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What is the dopant concentration in polycrystalline thin-film Cu(In,Ga)Se$_2$?

F. Werner *, T. Bertram, J. Mengozzi, S. Siebentritt

Laboratory for Photovoltaics, University of Luxembourg, Rue du Brill 41, L-4422 Belvaux, Luxembourg

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ABSTRACT

We compare the dopant concentration of polycrystalline Cu(In,Ga)Se$_2$ thin film absorbers derived from Hall and capacitance-voltage measurements. Although both measurements techniques appear to be reliable, dopant concentrations determined by capacitance-voltage analysis are significantly lower and vary with probing depth into the absorber. The doping profiles and differences between both measurement techniques are consistent with Cd in-diffusion from the CdS buffer layer during solar cell fabrication. Different doping profiles obtained after a variation of the CdS deposition process support this scenario.

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1. Introduction

The net dopant concentration of the absorber layer is a critical parameter for understanding and optimizing the performance of a thin film solar cell. The dopant concentration for example significantly affects the recombination rate and determines the properties of the space charge region (SCR) at the hetero junction. The two most commonly employed experimental techniques to determine the dopant concentration are electrical measurements of the Hall effect and of the voltage-dependent SCR capacitance (*C–V* measurements). Both are well-established standard characterization techniques and described in a large number of textbooks and review articles (see for example Refs. [1–6] for further information). However, both techniques are often applied to polycrystalline thin film absorbers without sufficient discussion of the validity of the approach, and the dopant concentrations obtained from both measurement techniques for comparable specimens often differ by more than one order of magnitude.

The basic equations governing interpretation of Hall and C–V measurements rely on simplified device models and make several assumptions, which are often not valid in realistic thin film photovoltaic devices. The original proof of the van-der-Pauw technique [7] by conformal mapping is based on the assumption of a homogeneous conductor. Due to the presence of grain boundaries, polycrystalline thin films can no longer be regarded as laterally homogeneous conductors, and care must be taken in the interpretation of Hall measurement on such films. Conventional capacitance-voltage analysis, on the other hand,

assumes a one-sided abrupt *p/n* junction, relies on an appropriate choice of equivalent electrical circuit, and is susceptible to capacitance contributions by deep defects. Particularly the assumption of a one-sided abrupt *p/n* junction is difficult to verify independently for typical chalcopyrite solar cells, as the *n*-doped side is formed by a complex multi-layer stack of differently doped buffer and window layers. To further complicate matters, Hall analysis is a lateral technique and requires an insulating substrate, while *C–V* analysis is a perpendicular technique and requires a conductive back contact.

In this contribution we compare Hall and *C–V* measurements of chalcopyrite thin film absorbers and solar cells, and assess the validity of the analysis.

2. Experimental details

Polycrystalline Cu(In,Ga)Se$_2$ (CIGSe) and CuInSe$_2$ absorbers were grown on blank and Mo-coated soda-lime glass (SLG) by physical vapor deposition in a molecular beam epitaxy system. We determine the chemical composition of the as-grown films by energy-dispersive X-ray (EDX) analysis. The Cu(In,Ga)Se$_2$ films are slightly Cu-poor with $[Cu]/([Ga] + [In]) \approx 0.98$ and a ratio of $[Ga]/([Ga] + [In]) \approx 0.3$. The CuInSe$_2$ films are grown under Cu-rich conditions and hence are assumed to be nearly stoichiometric.

We use pairs of blank and Mo-coated SLG substrates in the same deposition run to ensure identical deposition parameters on both types of substrates. The two different types of substrates are necessary because *C–V* analysis requires a conductive back contact, while Hall analysis requires an insulating substrate to prevent parasitic current flow through the back contact. The substrate temperature during growth is controlled

by an infrared heating source, and thus the additional metallic Mo layer might alter the sample temperature and influence the growth process. In order to exclude any influence of a temperature difference on the dopant concentration, we have mechanically detached the CIGSe film from a Mo-coated glass substrate for Hall measurements. This is achieved by gluing a glass substrate to the top of the CIGSe thin film. Application of mechanical force then leads to a detachment of the CIGSe from the smooth Mo surface.

All samples were etched in KCN after growth to remove any secondary copper-selenide phases and to ensure good electrical contacts. For the fabrication of Hall specimens, triangular gold contacts (contact area below 1 mm^2) with a thickness of 300 nm were defined on the corners of 5 × 5 mm^2 pieces of the sample by electron beam evaporation through a shadow mask. We determine the majority carrier concentration and Hall mobility by Hall measurements in the van der Pauw configuration [7] under varying magnetic fields of up to 9 T using a superconducting magnet in a closed-cycle cryostat. We assume a Hall scattering factor r of unity and infinitely small contacts. The sample temperature is measured at the back of the sample holder and is calibrated to be correct within ± 1 K. Due to the stabilization time required for the setup, all samples were kept in the dark for at least one day before the measurement.

For C–V analysis, absorbers grown on Mo-coated glass are processed into solar cells by chemical bath deposition of a CdS buffer layer and subsequent rf-sputtering of a double layer of i-ZnO/Al:ZnO. A Ni/Al grid is deposited as front contact by electron beam evaporation through a shadow mask. Individual cells with areas of 0.2–0.5 cm^2 are defined by mechanical scribing. After mounting in the shielded and evacuated cryostat, the sample is kept in the dark at a temperature of 300 K for at least one night before the measurement. The impedance spectrum is recorded with an Agilent E4980A Precision LCR Meter at frequencies of 100 Hz–1 MHz and an ac voltage of 30 mV, and the capacitance is extracted assuming a parallel equivalent circuit ("Cp-G" model).

3. Results and discussion

3.1. Hall analysis

Hall measurements of polycrystalline low-mobility thin films are challenging due to a small signal, limited by a small measurement current, compared to large offset voltages originating from imperfect alignment of the voltage probes on the highly resistive sample [7]. For the measurements in this study we have taken care to correct for these offsets: the sheet resistance is measured at each magnetic field in addition to the Hall voltage to account for resistivity variations, and the Hall coefficient is obtained from the linear slope of the magnetic-field-dependent Hall voltage over a wide range of magnetic fields between −9 T and +9 T. A detailed review of the correction procedures will be published in a separate manuscript. Fig. 1 shows the resulting effective hole concentration p and effective Hall mobility μ obtained by Hall measurements of three different samples as a function of inverse temperature 1000 / T. We compare one absorber grown on glass (black squares), the same device after chemical bath deposition of nominally 50 nm of CdS on top (red circles), and one other absorber grown in the same deposition run on Mo-coated glass and subsequently ripped off (blue triangles). Although we obtain somewhat comparable effective hole concentrations in the range of $3 \times 10^{16} – 1 \times 10^{17}$ cm^{-3}, the effective hole mobility differs by almost two orders of magnitude between the three different samples. For polycrystalline samples, however, the effect of grain boundaries on the Hall analysis has to be taken into account. We employ the model of Jerhot and Snejdar [8], where we assume thermionic emission over a potential barrier for majority carriers. As shown by the lines in Fig. 1 we can reproduce all three sets of data with a single set of material parameters, obtained from a fit to the data in Fig. 1 and summarized in Table 1, which only differ in the barrier height at the grain boundary (in addition, we have to assume a
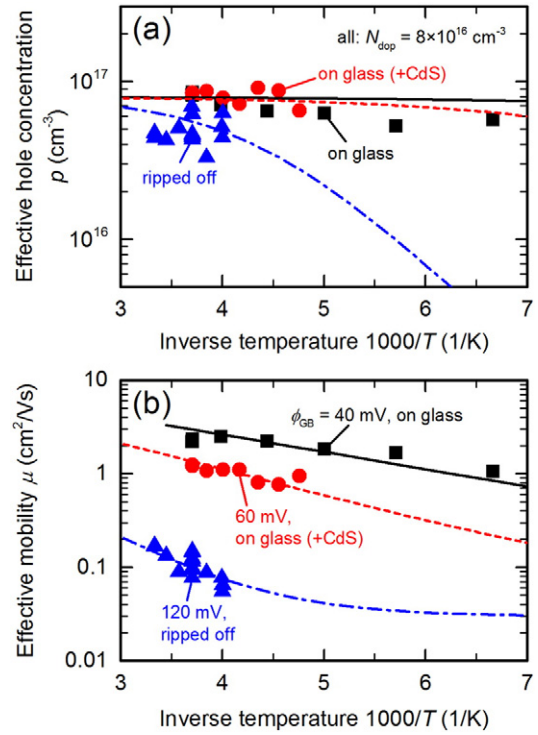
Fig. 1. (a) Effective hole concentration and (b) effective mobility obtained by Hall analysis of polycrystalline Cu(In,Ga)Se$_2$ thin film absorbers grown on glass (black squares, solid line), the same sample with nominally 50 nm CdS on top (red circles, dashed line); and grown on Mo-coated glass and then ripped off (blue triangles, dash-dotted line). Lines are best fits to a model of the Hall effect in polycrystalline films. The dopant concentration N_{dop} and barrier height at the grain boundary ϕ_{GB} are given in the graph, all parameters are summarized in Table 1.

slightly lower mobility within the grain boundaries after rip-off, which might be related to mechanical damage or glue entering the grain boundaries). The excellent agreement between model and experiment strongly supports the validity of the analysis and allows to derive the real in-grain carrier concentration from the measured apparent hole concentration. This leads to the conclusion that Hall analysis on polycrystalline CIGSe yields consistent and reliable results if grain boundaries are taken into account. Furthermore, the presence of a Mo back contact during the growth process does not significantly affect the dopant concentration in the absorber film, neither does ripping off the film modify the in-grain "bulk". The dopant concentration of all three films shown in Fig. 1, obtained by Hall analysis, is then $(8 \pm 3) \times 10^{16}$ cm^{-3}.

3.2. Capacitance–voltage analysis

For a direct comparison, we process solar cells from absorbers grown on Mo-coated glass in the same deposition run as those analyzed by Hall analysis in Section 3.1. Fig. 2(a) shows the inverse squared capacitance

Table 1
Model parameters for the Hall analysis taking into account the effect of grain boundaries (GB), obtained by fitting the temperature-dependent Hall data.

Model parameter	Value
Dopant concentration	8×10^{16} cm^{-3}
GB barrier height	40/60/120 mV
In-grain mobility	30 cm^2/Vs
GB mobility	0.9 cm^2/Vs
- after rip-off	*0.6 cm^2/Vs*
Relative size GB/grain	0.05