Combined electron backscatter diffraction and cathodoluminescence measurements on CuInS₂/Mo/glass stacks and CuInS₂ thin-film solar cells

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Electron backscatter diffraction (EBSD) and cathodoluminescence (CL) measurements in a scanning electron microscope were performed on cross sections of CuInS₂ thin films and ZnO/Cds/CuInS₂/Mo/glass thin-film solar cells. The CuInS₂ layers analyzed for the present study were grown by a rapid thermal process. The regions of the CuInS₂ layers emitting high CL intensity of band-band luminescence are situated near the top surface (or close to the interface with ZnO/CdS). This can be attributed to an enhanced crystal quality of the thin films in this region. The phenomenon may be related to the recrystallization via solid-state reactions with Cu₃S phases, which is assumed to run from the top to the bottom of the growing CuInS₂ layer. The distribution of CL intensities is independent of the sample temperature, the acceleration voltage of the electron beam, and of whether or not the ZnO/CdS window layers are present. When comparing CL images and EBSD maps on identical sample positions, pronounced intragrain CL contrast is found for individual grains. Also, it is shown that at random grain boundaries, the decreases in CL intensities are substantially larger than at Σ3 grain boundaries. © 2010 American Institute of Physics. [doi:10.1063/1.3275046]

I. INTRODUCTION

Chalcopyrites with the chemical formula AᴵBᴵᴵᴵCᴵ𝑉₂ have been investigated as absorbers in thin-film solar cells for more than 30 years. However, only recently, such solar cells have been commercialized by a rapidly growing industry. One of these chalcopyrite-type compounds is CuInS₂, which may be deposited by a so-called rapid thermal process (RTP) when aiming for high throughput in an industrial baseline. The best thin-film solar cells with RTP-CuInS₂ absorbers have exhibited conversion efficiencies of up to 11.4%.¹ Although the research on and development of these solar cells have been conducted for several decades, the detailed knowledge of the optoelectronic properties of CuInS₂ thin films is still limited.

For semiconductor devices, cathodoluminescence (CL) performed in a scanning or transmission electron microscope represents an important technique to obtain information on optical and electronic properties at a high spatial resolution down to several tens of nanometers. A general introduction into CL can be found in the review by Yacobi and Holt.² Another technique applied in scanning electron microscopy (SEM) is electron backscatter diffraction (EBSD), which gives information on the size and orientation of individual grains, also at a high spatial resolution of several tens of nanometers. Since the orientations of two adjacent grains can be determined, the EBSD technique allows for the classification of individual grain boundaries. A more extended overview on EBSD maps from chalcopyrite-type thin films in solar cells can be found in Ref. 3.

The present contribution reports on CL analyses performed on cross sections of CuInS₂/Mo/glass stacks and also on completed solar cells with the stacking sequence ZnO/Cds/CuInS₂/Mo/glass, where the p-n junction is formed at (or in the vicinity of) the interface between the n-type ZnO/CdS and the p-type CuInS₂. The cross-section configuration for the analyses was chosen in order to characterize directly spatially extended features that may impact the current transport and voltage in the solar cells. The influences of various acquisition parameters, as well as those of diverse cross-section sample preparation methods, on the CL signals were investigated. It will be shown that the acquisition of EBSD and CL maps on identical areas is useful if conclusions on the electronic properties of individual grains or grain boundaries are to be drawn.

II. EXPERIMENTAL DETAILS

The CuInS₂/Mo/glass stacks and the CuInS₂ thin-film solar cells studied in the present work were produced in the following way. Cu and In layers (with thicknesses of 550 and 650 nm) were sputtered on soda-lime glass substrates coated with a 0.5 μm Mo back contact layer. The Cu/In stack was exposed to sulfur during a rapid thermal annealing step (heating-up rate 10 K/s) with a final temperature of nominally 530 °C held for about 3 min, resulting in the formation of a 2–3 μm thick CuInS₂ film. Since the [Cu]/[In] ratio was about 1.6, Cu–S forms on top of the CuInS₂ layer, which is removed by a KCN etch after film preparation.

The solar cells were completed by chemical bath deposition of a CdS buffer layer (50 nm), sputtering of a transparent ZnO/ZnO:Al bilayer (100 nm/500 nm) front contact, and a Ni/Al contact grid. For further details on the solar-cell production, the reader is referred to Ref. 1. The solar-cell performances of all samples studied for the present work are summarized in Table 1.

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TABLE I. The solar-cell parameters (open-circuit voltage $V_{oc}$, short-circuit current density $J_{sc}$, fill factor $ff$, and solar-cell efficiency $\eta$) of the completed solar cells used for the present work.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>692</td>
<td>21.4</td>
<td>68</td>
<td>10.1</td>
</tr>
<tr>
<td>2</td>
<td>563</td>
<td>22.7</td>
<td>66</td>
<td>8.4</td>
</tr>
<tr>
<td>3</td>
<td>684</td>
<td>21.8</td>
<td>65</td>
<td>9.7</td>
</tr>
</tbody>
</table>

For CL and EBSD analyses, various preparation methods were applied.

1. Cutting stripes from the CuInS$_2$/Mo/glass stacks and the CuInS$_2$ solar cells, which were glued together face to face by the use of epoxy glue. The cross sections were polished mechanically using diamond lapping foils and also by the use of an Ar-ion polishing machine, using incident Ar-ion beam angles as low as 4°. Graphite layers of nominally 4–5 nm thickness were deposited on top of the cross-section samples in order to reduce the drift during the CL and EBSD measurements (sample 1).

2. Cutting a cross section at the edge of a ZnO/CdS/CuInS$_2$/Mo/glass stack by the use of a ZEISS CrossBeam 1540 scanning electron microscope, which is equipped with a focused ion beam (FIB Ga ions), at an ion beam voltage and current of 30 kV and 2 nA (sample 2).

3. Fracturing a CuInS$_2$/Mo/glass stack in order to obtain a cross section. For comparison, CL was also performed in plan-view configuration on this CuInS$_2$/Mo/glass stack (sample 3).

The CL analyses were performed on two setups:

I. a ZEISS DSM962 scanning electron microscope equipped with a tungsten filament and a MonoCL2 CL system (CL setup I) and on

II. a ZEISS ULTRA55 scanning electron microscope equipped with a field-emission gun (FEG) and a MonoCL3 system (CL setup II).

In setup I, the CL signal is detected by a liquid-nitrogen cooled photomultiplier tube (PMT) R5509-72 with an InP/InGaAs photocathode (spectral range: 300–1700 nm), while setup II consists of a PMT R943-02 with a GaAs photocathode (spectral range: 160–930 nm). Both scanning electron microscopes are equipped with a He-cooling stage allowing for sample temperatures between 6 and 300 K. The reason of combining setups I and II in the present study is that setup II (FEG) provides an enhanced spatial resolution compared with setup I (tungsten cathode), whereas setup I covers a larger spectral range than setup II.

The photoluminescence (PL) spectrum was recorded at 300 K using a 668 nm semiconductor laser as an excitation source. The luminescence radiation is analyzed by a grating monochromator and a low-noise InGaAs linear image sensor. The excitation spot had a diameter of approximately 100 μm, and the excitation intensity was about 100 W/cm².

![Image](https://via.placeholder.com/150.png?text=Image+of+a+sample+section)

FIG. 1. (Color online) EBSD pattern quality map with Σ3 grain boundaries highlighted by intensified (red) lines, acquired on a polished cross section (see method 1 above).

The EBSD maps were acquired on the identical sample areas as the corresponding CL measurements by using a LEO GEMINI 1530 scanning electron microscope equipped with a FEG and a NordlysII-S EBSD detector from Oxford Instruments HKL. The acceleration voltage applied was 20 kV, and the probe current was about 1 nA. The EBSD patterns were acquired and evaluated using the Oxford Instruments HKL software package CHANNEL5. EBSD maps were recorded with point-to-point distances of 50–100 nm and with recording durations of about 80–120 ms at each point.

III. RESULTS AND DISCUSSION

A. The RTP-CuInS$_2$ microstructure

An exemplary EBSD pattern quality map from a polished cross-section sample is given in Fig. 1. The high relative frequency of Σ3 (twin) boundaries (the Σ value is introduced in Ref. 4), given as (red) lines, can be attributed to the rapid growth rate of the RTP-CuInS$_2$ layer, which leads to large strains in the thin film. Since the chalcopyrite-type crystal structure of CuInS$_2$ exhibits a low enthalpy for stacking-fault formation, this mechanism (where twin boundaries are special cases of stacking faults) may help to reduce the strain in CuInS$_2$ thin films during growth and cooling down. Note that there is not any significant difference between the average grain sizes for CuInS$_2$ regions close to the ZnO/CdS layers and for those situated near the Mo back contact.

B. Influence of the stacking sequence and sample preparation methods on CL intensities

A comparison of CL spectra obtained from cross sections of a CuInS$_2$/Mo/glass stack and a completed solar cell (with stacking sequence ZnO/CdS/CuInS$_2$/Mo/glass), both prepared by method 1, at identical acquisition parameters [room temperature (RT) and 10 kV acceleration voltage] is given in Fig. 2. Background noise from the glass substrate was subtracted. Also included is a PL spectrum recorded at RT on a CuInS$_2$/Mo stack. Apparently, there are two intensity maxima, one at about 820 nm, which can be related to the band-band transition in CuInS$_2$, and the other one at about 1050 nm, which can be attributed to transitions via deep defects, which have not been identified so far. It is evident that the two spectra do not differ significantly in the vicinity of the peak at 820 nm; i.e., the properties of the luminescence spectrum of CuInS$_2$ in this wavelength range can be...
considered independent of whether ZnO/CdS layers are present or not in the layer stack. The positions of the dominant peaks of these CL spectra agree well with those of the PL spectrum acquired on a CuInS₂/Mo/glass stack comparable to the samples studied by CL.

Figure 3 shows the CL spectra acquired by the use of setup II, for cross sections prepared by methods 1–3 as well as for the plan-view sample. The CL acquisition parameters were kept identical for all these measurements (RT, 10 kV, and identical acquisition window size). Apparently, the peak intensities at about 820 nm (band-band transitions) are larger for the cross section prepared by polishing and for the plan-view sample. The fractioned cross section and the one prepared by FIB exhibit peak intensities that are substantially lower than that of the polished cross section. Furthermore, it is found that the CL intensities at 820 nm decrease from about 5000 (10 kV) to 100 (5 kV) for the FIB-prepared cross section (not shown here), whereas this decrease is much smaller for the polished cross section with a graphite layer (from about 13 000 at 10 kV to about 10 000 at 5 kV; data not shown here).

These differences hint to substantially differing influences of the cross-section surfaces on the radiative recombination for the samples prepared by methods 1–3. The cross sections prepared by FIB are known to contain a Ga contamination layer, which may be responsible for enhanced surface recombination. Although the thickness of the Ga contamination layer, in principle, may be reduced considerably by reducing the ion beam energy, this is to be optimized for future works. On the other hand, the polished cross sections exhibit the highest CL yield, which may be due to a thin graphite layer (4–5 nm) deposited on the sample surface. This graphite layer may modify the surface potential and/or change the charging of the surface caused by the impinging electron beam. In either case a change in the band bending at the surface of the p-type CuInS₂ absorber layer is expected, resulting in a reduced surface recombination velocity for minority carriers.

C. Spatial distribution of CL signals

A comparison of CL images obtained at 820 nm by CL setups I and II is given in Figs. 4(a) and 4(b), which show results from a stack formed by gluing two RTP-CuInS₂ solar cells face to face together. There, the CL signals are super-
imposed on the secondary electron (SE) image in order to illustrate where in the layer stack the CL signals are emitted from. Apparently, the lateral CL intensity distribution is similar for both detectors. The SE images in Figs. 4(b) and 4(c) are somewhat blurred since a high beam current was chosen on the SEM with the tungsten cathode in order to improve the spatial distribution of the CL intensity.

In Fig. 4, CL emission can be detected mainly from the CuInS2 layer (the glass substrate also emits very weak CL signals). Most of the regions in the CuInS2 layer with high CL intensity at 820 nm [Fig. 4(b)] are situated close to the interface with the ZnO/CdS layers. In contrast, most of the regions in the CuInS2 layer with high CL intensity at 1050 nm [Fig. 4(c)] are rather close to the interface with the Mo back contact. This behavior becomes apparent particularly when the CL signals in Figs. 4(b) and 4(c) are superimposed on each other [Fig. 4(d)].

The CL intensity distribution in CuInS2 at 820 nm with high intensities mainly close to the ZnO/CdS layers was confirmed on several other sample regions; see Fig. 5(a) for an example. The situation is still similar when lowering the nominal sample temperature from RT to 5 K [Fig. 5(b)]. CL maps obtained at both RT and 5 K resolve small features down to about 50–100 nm, and the resolution does not change substantially at very low temperatures. This indicates that the grain-boundary recombination velocity is large, and that the effective minority-carrier diffusion lengths in the RTP-CuInS2 are also in the order of 100 nm. A more detailed analysis of the relationship between CL contrast and minority-carrier recombination properties will be given in a forthcoming publication.

Also for the CuInS2/Mo/glass stack without ZnO/CdS, most of the regions in the CuInS2 layer with high CL intensity at 820 nm seem to be situated close to the CuInS2 surface, similar as for the completed solar cells. This result shows that the ZnO/CdS layers apparently do not influence the spatial distribution of the CL intensity.

D. Implications for RTP-CuInS2 growth mechanism

The emission of CL signals in a semiconductor is a process induced by the incident electron beam, which generates electron-hole pairs. These charge carriers diffuse and then recombine. Recombination of electrons and holes may be associated with the emission of photons, as expected if an electron and a hole from states close to the edges of the conduction and the valence bands recombine. However, when the recombination occurs via deep levels positioned close to the middle of the band gap of the semiconductor, the process is likely to be nonradiative (e.g., phonon assisted or accompanied by Auger-electron emission).

Therefore, the CL intensity depends on the generation rate of electron-hole pairs as well as on the probability of radiative and nonradiative recombinations. Assuming laterally homogenous generation rates, the CL intensities at RT and 820 nm (band-band transitions) can be expected to be high where only a few deep defects are present, as, e.g., in crystals with small densities of crystal defects. This may be the case for the major part of the near-surface regions (or those close to ZnO/CdS for completed solar cells) in the RTP-CuInS2 layers, as shown in Figs. 4 and 5 (note that there are some regions exhibiting high CL intensity at 820 nm also close to the Mo back contact).

On the other hand, from the results shown above, it can be concluded that the density of crystal defects is larger for the major part of the regions in RTP-CuInS2 close to the Mo back contact. Rudigier et al. found a correlation between the peak intensity around 1050 nm in the PL spectra with an increased full width at half maximum (FWHM) of the A1 Raman mode by combined PL and Raman spectrometry on RTP-CuInS2 layers. The increase in the FWHM of the A1 mode again can be attributed to a decrease in the phonon correlation length, caused by a larger density of localized and spatially extended defects in the lattice.

In order to understand why the crystalline quality of the sample regions close to the surface (close to the ZnO/CdS layers) may be enhanced compared with those close to the Mo back contact, it is helpful to consider the RTP-CuInS2 growth process in more detail. Sputtered Cu and In layers are deposited on Mo-coated glass substrates. Cu diffuses into the In top layer to form a Cu-In alloy. This layer stack is exposed to sulfur molecules in a closed reaction chamber (Fig. 6). For high sulfur partial pressures, it was found that...
CuInS$_2$ forms at an early stage of the process. Sulfur diffuses from the surface to the bottom of the layer stack, whereas Cu and In diffuse into the opposite direction. Since the Cu/[In] ratio is larger than 1, Cu$_x$S forms on top of the CuInS$_2$ layer. These two compounds exhibit crystal structures that resemble each other. It is assumed that the CuInS$_2$ grain growth is substantially assisted by an exothermic solid-state reaction between Cu$_x$S and CuInS$_2$, which includes the exchange of cations while the sulfur substructures remain nearly unaffected. Rodriguez-Alvarez et al. showed by EBSD maps acquired on cross sections of annealed CuInS$_2$/Cu$_x$S stacks (where the as-grown CuInS$_2$ layers exhibit rather small average grain sizes) that the average grain size of the recrystallized CuInS$_2$ (after annealing) increases for larger thicknesses of the Cu$_x$S layer.

It is important to point out here that EBSD maps of various RTP-CuInS$_2$ layers (see Fig. 1 for an example) do not reveal any significant difference in average grain size between the CuInS$_2$ regions close to the ZnO/CdS layers and those situated near the Mo back contact. Therefore, it can be assumed that after crystallization (running from the top to the bottom), point and extended defects (and not smaller average grain sizes) are to be found in the vicinity of the Mo back contact. On the contrary, CuInS$_2$ grains present in the near-surface region correspond to a crystallization seed layer; thus, they may exhibit an enhanced crystal quality with a significantly smaller density of crystal and electronic defects.

E. CL and EBSD measurements on identical sample positions

From the CL images shown in Figs. 4 and 5, it may be concluded that the intensity distributions represent closely the microstructure in the RTP-CuInS$_2$ thin films. In order to verify this assumption, identical sample positions in several ZnO/CdS/CuInS$_2$/Mo/glass and CuInS$_2$/Mo/glass stacks were analyzed by means of CL and EBSD. Figure 7 gives an
overview of the various details, which can be extracted from the CL images and EBSD maps. When reducing the sample temperature to 6 K and the acceleration voltage to 5 kV [Fig. 7b], much smaller details of down to 50 nm are resolved as compared to the CL map acquired at RT and 10 kV [Fig. 7a]. Note that the improvement of the resolution is attributed to the decrease in acceleration voltage, not to that of the sample temperature (see also Fig. 5). The distribution of the local orientations perpendicular to the Mo substrate [Fig. 7d] appears to be random, as it was also confirmed by EBSD texture measurements performed on large areas (not shown here). It was not possible to correlate the CL intensity distribution at 820 nm to that of the local orientations.

In CuInS₂ thin films, grain boundaries can be divided roughly into (near) Σ3 (twin) boundaries and other grain boundaries, in the following called “random” (see Ref. 3 for details). The Σ3 (twin) boundaries exhibit the most frequent grain-boundary type in RTP-CuInS₂, as visible in Fig. 7(c). From the EBSD data, their relative frequency can be estimated to about 75%–80%. Also, Σ3 (twin) boundaries can be expected to be less electrically active than random boundaries, due to a lower density of dangling and distorted atomic bonds.

Indeed, it has already been shown [15] that the CL intensity in RTP-CuInS₂ decreases more strongly at random than at Σ3 (twin) boundaries. This result is confirmed by the present work [see, e.g., Fig. 8(c)]. Moreover, it is shown in Fig. 8 that individual grains, as determined by EBSD [Fig. 8(b)], consist of regions with different CL intensity [Fig. 8(a)]. In the example given in Fig. 8, the CL signal from the grain highlighted by a (yellow) circle appears divided into a high-intensity part close to the ZnO/CdS layers and a low-intensity part near to the Mo back contact. The latter region seems to be again divided into smaller areas by lines of further decreased CL intensities. These phenomena may be attributed to planar crystal defects such as dislocations or other extended defects [probably not twin boundaries, which do not lead to strong decreases in CL intensity, as shown in Fig. 8(c)]. Obviously, these planar defects are not detected by EBSD but may contain a certain density of electronic defect states, which affect the CL signal.

A further example of how easily CL images may be misinterpreted without the knowledge of the corresponding microstructure is given in Fig. 9. At several positions, the CL map [Fig. 9(a)] exhibits regions containing lines of reduced CL intensity (two of such regions are highlighted by yellow circles). It appears that these lines can be attributed to grain boundaries. However, the EBSD map in Fig. 9(b) shows that the regions within the yellow circles are indeed single crystals without any grain boundary. By examining SEM images from the identical position (not shown here), it was also verified that the lines of reduced CL intensity are not due to...
However, this may explain only for some regions why EBSD detects a contiguous grain, while the CL results indicate extended defects at the identical sample position. Especially in view of the large grains present in Figs. 8–10 with 2–4 μm in diameter, this explanation seems not sufficient. Rather, it may be assumed that, in general, the CL intensity is affected considerably even by small defect densities that do not involve a change in crystal orientation, which again is the only information to be gathered by EBSD, apart from changes in crystal structure.

IV. CONCLUSIONS

CuInS₂ thin films grown by a RTP in ZnO/CdS/CuInS₂/Mo/glass and CuInS₂/Mo/glass stacks were analyzed by means of CL and EBSD. It was shown that the regions in the CuInS₂ layers emitting high CL intensity at 820 nm (band-band transitions) are situated near to their surface and close to the interface with ZnO/CdS, while at 1050 nm, the high intensities were detected rather close to the Mo back contact. This behavior is attributed to a better crystal quality close to the top surface of RTP-deposited CuInS₂ films. The spatial CL intensity distribution detected at 820 nm is independent of the measurement temperature, the acceleration voltage of the electron beam, and the cross-section preparation method. The CL intensity itself is found to be affected by the preparation method and hints toward differing levels of surface recombination for the samples. When combining monochromatic CL and EBSD on identical sample positions, it was found that individual grains exhibit additional CL features on several positions, which do not seem to be related to grain boundaries but to other kinds of extended defects.

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