Influence of copper excess on the absorber quality of CuInSe$_2$

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The compositional dependence of the optoelectronic quality of CuInSe$_2$ thin film absorbers is investigated on single- and polycrystalline films with varying [Cu]/[In]-ratios. We quantify the quality of the absorbers by the splitting of quasi-Fermi levels, determined by spectral photoluminescence. This quantity determines the maximum achievable open circuit voltage by an absorber. Our results indicate a significant increase of this value for growth under Cu-excess, indicating a decrease of recombination losses. By comparison of the predicted achievable open circuit voltage and the actually measured ones of finished solar cells, we find a huge “un-utilized potential” for the Cu-rich devices. © 2011 American Institute of Physics. [doi:10.1063/1.3648111]

The chalcopyrite absorber copper indium/gallium diselenide Cu(In,Ga)Se$_2$ (CIGSe) has entered the stage of thin film solar cell mass production with module efficiencies of up to 15.7% and world record efficiencies above 20% for small laboratory scale devices. Chalcopyrites are well known to form a stable phase at significant deviations from stoichiometry ranging from copper poor ([Cu]/[In] < 1) to copper rich ([Cu]/[In] > 1). In today’s best solar cells, the composition is in the range of [Cu]/[In] ≈ 0.9.

For Cu-poor samples, the resulting composition of the bulk is copper poor ([Cu]/[In] < 1). For Cu-rich growth processes, we always find a stoichiometric chalcopyrite bulk ([Cu]/[In] = 1) plus a Cu$_x$Se secondary phase on the surface, formed by the excess copper. Therefore, the term “Cu-rich” does not refer to the actual composition of the CIGSe bulk, but to the overall [Cu]/[In] ratio measured by energy-dispersive x-ray spectroscopy (EDX) as the average composition of the unetched film, containing CIGSe and Cu$_x$Se. Although the composition of CIGSe stays stoichiometric at Cu-rich growth, the electronic material properties of CIGSe absorbers are determined by the respective copper excess during growth. Several publications have reported on the role of the copper content on material properties investigated by Hall and photoluminescence (PL) studies. The results indicate an improvement of several single material properties of chalcopyrite absorbers grown under copper excess, i.e., increase of the charge carrier mobility, decrease of the defect concentration, and increased excess charge carrier concentration under illumination. Still, the overall effective influence of Cu-excess on general absorber and device quality has not been investigated in detail.

In this paper, we are focusing on the ternary chalcopyrite CuInSe$_2$ (CISe) and investigate the role of the Cu/In ratio on the resulting absorber quality, in terms of the effective quality of the photo excited state. This property is quantitatively determined by the splitting of quasi-Fermi levels, which we extract from PL measurements. The applied technique generally allows to predict the potential solar cell performance, particularly the maximum achievable open circuit voltage, already at a very early fabrication step, before the absorber undergoes the steps to a final device.

We investigate a sample series of single crystalline absorbers grown by metalorganic vapor phase epixp and a series of polycrystalline films grown by co-evaporation. Each sample series contains specimen grown at various copper contents ranging from copper poor ([Cu]/[In] < 1) to copper rich ([Cu]/[In] > 1).

The analysis of single crystalline layers allows for investigation of bulk properties in the absence of grain boundaries. Furthermore, disturbances of the optical measurements due to different grain sizes and surface roughness can be neglected. The analysis of the polycrystalline absorber series allows for a comparison with the actual solar cell parameters of devices, which are fabricated from the same polycrystalline absorbers. This comparison is limited to the polycrystalline sample series as devices fabricated from epitaxial absorbers achieve only marginal efficiencies, suffering from contact problems.

The single crystalline epitaxial CISe thin films were grown on GaAs (001) wafers in a horizontal metalorganic chemical vapor deposition (MOCVD) reactor at 50 mbar pressure and 470°C. Precursors are Cyclopentadienyl-Copper-Triethyl-Phosphine, Trimethyl-Indium, and Diterti-ary-Butyl-Selenide. The samples have a thickness of 700–800 nm. All flows and partial pressures are kept constant during the growth process. More details about this process and a general description of the resulting structure of epitaxial chalcopyrite films were reported elsewhere.

The polycrystalline CuInSe$_2$ thin films were grown on molybdenum/soda lime glass substrates in a molecular beam epitaxy (MBE) chamber by co-evaporation via a modified three-stage process. Cu rich films are obtained by processes finishing after the second stage with varying the duration of the second stage. Cu poor films are grown by the full three-stage process. Cu-rich films are obtained by processes finishing after the second stage with varying the duration of the second stage. Cu poor films are grown by the full three-stage process with different durations of the second stage. Cu-rich films are obtained by processes finishing after the second stage with varying the duration of the second stage. Cu poor films are grown by the full three-stage process with different durations of the second stage.
very thin epitaxial films, additional PL measurements at 10 K were done to compare specific PL fingerprints for different compositions, as described by Rega et al.\textsuperscript{5}

Solar cells are prepared in standard CIS/Se/CdS/ZnO design. However, the Cu-rich samples were treated with an aqueous KCN solution before to remove any Cu,Se.\textsuperscript{18}

PL measurements are performed at room temperature and at T = 10 K using the 514.5 nm line of an argon ion laser as excitation source. The collected PL photons are dispersed in a 0.3 m spectrometer and detected by an InGaAs detector array. To allow for the evaluation of the quasi-Fermi level splitting from the measured PL, the setup is spectrally calibrated with a calibration lamp for counting absolute photon numbers. At room temperature, the samples are excited with a photon flux of $3 \times 10^{17} \text{cm}^{-2} \text{s}^{-1}$, which is equivalent to AM1.5. All PL measurements are performed on blank absorbers, without any surface coverage.

The PL spectra are evaluated with respect to Planck’s generalized law\textsuperscript{19}

\begin{equation}
Y_{\text{PL}}(\omega) = A(\omega) \frac{\Omega}{4\pi} \frac{(h\omega)^2}{e^{(h\omega/E_F)} - 1},
\end{equation}

Here, $A(\omega)$ is the absorptivity, $\Omega$ is the solid angle of detection, $h\omega$ is the photon energy, and $E_F$ is the splitting of quasi-Fermi levels. As described elsewhere in detail,\textsuperscript{11,12,20} the splitting of the quasi-Fermi levels is evaluated by Eq. (1). The absorptivity $A(\omega)$ can be approximated as unity, as only the spectral regime above the band gap is relevant for this evaluation. Accordingly, the high energy wing of the spectra is evaluated by fitting the effective sample temperature $T$ and the splitting of the quasi-Fermi levels $\mu = E_{Fp} - E_{Fp}$.\textsuperscript{15}

In Figs. 1(a) and 1(b), we show the results for both sample series, as a function of the composition. The results for the epitaxial samples show a clear trend in the range $[\text{Cu}] / [\text{In}] < 1.1$, increasing significantly towards higher copper contents from $\approx 400 \text{meV}$ to $\approx 570 \text{meV}$ in an approximately linear behaviour. The one sample grown at very high copper supply ($[\text{Cu}] / [\text{In}] \approx 1.5$) departs clearly from this behaviour showing a decreased value. The results for the polycrystalline sample series in Fig. 1(b) show a similar behaviour: a clear increasing trend in the range $[\text{Cu}] / [\text{In}] < 1.2$ from $\approx 300 \text{meV}$ to $\approx 450 \text{meV}$ and a levelling off for samples grown at highest copper supply. The polycrystalline sample indicated with a filled circle is excluded from this observation, as it shows a clear departure from the trend of the neighbouring samples of $\approx -100 \text{meV}$. This discrepancy is observed in the solar cell results as well and will be discussed below.

That is to say that both sample types show a clear trend: an increase of the splitting of the quasi-Fermi levels when going from Cu-poor to Cu-rich absorbers. For very high copper supply, we find a stagnation and deterioration of the absorber quality. In the entire region $[\text{Cu}] / [\text{In}] < 1.2$, the values of the epitaxial series are $\approx 100 \text{meV}$ higher than the polycrystalline samples, indicating a higher absorber quality and less recombination for the epitaxial films, confirming an increase of recombination due to grain boundaries.\textsuperscript{21,22} The drop of the quasi-Fermi level splitting for the epitaxial sample at the highest copper content can be due to a strong increase of surface roughness and facets at higher Cu-excess,\textsuperscript{15} which may reduce the quality of the epitaxial films.

As the splitting of the quasi-Fermi levels determine the maximum achievable open circuit voltage in a device,\textsuperscript{19} these results allow the prediction that devices prepared from Cu-rich absorbers should achieve higher open circuit voltages than the Cu-poor specimen, given that nothing else during device preparation changes. Note that blank absorbers (no CdS cover) usually have unpassivated surface defects,\textsuperscript{23} which reduce the effective splitting of quasi-Fermi levels. This reduction was quantified for two polycrystalline samples by measuring after etching and after aging and amounts to around $\approx 180 \text{meV}$.

Fig. 2(a) depicts the measured open circuit voltages ($V_{\text{oc}}$) of the final solar cells. In the range of $[\text{Cu}] / [\text{In}] \approx 0.9–0.95$, where usually good devices are fabricated, we find values in the range of $V_{\text{oc}} \approx 450–500 \text{mV}$. For samples grown at higher Cu/In ratios, we observe a significant decrease of the values down to $V_{\text{oc}} \approx 350 \text{mV}$ for the highest copper contents.

The sample indicated with a filled circle shows a significant drop of the device performance for this sample, not fitting into the observed general trend. This sample shows a $V_{\text{oc}}$ of $\approx 150 \text{mV}$ below the neighbouring samples. The rather poor performance of this specimen could be expected already by the observation of the quasi-Fermi level splitting of the same sample in Fig. 2(b). There we already see a lower value of $\approx 100 \text{meV}$ when compared to the general trend line. This demonstrates that the PL method can be applied as a useful tool on chalcopyrite fabrication to sort out poor quality absorbers directly after growth.
The trend of the resulting $V_{oc}$ is in clear contradiction to the predicted behaviour and was reported earlier.\textsuperscript{24,25} The efficiency drop for higher copper contents was explained by higher recombination losses at the interface between CdS and Cu-rich CISE.

Concluding these results, we can state that the absorbers grown at reasonable copper excess show the largest quasi-Fermi level splitting, promising a higher $V_{oc}$. Simultaneously recombination losses occur at the CdS/CISE interface as the copper content is increased.\textsuperscript{24,25} Therefore, it can be interpreted that this loss mechanism is much more deteriorating for the efficiency than the shown improvement of the bulk absorber quality, quantified by the quasi-Fermi level splitting.

In Fig. 2(b), we plot the relative difference of the splitting of quasi-Fermi levels in the absorbers and the resulting open circuit voltage ($E_{Fp}$–$E_{Fn}$) – $eV_{oc}$ for the finished devices. We observe a significant increase of the departure between predicted and resulting values for increasing [Cu]/[In] ratios. This can be interpreted as an un-utilized potential for achieving a higher $V_{oc}$, which is being hampered by the mentioned recombination losses at the interface. This un-utilized potential which is not accessible with the standard CISE/CdS/ZnO configuration is $\approx 200$ meV larger for the Cu-rich devices than for the Cu-poor specimen.

It appears that the heterojunction in today’s devices is well optimized only for Cu-poor devices but suffers significant losses with Cu-rich absorbers. According to the quasi-Fermi level splitting, the absorbers grown in the range [Cu]/[In] $\approx 1.1$–$1.2$ promise a maximum achievable $V_{oc}$ which is in the range of $\approx 100$ mV higher than the samples from today’s high efficiency region at [Cu]/[In] $\approx 0.9$.

It appears that either the CdS/CISE interface has to be improved to suite Cu-rich grown CISE absorbers or alternative buffers and/or window layers have to be tested for the Cu-rich case to access the un-utilized potential. In a recently reported approach, the surface of copper rich absorbers is switched to copper poor by an In-Se treatment, whereas the bulk maintains the copper rich properties. This leads to a significant improvement of the performance of cells from copper rich grown absorbers\textsuperscript{26} and towards a higher exploitation of the un-utilized potential discussed in this manuscript.

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\textsuperscript{1}M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, \textit{Prog. Photovoltaics} \textbf{19}(1), 84 (2011).