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Correlative Transmission EBSD-APT Analysis of Grain Boundaries in $Cu(In,Ga)Se_2$ and $Cu_2ZnSnSe_4$ Based Thin-film Solar Cells

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The compound semiconductors $Cu(In,Ga)(S,Se)_2$ (CIGS) and $Cu_2ZnSn(S,Se)_4$ (CZTS) are used as alternative absorber materials in thin-film solar cells. Currently, record efficiencies of 22.6% and 12.6% are achieved for CIGS and CZTS based solar cells, respectively.[1]

When considering the polycrystalline nature of the CIGS and CZTS thin-films, those efficiencies are surprisingly high. For further enhancement of the efficiency it is important to understand how the microstructure affects the electrical properties of the absorber films and, hence, the device performance. Therefore, as one part, one needs to study the relationship between structural and chemical properties of grain boundaries (GB).

Compositional changes at GBs in CIGS thin-films have been already reported.[2] Cu-enrichment and In-depletion or Cu-depletion and In-enrichment are detected as well as segregation of impurities such as alkali metals. Similar observations are observed for CZTS GBs.[3] However, there are only few studies which correlate structural and chemical properties of GBs in the CIGS system. For the CZTS system, there is even no such study available.

Therefore, we investigate the correlation between crystallographic and chemical information of GBs in CIGS and CZTS thin-films by using electron backscatter diffraction in transmission (t-EBSD) and atom probe tomography (APT). We address practical issues related to the preparation of APT tips from CIGS and CZTS thin-films for t-ESBD investigations and how to resolve them. Furthermore, we discuss the different compositional changes of the matrix elements and segregation phenomena detected at random high-angle GBs and twin boundaries.

Figure 1 shows a representative t-EBSD-APT study of a CIGS GB. The image quality maps in Figure 1 a) show clearly the presence of a GB as indicated by the darker contrast caused by the blurring of overlapping Kikuchi patterns of the adjacent grains. In a second step the GB was placed ~300 nm closer to the apex of the APT tip by an additional focused-ion-beam milling step (Figure 1 b)). The corresponding inverse pole figure map oriented along the APT tip direction is shown in Figure 1 c), which reveals a misorienation angle of 37° of the GB, i.e. a random high-angle GB (HAGB). By APT we detect clearly segregation of Na, which diffused out from the soda-lime glass substrate into the CIGS absorber, at the GB as shown in the reconstructed 3D APT data in Figure 1 d). Furthermore, the 1D concentration profile across the random HAGB (Figure 1 e)) exhibit an atomic redistribution. We detect Cu-depletion and In- as well as Se-enrichment at the GB compared to the grain interior. Moreover, we observe co-segregation of Na and K. In contrast to random HAGBs, we detect no compositional changes

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as well as no segregation of impurities at Σ3 twin boundaries for the here studied CIGS sample.
For CZTS thin-films we have also observed an atomic redistribution at CZTS GBs in a previous study [3]. For low-temperature co-evaporated precursor films we detected Cu-enrichment at CZTSe GBs. After annealing we detected in the final absorber either Zn-enrichment at CZTS GBs without impurity segregation or segregation of Na and K at CZTSe GBs without any change in the concentration of the matrix elements. Whether the different compositional changes at CZTS GBs are related to different GB types, i.e. random HAGBs or twin boundaries, will be studied by t-EBSD-APT as well.

Deep defects within the band gap at GBs can cause non-radiative Shockley-Read-Hall recombination of photogenerated charge carriers, limiting the open-circuit voltage and, hence, the power conversion efficiency. Cu-depletion at CIGS and CZTS GBs can cause a downward shift of the valence band maximum at the GB. This valence band offset can act as neutral hole barrier.[4] Furthermore, although the defect density is increased at GBs, *ab initio* density functional theory calculations by Yan et al. [5] and Wei et al. [6] suggest that an atomic reconstruction at CIGS GBs does not increase the density of deep defects and that Na can even eliminate defects. Hence, the by APT detected compositional changes at GBs might passivate the GBs electrically, i.e. non-radiative recombination is reduced.

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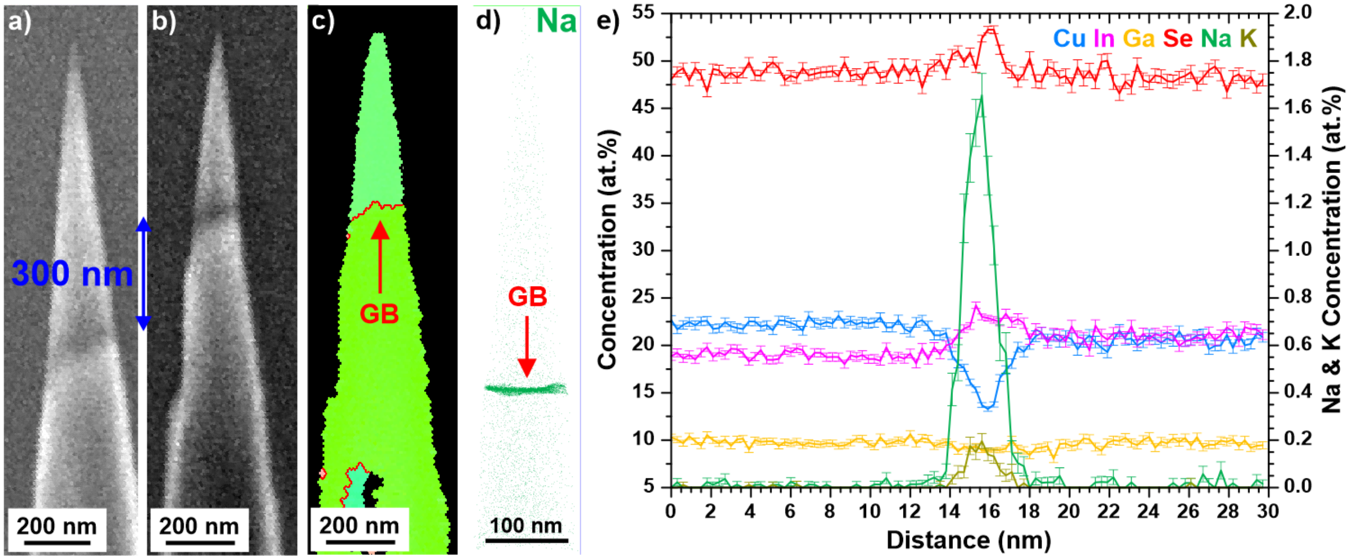

Figure 1. a)-b) Image quality (IQ) maps of the same APT tip from a CIGS sample after a first and second low-kV milling. The dark contrast in the middle of the IQ map of the APT tip marks a GB, which was placed closer to the apex of the APT tip after an additional milling step. c) Inverse pole figure map to b) orientated along APT tip direction: the misorientation angle of the GB is 37°. d) 3D distribution map of Na of the corresponding reconstructed APT tip. Na is detected at the grain boundary. e) 1D concentration profile across the GB shown in d) showing compositional changes at the GB.

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