HL 68: Photovoltaics: Chalcopyrites II

Time: Thursday 10:15–13:30 Location: FOE Anorg

HL 68.1 Thu 10:15 FOE Anorg

Radiative recombination of Cu_2ZnSnS_4 thin films and single crystals — •Steffen Kretzschmar[1], Justus Just[1], Björn Schubert[1], Susan Schorr[1], Thomas Unold[1], Serghei Levcenko[2], Victor E. Tezlevan[2], and Ernest Arushanov[2] — [1]Helmholtz Zentrum Berlin für Materialien und Energie, 14109 Berlin — [2]Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD 2028, Moldova

Cu_2ZnSnS_4 is an interesting absorber material for thin film solar cells, because it uses non-toxic and earth abundant elements. The best efficiencies reached so far are much lower than the record efficiencies of chalcopyrite thin film solar cells, 6.8% for Cu_2ZnSnS_4 and 9.6% for $Cu_2ZnSn(S,Se)_4$ have been reported in the literature. So far there is little knowledge about the optical and electronic properties of these materials. In this work Cu_2ZnSnS_4 thin films grown by coevaporation and Cu_2ZnSnS_4 single crystals grown by iodine transport chemical vapour deposition are investigated by photoluminescence spectroscopy. At low temperature shallow and deep transitions are observed. By temperature and intensity dependent measurements these transitions are identified as excitons and free-bound transitions, respectively.

HL 68.2 Thu 10:30 FOE Anorg

Untersuchung der kristallographischen und elektronischen Struktur von Cu_2ZnSnS_4 mittels Röntgenabsorptionspektroskopie — •Justus Just[1,2], Thomas Unold[2], Dirk Lützenkirchen-Hecht[1], Hans-Werner Schock[2], Susan Schorr[2] und Ronald Frahm[1] — [1]Bergische Universität Wuppertal — [2]Helmholtz-Zentrum-Berlin, Institut für Technologie E-I3

Als alternatives Absorbermaterial für Dünnschichtsolarzellen im Vergleich zu herkömmlichen Chalkopyriten $Cu_2(In,Ga)(S,Se)_4$, bietet sich Cu_2ZnSnS_4 (CZTS) in chalkopyrit-verwandter Kesterit-Struktur an, und ist bislang kaum erforscht. Alle enthaltenen Elemente bzw. deren Verbindungen sind ungiftig und zu genüge in der Erdkruste enthalten, daher ist eine besonders kostengünstige Herstellung denkbar. Weiterhin hat CZTS eine zum Sonnenspektrum ideal angepasste Bandlücke von ca. 1,5eV und bietet einen hohen Absorptionskoeffizienten $\sim 10^4$/cm für sichtbares Licht. Somit eignet sich diese Verbindung ideal zur Herstellung von Dünnschichtsolarzellen. CZTS und dessen strukturverwandte Fremdphasen wurden mittels Röntgenabsorptionsspektroskopie bezüglich ihrer kristallografischen Struktur (EXAFS und Röntgenbeugung) und ihrer elektronischen Struktur nahe der Leitungsbandkante (XANES) untersucht. Die präsentierten Ergebnisse zeigen einen deutlichen Zusammenhang zwischen der aus theoretischen Kalkulationen bestimmten elektronischen Zustandsdichte unbesetzter Zustände und der gemessenen Röntgenabsorption. Dies ermöglicht eine quantitative Identifikation von Fremdphasen in den mittels Ko-Verdampfung hergestellten Dünnschichten.

HL 68.3 Thu 10:45 FOE Anorg

Ab initio based Monte Carlo studies of Cu-depleted CIS phases for solar cells — Christian Ludwig[1], •Thomas Gruhn[1], Claudia Felser[1], and Johannes Windeln[2] — [1]Institut für Anorganische and Analytische Chemie, Johannes Gutenberg-Universität Mainz, Deutschland — [2]IBM Mainz, Deutschland

Thin film solar cells with a $CuInSe_2$ (CIS) absorber layer have an increasing share of the solar cell market because of their low production costs and the high efficiency. One interesting aspect of CIS is the inherent resilience to defects and composition fluctuations. Beside the stable $CuInSe_2$ phase, there are various Cu-poor phases along the Cu_2Se–In_2Se_3 tie line, including the $CuIn_3Se_5$ and the $CuIn_5Se_8$ phase.

We have used ab initio calculations of Cu-poor CIS configurations to make a cluster expansion of the configurational energy. In the configurations, Cu atoms, In atoms, and vacancies are distributed over the Cu and In sites of a CIS cell with fixed Se atoms. With the resulting energy expression, $CuIn_3Se_5$ and $CuIn_5Se_8$ systems have been studied in the canonical ensemble. By analyzing the free energy landscape the transition temperature between a low-temperature ordered and a high-temperature disordered $CuIn_5Se_8$ phase has been determined.

Furthermore, grandcanonical ensemble simulations have been carried out, which provide the equilibrium Cu and In concentrations as a function of the chemical potentials μ_{Cu} and μ_{In}. Plateau regions for the $CuInSe_2$ and the $CuIn_5Se_8$ phases have been found and analyzed for different temperatures.

HL 68.4 Thu 11:00 FOE Anorg

The influence of sodium in Cu(In,Ga)Se_2 solar cells investigated by quantum efficiency measurements — •Stefan Puttnins[1,2], Hendrik Zachmann[1], Felix Daume[1,2], Andreas Rahm[1], and Marius Grundmann[2] — [1]Solarion AG, Ostende 5, 04288 Leipzig, Germany — [2]Institut für Experimentelle Physik II, Universität Leipzig, Linnéstr. 5, 04103 Leipzig, Germany

Thin film solar cells based on Cu(In,Ga)Se_2 (CIGSe) absorbers can be deposited on flexible plastic foils reaching efficiencies up to 17.6 %. The addition of sodium plays a key role for enhancing CIGSe solar cell perfomance.

As polyimide is a sodium free substrate (in contrast to soda-lime glass) extrinsic incorporation of sodium is indispensable to achieve high efficiencies.

The aim of this work is to analyze the influence of different sodium contents on photocurrent and defect characteristics by quantum efficiency (QE) measurements. We show that the sodium content influences the CIGSe bandgap, carrier collection in the long wavelength region of the QE spectra and the Urbach energy as a measure of structual disorder.

Furthermore, we show how luminescence spectra can be calculated from QE data and how the sodium content affects peak intensities and energetic peak positions in those spectra.

HL 68.5 Thu 11:15 FOE Anorg

Kathodolumineszenz-Mikroskopie von polykristallinen Cu(In,Ga)Se_2 -Absorberschichten — •Stefan Ribbe[1], Mathias Müller[1], Frank Bertram[1], Thomas Hempel[1], Wolfram Witte[2], Dimitrios Hariskos[2] und Jürgen Christen[1] — [1]Institut für Experimentelle Physik, Otto-von-Guericke Universität, Magdeburg, Deutschland — [2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung, Baden Württemberg (ZSW), Stuttgart, Deutschland

Die Lumineszenzeigenschaften von Cu(In,Ga)Se_2-Schichten unterschiedlicher Schichtdicke als Absorber für hocheffiziente Dünnschichtsolarzellen wurden mittels hoch orts- und spektral-aufgelöster Kathodolumineszenz (KL) untersucht. Die Absorberschichten wurden in einem Durchlaufprozess mittels Koverdampfung auf Mobeschichtetes Kalk-Natron-Glas hergestellt. Unterschiedliche Schichtdicken von 1.0 und 3.0 μm wurden durch Variation der Durchlaufgeschwindigkeit realisiert. Auf den Oberflächen der polykristallinen Schichten ließen sich neben der typisch körnigen Struktur einzelne Facetten erkennen. Die ortsintegralen Tieftemperatur-KL-Spektren sind durch einen, für kupferarme Schichten typischen, breiten Peak um 1.13 eV (1.1 μm) gekennzeichnet. Durch Variation von Temperatur bzw. Anregungsdichte ließen sich DAP-Übergänge mit Beteiligung der Kupfervakanz und der Antisite-Defekt In_{Cu} identifizieren. Die laterale Lumineszenzverteilung ist sowohl hinsichtlich der Intensitäten als auch der Peakenergien mikroskopisch inhomogen. Hierbei sind sowohl Fluktuationen von Korn zu Korn, als auch eine Variation der Emissionswellenlänge innerhalb der einzelnen Partikeln zu erkennen.

HL 68.6 Thu 11:30 FOE Anorg

Investigations of lateral and vertical compositional gradients in Cu(In,Ga)Se_2 by highly spatially, spectrally and time resolved cathodoluminescence spectroscopy — •Mathias Müller[1], Stefan Ribbe[1], Thomas Hempel[1], Frank Bertram[1], Wolfram Witte[2], Dimitrios Hariskos[2], and Jürgen Christen[1] — [1]Institute for Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany — [2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung, Baden Württemberg (ZSW), Stuttgart, Germany

Luminescence properties of Cu(In,Ga)Se_2 (CIGS) layers with different thicknesses were investigated by means of highly spatially, spectrally and time resolved cathodoluminescence (CL) spectroscopy at low temperature (T = 5 K). A polycrystalline CIGS thin film with a thickness of 2.4 μm was grown using an in-line co-evaporation process with a final Cu-poor composition on top of a sputtered Mo layer on a soda lime glass substrate. The layer thickness was then reduced by highly controlled bromine methanol etching. The typical grainy ($d_{average}$ =

3 μm) structure of the untouched sample develops thin longish structures under the influence of the etchant. Integral CL spectra of the samples are dominated by donor-acceptor pair (DAP) luminescence. The peak energies of these spectra are ranging from 1.13 eV to 1.22 eV with decreasing layer thickness. The lateral distribution of the luminescence is inhomogeneous regarding the intensity as well as the peak energy. Time resolved CL shows a strong dependence of the initial lifetime from the emission energy.

15 min. break

HL 68.7 Thu 12:00 FOE Anorg

Band-lineup and junction formation between Zn-VI (VI = O, S, Se) and epitaxial $CuInSe_2$ — •Andreas Hofmann and Christian Pettenkofer — Helmholtz-Zentrum Berlin, Institut für Ladungsträgerdynamik, 12489 Berlin

The crucial interface in chalcopyrite-based solar cells is the one between Cu(In,Ga)Se_2 absorber and CdS buffer layer, where the p/n junction is situated and which should provide a beneficial energetic lineup among absorber and ZnO window. Due to its toxicity, Cd-free buffer layers are desirable.
Single-crystalline $CuInSe_2$(112) and (001) films were grown by molecular beam epitaxy as well-defined model systems to study the band alignment with alternative buffer layer materials. The Zn-VI layers were deposited stepwise with intermediate analysis by combined XPS/UPS and LEED, completely under UHV conditions. ZnO deposition by Metal-Organic MBE leads to the formation of an ultra-thin intrinsic ZnSe buffer layer (1-2 nm thickness), consistent with our findings for $CuInS_2$(112) [1]. The valence band offset for the intrinsic buffer layer of 0.7 eV is conform with our result for the bulk and agrees well with theory [2]. On $CuInSe_2$(112) substrates, ZnO grows in registry with ZnSe(111) with its own lattice constant in the (0001) direction, as confirmed by the LEED pattern. From our measurements, the band alignment is largely independent on orientation.

[1] S. Andres *et al.*, Thin Solid Films **518**, 1032 (2009).
[2] W. Mönch, Appl. Phys. A **87**, 359-366 (2007).

HL 68.8 Thu 12:15 FOE Anorg

Band alignment of epitaxial ZnS on $CuInS_2$(001) and $CuInS_2$(112) — •Carsten Lehmann, Frank Kelleter, and Christian Pettenkofer — Helmholtz-Zentrum Berlin, Berlin, Deutschland

With respect to thin film solar cells based on $CuInS_2$ and ZnO ZnS is a promising alternative to CdS as buffer layer material [1,2]. We report on the band aligment of epitaxial ZnS prepared by molecular beam epitaxy (MBE) on $CuInS_2$ (001) and $CuInS_2$(112). The preparation and investigation of the samples were performed in an ultra high vacuum system at the Helmholtz-Zentrum Berlin. An alternating step-by-step growth and investigation by photoelectron spectroscopy (PES) and low energy electron diffraction (LEED) provided insight on the band line up of the $CuInS_2$-ZnS interface. The $CuInS_2$ substrates were prepared on GaAs by gas source molecular beam epitaxy (GSMBE) using di-tert butyl disulfide (TBDS) as sulfur precursor. Furthermore, the derived data were used to determine the band alignment of the corresponding $CuInS_2$-ZnS-ZnO interfaces prepared by metal organic molecular beam epitaxy (MOMBE) based on diethylzinc and water [2]. [1] M. Bär, et. al., Journal of Applied Physics 99 (2006) [2] S. Andres, et. al., Thin Solid Films 518 (2009)

HL 68.9 Thu 12:30 FOE Anorg

Spatially resolved photoluminescence studies on $CuGaSe_2$ and $CuInSe_2$ thin-films — •Christian Gutsche[1], Raquel Caballero[2], and Gottfried H. Bauer[1] — [1]Insitute of Physics, Carl von Ossietzky University Oldenburg, Germany — [2]Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany

Chalcopyrite absorbers such as Cu(In_{1-x} Ga_x)Se_2 as convincingly promising candidates for solar light harvesting due to the grainy structure exhibit a high degree of compositional, optical and electronic inhomogeneities.

We have studied samples of the extreme values of stoichiometry, say x=0, and x=1 by steady state spectrally resolved photoluminescence with lateral resolution of $\leq$ 1 μm in a confocal cryostat setup. We compare the experimental observations of these two types of absorbers, $CuInSe_2$ with $CuGaSe_2$ with respect to laterally resolved luminescence yields, local splitting of quasi-Fermi levels, local absorption coefficients and local pseudo band gaps, as well as local recombination rates.

Furthermore we discuss the distribution of these magnitudes on the basis of histograms and Minkowski-operations like 'opening'-functions to extract lateral features and determine their pattern sizes.

HL 68.10 Thu 12:45 FOE Anorg

Cu(In,Ga)Se_2-based thin-film systems with different absorber thicknesses: spatially resolved photoluminescence and AFM measurements — •Oliver Neumann[1], Stephan J. Heise[1], Rudolf Brüggemann[1], Max Meessen[1], Wolfram Witte[2], Dimitrios Hariskos[2], and Gottfried H. Bauer[1] — [1]Institute of Physics, Carl von Ossietzky University Oldenburg, Germany — [2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Stuttgart, Germany

Chalcopyrite absorbers exhibit spatial inhomogeneities in structural, optical and optoelectronic properties. We study the absorber thickness dependent behavior of the local properties such as the splitting of the quasi-Fermi levels, optical threshold energies and surface roughness of Cu(In,Ga)Se2-based (CIGSe) thin-film systems with different absorber thicknesses, which are realized by etching traditionally prepared absorbers with nominal thicknesses of about 2 μm with bromine-methanol followed by a cadmium sulfide (CdS) passivation. AFM measurements reveal a decrease in the surface roughness with decreasing absorber thickness, i.e., increasing etching time. Photolumienscence experiments with high lateral resolution allow the extraction of the optical threshold energies and the splitting of the quasi-Fermi levels. Furthermore we verify a depth gradient of the gallium concentration and a variation of quasi-Fermi level splitting depending on the absorber thickness. Additionally, we show that the CdS/CIGSe junction formation of an unetched absorber in comparison to an etched absorber leads to higher quasi-Fermi level splitting.

HL 68.11 Thu 13:00 FOE Anorg

Photoelectric properties of variably RTP processed $CIGS_2$ solar cells — •Julia Riediger[1], Jörg Ohland[1], Martin Knipper[1], Jürgen Parisi[1], Ingo Riedel[1], Roland Mainz[2], Saoussen Merdes[2], and Joachim Klaer[2] — [1]Energy and Semiconductor Research Laboratory, Department of Physics, University of Oldenburg, 26111 Oldenburg, Germany — [2]Helmholtz-Zentrum Berlin für Materialien und Energie Berlin GmbH, Glienicker Straße100, 14109 Berlin, Germany

The open circuit voltage V_{oc} of $CuInS_2$ solar cells was found to improve via incorporation of gallium. The Cu(In,Ga)S_2 absorber of the samples studied in this work was prepared by sputtering (Cu,Ga) and In precursors subsequently sulfurized via rapid thermal processing (RTP) in sulfur vapor. Distinctive top/bottom $CuInS_2$/$CuGaS_2$ segregation has been observed which extent depends on the substrate temperature and holding time of the temperature during RTP-process. The insufficient gallium accumulation at the surface impedes high values of V_{oc}.We studied the consequences of RTP-process parameter variation in regard of the interdiffusion of $CuInS_2$ and $CuGaS_2$. Quantum efficiency (QE) and temperature-/illumination-dependent current-voltage (IV) profiling have been carried out for differently processed samples. These measurements provide the minimum band gap E_g of the graded absorber layer, the temperature dependent V_{oc} and the activation energy E_a for carrier recombination. Drive level capacitance (DLCP) profiling reveals the spatially resolved in-depth variation of the doping/defect concentration close to the space charge region.

HL 68.12 Thu 13:15 FOE Anorg

Comparison of Photovoltaic Parameters of Cu(In,Ga)Se2 Thin Film Solar Cells with Infrared Images Obtained with Lock-In Thermography — •Torben Klinkert[1], Jörg Ohland[1], Robin Knecht[1], Jürgen Parisi[1], Raymund Schäffler[2], and Bernhard Dimmler[2] — [1]Thin Film Photovoltaics, Energy- and Semiconductor Research Laboratory, University of Oldenburg, D-26111 Oldenburg — [2]Würth Solar GmbH & Co. KG, Alfred-Leikam-Straße 25, D-74523 Schwäbisch-Hall

The performance of photovoltaic modules comprised of monolithically series connected solar cells is basically determined by the weakest element in the circuit. In chalcopyrite thin film modules lateral film inhomogeneities and losses due to interconnection are likely to deteriorate the photovoltaic performance of individual cell stripes and, in consequence, to reduce the module efficiency. In this work we correlate microscopic features with the macroscopic device parameters of Cu(In,Ga)Se2 solar cells cut from large-area modules. Imaging of the film imperfections and regions of enhanced joule heating was re-

alized by applying infrared Lock-In Thermography (LIT) with optical (I-LIT) and electrical (D-LIT) excitation of the sample. Via comparison of the infrared LIT images with the photovoltaic cell parameters obtained from STC current voltage profiling and quantum efficiency measurements we try to correlate macroscopic junction failure with microscopic disruptions of the film properties. These problems will also be discussed on the module level by analysis of D-LIT results obtained for individual cell stripes in an integrated series compound of a CIGSe-module.