Luminescence properties of Ga-graded Cu(In,Ga)Se$_2$ thin films

J. Haarstrich [a],[*], H. Metzner [a], C. Ronning [a], A. Undisz [b], T. Rissom [c], C.A. Kaufmann [c], H.W. Schock [c]

[a] Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany
[b] Institut für Materialwissenschaft und Werkstofftechnologie, Metallische Werkstoffe, Friedrich-Schiller-Universität Jena, Löbdergraben 32, 07743 Jena, Germany
[c] Helmholtz-Zentrum Berlin für Materialien und Energie, Solar Energy Research, Institute for Technology, Lise-Meitner-Campus, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

ARTICLE INFO

ABSTRACT

Cathodoluminescence (CL) has been measured at 10 K in cross-section and plan-view configuration on Cu(In, Ga)Se$_2$ thin films with Ga-grading as they are used in high-efficiency solar cells. Measurements on cross-section samples show the vertical profile of the emission energy to correspond to the band-gap profile of the film as calculated from measurements of the Ga-grading. Hence, the CL method is capable to directly measure the band-gap grading in semiconductor thin-films, but often the influence of the grading on the emission energy is generally ignored in recent literature. At the same time, we observe a strong drift of excited charge carriers toward the minimum of the band-gap. The transport process can be explained by the quasi-electric field induced by the Ga-grading and applied to determine transport properties of the Cu(In,Ga)Se$_2$ material. Implications for luminescence investigations on band-gap graded thin-films are discussed.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

In today's high efficiency solar cells based on Cu(In,Ga)Se$_2$ (CIGSe) absorber layers, the ratio $[Ga]/([Ga]+[In])$ (GGI) varies with depth and, hence, a grading in composition is commonly present in the layer [1,2]. Since, in turn, the band-gap varies with GGI (CuInSe$_2$ $E_g = 1.0459$ eV, CuGaSe$_2$ $E_g = 1.7305$ eV [3]), the grading in composition also introduces a grading in the band-gap. The variation of the band-gap through the addition of gallium has been shown to primarily occur in the conduction band position while the valence band remains mainly unaffected [4,5] and is discussed to be beneficial for solar cell performance [6]. However, an improper grading shape has been shown to lead to serious degradation of the cell performance [7,8] and, hence, an efficient control of the grading by characterization techniques is needed. In luminescence methods, electron–hole pairs are excited and their radiative recombination is observed spectrally and/or spatially resolved. The photon energy corresponds to the energy difference of the initial and the final state and carries information on the band-gap energy. In the recent literature, numerous investigations on the luminescence of Ga-graded CIGSe thin-films can be found, which interpret the spectra in relation to the integral GGI ignoring the presence of the grading [9–12].

After excitation, electron–hole pairs are subject to drift and diffusion mechanisms within their lifetime [13] in the conduction and valence band, respectively. This means that the recombination may occur in a place different from the one of excitation. Furthermore, it must be considered for correct interpretation of the data, that cathodoluminescence (CL) is commonly performed in a scanning electron microscope (SEM) and, thus, in a scanning mode. Therefore, the image observed always displays the distribution of the luminescence intensity as a function of the point of excitation, although the luminescence signal might originate from recombination at a different spot. Carrier diffusion processes will take place in any semiconducting material, but as they are thermally activated, they will be strongly suppressed at low temperatures. Drift mechanisms only occur, if some accelerating force is present, such as the electric field in the space charge region of a p-n junction. It has been shown theoretically [14] and experimentally [15,16] that, in graded-gap materials, drift of excited carriers is introduced by the grading of electron and hole affinity, respectively. This effect is commonly referred to as drift field [7], effective force field [14] or quasi-electric field [16]. The latter term will be used throughout this work.

In this study, the impact of the Ga-grading on the luminescence properties of CIGSe is investigated including the influence of the charge-carrier drift in the quasi-electric field. Therefore, samples from the same absorber deposition process were measured in three different geometries: (i) as pure absorbers on Mo-coated glass from the front, (ii) after lift-off from the back and (iii) in cross-section configuration. Local material properties are commonly determined by

measuring luminescence spectra as a function of the point of excitation (spectral imaging). We will show that those point spectra as well as data obtained from plan-view measurements on band-gap graded thin-films have to be interpreted very carefully.

2. Review on luminescence of Cu-poor Cu(In,Ga)Se$_2$

In the CIGSe material system, photoluminescence has been applied most often and a fairly deep understanding of the underlying processes has been achieved. The low-temperature luminescence of slightly Cu-poor material (as used for solar cell production) has been shown to be dominated by a broad emission 50–70 meV below the band-gap, which is found to be a donor–acceptor (DA) transition [17,18]. Additionally, it has been shown that the luminescence peak energy continuously shifts with the band-gap through the addition of Ga, i.e. with the GGI [19]. Therefore, the energy of this so-called DA1-transition, which can be determined by luminescence measurement, can be related via the band-gap to the GGI-ratio as shown in Fig. 1, where the energy of the DA1-transition E_{DA1} at low temperature (4–10 K) is plotted as a function of the GGI [17–22]. This way, the DA1-transition energy can act as a finger print of the band-gap of the corresponding phase of origin. In addition, the band-gap is shown as a function of GGI featuring a bowing factor of -0.167 [23] and band gaps of $E_{gap,CISe} = 1.045$ eV and $E_{gap,CGSe} = 1.720$ eV [19]. Rega et al. have introduced a defect model for CIGSe, which has been used in Fig. 1 to obtain the interpolated energy E_{DA1} for the whole range of GGI for stoichiometric material.

The DA1-emission is increasingly affected by strong potential fluctuations with decreasing Cu-content due to the strong self-compensation of the material [17,18,20,22]. This leads to several unusual features of the emission, such as an asymmetric broadening of the peak, a shift to lower energies with increasing degree of compensation and a strong blue-shift with excitation power [20]. Most literature data were obtained on Cu-rich or near-stoichiometric samples, but the numerous data points from pure CuInSe$_2$ and CuGaSe$_2$ [17,18,20,22] originate from samples with varying [Cu]/[III] stoichiometry and point out the decrease in emission energy with decreasing Cu content. As it has been shown [20], this decrease can be compensated for high injection densities, since saturation of the energy E_{DA1} can be reached in CL measurements at $E_{DA1,sat}$ which equals E_{DA1} of the stoichiometric material.

In this work, the influence of the grading is investigated and interpreted on the basis of this common luminescence model for homogeneous CIGSe described above.
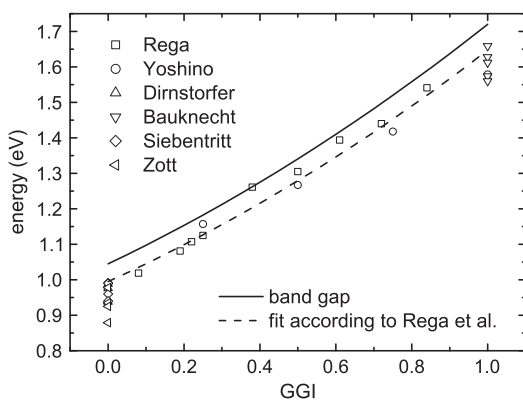

Fig. 1. Dependence of band-gap and DA1-energy of CIGSe as a function of GGI as determined by luminescence methods [17–22]. Rega [19] has introduced a defect model which allows to obtain the DA1-energy for any Ga-content (dashed line), the band-gap dependence was described according to the literature [19,23].

3. Experimental methods

Standard CIGSe thin-films with a thickness of about 2 μm were prepared by multi-stage co-evaporation onto Mo-coated soda-lime glass [2]. The integral stoichiometry was measured by means of X-ray fluorescence spectroscopy (XRF) to [Cu]/([In] + [Ga]) = 0.811(3) and GGI = 0.269(2). Solar cells made from these absorbers using the standard ZnO/CdS window structure [2] show efficiencies up to 17%. High-temperature absorbers as discussed toward the end of this study were prepared at increased substrate temperature of 610 °C compared to the standard process (530 °C) as described in Ref. [24].

The Ga-grading was measured by means of energy dispersive X-ray spectroscopy (EDS) using an Oxford device installed to a transmission electron microscope (TEM) JEOL JEM-3010 with LaB$_6$ cathode and using an EDAX device installed scanning electron microscope (SEM) JEOL SEM-6490 with LaB$_6$ cathode. The TEM-sample was prepared by lamella preparation with a focused ion beam FEI-Helios NanoLab 600i (using Ga-ions, final polishing at 5 kV, lamella thickness about 170 nm), whereas the SEM–EDS measurements were performed on a cross-section (broken from the sample) which was polished with diamond lapping foil. The measurement was performed in cross-section configuration; the absolute Ga-concentration of the profile was scaled through normalization to the XRF measured integral stoichiometry. The measurements were performed at an electron acceleration voltage U_e of 300 kV using the K-lines of the elements and 10 kV using the L-Lines for TEM and SEM data, respectively.

The CL measurements were performed in the same JEOL SEM-6490 with a Gatan monoCL3 attached. An (In,Ga)As photomultiplier was used for the detection of the infrared luminescent light. The samples were cooled to approx. 10 K and measured with an electron current I_e of 250 pA and an electron acceleration voltage U_e of 10 kV if not stated otherwise. The spectra were obtained while scanning an area of about 400 μm^2 and, hence, represent the luminescence averaged over a large number of grains.

As described in the introduction, samples from the same absorber deposition process were measured with CL in three different geometries. For configuration (ii) (from the back), the CIGSe absorber was glued with the front-side onto a sample holder using epoxy glue. Subsequent lift-off of the glass substrate made the Mo-layer come off the CIGSe layer and, thus, a pure CIGSe-surface was obtained. No molybdenum was detected by EDS measurement at 10 kV in an SEM. The cross-section samples (iii) were prepared by cutting stripes from the CIGSe-Mo stack which were glued together face to face using epoxy glue and then polished mechanically using diamond lapping foils in order to obtain a flat sample surface.

The EDS as well as all CL measurements were performed repeatedly and using samples from different absorber deposition processes. The data showed only minor differences between the individual thin-films and the model developed in this work was found to apply to all samples.

4. Results and discussion

4.1. Ga-grading and standard CL measurements

The GGI is shown as a function of depth z in Fig. 2 as it was determined using TEM–EDS and SEM–EDS on a cross-section sample, respectively. The two profiles are in very good agreement, also when compared to data obtained on comparable samples with secondary ion mass spectroscopy [25], and they illustrate the Ga-grading present in the CIGSe absorber layers used in this study. The grading has been identified to be due to real alloying of CuInSe$_2$ and CuGaSe$_2$ by X-ray diffraction at the very same samples [24]. The noise of the curves in Fig. 2 represents the error of the measurements. The shape of the grading is called double-grading with an increased GGI