shapes with a second maximum near the interface to the Mo contact layer. Similar observations are made for Zn in epitaxial CISe close to GaAs substrate. Experiments with the radiotracer Na-22 turn out to be difficult, because of its extremely fast transfer across the CIGSe film and the high solubility of Na in the glass substrate. Our results will be compared with data in the literature and discussed in terms of diffusion mechanisms. [1] K. Hiepko, J. Bastek, R. Schlesiger, G. Schmitz, R. Wuerz, N.A. Stolwijk, Appl. Phys. Lett. 99 (2011) 234101 [2] J. Bastek, N.A. Stolwijk, R. Wuerz, A. Eicke, J. Albert, S. Sadewasser, Appl. Phys. Lett. 101 (2012) 074105 [3] N.A. Stolwijk, Sh. Obeidi, J. Bastek, R. Wuerz, A. Eicke, Appl. Phys. Lett. 96 (2010) 244101

H17 1

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10:30 **The role of Ga content in CIGSe efficiency : an atom probe study**

Authors : Mohit Raghuwanshi, Emmanuel Cadel, Sébastien Duguay, Philippe Pareige, Nicolas Barreau

Affiliations : Groupe de Physique des Matériaux (GPM), University of Rouen; University of Nantes

Resume : Very high absorption coefficient and cost effective production makes Copper Indium Gallium Selenide (CIGS) semiconductor one of the most promising thin films photovoltaic device. With efficiency > 20%, it is currently the most efficient thin film solar cell produced. Na segregation along the Grain Boundaries (GBs) in polycrystalline CIGS is well known to improve efficiency. Efficiency of CIGS is very sensitive to Ga content in CIGS and is most efficient for x ≈ 0.25. In the present study, GB nano-chemistry for various Ga-concentrated CIGSe samples (from Ga/In+Ga=0 to Ga/In+Ga = 1) has been investigated by Atom Probe Tomography (APT). APT provides 3D atomic mapping of elements in a material at sub nanometer resolution and can therefore accurately characterize the composition profile across GB in CIGS cells. APT has already put into evidence the modification of the GB chemistry at different stages of the CIGS-growth process suggesting an important role of the In/Cu-CIGSe-content on its final efficiency. In the present study, a clear influence of the Ga content over the GB chemistry was observed by APT. The results will be discussed in terms of cell efficiency and quantum efficiency. AH 1

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10:45 **Strain measurements in CuInSe2 absorber layers by several diffraction techniques**

Authors : Norbert Schäfer1, Daniel Abou-Ras1, Manuela Klaus1, Christoph Genzel1, Julien Marquart1,2, Susan Schorr1,2, Thorsten Rissom1, Angus Wilkinson3, Tobias Schulli4

Affiliations : 1. Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany; 2. Freie Universitaet Berlin, Institute of Geological Sciences, Malteserstr. 74-100, 12249 Berlin, Germany; 3. Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.; 4. European Synchrotron Radiation Facility, BP 220, Grenoble Cedex, France

Resume : Thin-film solar cells based on CuInSe2 absorber layers, produced by co-evaporation, are subject to strain due to the evolution of the microstructure. For the investigation of the macrostrain and microstrain within the completed CuInSe2 thin films, electron and X-ray diffraction (XRD) measurements were performed. Since the ternary CuInSe2 layers do not exhibit substantial chemical gradients and a crystal structure with low pseudocubic distortion, this compound is suitable to compare different diffraction techniques applied at various scales. Also, coevaporated CuInSe2 thin films feature average grain sizes of typically more than 1 µm, which is feasible for X-ray microdiffraction within individual grains. While macroscopic XRD experiments were performed on a five-circle ETA diffractometer from GE Inspection Technologies, microdiffraction within individual grains was conducted at the ID01 Microdiffraction Imaging Beamline at the ESRF, Grenoble. In addition, information on strain was extracted by the Williamson-Hall method from XRD data acquired under grazing incidence using a PANalytical X'pert Pro diffractometer. Electron backscatter diffraction (EBSD) maps were measured using a Zeiss Ultra Plus scanning electron microscope equipped with a NordlysNano EBSD detector as well as using the Oxford Instruments AZtec acquisition and evaluation software. The recorded EBSD patterns were evaluated by means of the software CrossCourt (BLG Productions). Shifts in EBSD patterns can directly be correlated with strain distributions within individual grains. Based on a specific reference pattern, strain distributions can be calculated within individual grains with a spatial resolution of about 50 nm. The results on the strain distributions obtained by the different diffraction techniques were compared, also with respect to the relationships between macrostrain and microstrain. It is the aim to correlate the local strain distributions in CuInSe2 thin films to the optoelectronic properties of the corresponding solar cells obtained by means of electron-beam-induced current and cathodoluminescence measurements AH 2

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11:00 **EMRP - Thin Films - Project: Traceable Raman mappings on solar cell thin-film materials**

Authors : S. Zakel, S. Wundrack, B. Güttler, R. Stosch

Affiliations : Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany AH 3

Resume : Micro-Raman spectrometry has become a meaningful method in thin-film analysis, but variation in the measurement conditions as well as a lack of standards for effective integration into the process are still factors which have to be overcome to enable the routine use of this technique. A 2D-Scan representing the spatially resolved scattering intensity is easily created from an individual vibrational mode, separating the object from the non-object areas. Here, well known structured reference samples were assessed for the uncertainty analysis of such segmented areas to provide traceability of the results to the meter. Real CIGSe samples were then investigated with regard to inhomogeneities resulting from the production process. In this context, data pretreatment is a major issue as mapping spectra often shows a low S/N ratio due to the limited integration time. As the optical resolution is diffraction limited, blurry edges influence the area determination. It is crucial for the quality of the segmentation as well as for the size of the segmented areas to choose the right threshold value by the assessment of the histogram. Traceability of the chemical composition was achieved for the CIGSe thin films via high purity reference compounds, their spectra being traceable to existing standards with regard to the instrument response and Wavenumber accuracy. This work is funded through the European Metrology Research Programme (EMRP).

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11:15 **EMRP - Thin Films - Project: Reference-free quantification of in-depth matrix gradients – the uncertainty dependencies of the effective solid angle of detection**

Authors : C. Streeck 1, C. Herzog 2, B. Kanngießer 2, B. Beckhoff 1

Affiliations : 1 Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin 2 Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin

Resume : Synchrotron-radiation based Grazing Incidence X-ray Fluorescence analysis (GIXRF) with varying excitation angles provides non-destructive access to the compositional depth profile of thin film matrix elements in the nano- and micrometer range. Reference-free GIXRF in conjunction with fundamental parameter based quantification allows for an analysis without the need for any calibration standards. This XRF-methodology can be used e.g. for the non-preparative determination of elemental depth gradients with an In to Ga gradient in Cu(In,Ga)Se2 thin film solar cell absorber layers. As a key metrological aspect, the uncertainty of the components of the effective solid angle of detection and its impact on the uncertainty of the detected count rate will be presented: with varying angle of incidence the irradiated area on the sample changes over two order of magnitude, the Gaussian shape of the beam leads to an intensity distribution and the field of view of the detector is dependent on the distance from the sample. The uncertainty of all components shows a different angle dependency. Therefore, a detailed uncertainty analysis and their implication is prerequisite for a reliable calibration procedure.

AH 4

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11:30 **Lunch break**

Characterization techniques : R. Gordon, B. Vermang

14:00 **Characterization of Electronic Structure of CZTSSe Absorber Layers and CdS/CZTSSe Interfaces by PES/IPES**

Authors : N. Terada 1, 2, S. Yoshimoto 1, K. Chochi 1, T. Fukuyama 1, M. Mitsunaga 1, H. Tampo 2, H. Shibata 2, K. Matsubara 2, S. Niki 2, N. Sakai 3, T. Kato 3 and H. Sugimoto 3

Affiliations : 1. Kagoshima University, Kagoshima, Kagoshima 890-0065, Japan; 2. Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568; 3. Showa Shell Sekiyu K. K., Atsugi, Kanagawa 243-0206, Japan

Resume : For pursuing higher performances of CZTSSe-based solar cells, it has been pointed out that the clarifications of intrinsic features of this multinary absorber, and of junctions in the cells are crucial. In this study, dependence of electronic structure of CZTSSe layers on S/(S+Se) ratio and band alignment at interfaces between CdS buffer and CZTSSe have been studied by UPS, XPS and IPES. CZTSSe layers with S/(Se+S)= 0 ~ 1.0 were synthesized by sulfurization and/or selenization of metal precursors. Surfaces of them were cleaned by NH3 etching. Buffer/ absorber junctions were fabricated by step-deposition of CdS layer on the cleaned surface by MBE. In each step, electronic structure was examined in-situ. UPS/IPES results of the CZTSSe layers have revealed almost linear expansion of band gap energy Eg with an increase of S/(S+Se) ratio; Eg

A.O10 1

(CZTSe) = 0.9 ~ 1.0 eV, Eg(CZTS)=1.4 ~ 1.5 eV. This expansion mainly originates in the rise of conduction band minimum CBM; CBM(CZTSe) ~ 0.5 eV, CBM(CZTS) = 0.9 ~ 1.0 eV. The in-situ measurements of the interfaces have revealed that CdS/CZTSSe; S/(S+Se) ~ 0.3 has so-called "type I" band alignment with conduction band offset CBO and interface induced band bending of ~ +0.2 and ~ 0.4 eV, respectively. Sign-inversion of CBO is confirmed for the CdS/CZTS; S/(S+Se) = 1.0. The observed changes of band alignment are consistent that the variation of cell-performances; e.g. the cells using the absorber with S/(S+Se) ~ 0.3 show a high efficiency > 10 %.

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14:30

Investigation of Cu-poor and Cu-rich Cu(In, Ga)Se2/CdS interfaces using hard X-ray photoelectron spectroscopy (HAX-PES)

Authors : B. Ümsür1, W. Calvet1, B. Höpfner1, A. Steigert1, I. Lauermann1, K. Prietzel1, H. Allaf Navirian1, C. Kaufmann1, T. Unold1 and M. Lux-Steiner1,2

Affiliations : 1 Helmholtz-Zentrum-Berlin, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany; 2 Freie Universität Berlin, Department of Physics, Arnimallee 14, D-14195 Berlin, Germany

Resume : Thin film solar cells based on polycrystalline chalcopyrite absorbers reach maximum conversion efficiencies above 20% on the laboratory scale [1]. Nevertheless, besides defects in the absorber bulk material, the interface between the absorber and the CdS buffer layer plays an important role with respect to band alignment and appearance of interface states limiting the solar power conversion efficiency. In this work, we compare Cu-poor and Cu-rich grown CIGSe absorbers with a surface concentration [Cu]/([In]+[Ga]) of 0.79 and 1.03. Ultrathin CdS layers were deposited on the absorbers by chemical bath deposition (CBD) which allows the investigation of both, the absorber and the buffer layer at the same time using hard X-ray photoelectron spectroscopy (HAX-PES). The aim was to analyze the interface formation and diffusion processes of the involved species, namely Cd and Cu. Additionally, diffusion phenomena at temperatures of 200 °C, 300 °C and 400 °C were investigated in-situ under ultrahigh vacuum (UHV) conditions. It was found that the diffusion of Cd is strongly dependent on the bulk stoichiometry of the CIGSe absorber. Contrary to our expectation, no Cd was found on the Cu-poor surface after a 400 °C treatment, whereas remnants of Cd were still present on the Cu-rich sample. We explain this by the strongly increased diffusion of Cd ions into the bulk of the vacancy-rich, Cu-poor bulk CIGSe material, leading to a strong dilution of the Cd. The slower diffusion of Cd in the Cu-rich material leads to a higher concentration at the surface. This is also supported by a recent paper of Kiss et al. [2], where the diffusion of Cd in Cu-deficient CISe was examined theoretically. [1] M. A. Green et al., Solar cell efficiency tables (ver. 43), Prog. Photovolt: Res. Appl., 22, p.1-9 (2014) [2] J. Kiss et al., Theoretical Study on the Diffusion Mechanism of Cd in the Cu-Poor Phase of CuInSe2 Solar Cell Material, J. Phys. Chem. C , 117, p. 25933−25938 (2013)

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14:45

Characterization of local electronic properties of CIGS thin film solar cells by VEELS and in-line holography

Authors : Debora Keller 1,2, Stephan Buecheler 1, Patrick Reinhard 1, Fabian Pianezzi 1, Darius Pohl 3, Alexander Surrey 3,4, Bernd Rellinghaus 3, Rolf Erni 2, Ayodhya N. Tiwari 1

Affiliations : 1 Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland; 2 Electron Microscopy Center, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland; 3 Institute for Metallic Materials, IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany; 4 Institute for Solid State Physics, TU Dresden, Zellescher Weg 16, D-01062 Dresden, Germany;

Resume : The efficiency of Cu(In,Ga)Se2 (CIGS) solar cells is strongly affected by Cu and Ga concentration variations in the absorber layer, which locally influence the electronic properties such as the band gap energy (Eg) and the mean inner potential (MIP). Therefore, the measurement of nanoscale variations of these properties is of high interest to improve the understanding of local mechanisms related to compositional inhomogeneities and structural defects. Valence electron energy loss spectroscopy (VEELS) provides a promising tool to measure Eg variations on the nanometer scale. However, VEEL spectra can be influenced by various artifacts which complicate the data interpretation. Based on a systematic study, we discuss the feasibility and reliability of local Eg measurement in CIGS by VEELS. Further, we assess the precision and accuracy of the results in consideration of error estimations and compare the results with

A.O10 3

simulations. The obtained measurement precision allows detecting relative Eg variations in CIGS and the measured variation corresponds well to the expectations based on compositional gradients measured by energy dispersive x-ray (EDX) spectroscopy. As a second method, local variations of the MIP can be accessed by in-line electron holography in transmission electron microscopy (TEM) using the transport of intensity equation. First results of local MIP measurements are presented and the impact of fluctuations in Eg and MIP on the solar cell efficiency is discussed.

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15:00 **Chemistry of structural defects in Cu(In,Ga)Se2 by means of STEM**

Authors : E. Simsek, Q.M. Ramasse, R. Mainz, A. Weber, D. Abou-Ras, P.A. van Aken

Affiliations : E. Simsek; P.A. van Aken Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, 70569 Stuttgart, Germany; Q. M. Ramasse SuperSTEM, STFC Daresbury Laboratories, Keckwick Lane, Warrington, WA4 4AD, United Kingdom; R. Mainz; A. Weber; D. Abou-Ras Helmholtz Zentrum Berlin, Hahn Meitner Platz 1, 14109 Berlin, Germany

Resume : Cu(In,Ga)Se2 (CIGSe) based chalcopyrite-type solar cells fabricated with multi-stage co-evaporation show high power-conversion efficiencies of more than 20%. However, in many cases efficiencies obtained with CIGSe fall behind this value. This is in particular true in low-temperatures processes without a Cu-rich stage. Reasons for efficiency loss as well as limitations for further efficiency increase are not fully understood. In this work, we analyse structural defects in CIGSe absorber layers with sub-nanometer resolution to gain a better understanding of the defects’ chemical characteristics. For that purpose we use electron energy loss spectroscopy (EELS) combined with high-resolution scanning transmission electron microscopy (HR-STEM). HR-STEM and EELS analyses show striking chemical characteristics for a number of observed defects in the Cu-poor CIGSe thin films. The chemistry of twin boundaries along the {112} planes of the chalcopyrite structure, which are very frequent in these samples, is entirely identical to the rest of the grains, with a homogeneous distribution of all the elements. By contrast, Cu enrichment in combination with In and Se depletion were systematically observed within complex defects closely related to stacking faults, as well as at random grain boundaries. Finally, CuxSe-rich channels seem to form immediately outside (not within) dislocation cores suggesting these defects play a crucial role for the photovoltaic properties of the material. A.O10 4

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15:15 **3-Dimensional Microstructural and Crystallographic Characterization of CdTe Absorber Layers from CdTe/CdS Solar Cells Grown in Substrate Configuration.**

Authors : Guillaume Stechmann, Stefan Zaefferer, Peter Konijnenberg, Dierk Raabe, Christina Gretener, Lukas Kranz, Julian Perrenoud, Stephan Buecheler, Ayodhya Tiwari

Affiliations : Max Planck Institute for Iron Research, Düsseldorf, Germany; Max Planck Institute for Iron Research, Düsseldorf, Germany; Max Planck Institute for Iron Research, Düsseldorf, Germany; Max Planck Institute for Iron Research, Düsseldorf, Germany; Laboratory for Thin Films and Photovoltaics, Empa, Duebendorf, Switzerland; Laboratory for Thin Films and Photovoltaics, Empa, Duebendorf, Switzerland Laboratory for Thin Films and Photovoltaics, Empa, Duebendorf, Switzerland Laboratory for Thin Films and Photovoltaics, Empa, Duebendorf, Switzerland Laboratory for Thin Films and Photovoltaics, Empa, Duebendorf, Switzerland

Resume : Grain boundaries (GB), may play a decisive role on CdTe/CdS solar cells efficiency. They can be described using 8 parameters including 5 crystallographic, rotational degrees of freedom and 3 atomistic ones. It may be assumed that their properties depend on all 5 rotational parameters; their determination is therefore crucial. 2D electron backscatter diffraction (EBSD) allows the classification of GB based on the misorientation between the related two abutting grains (3 parameters). Furthermore, the orientation of the GB trace delivers a 4th parameter. A more comprehensive characterization is possible by focused ion beam/EBSD tomography which reveals the full GB character. CdCl2-treated CdTe/CdS solar cells in substrate configuration were investigated using these techniques. Results show an evolution of the texture across the thickness of the CdTe layer: the strong {111} fiber texture near the back contact being no longer present near the p-n junction. The 5-parameter GB analysis shows that this decrease of texture sharpness is due to successive twinning inside columnar grains during the growth or post-treatments. A second method to fully characterize twin boundaries is quantitative trace analysis. In contrast to 3D EBSD, it can be performed non-destructively on 2D orientation maps, which opens the possibility to further investigate the physical properties A.O10 5 of the GB. Several incoherent twin boundaries, previously reported from TEM or etching experiments, have been identified.

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15:30 **coffee break**

Poster 4: Electrical characterization, device studies and modelling, novel materials, and ultra-thin absorbers : Alessandro Romeo, Daniel Abou-Ras

16:00 **Electrical modeling of CuIn1-xGaxSe2 based solar cells with ZnO1-ySy buffer layer.**

Authors : S. Ouédraogo, F. Zougmoré, J.M. Ndjaka

Affiliations : S. Ouédraogo; F. Zougmoré: Laboratoire de Matériaux et Environnement (LA.M.E), UFR-SEA, Université de Ouagadougou, 03 B.P. 7021 Ouaga 03, Burkina Faso. S.Ouédraogo, J.M. Ndjaka: Département de Physique, Faculté des sciences, Université de Yaoundé I, B.P.812 Yaoundé, Cameroun

Resume : CdS is widely used as a buffer layer in CIGS based solar cells. Appreciable efficiencies are obtained using this buffer layer. In view of the detrimental environment impact of Cd, Cd-free buffer layers are attractive. ZnO1-ySy is considered as the best material that can replace the CdS but the conversion efficiencies obtained with this alternative buffer layer are generally lower than those of the conventional CdS layer. In this paper, device modeling and simulation were conducted to investigate the performance of CuIn1-xGaxSe2/ZnO1-xSy solar cells by varying the sulfur content, doping concentration, as well as Zn(O,S) layer bulk defect densities. Furthermore, an inverted surface layer, n-type CIGS, is inserted between the buffer layer and the absorber layer. Donor interface defects were placed 0.2 eV below the conduction band to pin the Fermi-level at the absorber/Zn(O,S) interface. The resulting performance parameters of open-circuit voltage (Voc), short-circuit density (Jsc), fill factor (FF) and efficiency (η) are determined using current density-voltage (J-V) characteristics. The obtained results show that the best solar cells with the Zn(O,S) buffer layer can be achieved when the S content in the buffer layer is approximately 0.2. In comparison to the conventional CdS buffer layer, the best solar cells with the Zn(O,S) buffer layer has slightly lower Voc, FF, and higher Jsc which result in slightly lower conversion efficiency. The simulation results suggest that the high defect density in the Zn(O,S) buffer layer may be the cause of poor performances of Zn(O,S)/CIGS based solar cells. A comparison of the simulation results with published data for the CIGS cells with the Zn(O,S) buffer layer shows an excellent agreement. A.P4 1

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16:00 **An optimization-based approach to enhancing carriers collection in superstrate Cu(In,Ga)Se2 solar cells**

Authors : Idris Bouchama1,2,*, Kamal Djessas3,4, Ammar Messous2, Abdessalam Bouloufa2

Affiliations : 1 Département d’Electronique, Faculté de Technologie, Université de Msila, Alegria. 2 Laboratoire d’Electrochimie et Matériaux, Université Ferhat Abbas de Sétif, Algeria. 3 Laboratoire Procédés Matériaux et Energie Solaire PROMES-CNRS, Rambla de la Thermodynamique, Technosud, 66100 Perpignan, France. 4 Université de Perpignan Via Domitia, 52 avenue Paul Alduy, 68860, Perpignan Cedex9, France. *Bouchama.idris@yahoo.fr

Resume : In this work, one-dimensional device simulator AMPS-1D (Analysis of Microelectronic and Photonic Structures) was employed to study the performances of superstrate SLG/TCO/Cu(In,Ga)Se2 (CIGS)/ODC/In2Se3/Metal thin film solar cells. The impact of TCO/p-CIGS and n-In2Se3/Metal interfaces has been investigated. The combination of optical transparency and electrical conductivity for TCO front contact layer is capable of yielding high efficiency. Several transparent conducting oxides (TCOs) materials and metals have been tested respectively as a front and buck contact layers for superstrate CIGS solar cells. The presence of barrie rs in the front and back contact in the structure can significantly affect the cell performance by limit the carriers current flow. The influence of various parameters for the front and the back structures was studied and the corresponding design optimization was provided. The depletion region overlapping between the TCO/CIGS and In2Se3/Metal junctions will result in the decrease of the solar cell performance. The In2Se3/Metal Schottky contact can be utilized as the back reflector in the buffer layer. The best energy conversion efficiencies have been obtained with ZnSnO3 front contact layer. An A.P4 2 efficiency of 20.17% (with Voc ≈ 0.71 V, Jsc ≈ 35.35 mA/cm2 and FF ≈ 0.80) has been achieved with ZnSnO3-based as TCO front contact layer and Zn-based back contact layer. All these simulation results give some important indication to lead to higher efficiency of superstrate CIGS solar cells for feasible fabrication. Key words: Superstrate solar cells, Cu(In,Ga)Se2, Thin films, AMPS-1D.

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16:00

Fabrication and characterization of photosensitive n-ZnO/p-InSe heterojunctions

Authors : Z. Kudrynskyi (1), V. Khomyak (2), V. Katerynchuk (1), M. Kovalyuk (1), V. Netyaga (1), B. Kushnir (1)

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Resume : Indium monochalcogenide (InSe) with a band gap of 1.25 eV is a promising material for photovoltaic applications. In this work, photosensitive anisotype n-ZnO/p-InSe heterojunctions were fabricated for the first time by means of radio-frequency magnetron sputtering of the zinc oxide onto freshly cleaved (0001) van der Waals surface of p-InSe single-crystal. Structural properties of the obtained heterostructures were investigated by means of X-ray diffraction. Surface morphology of the grown ZnO thin films was studied by means of atomic force microscopy. The electrical and photoelectrical properties of the heterojunctions were investigated using the I-V characteristics measured at different temperatures, C-V characteristics and photoresponse spectra. The dominating current transport mechanisms through the heterojunctions under investigation were determined at forward and reverse bias. It was found that the developed heterojunctions n-ZnO/p-InSe show photosensitivity in the photon energy range (1.25 - 3.20) eV at room temperature. The energy diagram of the n-ZnO/p-InSe heterojunction was built using the obtained experimental data. In addition, we analyzed the influence of vacuum annealing of the heterojunctions at different temperatures on their photoelectric properties.

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16:00

Modulated Photo current experiments – what is the correct data treatment?

Authors : Jennifer Luckas, Christophe Longeaud, Tobias Bertram, Valérie Depredurand,Susanne Siebentritt

Affiliations : Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg ; Laboratoire de Génie Electrique de Paris (CNRS UMR 8507), Supelec, Universités Paris VI et XI, Plateau de Moulon, 11 rue Joliot Curie, 91190 Gif sur Yvette, France ; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg ; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg ; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg ;

Resume : Modulated photocurrent experiments offer a sophisticated approach to study localized defect states within the band gap of semiconductors. In these experiments a semiconducting thin film is illuminated by a modulated light source, while the induced alternating photo current is measured for different temperatures and modulation frequencies. The interaction of photo generated carriers with localized trap states within the band gap, results in a phase shift between modulated photo current and excitation light. Consequently, the phase shift holds information on trap states interacting with free carriers. However, in recent years two different data analysis procedures have been established. The method proposed by Brüggemann et al. analyses phase shifts and amplitudes of modulated photo currents to resolve a reduced density of trap states[1]. In contrast the method proposed by Herberholz et al. concentrates on phase shifts only, and determines the attempt-to-escape frequency and the energetic position of the trap [2]. As Herberholz claimed that the method proposed by Brüggemann is not applicable to crystalline Cu(In,Ga)Se2, this class of materials is generally studied employing the method proposed by Herberholz [3,4]. In this study we use both data treatments to analyse modulated photocurrent experiments performed on amorphous GeTe, amorphous hydrogenated silicon a-Si:H and stoichiometric polycrystalline CuInSe2 grown either under Cu excess or Cu deficiency followed by an etching step in KCN. This comparison shows that both methods lead to equivalent results as long as simple defects, such as acceptor or donor like monovalent traps are dominant. However, the Herberholz method fails for more complex defect arrangements such as the defect pool probed in a-Si:H as well as a complex defect signature present in Cu rich

A.P4 4

CuInSe2. [1] R. Brüggemann, C. Main, J. Berkin and S. Reynolds, Phil. Mag. B 62, 29-45 (1990). [2] R. Herberholz, T. Walter and H.W. Schock, J. Appl. Phys. 76, 2904-2911 (1994). [3] A. Krysztopa, M. Igalson, Y. Aida, J. K. Larsen, L. Gütay and S. Siebentritt, J. Appl. Phys. 110, 103711 (2011). [4] A. Krysztopa, M.Igalson, L. Gütay, J.K. Larsen and Y. Aida, Thin Solid Films 535, 366–370 (2013).

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16:00

RF sputtered single phase CuSbS thin films

Authors : F. Al-Saab, C.C. Huang, J. Yao, B.E. Hayden, D.W. Hewak

Affiliations : University of Southampton, Southampton, SO17 1BJ, United Kingdom

Resume : Second generation thin-film chalcogenide materials, in particular CuInGa(S,Se)2 (CIGS) and CdTe2 have been among the most promising candidates for large-scale PV manufacturing and are quickly becoming commercial products. These materials offer stable and efficient (above 10%) photovoltaic modules fabricated by scalable thin-film technologies and cell efficiencies above 20 % (CIGS). CuSbS2 is a chalcogenide that was discovered in 1942 as a dark gray mineral in Morocco and Tunisia. CuSbS2 is a relatively new material with little research published but is expected to be interesting for environmentally amenable solar cells, as its constituents are nontoxic and are relatively abundant in the earth’s crust. CuSbS2 thin films show p-type conductivity, a band gap of around 1.5 eV, which is ideal to achieve the highest solar-cell conversion efficiency, and a relatively high optical absorption in the visible light range. It also benefits from a low crystallization temperature of 250 ☐C, which allows easier synthesis for flexible solar cells. Various techniques have been developed for synthesizing CuSbS2 but to meet the goal of cost effective fabrication, suitable thin film in-line coating and processing techniques have to be realized. Among possible deposition methods, sputtering can provide good control on film composition at a relatively low cost and is suitable for large -area, continuous and multi-component deposition. This method is already an established technique for the preparation for thin films for magnetic, optical and contact applications. Annealing by rapid thermal processing is a method that significantly reduces the thermal budget of the sample as compared to conventional furnace annealing. In addition to production related issues, the principal advantages of low thermal budget processing is the minimization of interdiffusion and impurity diffusion from the substrate as well as better control of the process kinetics. In this work, CuSbS2 thin films were first deposited by RF magnetron sputtering at room temperature from a single ternary target on molybdenum coated substrates using a Kurt Lesker NANO-38 thin film deposition system. The films were annealed in a Jipelec JetFirst 100 bench top rapid thermal processor at various temperatures (250 to 325 ℃) and times (5 to 60 min). The annealing was done without any toxic gases or reactive sulfur. The compositional, optical, electrical and structural properties of the films were analyzed using SEM, EDX and XRD. Single phase CuSbS2 films with good adhesion, good crystallinity and with no apparent sulfur loss can be achieved.

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16:00

Electroreflectance Spectroscopy on Cu(In,Ga)Se2 Solar Cells with Different Buffer Layers

Authors : Oliver Kiowski1, Wolfram Witte1, Andreas Bauer1, David Sperber2, Christoph Krämmer2, Michael Hetterich2 and Michael Powalla1,2

Affiliations : 1 Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg (ZSW), Stuttgart, Germany. 2 Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany.

Resume : We use electroreflectance (ER) spectroscopy at room temperature to compare CdS/i-ZnO and Zn(O,S)/(Zn,Mg)O buffer layers in complete Cu(In,Ga) Se2 (CIGS) thin-film solar cells with a Mo back contact and ZnO:Al as transparent front contact. CdS buffer layers are deposited by chemical bath deposition (CBD). Zn(O,S) buffer layers are deposited by either CBD or sputtering and exhibit different S/(S+O) ratios. CIGS absorber layers are coevaporated from elemental sources and exhibit a Ga/(Ga+In) ratio of ~0.3. In our ER set-up, we measure the change in reflectivity (as a function of photon energy) of a solar cell when a negative bias is applied. ER signals from absorber and buffer layers are well separated due to their different band gaps. Low ER signals can be masked by interference patterns which we reduce by using rough absorber layers, MgF2 anti-reflective coatings, and an off-axis detector alignment. For solar cells with a CdS/i-ZnO buffer, ER signals are superimposed by a photoluminescence background of CdS. ER signals of Zn(O,S) grown by CBD and sputtering are very weak compared to CdS which could be due to a smaller variation of the electrical field inside that buffer layer. We determine

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band gaps, critical point energies, and broadening parameters describing the band structure of CdS/i-ZnO and Zn(O,S)/(Zn,Mg)O buffer films by fitting the ER spectra to the third derivative of the undisturbed dielectric function.

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16:00

The impact of Na and K on the degradation of CIGS solar cells

Authors : Mirjam Theelen, Nicolas Barreau, Henk Steijvers, Zeger Vroon, Miro Zeman

Affiliations : Mirjam Theelen 1,2,3; Nicolas Barreau 4; Henk Steijvers 1; Zeger Vroon 1; Miro Zeman 2; 1 TNO, dept. Thin Film Technology - De Rondom 1, 5612 AP, Eindhoven, The Netherlands 2 Delft University of Technology, Photovoltaic Materials and Devices, Mekelweg 4, 2628 CD Delft, The Netherlands 3 Materials innovation institute (M2i), Mekelweg 2 2628 CD DELFT, The Netherlands 4 Institut des Matériaux Jean Rouxel (IMN)—UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière B.P. 32229, 44322 Nantes Cedex 3 France

Resume : The incorporation of sodium (Na) and potassium (K) into CIGS leads to enhanced cell performance, but the influence of these alkali on degradation is unclear. Therefore, three types of CIGS cells were prepared with different K and Na contents (high, low and alkali poor) by changing the molybdenum microstructure [1] or adding a SiNx barrier for the alkali poor CIGS. The cells have been degraded in a hybrid damp heat – illumination setup, which allowed continuous in-situ monitoring of the degradation [2]. It was observed that the alkali poor samples had a relatively low initial efficiency, mainly caused by a lower Voc (average 11.4% & 553 mV for alkali free vs 13.2/11.9% & 646/607 mV for low/high alkali content). After 500 hours of degradation, it was observed that the alkali poor cells' efficiency had decreased to 8.4%, while the other cells had average efficiencies as low as 1.1% (low) and 3.0% (high). In order to better understand the degradation behavior, SIMS measurements were executed on similar samples before and after degradation. It was observed that the Na had migrated from the CIGS bulk to the CdS/CIGS interface and the ZnO:Al layer. This effect was of course very limited for the alkali poor samples, which is likely linked to the stability of these samples. Alkali poor CIGS cells are thus much more stable than CIGS containing K and Na. [1] Bommersbach, Prog. Photovolt: Res. Appl. 21 (2013) 332–343 [2] Theelen, proc. 39th IEEE PVSC (2013)

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16:00

Metastable behavior of defects in n-CdTe/p-ZnTe photodiodes grown by MBE method

Authors : E. Zielony1, E. Płaczek-Popko1, A. Racino1, K. Paradowska1, Z. Gumienny1, S. Chusnutdionow2 and G. Karczewski2

Affiliations : 1 Institute of Physics, Wroclaw University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland 2 Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, 02-668 Warsaw, Poland

Resume : The n-i-p junctions based on CdTe/ZnTe heterostructures has been studied as potential candidates for solar cells. The layer structure of the diodes grown by MBE technique was as follows: 14□m thick n-type CdTe:I buffer deposited on the semi-insulating (100)-GaAs substrate, undoped CdTe absorber and 1.5□m thick p-type ZnTe:N layer. Dark I-V characteristics of the studied junctions exhibit diode-like behavior and strong rectifying properties. I-V characteristics measured under 1-sun illumination yield low efficiencies of the junctions not exceeding 5%. In order to verify the origin of the low efficiency DLTS method has been applied. The capacitance - voltage measurements yield net dopant concentration ~1016cm-3. This means that the depletion region of the diodes, which is probed during DLTS measurements, is located within the absorber layer since the n and p layers of the junctions were doped up to 1018cm-3. DLTS results yield the presence of a trap acting as a recombination center. Moreover, it was found that at low temperatures the I-V characteristics reveal metastable character. The structures exhibit also a persistent photocapacitance within a broad temperature range of 20–300K. The latter observation points out on the presence of a continuum of defect states, presumably located at the absorber heterointerfaces. Summarizing, the deep defects located in the absorber layer and at its heterointerfaces may be responsible for the low efficiency of the studied solar cells.

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16:00

Deep-level transient spectroscopy measurements on Mo/CIGS/Metal Schottky diodes

A.P49

Authors : L. Van Puyvelde 1, J. Lauwaert 1, F. Pianezzi 2, A.N. Tiwari 2 and H. Vrielinck 1

Affiliations : 1 Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, 9000 Gent Belgium 2 Laboratory for Thin Films and Photovoltaics, Swiss Federal

Laboratories for Materials Science and Technology (Empa), Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland

Resume : Thin-film Cu(In,Ga)Se2 (CIGS) solar cells are multiple-layer structures. In such complicated structures the presence of capacitance spectroscopy signals originating from non-ideal contacts hamper the detection of defect related signals [1]. Still, a numerous types of intrinsic defects are possible in the chalcopyrite structure, that very probably influence the efficiency of the solar cell. Therefore, we made Mo/CIGS/Metal structures from (the original) cells by etching away the buffer and window layer and evaporating gold or aluminum directly on the p-type CIGS absorber. The N1 signal, observed at low temperature (T<120K) is still present in these Schottky diodes, confirming its assignment to the non-ohmic Mo/CIGS back contact [2,3]. Besides N1 no other DLTS signal that exhibits the properties of a non-ohmic contact is observed in these simplified devices. The signals observed at near room temperature where the N2 signal is expected, do no longer obey the model for the back contact. Hence, these Mo/CIGS/Metal diodes appear favorable for studying defects that induce deep levels which can be detrimental for the solar cell efficiency, and that were masked by the presence of contact related signals near room temperature, when measuring on complete solar cells. [1] J. Lauwaert et al. Sol. Energy Mater. Sol. Cell. 112 (2013) 79-83 [2] T. Eisenbarth et al. J. Appl. Phys. 107 (2010) 034509 [3] J. Lauwaert et al. Prog. Photovoltaics 20 (2012) 588

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16:00 **Behavior of Deep Level Defects on Voltage-Induced Stress of CIGS Solar Cells** A.P4 10

Authors : D.W. Lee, S.E. Cho, J.H. Jeong, and H.Y. Cho

Affiliations : Department of Physics, Dongguk University, Solar Cell Center, KIST, Seoul, Korea

Resume : The behavior of deep level defects by a voltage-induced stress for CuInGa(SSe)2 solar cells has been demonstrated. CIGS samples were used with standard structures which are AZO/i-ZnO/CdS(or ZnS)/CIG(SSe)2/Mo on glasses, resulted in the conversion efficiency as high as 15%. The samples with the same structure were stressed at 90℃ under the reverse voltages according to the stressing time and were kept under an ordinary fluorescent light at room-temperature and were characterized for 1-hour, 1-day, and 1-month-past samples after the stress. The voltage-induced stressing CIGS solar cells showed about the 15% decrease of hole carrier density and the conversion efficiency. To investigate the behavior of deep level defects in the stressed CIGS cells, photo-induced current transient spectroscopy on CIGS cells was utilized, and normally 3 traps (including 2 hole traps and 1 electron trap) were found to be located at 0.16eV and 0.24eV above the valence band maximum (and 0.30eV below the conduction band), respectively. In the voltage-induced cells, especially, the 0.24eV defect which is known to attribute to a charge-trap site of CIGS solar cells significantly increases in intensity, resulting in the decrease of the conversion efficiency. And the increase of the defect is reversible with the recovery of the efficiency. And we will present the relation between reversible defects and the degradation of CIGS cells and discuss the origin of the defects generated by the stress.

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16:00 **Temperature dependent current transport properties in Cu2ZnSnS4 solar cells** A.P4 11

Authors : Mati Danilson (1), Erkki Kask (2), Nikhil Pokharel (1,3), Maarja Grossberg (1), Jüri Krustok (1,2)

Affiliations : (1) Department of Materials Science, Tallinn University of Technology, Estonia; (2) Department of Physics, Tallinn University of Technology, Estonia; (3) Department of Natural Sciences (Physics), Kathmandu University,Nepal

Resume : The quaternary compound Cu2ZnSnS4 (CZTS) is a promising non-toxic absorber material for solar cells made from earth abundant elements. In this study temperature dependencies of current-voltage (J-V), impedance and quantum efficiency (QE) of CZTS monograin layer solar cells were measured in order to clarify current transport in CZTS that is still not fully understood. The temperatures and frequencies were in the range of T=10-300K and f=10Hz-10MHz, respectively. Three different conductivity types can be distinguished from the temperature dependence of the series resistance (Rs) obtained from J-V and impedance measurements. At high temperatures (T>90K), the thermally activated conductivity was detected with Ea≈40-50 meV depending on sample. The possible origin of this process is discussed. According to the QE spectra the effective bandgap energy starts to show abnormal behaviour with temperature in this region. At intermediate temperatures (T≈90–40K), a typical Mott’s variable-range hopping conductivity starts to dominate while the effective bandgap energy has lowest value in this temperature region. At very low temperatures (T<40K) the impurity band conductivity appears and the effective bandgap energy increases rapidly. At the same time, the impedance and J-V measurements reveal a strong decrease of Rs. It is proposed that the current transport at this low temperature region is related to very shallow acceptor defects with very high concentration.

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16:00

An approach using point contact back reflector for efficiency improvements in submicron Cu(In,Ga)Se2-based solar cells

Authors : E. Leonard, L. Arzel, N. Barreau

Affiliations : Institut des Matériaux Jean Rouxel (IMN)-UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

Resume : The decrease of absorber thickness in co-evaporated Cu(In,Ga)Se2 (CIGS)-based solar cell is important for both material consumption and production cycle time issues. Since the short circuit current (Jsc) progressively decreases with the absorber thinning due to the reduction of low energy photon absorption, optical management is a major issue to keep high efficiencies in CIGS cells with submicron absorber. The approach we followed in the present study consists in increasing the back contact reflectance. Our work shows that the use of Mo/ZnO:Al/CIGS structure yields improved Jsc thanks to the optical properties of the TCO layer. However, as could be expected, this gain is accompanied with Voc and FF losses inherent to the resulting additional potential barrier at the back contact. Nevertheless, it will be shown that Voc and FF losses can be overcome with the help of Mo/CIGS point contacts throughout the ZnO:Al interlayer. The density and size of the pinholes have been optimized to combine both good Ohmic contact and high reflectance in the long wavelengths. Thereby, the performance of submicron CIGS based cells has been improved.

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16:00

Photomodulated Photoelectron Spectroscopy of Ag/CuInSe2 to Probe Atomic Charge State

Authors : Aydogan, Pinar, Johnson, Nicole, Rockett, Angus, Suzer, Sefik

Affiliations : Aydogan, Pinar: Department of Chemistry, Bilkent University, 06800 Ankara. Turkey; Johnson, Nicole: Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign; Rockett, Angus: Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign; Suzer, Sefik: Department of Chemistry, Bilkent University, 06800 Ankara. Turkey

Resume : Epitaxial thin films of AgInSe2 and CuInSe2 were grown by a hybrid sputtering and evaporation technique on (001), (100), (110) and (111) GaAs substrates. Film thicknesses were between 500-1000 nm and the substrate temperature was varied from 560-712°C. Aligned surface morphology features matching the substrate geometry in scanning electron microscopy (SEM) images indicate epitaxial growth, which was confirmed by x-ray diffraction (XRD). Chemical information was gathered using x-ray photoelectron spectroscopy (XPS) with monochromatic AlKα x-rays. During measurement of photoelectron spectra, all samples could be illuminated by one of four continuous wave lasers of wavelengths 405, 532, 635 and 980 nm with a rated power of >25mW. Under illumination, relative to in the dark, each element in the films was observed to exhibit binding energy shifts that were wavelength and intensity sensitive. For a CuInSe2/CdS heterojunction, Cd, Cu, In and S showed different binding energy shifts. The highest shift for Cd was under 532 nm illumination while the highest shift for Cu was under 405 nm illumination. Similar measurements of the AgInSe2/CdS heterojunction yielded binding energy shifts in similar directions but were much lower. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No:1312539 TUBITAK Grant No: 212M051).

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16:00

Investigation of defect-related recombination process around pn-interface of CIGS solar cells by impedance spectroscopy

Authors : H. Sakakura, Y. Kondo, S. Aihara, M. Itagaki, M. Sugiyama

Affiliations : Research Institute for Science and Technology / Faculty of Science & Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510, Japan

Resume : We propose to utilize an impedance spectroscopy for revealing the interface defects/recombination properties of CIGS solar cells. The electrical properties of CIGS or CZTS solar cells, especially around pn-interfaces, have yet to be comprehensively clarified because these solar cells exhibit a complex structure comprising stacked layers of several materials. Electrochemical impedance spectroscopy (EIS) is a nondestructive method of investigating

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electrochemical devices, using transfer functions such as impedance and admittance of the equivalent circuits of these devices. In fact, EIS is applicable to various inhomogeneous phenomena such as organic electroluminescence devices and dye-sensitized solar cells. One of the advantages of EIS is that it can measure which capacitance and resistance is changed by the existence of defects, grains, and diffusion of atoms. Therefore, applying EIS as a way to examine CIGS solar cells is a promising tool for direct observation of the pn interface. In fact, we have been using this convenient technique to reveal several interface properties such as defects, impurities, uniformity, and ideality of CIGS solar cells. In this study, we determine the carrier-transfer time-constant (quasi-lifetime) of CIGS solar cells measured by EIS. This quasi-lifetime strongly depends on pn-interface properties. We also describe the relationship between the quasi-lifetime and interface defects of CIGS solar cell.

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16:00 **Ultrafast Carrier Dynamics in CdS/Cu(In,Ga)Se2 Grown on Different Substrate Types (Soda lime glass, Borosilicate)**

Authors : Woo-jung Lee1, Dae-Hyung Cho1, Jae-Hyung Wi1, Won Seok Han1, Yong-Duck Chung1,2, Seonghoon Jung3, Jaehun Park3

Affiliations : 1Solar Cell Technology Research Section, Electronics and Telecommunications Research Institute, Daejeon 305-700, Korea; 2Department of Advanced Device Engineering, University of Science and Technology, Daejeon 305-350, Korea; 3fs-THz Laboratory, Pohang Accelerator Laboratory, POSTECH, Pohang 790-784, Korea

Resume : An understanding of carrier dynamics is of vital interest for improving the efficiency of the solar cell. To realize behavior of e-h pair excited by photon, femtosecond optical technique using THz spectroscopy is very useful but, not applied in the studies of dynamics of nonequilibrium carrier relaxation in chalcogenide-based solar cell. Interestingly, Na incorporation is considered as an important variable to enhance the cell performance in Cu(In,Ga)Se2 (CIGS) thin-film solar cell. Na is typically supplied from the soda lime glass (SLG) widely used as a substrate of solar cell. Although Na is known to have positive influences on CIGS-based solar cell, a deep understanding of their response to optical excitation on a sub-picosecond time scale has not yet been studied. In this study, we performed the comparative experiment by depositing the same CIGS on different substrates of Na-containing SLG and Na-free borosilicate (BS), respectively, and then forming CdS on CIGS using chemical method. Optical pump-THz probe spectroscopy (OPTP) and photoluminescence (PL) were used to investigate the Na effect on ultrafast carrier dynamics at interface between CIGS and CdS. We found that different defect states were formed in the band gap of CIGS depending on Na presence from the PL spectra. The relaxation time of the carriers excited by optical pump beam (400 nm) was significantly increased at CdS/CIGS on SLG as compared with that on BS from the OPTP results. A.P4 16

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16:00 **How post deposition treatment with NaF and KF improves the electronic properties of low temperature grown Cu(In,Ga)Se2 solar cells**

Authors : Fabian Pianezzi, Patrick Reinhard, Benjamin Bissig, Shiro Nishiwaki, Adrian Chirila, Stephan Buecheler, Ayodhya N. Tiwari

Affiliations : Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland

Resume : In order to produce high efficiency Cu(In,Ga)Se2 (CIGS) solar cells the absorber layer has to be doped with alkaline material. A possibility to incorporate the alkaline elements is to deposit a thin layer of an alkali-precursor onto the completely grown CIGS layer and to anneal it, the so-called post deposition treatment (PDT). Using this approach our group recently demonstrated that sequential PDT with NaF and KF allows producing low temperature grown CIGS solar cells on flexible polyimide substrate with efficiency exceeding 20%. In this study we investigate the distinct effects of PDT with NaF and/or KF on the electronic properties of CIGS solar cells. We show that whereas Na is more effective in increasing the hole concentration in the absorber layer, as revealed by C-V measurements, K has significant impact on the pn-junction quality. We investigate the beneficial effect of K to improve the PV performance in view of the recombination mechanisms in the device by temperature dependent J-V measurements. In addition we perform device simulations with the software SCAPS to verify our model of the electronic transport. The PDT with either KF or NaF has also distinct influence on the energetic position of the N1 signal in admittance spectroscopy and the roll-over A.P4 17 of the J-V curve at low temperature. Based on these results we discuss the origin of these two features.

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16:00

Sulfurization growth mechanism and defect properties of SnS thin films

Authors : M. Sugiyama, H. Nagayasu, T. Tsugawa, T. Hiramatsu, K. Hisatomi, S. Aihara

Affiliations : Research Institute for Science and Technology / Faculty of Science & Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510, Japan

Resume : in monosulfide (SnS) is considered to be a promising candidate for a cost-effective and earth-abundant inorganic material to fabricate next-generation solar cells. Although the theoretical conversion efficiency of SnS-based solar cells is high, the demonstrated efficiencies of such cells are still low. One of the reasons for low efficiencies is the poor crystal quality of a SnS layer. In fact, the morphology and crystal structure of SnS thin films strongly depend on the heating profile and the time of each step during the sulfurization process. However, few experimental results using the sulfurization technique have been reported compared to other growth techniques such as co-evaporation or chemical vapor deposition. In this presentation, we reveal the growth mechanism of SnS thin films by a simple and commercial-friendly sulfurization technique. As well, defect-related PL peaks in the as-grown SnS thin films will be investigated. In this way, we found that sulfurization conditions, especially the S flow rate, strongly affected orientation and electrical properties such as carrier density or mobility of SnS thin films. These results indicated that Sn vacancy (VSn) and S vacancy (VS) act as a shallow acceptor and deep donor, respectively. These investigations will greatly assist our ability to optimize the conditions required for the production of SnS-based solar cells.

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16:00

SnS absorber thin films by co-evaporation: optimization of the growth rate and influence of the annealing

Authors : Víctor Robles, Juan Francisco Trigo, Cecilia Guillén, José Herrero

Affiliations : CIEMAT

Resume : Tin monosulfide (SnS) is a chalcogenide material which has reached great interest because it is made up of cheap and non-toxic elements. This material is used as absorber layer in thin film solar cells because its high absorption coefficient above 10-5 cm-1 and its band gap of 1,3 eV, being a potential substitute for other chalcogenides such as CdTe or CIS. This work has been focused on the synthesis by co-evaporation on glass substrate of tin sulfide films for use as absorber layers, with a substrate temperature of 350 °C and varying the growth rate in the 2-6 A/s, adjusting the deposition time in order to obtain thicknesses in the 700-1500 nm range. After evaporation, the samples were heated at 400 and 500 °C under various atmospheres. The evolution of the morphological, structural and optical properties has been analyzed as a function of the thickness and deposition rate, before and after annealing. For the samples grown at the lowest rates, some sulfur-rich phase mixing has been observed by XRD. Samples with reduced thickness preferably crystallize in the SnS phase, whereas thicker layers become richer in the Sn2S3 phase. Sulfur annealing of these samples obtained at the lowest rates evolves toward SnS2 phase. Otherwise, the samples obtained at the highest rates show phase mixing of Sn and SnS that evolves towards monophase SnS after heating at 400 ° C in sulfur atmosphere, with gap energy values around 1.3 eV, while at 500 ° C is formed mainly SnS2.

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16:00

DEGRADATION OF CIGS THIN-FILM SOLAR CELLS DUE TO THE IONIZATION EFFECT OF ELECTRON IRRADIATION

Authors : Shirou Kawakita1, Mitsuru Imaizumi1, Shogo Ishizuka2, Shigeru Niki2, Shuichi Okuda3, Hiroaki Kusawake1

Affiliations : 1 Japan Aerospace Exploration Agency; 2 National Institute of Advanced Industrial Science and Technology; 3 Osaka Prefecture University

Resume : CIGS solar cells have excellent radiation tolerance, although the radiation defects which impair their performance has been reported as an In antisite defect. However, whether the other types of defects in CIGS simultaneously generated by radiation, namely Cu, Ga and Se Frenkel-pair, degrades cell performance or not remains unclear. CIGS solar cells were irradiated with less than 1×1016 cm-2 electrons of the energy of 250 keV. The results indicated an increase in carrier density in CIGS and reduction of roll-over in I-V characteristics in CIGS. Equivalent behavior was reported for the light-soaking effect of CIGS solar cells. The results of electron irradiation tests suggest that the mechanism is considered equivalent to that of the light soaking effect. The CIGS solar cells were irradiated with over 1×1016 cm-2 electrons.

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Conversely, a degradation of electrical performance was observed. The same result was obtained by 100 keV electrons, which could not generate the replacement defects in CIGS semiconductors. Carrier profiles of the CIGS absorbing layer in the cells were studied before and after electron irradiation with C-V measurement. Consequently, the carrier density was shown to decline with increasing electron fluence and it emerged that electron irradiation produces donor-like defects in CIGS absorbers. The defects due to the ionization effect induced by low-energy electrons impair the performance of CIGS solar cells.

add to my program **(close full abstract)**

16:00 **Growth and characterization of SnSe2 by selenization of sputtered metallic precursors**

Authors : P. A. Fernandes (a,b), M. G. Sousa (a), P. M. P. Salomé (c), J. P. Teixeira (a), J. P. Leitão (a) and A. F. da Cunha (a)

Affiliations : (a) I3N and Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal;(b) Departamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal;(c) International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga, 4715-330 Braga, Portugal

Resume : Metal selenide compounds have received a great deal of attention due to their great versatility and potential use in microelectronics applications. Photovoltaic application is also an interesting possibility for the binary compounds SnSe and SnSe2. To confirm that possibility a better understanding of the suitable growth conditions and fundamental properties is needed. In this work, we present a process to grow tin diselenide thin films by selenization, at a maximum temperature of 470 ºC, of tin metallic precursor layers deposited by dc-magnetron sputtering and the results of their characterization. The morphological and structural properties of the SnSe2 layers were investigated by scanning electron microscopy, X-ray diffraction (XRD) and Raman scattering. For this growth temperature, disk-like grain morphologies were observed. Prominent XRD reflections at 2θ=30.75º, 40.10º and 47.72º and vibration modes located at 119 cm-1 and 185 cm-1, were observed. These results allowed the conclusion that under the preparation conditions used the dominant phase is SnSe2. The composition analysis, done by energy dispersive spectroscopy, showed that the films were close to stoichiometric SnSe2 with a Se to Sn ratio of 1.95. Photoluminescence characterization revealed two bands with low intensity at photon energies lower than 0.92 eV. This emission is compatible with an indirect energy gap in the 0.9-1.0 eV range. The nature of the radiative transitions for both bands will be discussed.

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16:00 **PVTEAM - Photovoltaic Technology based on Earth Abundant Materials**

Authors : Aron Walsh (1), Laurence Peter (1), David Fermin (2), Ralph Gottschalg (3), Jake Bowers (3), Michael Walls (3), Ian Forbes (4), David Worseley (5), Trystan Watson (5)

Affiliations : 1. University of Bath 2. University of Bristol 3. Loughborough University 4. Northumbria University 5. Swansea University

Resume : Forbes and Peter [1] have predicted that the market share of CdTe and CIGSe PV will peak and then fall as supply limitations begin to impact as the global installation rate of PV increases. It follows that materials substitution needs to be addressed now if thin film PV is to take on the rapidly emerging challenge of TW renewable energy production. PVTEAM will use semiconductor materials based on abundant sustainable low-cost elements such as copper, tin, zinc and bismuth as substitute layers in thin-film devices. PVTEAM will accelerate the adoption of new earth-abundant PV by developing processes technologies for materials and systems to a level where they can be taken up by manufacturing industries. The programme covers materials specifications and performance, integration into cells and mini-modules and scale up. Using a multi-level screening approach, PVTEAM will choose substitute materials and incorporate the best performing candidates into a generic, industrially-oriented process coupled with appropriate in-line metrology, calibration and stability testing. The PVTEAM work programme consists of three themes: material specification, integration at cell and module level and scale-up towards manufacture. The overall objectives of the programme are: ? To specify and assess high quality binary, ternary and quaternary PV layers produced by scalable solution based processing. ? To develop sustainable non-vacuum routes to the fabrication of viable thin film architectures (t

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add to my program **(close full abstract)**

16:00 **CdS segregation in CZTS solar cells**

Authors : Dahyun Nam1, Mungunshagai Gansukh1, Dae-Ho Son2, Jun-Hyoung Sim2, Dong-Hwan Jeon2, Byoung-Soo Ko2, Dae-Hwan Kim3, Kee-Jeong Yang2,3, Dae-Kue Hwang2, Jin-Kyu Kang 2,3, Hyeonsik Cheong1

Affiliations : 1Department of Physics, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul, 121-742, Republic of Korea; 2Advanced Convergence Technology Center, Daegu Gyeongbuk Institute of Science & Technology, 223 Sang-ri, Hyeonpung-myeon, Dalseong -gun, Daegu 711-873, Republic of Korea; 3Energy Research Division, Daegu Gyeongbuk Institute of Science & Technology, 223 Sang-ri, Hyeonpung-myeon, Dalseong-gun, Daegu 711-873, Republic of Korea

Resume : A CdS layer prepared by the chemical bath deposition (CBD) method has been widely used as a buffer layer for Cu(In,Ga)Se2 (CIGS) solar cells for it is relatively convenient to deposit thin films a high homogeneity. Since the crystal structure is quite similar, the CdS buffer layer was easily adapted to Cu2ZnSnS4 (CZTS) solar cells. However, whether the CBD-CdS is a good match for the CZTS absorber layer is not fully established yet. In this work, we investigated the homogeneity of the CdS layer in a CZTS solar cell with an efficiency of 4.8%. The CZTS thin film was deposited in a two-step process - sputtering and sulfurization - and the cell was fabricated using a typical procedure, CBD-CdS and sputtered-ZnO. Micro-Raman imaging, atomic force microscopy, and laser beam induced current (LBIC) images were compared in the same area of the cell. We found CdS segregation of CdS clusters in the solar cell. The current was reduced where there are CdS clusters. The results of the CZTS solar cell were compared with a co-evaporated CIGS solar cell with an efficiency of ~15%. The CdS clusters were much smaller and fewer than in the CZTS cell. The LBIC image did not show clear correlation with the CdS inhomogeneity. The results suggest that the efficiency of CZTS solar cells are limited by the presence of CdS clusters.

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16:00 **p-n junction improvements of Cu2ZnSnS4/CdS monograin layer solar cells**

Authors : M.Kauk-Kuusik1, K.Timmo1, M. Danilson1 M. Altosaar1, K. Ernits2, T.Holopainen2

Affiliations : 1 Department of Materials Science, Tallinn University of Technology Ehitajate tee 5, 19086 Tallinn, Estonia; 2 crystalsol GmbH, Tallinn

Resume : The formation of interface Cu2ZnSnS4/CdS in monograin layer solar cells is not well understood but seems to be the key to further improvements of their performances. Cu2ZnSnS4 monograin powders were synthesized from elemental precursors in molten KI as flux materials in sealed quartz ampoules at 740 C. In the present work, chemistry of Cu2ZnSnS4 monograin powder surfaces submitted to various chemical treatments was investigated by X-ray photoelectron spectroscopy. The surface analysis allowed us to compare the surface composition with the bulk one as a function of the treatments. The chemical nature of the etchant had a dramatic influence on both, surface composition and interface chemistry. The CdS film formed by chemical bath deposition is reproducible and yields good photovoltaic performance. Due to the aqueous environment, however, the as-deposited CdS film may contain significant amounts of oxygen and hydrogen which degrade the quality of the film. The effect of heat treatment on Cu2ZnSnS4/CdS interfaces in air and vacuum has been also studied. We have developed a combined process based on chemical etching and Cu2ZnSnS4/CdS interface annealing, which improved the active area efficiency to more than 8 %.

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16:00 **CZTS solar cells with efficiency of 5.7% obtained from binary sulfides co-sputtered precursors**

Authors : M. Valentini, C. Malerba, A. Mittiga

Affiliations : SAPIENZA – University of Rome, Department of Physics, P.le Aldo Moro 5, 00156 Roma, ITALY; University of Trento, DICAM, via Mesiano 77, 38123, Trento, ITALY; ENEA, Casaccia Research Center, via Anguillarese 301, 00123, Roma, ITALY;

Resume : Cu2ZnSnS4 (CZTS) is an interesting photovoltaic material owing to its earth abundant and environmentally friendly constituents and an optimal direct band gap of about 1.5 eV. We have grown CZTS thin films using a two-steps process, which consists in the precursor deposition, followed by a thermal treatment. The precursors are deposited by a co-sputtering process from three sulfides sources (CuS, ZnS, SnS) giving films with a homogeneous elements distribution and nearly stoichiometric sulfur content. This is not a widely explored route and nevertheless it gives, after a suitable thermal treatment, CZTS thin films with easily controllable stoichiometry, good homogeneity and large grain size. CZTS films and the respective precursors are investigated by

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XRD, Raman, SEM-EDX and Spectrophotometric measurements. Compositional depth profiles are obtained by XPS. The films have also been employed to fabricate solar cells, with a standard structure: Mo/CZTS/CdS/iZnO/Al:ZnO/Al-grid. The device performances are evaluated by measuring the J-V characteristic curves, under both AM1.5G illumination and dark condition, and External Quantum Efficiency. CZTS films composition and thickness have been optimized in terms of cell efficiency. Up to now our best CZTS-based photovoltaic device has shown an efficiency of 5.7%. The optimization of the material stoichiometry is still ongoing and its relation with the optical properties of the material and with the device performances will be discussed.

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16:00

N-type conduction in SnS-based thin films

Authors : Fan-Yong Ran (1), Zewen Xiao (1), Hidenori Hiramatsu (1,2), Hideo Hosono (1,2), and Toshio Kamiya(1,2*)

Affiliations : (1) Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan; (2) Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.

Resume : SnS is a p-type semiconductor. Since it has a reasonably bandgap of 1.07 eV and a strong absorption coefficients > 105 cm-1, it is expected for photovoltaic layers in solar cells; whereas the highest conversion efficiency reported is only 2 %.[1] The low efficiency might suffer from large lattice mismatch and unfavorable band alignment in heterjunction structure.[2] Fabricating a homojunction solar cell with p-SnS / n-SnS structure might solve the problems, but no reliable n-type conduction has been achieved in SnS-based materials so far. In this work, n-type SnS-based films were successfully fabricated. Sn1-xPbxS films were grown by pulsed laser deposition with (Sn,Pb) S ceramics targets in a H2S gas. The substrate temperature and the partial pressure of a Ar / H2S mixing gas (80 / 20 %) were varied from 200 to 400 oC and from 5 to 20 Pa, respectively. The Sn1-xPbxS (0.08

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16:00

Photovoltaic Performance of a Cd1-xMgxTe/CdS device

Authors : Omar S. Martinez1, 2, Eulises Regalado-Pérez1, Erik R. Morales1, 3, Xavier Mathew1

Affiliations : 1 Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Temixco, Morelos, 62580, México 2 Centro del Cambio Global y la Sustentabilidad en el Sureste, Villahermosa, Tabasco, 86080, México 3 División Académica de Ingeniería y Arquitectura- Universidad Juárez Autónoma de Tabasco, Cunduacán, Tabasco, 86690, México

Resume : In this paper we report the progress in developing a wide band gap alloy material based on CdTe for possible application as top-cell absorber in tandem devices. The ternary alloy film Cd1-xMgxTe was deposited by co-evaporation of CdTe and Mg and the composition was adjusted to obtain a band gap near to 1.6 eV by controlling the Mg concentration. XRD studies confirmed that the alloy film maintained the structural properties CdTe even after incorporating 4% Mg in the CdTe film. The photovoltaic properties of the material were studied by developing a working solar cell of the type Tec7/CdS/Cd1-xMgxTe/Cu-Au. We have studied the effect of post deposition treatments of the film with CdCl2 at different temperatures as well as the diffusion of Cu contacts on the opto-electronic properties of the device. C-V studies showed that the net carrier density varies with depth in Cd1-xMgxTe layer; both interface and back contact regions having higher carrier density. Cu related acceptors play a major role in controlling the carrier concentration. We were able to achieve efficiencies over 9% for the Cd1-xMgxTe/CdS solar cell through improved contact processing and post deposition treatments. Acknowledgements:- This work at IER-UNAM is part of the projects CeMIE-Sol, and SENER-CONACyT 117891.

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16:00

The Frequency-time-resolved microwave photoconductivity and the Broad band photodielectric spectroscopy are two advanced techniques for research of loss process of charge carriers in semiconductors on examples of CIGS and CdS.

Authors : G.F. Novikov

Affiliations : Dr.Sci., Prof., Head of Lab of Photoelectrophysics. The Institute of Problems of Chemical Physics, RAS. Chernogolovka, Moscow region, Russia, 142432. e-mail: ngf@icp.ac.ru; tel./fax: +7 (49652)21842.

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Resume : To date the achieved photovoltaic characteristics of thin-film solar cells (TSCs) are far from those theoretically possible. One of the causes is that the mechanisms of the carrier loss are not fully understood in working layers of

TSCs, so as the roles in these processes of grain boundaries and structure of grain (crystallite) interior. The lack of quantitative data on the mechanism of reactions, on processes of generation and transport of carriers, on processes of their death affects not in the best way characteristics of developed devices. The corresponding methods are necessary for obtaining such data. In this report for the example of Cu(In,Ga)Se2 (CIGS) and CdS the review of two modified methods are shown: the frequency-time-resolved microwave photoconductivity (FTRMC) method and the broadband photodielectric spectroscopy (BPDS) method. A nearly linear dependence of the FTRMC amplitude on the mean sizes of coherent scattering regions (CSR) in the range of 20 to 120 nm was found. The CSR sizes were much smaller than the grain sizes in those CIGS films. This result is an important evidence of the essential role of the CSR boundaries in the carriers loss processes. The best agreement between the theory and the experiment was observed at a value of electron mobility of μ=2·10^{4} cm^{2}V^{-1}s^{-1} in CSR. The BPDS method gives the opportunity to receive the time distribution of dielectric relaxation oscillators caused by excess current carriers.

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16:00

Crystallographic and optical properties of CuSbS2 and CuSb(S1-xSex)2 solid solution

Authors : K. Takei, T. Maeda, T. Wada

Affiliations : Department of Materials Chemistry, Ryukoku University

Resume : Recently, Septina et al. fabricated a CuSbS2 (CAS) solar cell with an efficiency of 3.1% [1]. CAS is an In-free and low-toxic photovoltaic material because it has a band gap of 1.52 eV and high absorption coefficient of >10^4 cm^{-1}. They fabricated CAS films by sulfurization of an electrodeposited metallic stack precursor film composed of Cu and Sb on a Mo-coated glass substrate. They fabricated the solar cell with a device structure of Al:ZnO/CdS/CuSbS2/Mo/glass. In this study, we synthesized CAS and CuSb(S1-xSex)2 (CASSe) solid solutions and characterized their crystal structures and band gap energies.

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We synthesized CASSe powders by planetary ball milling and post-heating at 450 °C in an N2 gas atmosphere. The crystal structures of CASSe were analyzed by Rietveld analysis using X-ray diffraction data. CASSe has a chalcostibite-type structure with an orthorhombic unit cell (space group: Pnma). The refined lattice constants of the CASSe increased from a = 6.0142 Å, b = 3.7965 Å, and c = 14.4841 Å for CAS to a = 6.2973 Å, b = 3.9786 Å, and c =14.9898 Å for CuSbSe2 with increasing Se content. The band gaps of CASSe were estimated by a diffuse reflectance spectrum of the powders. The reflectance edge shifted to a longer wavelength with increasing Se content. The band gap of the CASSe solid solution linearly decreased from 1.45 eV of CAS (x = 0.0) to 1.08 eV of CuSbSe2 (x = 1.0).

[1] W. Septina et al., Thin Solid Films 550 (2014) 700.

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16:00

OPTIMIZATION OF FLEXIBLE CIGS SOLAR CELLS/MODULES

Authors : N.Severino [1], N.Bednar [1], M.Acciarri [2], N.Adamovic [1]

Affiliations : [1]Institute of Sensor and Actuator Systems, Vienna University of Technology Floragasse 7, A-1040 Vienna, AUSTRIA; [2]Department of Material Science and Solar Energy Research Center, University of Milano Bicocca Via Cozzi 53, 20125 Milan, ITALY

Resume : In this work, CIGS thin film was deposited by a sputtering/co-evaporation process. Using the three-stage deposition method solar cells with efficiencies of 11% were obtained on polyimide substrate. In order to improve the current fabrication technology and allow the exploration of new cell/module concepts numerical calculations were carried out. The baseline set of parameters used for the simulations was obtained from the performed measurements. A good agreement with the experimental results was found considering bulk and interface recombination. A layer formed by the interface defects states between CIGS/CdS was introduced to match the measured data. The possibility to enhance the open circuit voltage, and hence the efficiency of the device, was also investigated. A theoretical analysis of the influence of the conduction band offset on performances of solar cells was carried out and an improved band alignment was proposed. The Ga profile obtained from secondary ion mass spectrometry measurements was investigated using simulations in order to improve the transport properties of photo-generated carriers. Results from the calculations performed on the material level were used as input data for simulations of the module. Optimization of the collection grid was done, using a hybrid model approach, to find a compromise between

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optical (shading) and electrical (resistivity of the material) losses on the module level.

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16:00 **Analysis of the back contact properties of Cu(In,Ga)Se2 solar cells employing the thermionic emission model** A.P4 31

Authors : Nils Neugebohrn, Maria S. Hammer, Janet Neerken, Jürgen Parisi, Ingo Riedel

Affiliations : Laboratory for Chalcogenide Photovoltaics, Energy and Semiconductor Research Laboratory, Department of Physics, University of Oldenburg, 26111 Oldenburg, Germany

Resume : Despite 20 years of research on Cu(In,Ga)Se2 (CIGSe) solar cells there is no conclusive model to explain the electronic properties of the back contact which forms between CIGSe and molybdenum during growth of the chalcopyrite absorber. For this interface Schottky-type as well as ohmic behavior has been reported previously. In particular, the intermediate MoSe2 layer which forms between the absorber and the metal during growth of the CIGSe layer determines the contact characteristics and might be critical for the device performance. In this study Au/CIGSe/MoSe2/Mo samples have been prepared via etch removal of the ZnO/CdS window layer from the completed cell stack and subsequent deposition of Au contacts on top of the CIGSe layer. To study a potential barrier-induced current limitation we performed temperature-dependent current-voltage measurements (IVT) between 80 K and 300 K. We observed an exponential dependence of the injection current indicating the presence of a contact barrier which height is estimated using the thermionic emission model. To verify the location of this barrier, either at the CIGSe/MoSe2 or at the MoSe2/Mo interface, additional MoSe2/Mo samples were prepared by lift-off of the CIGSe layer and studied with analogue IVT measurements.

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16:00 **Impact of Sulphur and Gallium Gradients on the Performance of Thin Film Cu (In,Ga)(Se,S)2 Solar Cells** A.P4 32

Authors : Tetiana Lavrenko, Thomas Walter

Affiliations : University of Applied Sciences Ulm, Albert-Einstein-Allee 55, 89081 Ulm, Germany; University of Applied Sciences Ulm, Albert-Einstein-Allee 55, 89081 Ulm, Germany.

Resume : A graded bandgap structure proved to be an important factor for increasing an overall efficiency of the chalcopyrite-based thin film solar cells. This contribution will be focused on the effects of sulphur incorporation into the surface region of industrial sequentially grown Cu(In,Ga)(Se,S)2 absorbers. A front grading due to such a sulphurization step enhances the bandgap in the space charge region, whereas the bulk of the absorber exhibits a lower bandgap which determines absorption and photocurrent. The question which will be addressed in this contribution is whether such graded bandgap structures allow to separate the absorption and recombination processes, therefore resulting in highly efficient solar cells with improved open circuit voltages without compromising short circuit currents. In order to assess the effective bandgap for nonradiative recombination low temperature measurements have been performed on the Cu(In,Ga)(Se,S)2 and Cu(In,Ga)Se2 – based solar cells. The extrapolated open circuit voltages at 0K demonstrate a shift of the activation energies of about 50 meV for the device with a S-gradient at the interface. However, the effective bandgaps for current collection of the same devices determined from external quantum efficiency measurements showed a negligible difference and roughly corresponded to the pure CuInSe2 material. Furthermore, a high Ga content at the back contact will be discussed in terms of a back contact passivation preventing injection of electrons to the back contact.

add to my program **(close full abstract)**

16:00 **Influence of different Na-Treatments on CIGSe Solar Cells: Experiment and Simulation** A.P4 33

Authors : Hengameh Allaf Navirian, Stephan Brunken, Dieter Greiner, Volker Hoffmann, Varvara Brackmann, Christian Kaufmann, Thomas Unold

Affiliations : Helmholtz-Zentrum Berlin für Materialien und Energie Hahn-Meitner-Platz 1 14109 Berlin Germany

Resume : Cu(In,Ga)Se2 films were prepared by a 3-stage-coevaporation process followed by a NaF-post-deposition treatment. We used glass substrates with a NaF-diffusion barrier to allow Na-free growth. A 4 nm thin NaF precursor layer, which was deposited onto the Mo back contact prior to CIGSe deposition, caused an absorber growth with a strong 112 texture. For samples without NaF precursor a dominant orientation was not observed. Selenization of a NaF-coated Mo back contact before absorber deposition also leads to an absorber growth without any remarkably dominating orientation. Independently of the pre-selenization, the NaF precursor layer lead to absorber layers with a more pronounced Ga-grading and higher charge carrier concentration and higher life time, which were measured by glow discharge optical emission spectroscopy (GDOES), Capacitance-Voltage (CV) measurements and time-resolved photo-luminescence (TRPL), respectively. Results of CV, GDOES and TRPL were used as inputs for device simulations using SCAPS1D. In the device model, parameters such as carrier concentration, lifetime, Ga-grading and interface recombination were then modified to optimize the conversion efficiency. The simulation results suggest modifications to the 3-stage growth in order to achieve optimal device performance.

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16:00 **TiO2 / CuInS2 heterostructures for solar cell applications**

Authors : Anna Frank1, Angela Wochnik2, Sophia Betzler2, Christina Scheu2

Affiliations : 1 Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany.; 2 Ludwig-Maximilians-University Munich, Department of Chemistry and Center for NanoScience, Butenandtstraße 5-13, 81377 Munich, Germany.

Resume : Nanostructured interfaces between semiconductors offer many advantages compared to planar solar cell devices. An enhanced surface area for charge carrier separation allows to obtain higher efficiencies. In addition, enhanced light scattering occurs due to nanostructuring and the migration distances of the charge carriers are decreased.[1] In our work we fill hydrothermally grown n-type TiO2 nanowires in Rutile modification with p-type CuInS2 via an easy solvothermal process. The single crystalline Rutile nanowires have a wide band gap of 3.1 eV and offer a direct path for the electrons toward the electrode.[2] CuInS2 is a p-type material with a band gap of 1.5 eV and a high absorption coefficient.[3] Preliminary results obtained by scanning and transmission electron microscopy (TEM) show a complete filling of the nanowire array with CuInS2. Rutile respectively Chalcopyrite crystal structures are proven to occur within the layer using electron and X-ray diffraction. Energy-dispersive X-ray measurements performed in TEM verify the existence of a thin Ti and O containing layer on the bottom of the nanowire arrays which can work as a blocking layer in solar cells. Further work will focus on the insertion of buffer layers such as In2S3 between TiO2 and CuInS2 to suppress interfacial recombination and hence improve the solar cell performance.[1] Literature: [1] Nanu et al. Adv Funct Mater 2005, 15, 95. [2] Cromer et al. JACS 1955, 77, 4708. [3] Tell et al. Phys Rev B 1971, 4, 2463. A.P4 34

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16:00 **Light-induced doping increase in Cu(In,Ga)Se2-based thin film solar cells**

Authors : Si Chen, Tobias Jarmar, Sven Södergren, Ulf Malm, Erik Wallin, Olle Lundberg, Sebastian Jander, Ralf Hunger, Lars Stolt

Affiliations : Si Chen; Tobias Jarmar; Sven Södergren; Ulf Malm; Erik Wallin; Olle Lundberg;Lars Stolt; Solibro Research AB, Vallvägen 5, SE-756 51 Uppsala, Sweden Sebastian Jander; Ralf Hunger; Solibro GmbH, Sonnenallee 32-36, 06766 Bitterfeld-Wolfen, Germany

Resume : Light-induced metastabilities of Cu(In,Ga)Se2 (CIGS)-based thin film solar cells have been extensively investigated for many years. It is commonly observed that junction capacitance and p-doping level in CIGS absorbers increase considerably after light soaking (LS). For medium to low minority carrier diffusion lengths, this leads to losses in the long wavelength region due to a reduced SCR width and thus carrier collection length. This work focuses on how cell performance and sodium distribution are affected by LS and how changes in electrical parameters can be explained with device simulation. Experiments show that high efficiency cells with good long wavelength EQE lose Voc and FF upon LS, whereas low efficiency cells with poor long wavelength EQE lose less or even gain Voc and FF. We also observe that the LS behavior is sensitive to differences in the CdS buffer layer process. The sodium content measured with GD-OES increases in the CIGS-CdS region with LS and may contribute to changes in the doping characteristics. The change in electrical parameters is explained with simulations, which relate the Voc and FF changes to a reduced recombination rate in the SCR due to the light induced change of the CIGS-CdS doping profile. The simulations also suggest that cells with higher n-doping in the CdS are less sensitive to changes in interface recombination rate and doping of CIGS, which agrees with the hypothesis that the CdS buffer deposition is important for the LS behavior. A.P4 35

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16:00 **Verification of Phototransistor Model for CIGS Solar Cells** A.P4 36

Authors : Thomas Ott 1, Francillina Schoenberger 1, Thomas Walter 1, Dimitrios Hariskos 2, Oliver Kiowski 2, Oliver Salomon 2 and Raymund Schaeffler 3

Affiliations : 1 University of Applied Sciences Ulm, Albert-Einstein-Allee 55, 89081 Ulm, Germany 2 Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung Baden Wuerttemberg, Industriestr. 6, 70565 Stuttgart, Germany 3 Manz CIGS Technology GmbH, Alfred-Leikam-Str.25, 74523 Schw?bisch Hall, Germany

Resume : With a new record efficiency of 20.8% on laboratory scale in 2013 CIGS passes multicrystalline Si and consolidates its position as the most promising thin-film technology for the future. Besides efficiency the long term stability is a crucial issue for the competitiveness of a solar cell technology. Previous studies showed that the long term stability critically depends on the bias across the junction. As a result of a dark anneal the IV-characteristics in the dark showed a blocking behavior with increasing anneal time. In the final stage the device exhibits an open circuit voltage (Voc) which is independent from the illumination intensity, a cross-over of the dark and illuminated IV-characteristics and Voc saturation for decreasing temperatures. These characteristics also occur in the initial state prior to the endurance test, however, at low temperature (<200K) measurements. We suggested a phototransistor model to explain the observed characteristics. The prerequisite of this model is the existence of a Schottky barrier at the back contact. In this contribution more insights into this phototransistor model and its experimental verification will be given and discussed. Finally we suggest how to avoid the effects of the back barrier with the help of a CuGaSe2 layer at the back of the absorber, a Ga gradient through the absorber or a passivation of the back contact. These measures will be verified with simulations in SCAPS and compared to measurements on co-evaporated devices.

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16:00 **Annealing of wet treated CIGSSe solar cells with an indium sulfide buffer**

Authors : Christian Hönes (a), Susanne Siebentritt (a)

Affiliations : (a) Université du Luxembourg, Luxembourg

Resume : Compound evaporated indium sulfide is one commonly utilized cadmium free buffer layer for CIGSSe solar cells. However, cells with such a buffer layer usually need a post deposition annealing step to reach the maximum short curcuit current, fill factor and open circuit voltage. In this work the annealing behaviour of such cells fabricated on commercially available absorber material is compared to the behavior of cells which were treated in a chemical bath, partly containing divalent cations, before buffer layer deposition. The latter cells show maximum open circuit voltage directly after window layer deposition and a drop is observed upon annealing. All samples, however, show an increased collection length and higher fill factor after annealing. A one diode model fit to the IV curves gives large ideality factors above 2 for the as-deposited samples which are reduced to values around 1.5 after annealing. Supporting SCAPS calculations show that the changes upon annealing can be explained within a model consisting of a highly p-doped absorber surface layer combined with a low conductivity window layer. During annealing the acceptor density at the absorber surface might be reduced thus leading to a larger space charge region and thereby increasing the fill factor and collection length while reducing the open circuit voltage.

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16:00 **Characterization of defects in CuInGaSe2 thin films by the charge-based Deep Level Transient Spectroscopy**

Authors : Yan Xu1,3, Cédric Renaud2, Abdeljalil Lahmar3, Thien-Phap Nguyen1*

Affiliations : 1Institut des Matériaux Jean Rouxel, 2 Rue de la Houssinière 44322 Nantes, France. ; 2LAPLACE, University of Toulouse, 118 Route de Narbonne 31062 Toulouse Cedex 9 France. ; 3LTN, 18 Bd Gaston Defferre 85000 La Roche-sur-Yon, France

Resume : Control of defects in CuInGaSe2 (CIGS) solar cells is of prime importance to improve their electrical properties and they have been extensively investigated using different analytical methods. Despite these efforts, the properties of traps in devices have not been fully understood yet, partly because of the complex structure of the active layer as well as that of the cells. In this work, we have investigated traps in Metal-CIGS-Metal (M1-S-M2) diodes (M1 = Mo, M2 = Al or Mo) by using the charge based Deep Level Transient spectroscopy (Q-DLTS), a variation of the conventional DLTS technique. Two sets of distributed traps A and B have been determined in diodes with different metal electrodes. Type A defects contain several levels of shallow traps with a mean activation energy of 25mV while type B contains deep traps with a mean activation energy of 370 mV. The capture cross sections of both types are determined to be in the range of 10-21-10-22 cm2 and their density in the range of 1015-10-16 cm-3. The trap filling process of the two trap

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sets was found to be strongly dependent of the temperature conditions. Replacing Mo top electrode by Al one did not modify significantly the trap distributions but decreased the trap density, suggesting that interfacial interactions between the active layer and electrode may have occurred in the devices. Q-DLTS spectra of a Mo-CIGS-Mo device measured at T = 300 K and by using a charging voltage of ΔV = 3 V and different charging times tC in the range 500 μs (○) – 1 s (▼).

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16:00

Transient surface photovoltage on the nanometer scale on Cu(In,Ga)Se2 solar cells

Authors : Nicoleta Nicoara (1), Pedro Salome (1,2), Humberto Rodriguez Alvarez (1), Viktor Fjällström (2), Bart Vermang (2), Marika Edoff (2), Sascha Sadewasser (1)

Affiliations : (1) International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, 4715-330 Braga, Portugal; (2) Ångström Solar Center, Uppsala University, P.O. Box 534, 751 21 Uppsala, Sweden

Resume : Kelvin probe force microscopy (KPFM) has contributed significantly to the understanding of Cu(In,Ga)Se2 (CIGSe) materials on the nanometer length scale throughout the last 15 years. In combination with sample illumination, some important fundamental properties like charge carrier generation and separation processes can be investigated. While previously KPFM with illumination has been applied as a static technique, here we present the investigation of the dynamics of the surface photovoltage in the range between nanoseconds and milliseconds. We present results on different sets of CIGSe samples from different growth processes and with stacks of CIGSe/CdS and CIGSe/CdS/ZnO. For lower efficiency CIGSe we measure relaxation times of excited and separated charge carriers on the order of a few tens of microseconds. For higher efficiency CIGSe we obtain 10 times faster relaxation times. Analysis of spatially resolved transient surface photovoltage shows a homogeneous distribution of relaxation times, without significant differences between grains and grain boundaries. We discuss the differences of the physical origin of the measured relaxation times with respect to relaxation times obtained from other techniques, such as transient photoluminescence and deep level transient spectroscopy.

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16:00

Characterization of the properties of CdS/CdTe solar cells grown by close space vapour sublimation using resistive elements

Authors : O. Martínez1, J.L. Plaza2, S. Rubio2, P. Iñiguez1, J. Jiménez1, E. Diéguez2

Affiliations : 1 GdS-Optronlab, Dpto. Física Materia Condensada, Univ. de Valladolid, Edificio I+D, 47011 Valladolid (Spain). 2 Laboratorio de Crecimiento de Cristales, Departamento de Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid.

Resume : Thin Film Photovoltaic Cells (TFPV) with a reduced peak efficiency of 11%, represent nearly 8% world share of the actual solar cell market. Moreover, it seems it will reach the 20% of the market in the next few years, due to the scarcity of Si and the cost-cutting potential that many people perceive in TF technology. For these reasons, a strong effort must be carried out in the research and development of TFPV experimental approaches which do not use Si as the matrix element. In this work we analyze the growth of CdTe/CdS films by CSS as well as the modification of their properties by using Low Energy Ion Sputtering. This technique has proved to be a very cost-effective in order to produce semiconductor nanostructures and has already shown to provide the enhancement of the luminescent properties of CdTe and CdZnTe single crystals. The CdS and CdTe films were grown on top of 10x10 mm FTO comertial conductive substrates by a novel technique using resistive heat elements. CdTe and CdS layers with quite good compositional properties have been obtained for optimized growth parameters. The rectifying character of the CdTe/CdS juction is also studied, observing a great influence of the porous structure observed in the CdS layer. The modification of the properties of the layers after ion beam irradiation, and the benefits for improving the properties of the juction, are studied by luminescence (PL, CL, μRaman) and electrical (LBIC, EBIC) techniques.

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16:00

Influence post-deposition selenium supply on CIGSe-based solar cell properties

Authors : 1- N. Barreau, L. Arzel, T. Lepetit, T. Painchaud, F. Couzinié-Devy 2- J. Kessler 3- P. Zabierowski, M. Igalson, A. Urbaniak, K. Macielak

Affiliations : 1- Institut des Mat?riaux Jean Rouxel, (IMN-UMR6502), CNRS, Universit? de Nantes, France 2- 44solar, France 3- Warsaw University of Technology, Faculty of Physics, Warsaw, Poland

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Resume : If the need of Se supply during CIGSe co-evaporation has been widely investigated and discussed, its need after the deposition, while the substrate is still at high temperature, remains unclear. The present contribution investigates the impact of chalcogen supply after CIGSe growth on cells properties. With this aim, absorber layers have been deposited by the 3-stage process and once the growth completed, the SLG/Mo/CIGSe structures have been kept at high temperature for one hour with or without Se supply. Both the resulting CIGSe layer and related device properties have been compared to those obtained when the substrate is cooled down right after the deposition (i.e. standard process). Moreover, such experiments have been performed using substrates yielding different CIGSe alkali content (i.e. Na-free, high and low Na). The results show that keeping the absorber at high temperature impacts Ga/III gradients differently depending on whether Se is supplied. More surprising is the impact on the cells, this work indeed shows chalcogen supply can be detrimental for cells performance when the CIGSe contains Na. This latter observation suggests an intimate relationship between Na and Se, which will be discussed with the help of advanced material and device characterization.

add to my program **(close full abstract)**

16:00 **Influence of the n-side doping on space charge profiles in CIGS-based solar cells**

Authors : Marek Maciaszek, Pawel Zabierowski

Affiliations : Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland

Resume : Determination of free hole and defect distributions in CIGS devices is problematic due to the amphoteric character of VSe - related defects. Recently we have proposed a method, based on measurements of capacitance profiles in different metastable states, which allows for a quantitative evaluation of densities of metastable defects (Nt), and net shallow acceptors (Na). A standard analysis of C-V measurements assumes high asymmetry in the doping level between both sides of the junction. However, after illumination, when the free hole concentration in CIGS is significantly increased, the r-ZnO/CdS/CIGS structure cannot be treated as a one-sided n+p junction. Hence, in order to accurately estimate Nt and Na, we take into account in this contribution the influence of the n-side on capacitance space charge profiles. We analyze the junction assuming both, fully and partially depleted buffer layer. We show that the explanation of the shape of the space charge profiles close to the interface is possible only by taking into account free carriers diffusing into the depletion layer. Analysis of profiles obtained for positive voltages can provide information about concentration of donors in CdS. We develop an analytical model and juxtapose it to numerical simulations. Basing on this we indicate in which conditions capacitance profiling gives reliable results, in particular free hole and metastable VSe defect densities.

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16:00 **Enhanced solar efficiency by Au@SiO2 core shell Nanoparticles in Non-Vacuum Process CISSe Solar Cell**

Authors : Yi-Ju Chen, Yu-Ting Yen, Chen Chia-Wei, Manikandan Arumugam, and Yu-Lun Chueh*

Affiliations : Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

Resume : Plasmonic solar cell has been demonstrated on many kinds of materials such as silicon solar cell, DSSC, and organic solar cell. However, it remains challenges for applying to Cu(InGa)Se2-based solar cells. One of the reasons is that Au will react with In and Cu during inevitable high temperature processes. In order to address this issue, development of thermal-stable protection shell is necessary. Here, we successfully demonstrate plasmonic CISSe solar cell with enhanced conversion efficiency by employing Au-core/SiO2 -shell nanoparticles (Au@SiO2 NPs). CISSe layer with different shell thickness and morphologies of Au-core/SiO2-shell was fabricated via non-vacuum process and characterized by HR-TEM and UV-Visible spectrometer, respectively. Afterwards, Au@SiO2 NPs were mixed with CuInS2 nanocrystal ink homogenously and experienced at high temperature selenization process to form CISSe layer. Compared to the pristine, Au@SiO2 NPs - embedded CISSe layer shows an enhanced device performance. SEM images reveal that the SiO2 layer can protect Au NPs intact after the high temperature annealing process. Consequently, under AM1.5G irradiation, the short circuit current (Jsc), open circuit voltage (Voc) and power conversion efficiency (η) have been improved by 13 %, 5 % and 17 % in average, respectively. This work successfully

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demonstrated enhanced light absorption scheme utilizing Au@SiO2 NPs within CISSe solar cells and may have a potential to other thin film photovoltaic devices.

add to my program **(close full abstract)**

16:00 **CdTe/CdS/ZnO:Al solar cells in substrate and superstrate configuration: thin film and device characterization** A.P4 44

Authors : C. Rotaru 1, V. Palekis 2, S. Vatavu 1,2, C. Ferekides 2, P. Petrenko 3, P. Gasin and M. Rusu 1,4

Affiliations : 1 Faculty of Physics and Engineering, Moldova State University, 60 A. Mateevici str., Chisinau, MD-2009, MOLDOVA; 2 Department of Electrical Engineering, University of South Florida, 4202 East Fowler Ave, Tampa, FL 33620, USA; 3 Institute of Applied Physics of the, Academy of Sciences of Moldova, 5 Academiei str., Chisinau, MD-2028, MOLDOVA; 4 Institut für Heterogene Materialsysteme, Helmholtz-Zentrum Berlin für Materialien und Energie, Lise-Meitner-Campus, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Resume : CdTe/CdS/ZnO:Al thin film solar cells have been prepared by CSS in substrate and superstrate configuration. The deposition temperatures were kept the same for both configurations of the cells, namely two batches of CdTe films have been deposited at source temperatures of 535C and 580C, while the substrate temperature varied from 265C to 440C. Mo/Glass and CdS/ZnO:Al/Glass structures have been used as substrates in substrate and superstrate configuration respectively. CdS has been sublimated at 650C onto ZnO:Al/Glass substrates heated up from 260C to 450C. Morphological and structural investigations has been carried out by XRD (FeKa, CuKa), GI-XRD (CuKa), AFM, SEM and optical transmitance. Briefly, XRD analysis for CdTe on Mo/Glass substrates show that the decrease of the substrate temperature results in a XRD pattern consisting of only two peaks determined by (111) and (511). The high (substrate) temperature samples have peaks due to (111), (220), (311), (400), (331), (422), (511). As deposited CdTe in CdTe/CdS/ZnO:Al, as well as CdTe annealed in presence of chlorides at 400C have been studied both by XRD and GI-XRD (angles of 0.7 to 1.5 degree have been used). A comparison analysis of the morphology and structure of CSS CdTe and CdTe single crystal used as a source material is given. The structural investigations are directly correlated to photovoltaic parameters. A comparative JV and QE analysis is presented.

add to my program **(close full abstract)**

16:00 **Numerical Analysis of Photovoltaic Solar Cells based on low cost thin film sulfides** A.P4 45

Authors : HANIF ULLAH1,2 , SHAFI ULLAH1,2 and BERNABÉ MARÍ SOUCASE 1

Affiliations : 1) Departament de Física Aplicada-IDF, Universitat Politècnica de València, València, Spain. 2) Electrical Engineering Department, Federal Urdu University Islamabad Pakistan.

Resume : SnS is a promising semiconductor for photovoltaic (PV) applications. Owing to its bangap value, SnS is well suited to be used as efficient absorber in thin film photovoltaic solar cells. Besides SnS is nontoxic and earth-abundant material. The purpose of this work is to check the effectiveness of SnS-based PV devices. Different configurations have been analyzed by using dedicated software, such as Solar Cell Capacitance Simulator (SCAPS). The proposed solar cell consist of an SnS absorber layer with a bandgap of 1.4 eV, a thin buffer layer of about 50 nm based on a n-type semiconductor without containing heavy metals and a window layer of about 100 nm. Two structures were studied. One containing the standard and well-known CdS buffer (SnS/CdS/SnOx) and a second one made of layers containing Sn in all layers in order to avoid diffusion (SnS/SnS2/SnOx). After optimization of different parameters a conversion efficiency of 10.50%, VOC of 0.91-volts, JSC 0.0134 A/cm2 and Fill-Factor (FF) of 86.48% was obtained for the SnS/CdS/SnOx structure. These results will be compared with that obtained for the greener SnS/SnS2/SnOx structure. It is worth noting that simulation studies are based of experimental data available in the literature. As SnS material has just being produced as thin film, its characteristics will be still improved for its use in PV devices and therefore the performance of related devices would be further enhanced.

add to my program **(close full abstract)**

16:00 **Thermal stability of CZTS-monograins in photovoltaic devices, investigation of diffusion processes in the photoactive region** A.P4 46

Authors : Lukas Plessing; Stöger Pollach; Christian Bühlmeyer; Christoph Waldauf; Axel Neisser;

Affiliations : crystalsol GmbH; TU Wien; crystalsol GmbH; crystalsol GmbH; crystalsol GmbH;

Resume : crystalsol's technology is based on mono-crystalline growth of CZTS particles (Cu2ZnSn(S,Se)4) in a flux-melt process at moderate temperatures. The device manufacturing is done from this photoactive monocrystalline powder by embedding it into a printed isolating polymer thereby forming highly flexible, light weight, monolithically integrated photovoltaic modules. The production process can be done roll-to-roll and customized shaped. The versatility of this concept allows us to imagine different applications starting from small mobile devices to building integrated PV. For successful entry into the PV market a core criterion beside costs and efficiency is the lifetime of the product. Especially interfaces are prone to degradation and require detailed investigation. Here we present TEM measurements on FIB-sliced samples from real photovoltaic devices with regard to jV-data measured on the very same devices. TEM pictures enable us to compare the elemental distribution along the junction prior and after accelerated thermal degradation studies. The comparison with appropriate jV-behavior allows for the conclusion on the impact on device performance. By optimized grain growth and the identification of an improved buffer layer deposition diffusion processes at the photoactive interface can be frozen out in order to achieve long term stability. In conclusion the carried out improvements enable the qualification of CZTS based technology for first product applications.

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16:00 **On the thin films based solar cell main recombination mechanisms characterization with the temperature-dependent open circuit voltage measurements technique**

Authors : Djicknoum Diouf, A. Darga

Affiliations : UFR Sciences Appliqu?es et Technologie Universit? Gaston Berger Saint-Louis SENEGAL; Sorbonne Universit?s, UPMC Univ Paris 06, UMR 8507, Laboratoire de G?nie Electrique de Paris, F-91190 Gif sur Yvette, France

Resume : The temperature-dependent open circuit voltage (Voc (T)) measurements technique is a powerful method to characterize recombination mechanisms. Indeed, it does not require a complex fitting procedure. Voc (T) measurements technique has been widely used to characterize the recombination mechanisms in thin films solar cells, including CIGS, CdTe and CZTS devices. The most common analysis methods, based on the work of V. Nadenau et al., consist of comparing the activation energy Ea (Extrapolated Voc (T=0)) to the absorber band gap (Eg), which allow to localize the main recombination at the heterointerface (Ea A.P4 47

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16:00 **Effects of air-annealing on photovoltaic performance of sputtered In2S3/CIGSe device**

Authors : Wei-Hao Ho, Chia-Hao Hsu, Tzu-Ying Lin and Chih-Huang Lai

Affiliations : Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

Resume : This work presents the effects of air-annealing on photovoltaic performances for CIGSe devices with sputtered In2S3 buffer. In2S3 thin films were deposited by pulse-DC sputtering onto selenized CIGSe absorbers at room temperature. Air-annealing treatments were achieved on In2S3/CIGSe samples prior to i-ZnO/AZO deposition. The influences of annealing temperature and duration have been investigated by using current-voltage measurement(J-V), external-quantum efficiency(EQE) and time-resolved photoluminescence(TRPL). After air-annealing, the enhancement of carrier collection blue wavelength range and minority carrier lifetime was observed. Additionally, as annealing temperature raised form room temperature(without annealing) to 135℃, all photovoltaic parameters of CIGSe solar cell were significantly improved resulting in the efficiency increased form 5.3±0.5% to 10.8±0.3%. However, the decline on cell performance was found when temperature higher than 145℃ and duration longer than 10min. A.P4 48

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16:00 **Device performance improvement in low-temperature grown CuInGaSe2 solar cells by Ag alloying**

Authors : Kihwan Kim (a), Joo Wan Park (a,b), Jin Su Yu (a), Jun-sik Cho (a), Jihye Gwak (a), Sejin Ahn (a), Ara Cho (a), Seung Kyu Ahn (a), Young-joo Eo (a), Joo Hyung Park (a), Keeshik Shin (a), Kyung Hoon Yoon (a), Hi-Deok Lee (b), and Jae Ho Yun (a) A.P4 49

Affiliations : (a)Photovoltaic Laboratory, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea ; (b) (b)Department of Electronic Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

Resume : In the past decade the CIGS-based solar cells have proven that they are one of the promising cost-effective thin-film solar cells by demonstrating significant technological advances from manufacturing as well as laboratory scale. In this work, with Ag alloying we attempted to improve the microstructure and device performance of low-temperature grown CIGS solar cells. Ag precursors with various thicknesses were deposited onto Mo prior to CIGS growth. CIGSS absorbers were then formed onto Mo/Ag with a single-step co-evaporation at the substrate temperature of 450 ?C. The surface morphologies and microstructures of the CIGS films were changed by the Ag alloying. A CIGS film without the Ag-alloying was found to have quite a fine microstructure, while Ag-alloyed films exhibited significant recrystallization. Devices were also fabricated with the CIGS films to elucidate the effects of the Ag-alloying to device performances. A CIGS cell without the Ag-alloying turned out to have a poor device performance as an efficiency of about 3.0% and a VOC of 310 mV. In contrast, a CIGS cell with Ag/(Ag Cu) = 0.2 exhibited a significantly improved device performance as an efficiency of about 8.6% and a VOC of 530 mV. This improvement by the Ag alloying appeared to be associated with the improved crystallinity and defect passivation. The more details of the Ag-alloying effects to a CIGSS film will be discussed in the conference.

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PROGRAM VIEW : 2014 Spring

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Thin film chalcogenide photovoltaic materials

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Ab-initio calculations + point defects : M. Maciaszek, T. Wada

08:30

Intrinsic point defects of CuInSe2 and CuGaSe2 revisited

Authors : Karsten Albe, Johan Pohl

Affiliations : Technische Universität Darmstadt, FB Material- und Geowissenschaften, FG Materialmodellierung, Jovanka-Bontschits-Str. 2, D-64287 Germany

Resume : A comprehensive study of the thermodynamic and electronic properties of intrinsic point defects in the solar absorber materials CuInSe2 and CuGaSe2 based on screened-exchange hybrid density functional theory is presented. GaCu is found to be the most detrimental intrinsic point defect in CuGaSe2 and high-gallium Cu(In,Ga)Se2 above approximately 50% gallium, since it constitutes a minority carrier trap. In contrast with results in the literature, InCu is a very shallow donor, which explains the good tolerance of CuInSe2 to off-stoichiometry rather than complex formation with vacancies. Complex formation with copper vacancies cannot occur under thermodynamic equilibrium conditions, because the formation energies are higher than that of the individual point defects. CuIn and CuGa hole traps and Cui may be contained in high quantities under certain preparation conditions such that they can significantly alter the properties of the material. Based on these results optimal preparation conditions in terms of the point defect physics of CuInSe2 and CuGaSe2 are discussed.

A.O111

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09:00

Direct Observation of Band Tails – a Comparative Study of Chalcopyrite and Kesterite Absorbers

Authors : J.H. Alsmeier, I. Repins, L. Mansfield, L. Korte, R.G. Wilks, R. Noufi and M. Bär

Affiliations : Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; National Renewable Energy Laboratory, Golden, CO, USA;National Renewable Energy Laboratory, Golden, CO, USA; Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany;National Renewable Energy Laboratory, Golden, CO, USA;Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany and Institut für Physik und Chemie, Brandenburgische Technische Universität Cottbus-Senftenberg, Cottbus, Germany

Resume : The best chalcogen-based photovoltaic devices use chalcopyrite CuIn1-xGaxSe2 ("CIGSe") absorbers and reach efficiencies up to 20.8 %.1 The related but more earth-abundant Cu2ZnSnSe4 ("CZTSe") kesterite system has reached efficiencies up to 12.6 %.2 Good CZTSe cells usually show similar short -circuit currents as do CIGSe devices but significantly lower open-circuit voltages (VOC). Recently, "band tails" (so-called Urbach tails) have drawn attention as a potential explanation for this VOC limitation.3,4 So far, the presence of band tails has been indirectly inferred from photoluminescence (PL) peak shifts and shallow quantum efficiency (QE) slopes. We will present constant final state yield spectroscopy (CFSYS) data for CIGSe and CZTSe absorbers. The high cross section of the photoemission process at low photon energies allows for a direct measurement of the band tail density of states (DOS), showing that the kesterite absorbers have a 3-5 times higher DOS in the band gap than do the chalcopyrites. These results are in good agreement with PL and QE findings3 and point to band tail DOS as a factor limiting the VOC of CZTSe solar cells. We will relate our CFSYS results with QE data and the device

A.O112

performance of corresponding solar cells. 1ZSW press release 18/2013, Stuttgart, 24 October 2013 2W. Wang et al., Adv. Energy Mater., DOI: 10.1002/aenm.201301465 (2013) 3T. Gokmen et al., Appl. Phys. Lett., 103, 103506 (2013) 4M. Grossberg et al., J. Photon. Energy. 3, 030599 (2013)

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09:15 First-principles study of point defects in Cu(In,Ga)Se2

Authors : Jonas Bekaert, Rolando Saniz, Bart Partoens

Affiliations : University of Antwerp, Department of Physics, Groenenborgerlaan 171, 2020 Antwerp, Belgium

Resume : We have performed a DFT study of point defects in Cu(In,Ga)Se2 (CIGS), using the HSE06 hybrid functional. Our calculations support the claim that Cu vacancies have low formation energies and act as shallow acceptors, accounting for p-type conductivity in Cu poor conditions. In these conditions, In_Cu and Ga_Cu are also defects with low formation energies and thus prevalent. These defects act as compensating shallow donors. Ga_Cu is likely to be the shallow donor level responsible for the broadened PL spectra in Ref. [1]. When the amount of Cu increases, their formation energy increases, consistent with the peaked PL spectra for increased Cu richness in Ref. [1]. Our study also indicates that p-type behavior is not restricted to Cu poor conditions. Cu_In and Cu_Ga, shallow acceptors as well, occur more frequently in Cu rich conditions. At the same time, less acceptor states are compensated. It may explain the experimental observation of the increasing hole concentration with Cu/Ga ratio in Ref. [2]. Finally, we have studied C impurities, motivated by growth methods based on nanoparticle inks. We find that C_Cu is a shallow donor, while C_In and C_Ga form deep donor levels. Interstitial C is an amphoteric defect. All C impurities can in principle harm the p-type conductivity. However, their formation energies are high leading to the prediction that C is expelled. [1] A. Bauknecht et al, J. of Appl. Phys. 89, 4391 (2001). [2] A. Gerhard et al, Thin Solid Films 387, 67 (2001).

A.O113

add to my program **(close full abstract)**

09:30 Defect levels in Cu(In,Ga)Se2 polycrystalline layers by sub-bandgap photo-induced current transient spectroscopy

Authors : K. Macielak 1, M. Igalson 1, P. Zabierowski 1, N. Barreau 2, L. Arzel 2

Affiliations : 1 Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warszawa, Poland; 2 Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, 44322 Nantes cedex 3, France

Resume : Intrinsic defects in Cu(In,Ga)Se2 have been a subject of intense investigation for decades. Junction capacitance techniques allowed to determine some characteristics of defect levels, but at the same time proved to be insufficient to reach unambiguous conclusions. Recently photocurrent-based methods as complimentary tools were proposed and successfully implemented for investigation of defect levels in the epitaxial and polycrystalline CuInSe2 and CuGaSe2 layers [1,2]. It was also shown that persistent photoconductivity effect accompanying photocurrent measurements distorted and often totally obscured PICTS spectra in case of copper-poor polycrystalline layers. In order to overcome this difficulty, the use of sub-bandgap light in PICTS measurements is proposed and presented in the following work. The results for a set of CIGS polycrystalline layers fabricated using various preparation protocols are shown and discussed. Both types of excitation – sub-bandgap (wavelength 1300nm) and above bandgap (wavelength 975nm) – have been used. We show that as expected sub-bandgap light allows to obtain better-resolved PICTS spectra than in case of standard measurements. Moreover an attempt to measure the excitation spectra for specific defect levels in order to find differences between thermal and optical transition energies will be made. [1] A. Krysztopa, et. al. J. Appl. Phys. 110 (2011) 103711. [2] A. Krysztopa, et. al., J. Phys. D: Appl. Phys. 45 (2012) 335101.

A.O114

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09:45 Metastable defect in CuInSe2 probed by Modulated Photo current experiments above 390 K

Authors : Jennifer Luckas, Christophe Longeaud, Tobias Bertram, Thomas Paul Weiss, Valérie Depredurand, Susanne Siebentritt

Affiliations : Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg ; Laboratoire de Génie Electrique de Paris (CNRS UMR 8507), Supelec, Universités Paris VI et XI, Plateau de Moulon, 11 rue Joliot Curie, 91190 Gif sur Yvette, France ; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill,

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Luxembourg; Laboratory of Photovoltaics, University of Luxembourg, 41 Rue de Brill, Luxembourg

Resume : Modulated Photocurrent experiments (MPC) have been largely used to study defects in semiconductors [1-4]. However, existing studies on Cu(In1-xGax)Se2 have been limited to measurement temperatures below 350 K[2-3]. In this study we present MPC spectra in a higher temperature range, from 390 K to 430 K, measured on a Cu poor CuInSe2 thin film grown on soda lime glass. In this higher temperature range, MPC measurements reveal a defect distribution located at 260 meV from the band edge. The measured MPC DoS defined by the product of defect distribution N, their capture coefficient for holes cp and inverse free carrier mobility[1] is observed to increase with time. By means of simulations the MPC defect response could be assigned to a hole trap having a rather low capture coefficient cp= 1x10-12 cm-3s-1. At 300 K cell structures fabricated from absorbers grown in the same deposition process as the MPC sample demonstrate a rise in cell capacitance for frequencies below 1000 Hz. SCAPS simulations [5] show that the hole trap nature of the defect probed by MPC 260 meV from the valence band edge is also responsible for the low frequency signature in room temperature admittance spectroscopy. Furthermore, the cell efficiency is observed to decrease by ~1% over two months as a result of a decrease in short circuit current and open circuit voltage. SCAPS simulations support that this decrease in cell parameters may arise from an increasing hole trap concentration centred 260 meV above the valence band edge as revealed by Modulated Photo current experiments performed above 390 K. [1] R. Brüggemann, C. Main, J. Berkin and S. Reynolds, Phil. Mag. B 62, 29-45 (1990). [2] R. Herberholz, T. Walter and H.W. Schock, J. Appl. Phys. 76, 2904-2911 (1994). [3] A. Krysztopa, M. Igalson, Y. Aida, J. K. Larsen, L. Gütay and S. Siebentritt, J. Appl. Phys. 110, 103711 (2011). [4] A. Krysztopa, M. Igalson, L. Gütay, J.K. Larsen and Y. Aida, Thin Solid Films 535, 366–370 (2013). [5] M. Burgelman, P. Nollet and S. Degrave, Thin Solid Films, 361-362, 527–532 (2000).

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10:00 **Coffee break**

Electrical characterization : N. Terada, I. Repins

10:30

Integration of device characterization into development methodology of CIGS solar cells

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Authors : A. Bayman
Affiliations : Miasole

Resume : CuIn1-xGaxSe2 (CIGS) based solar cell technology has emerged as a promising thin-film technology with world-record efficiencies for small laboratory solar cells of 20.3% and 15.7% for commercial-size PV modules. In order to continually drive down the cost of solar energy the efficiency of commercial PV modules has to approach champion device performance. MiaSolé's thin film technology is based on a "roll-to-cell" platform where all the films that comprise the CIGS solar cell are sputter deposited sequentially onto a flexible stainless steel substrate in a single pass in our all-PVD process system followed by automated cell formation and 100% inline IV testing. The architecture of the continuous operation roll-to-cell process flow used at MiaSolé is uniquely suited to design of experiment (DOE) methods. These methods reduce ambiguities from noise factors and enables repeatable testing of interacting factors. For example, multiple factors such as chemical composition, deposition rate, film thickness, operating pressure, and growth temperature can be tested simultaneously. Use of a production system for development has additional advantages (i) large volume of repeatable results due to a stable and high output operation (ii) fast turn-around of experimental results (substrate to full tested cell within 60minutes) and (iii) reduction of further scale up issues when transitioning to full manufacturing of a new process. At MiaSolé one of our goals is to understand the physical and device differences between champion and production cells and engineer meaningful process modifications to drive production cell efficiency towards champion level performance. The most common solar cell characterization techniques used at MiaSolé comprise IV, CV, QE, and AES. These techniques are extremely valuable in elucidating the chemical and electrical characteristics of record devices. Due to the high volume of samples from our production roll-to-cell system we have developed automated data analysis tools for these commonly used measurements which

have accelerated our data reporting time and increased our cycles of learning. Our automated approach to device characterization allows batch analysis of large sets of samples with a high level of consistency. In addition, our device characterization tools also include iterative curve fitting and solution finding capabilities to extract physical parameters from simple models and/or make the best estimate on some physical parameters that are challenging to measure directly. The extracted parameters include the diode parameters (diode ideality factor, saturation current, shunt conductance, series resistance), depletion width, carrier concentration profile and diffusion length, composition and band gap profile. These values can be used as inputs into a custom device model that allows us to partition out different mechanisms that contribute to the performance difference with record CIGS cells. The device characterization comparison of development cells made using our roll-to-cell process with high performance small scale cells (such as a record NREL CIGS device) has been used to generate an estimate of the power loss mechanisms and highlight non-optimum characteristics of our thin film device stack. We will present the device characterization and analysis tools used in this comparison of champion and development cells.

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11:00 **The Fermi level in CdS buffer layers**

Authors : A. Fuchs, J. Pohl, W. Witte, D. Hariskos, T. Adler, E. Feldmeier, J. Schaffner, A. Schneikart, S. Siol, J. Türck, K. Albe, W. Jaegermann, A. Klein

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Resume : CdS is a frequently used buffer layer in chalcogenide thin film solar cells. It can be prepared by a variety of deposition techniques as thermal evaporation (TE), close-spaced sublimation (CSS), chemical bath deposition (CBD), magnetron sputtering (MS), and others. This contribution summarizes extended studies of the Fermi level position at the surfaces of CdS layers using photoelectron spectroscopy. Different substrates and different deposition conditions are compared. It will be shown that the Fermi level depends noticeably on the deposition technique. In particular, as-deposited films grown on fluorine doped SnO2 show Fermi levels of EF-EVB = 1.8-2.2 eV (TE), 2.1-2.5 eV (CSS), 1.7-2.4 eV (MS), and ≈2.0 eV (CBD), respectively. The Fermi level of TE-CdS shows no apparent dependence on substrate material. Considerably lower Fermi level positions of EF-EVB ≈ 1.5 eV are reproducibly found for CBD-CdS grown on Cu(In,Ga)Se2. The results show that the Fermi level in CdS can be strongly pinned by intrinsic defects, which can even lead to a modification of energy band alignment at interfaces. It will furthermore be demonstrated that annealing in oxygen modifies the pinning position and changes the energy band alignment to the underlying substrate. A discussion of the observations in terms of intrinsic defects in CdS calculated using density functional theory will be provided.

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11:15 **Influence of solution-grown Zn(O,S) buffer layer thickness on the electrical properties of Cu(In,Ga)Se2 solar cells**

Authors : Wolfram Witte, Oliver Kiowski, Richard Menner, and Dimitrios Hariskos

Affiliations : Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Industriestraße 6, D-70565 Stuttgart, Germany

Resume : Zn(O,S) grown by chemical bath deposition (CBD) is well established as an alternative buffer to CdS in Cu(In,Ga)Se2 (CIGS) solar cells. Nevertheless, these devices often have a lower open-circuit voltage Voc than CdS-buffered references. This contribution promotes the understanding of Voc loss in CIGS cells buffered with Zn(O,S). A series of CIGS cells with different Zn (O,S) buffer thicknesses between 0 and 40 nm was generated by varying the time of the CBD process. All other layers of the cell stack were processed similarly: sputtered Mo, co-evaporated CIGS, as well as (Zn,Mg)O and ZnO:Al by sputtering. Reference cells from the same CIGS run were fabricated with CdS/i-ZnO/ZnO:Al. The Voc of the CIGS cells with increasing Zn(O,S) buffer thickness increases significantly from values below 500 mV for the 0 nm to 660-670 mV for the 40 nm samples. The latter values are close to the 690-700 mV found for the CdS-buffered references. Voltage-dependent external quantum efficiency (EQE(V)) measurements reveal almost no bias dependence for the cells with thick Zn(O,S), very similar to the CdS-buffered cells. The EQE(V) curves of CIGS cells with thin Zn(O,S) buffers, however, exhibit a distinct

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dependency on the applied bias voltage. Collection losses at positive bias voltages are possibly a result of interface recombination. This topic will be discussed with the focus on Voc of the Zn(O,S) series, complemented by the influence of a post-annealing step on the electrical cell properties.

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11:30 **Heat Induced Passivation of CuInSe2 Surfaces: A Strategy to Optimize the Efficiency of Chalcopyrite Thin Film Solar Cells?**

Authors : Harry Mönig, David Lockhorn, Nabi Aghdassi, Alexander Timmer, Christian A. Kaufmann, Raquel Caballero, Helmut Zacharias, and Harald Fuchs

Affiliations : Physikalisches Institut and Center for Nanotechnology (CeNTech) Universität Münster; Physikalisches Institut and Center for Nanotechnology (CeNTech) Universität Münster; Physikalisches Institut and Center for Nanotechnology (CeNTech) Universität Münster; Physikalisches Institut and Center for Nanotechnology (CeNTech) Universität Münster; Helmholtz-Zentrum Berlin für Materialien und Energie; Departamento de Física Aplicada, Universidad Autónoma de Madrid; Physikalisches Institut and Center for Nanotechnology (CeNTech) Universität Münster; Physikalisches Institut and Center for Nanotechnology (CeNTech) Universität Münster

Resume : Despite the success of chalcopyrite thin film solar cells, many open questions are related to the complex defect physics at the interface between the n-type window layer and the p-type chalcopyrite absorber, which largely determines the device efficiency. Therefore, our study aims to clarify the defect physics of chalcopyrite thin film surfaces, which is investigated by scanning tunneling spectroscopy, photoelectron, and inverse photoelectron spectroscopy. After removing surface oxides by a wet chemical KCN treatment and subsequent annealing at 280°C in ultrahigh vacuum, a complete passivation of defect levels is observed, which goes along with a type inversion and an enlarged band gap at the surface. Therefore, this sample state consolidates three exclusively beneficial properties, which potentially minimize interface recombination losses and increase the open circuit voltage in completed devices. In contrast, oxidation of the surface by annealing in air reduces the surface band bending and creates a high density of charge compensated defect levels, implying exclusively detrimental effects on the device performance due to the presence of oxygen at the window/absorber heterojunction. These results are discussed in view of previous models suggesting a passivation of defect levels upon oxygenation of the interface. A.O12 4

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11:45 **Electrical characterization of Cu(In,Ga)Se2-solar cells by voltage dependent time-resolved photoluminescence**

Authors : Matthias Maiberg, Conrad Spindler, Roland Scheer

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Resume : Time resolved photoluminescence (TRPL) is a promising method for the investigation of carrier dynamics and recombination kinetics in semiconductor devices. To characterize Cu(In,Ga)Se2 (short: CIGS) solar cells, we measured the TRPL for different applied external forward voltages and excitation intensities. We show that the TRPL decay time increases with increasing voltage in case of a high excitation intensity. This result is valid for a wide range of excitation frequencies of the laser. However, for low excitation intensity the decay time is unchanged by an external voltage. By simulation of the measured transients with Synopsys TCAD we determined a set of third level parameters which allow to fit the experimental photoluminescence transients for different voltages. The calculated quantities were Schockley-Read-Hall lifetime, doping density and minority carrier mobility of the solar cell's absorber layer with values of 10ns, 10E15/cm3 and 5cm2/Vs, respectively for a standard CIGS solar cell. We note that the minority carrier mobility is difficult to obtain by other methods. We further studied the appearance of a photovoltage in TRPL experiments with single-photon-counting-methods. By experimental and theoretical results we show, that the voltage externally applied gives the same transient than the internal photovoltage at open-circuit conditions. Moreover the open-circuit voltage shows a dependence of the laser repetition rate. A.O12 5

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12:00 **Lunch break**

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