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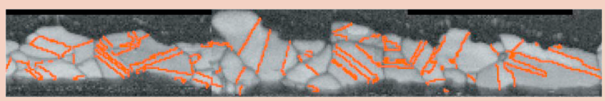

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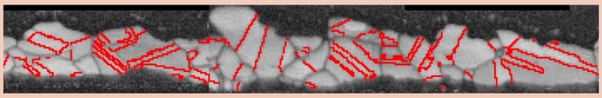
Twinning in a $CuInS_2$ layer in a completed thin-film solar cell was analyzed by means of electron backscatter diffraction. This technique revealed the microstructure of the $CuInS_2$ thin films and local orientation relationships between the grains. At various locations within the layer it was possible to retrace how twinning occurred comparing the local orientations with the theoretically possible changes in orientation by twinning.



EBSD map of a $CuInS_2$ cross-section with Σ3 boundaries highlighted by red lines.

Thin films based on ternary or multinary chalcopyrite-type materials have been used as solar absorbers in thin-film solar cells for over 30 years now [1]. Especially $CuInSe_2$, $CuGaSe_2$, $CuInS_2$, $CuGaS_2$ as well as their solid solutions $Cu(In,Ga)Se_2$, $Cu(In,Ga)S_2$, $CuIn(S,Se)_2$, and $Cu(In,Ga)(S,Se)_2$ have been successfully employed, also in industrial products. In spite of the enormous technical progress of the thin-film solar cells based on chalcopyrite-type materials, there is still considerable lack in understanding their material science, e.g., considering the impact of the various growth parameters of chalcopyrite-type thin-films on their microstructure.

The crystal structure of chalcopyrites (chemical formula $A^{I}B^{III}C^{VI}{}_2$) is very similar to the sphalerite crystal structure. Its unit cell consists essentially of two sphalerite unit cells, in which the A^{I} and B^{III} atoms are ordered on the two different cation sites. Generally, the c/a ratio differs slightly from the ideal value 2, i.e., the crystal structure is pseudo-cubic.

In a previous work [2], it was shown that the most frequent grain-boundary types in chalcopyrites are two different classes of Σ3 twin boundaries, which can be denoted in the angle-axis notation by $60°–\langle 221\rangle$ and $70.53°–\langle 110\rangle$ ($70.53°$ for $c/a = 2$; this angle varies for the different chalcopyrite-type materials). Medvedeva et al. [3] reported on calculations based on density functional theory showing that $CuInSe_2$ and $Cu(In,Ga)Se_2$ exhibit quite low stacking fault energies. Thus, the crystal structures of these compounds favor the formation of twins. However, it has not been clarified what impact the twinning of chalcopyrite-type materials has on their local texture. Taking a $CuInS_2$ layer in a completed solar cell as an example, the present work reports on electron backscatter diffraction (EBSD) measurements which enlighten this issue.

$CuInS_2$ absorbers studied in the present work were deposited on Mo-coated soda-lime glass substrates using rapid-thermal processing (RTP) [4]. In this deposition method, a sputtered Cu/In stack is exposed to sulfur gas at a temperature of 530 °C for only about 3 min, resulting in the growth of $CuInS_2$. The heating-up velocity is considerably high with about 10 K/s. The solar cells were completed by consecutive deposition of a CdS buffer layer, a transparent ZnO/ZnO:Al bilayer front contact and a Ni/Al contact grid.

For EBSD measurements, the sample was prepared by cutting slices from the thin-film solar cell, forming a stack by face-to-face gluing of two slices, mechanical polishing of the cross-section, and Ar-ion polishing. Deposition of a

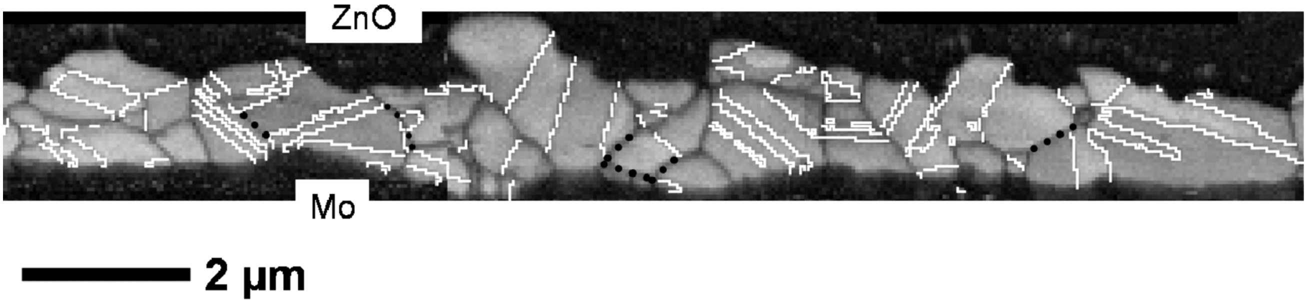


Figure 1 Pattern-quality map acquired by EBSD on a cross-section of a completed $CuInS_2$ thin-film solar cell. Highlighted by white lines are Σ3 twin boundaries, which apparently represent the most frequent grain-boundary types in this $CuInS_2$ thin film, and also 38.94°–⟨201⟩ and 96.38°–⟨210⟩ Σ9 boundaries (black, dotted lines).

very thin (about 4–5 nm) graphite layer on the cross-section reduced the sample drift during the acquisitions.

The EBSD measurements were performed on a LEO GEMINI 1530 scanning electron microscope equipped with a NordlysII-S EBSD detector from Oxford Instruments HKL Technology A/S. The acceleration voltage applied was 20 kV, and the probe current 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 nm and with recording durations of about 120 ms at each point.

A section of an EBSD pattern-quality map showing the microstructure of a $CuInS_2$ thin film is given in Fig. 1. The intensity on each measuring point in this map is related to the quality of the EBSD pattern acquired. Grain boundaries are well resolved since at the corresponding measuring points, EBSD patterns of two adjacent grains superimpose each other, which results in a zero solution and low intensity in the pattern-quality map. Highlighted in white lines are Σ3 twin boundaries. Apparently, the relative frequency of these grain-boundary types with respect to all grain boundaries visible in the EBSD map is very large. Apart from Σ3, also Σ9 grain boundaries were identified (indicated by black, dotted lines in Fig. 1).

In general, twinning in chalcopyrite-type thin films may occur during growth or also during cooling down. For both cases, the driving forces are strains in the thin films, which are reduced by forming stacking faults along predominant gliding planes of the crystal structure [3], leading to crystalline twin interfaces. The twinning of a single grain implies a change of the grain orientation. All possible changes in orientations induced by twinning were calculated by use of the rotation matrix describing the rotation transformation between the point lattice of the original grain and the one of the twinned part, i.e. rotations through 60° about [221] (corresponding to $[111]_{cub}$ for the cubic crystal structure). In order to facilitate the calculations, orientations $\langle uvw \rangle$ in the chalcopyrite-type crystal structure were transformed into corresponding orientations in the cubic crystal structure $\langle uvw \rangle_{cub}$ by multiplying the third component w by a/c (the lattice constants a and c of $CuInS_2$, taken from Ref. [5]). The cubic orientations resulting from the twinning calculations were then similarly transformed back to the chalcopyrite-type system. The results of this calculation are given in Fig. 2, where multiple twinning up to the second generation is indicated. Original orientations of ⟨110⟩/⟨201⟩ (corresponding to $\langle 110 \rangle_{cub}$ for the cubic crystal structure), ⟨221⟩ ($\langle 111 \rangle_{cub}$) and ⟨100⟩/⟨001⟩ ($\langle 100 \rangle_{cub}$) were chosen since the planes in the chalcopyrite-type crystal structure to which these directions are oriented perpendicularly, {110}/{102}, {112}, and {100}/{001}, are closest packed. Therefore, the growth along these directions is most likely.

In Fig. 3, EBSD pattern-quality maps from the same area as in Fig. 1 are shown with original orientations and their first and second generation twins, each highlighted in different colors for the ⟨110⟩/⟨201⟩, ⟨221⟩, and ⟨100⟩/⟨001⟩ twin series. A 10° deviation from the ideal orientations was allowed. Although the original orientations are possible orientations of the twinned states (Fig. 2), they were only highlighted as original orientations in Fig. 3. In the regions emphasized by yellow circles, it is possible to retrace how the twinning occurred from originally ⟨110⟩/⟨201⟩, ⟨221⟩, and ⟨100⟩/⟨001⟩ oriented grains. Neighboring grains clearly

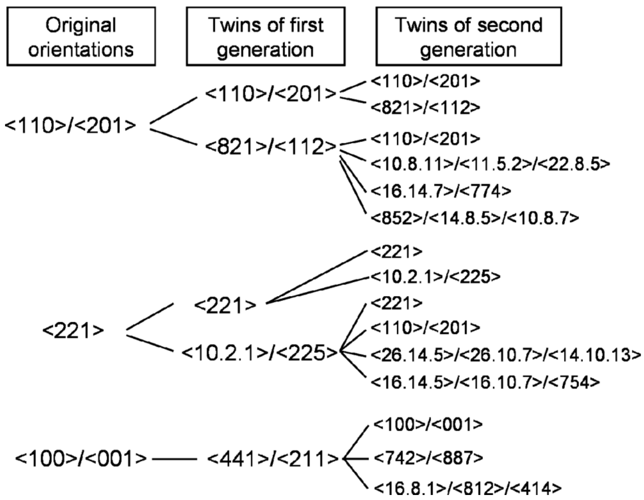


Figure 2 Scheme of possible grain orientations in chalcopyrite-type materials, which were obtained by single or two-fold twinning of ⟨110⟩/⟨201⟩, ⟨221⟩, and ⟨100⟩/⟨001⟩ oriented grains.

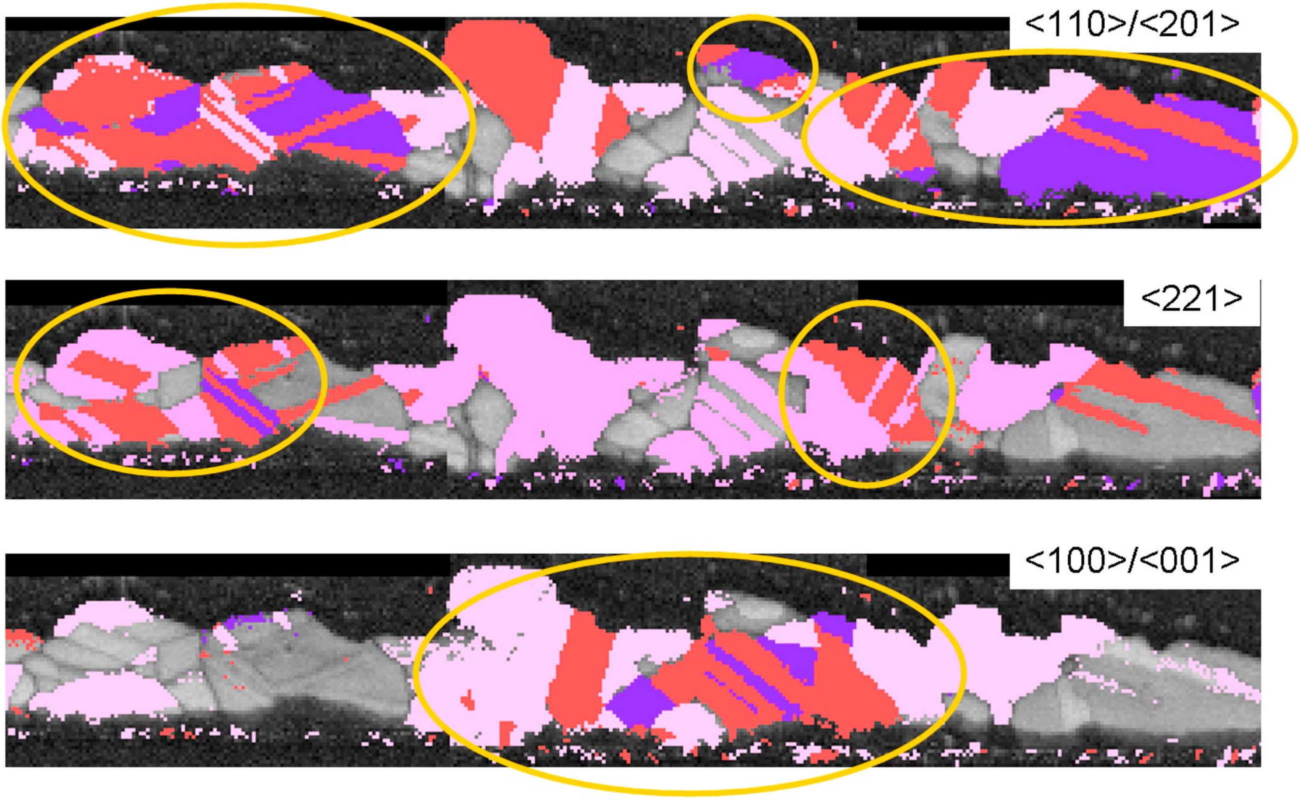


Figure 3 (online colour at: www.pss-rapid.com) Orientation distribution maps acquired by EBSD on the same area as the one shown in Fig. 1. Highlighted are the original orientations and their first and second order twins. For each of the ⟨110⟩/⟨201⟩, ⟨221⟩, and ⟨100⟩/⟨001⟩ twin series, the different colors indicate original orientations (violet), first order twins (red) and second order twins (pink).

show twin-orientation relationships. However, due to partly very small deviations between the various orientations, especially of the second generation twinned states, the orientations of single grains and subgrains cannot always be determined unambiguously and obviously, not all grains have twin orientations as given in Fig. 2. However, most of the interfaces between grains exhibiting original orientations and those associated with second-generation twins are identified as Σ9 grain boundaries (see Figs. 1 and 3). This result is an additional proof that neighboring grains in $CuInS_2$ are related by twins and indicates the presence of multiple twinning.

Similarly as for this $CuInS_2$ thin film, also for various other chalcopyrite-type thin films such orientation relationships as those depicted in Fig. 3 which can be related to twinning were revealed in corresponding EBSD orientation distribution maps. Of all these layers, RTP-grown $CuInS_2$ shows the highest density of twins.

The large density of twins in $CuInS_2$ can be attributed to very short processing durations of only few minutes. The growing layer has very reduced time to compensate strains, which can be related to crystal-structure changes from binary Cu–In, Cu–S or In–S precursors to the chalcopyrite-type material. On the other hand, also during the cooling-down phase, crystal-structure changes occur in the thin film, which may lead to further twinning. It remains unclear whether twinning is more enhanced during growth or during cooling-down. This issue needs further study.

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