

Nano-scale Characterization of Thin-Film Solar Cells

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Thin-film solar cells based on the compound semiconductors Cu(In,Ga)Se₂ (CIGSe) and Cu₂ZnSnSe₄ (CZTSe) exhibit a high efficiency, despite their polycrystalline defect-rich structure. Key factor for further efficiency improvements is a more profound knowledge about the chemical and structural state of the internal interfaces (p-n junction, grain and phase boundaries), diffusion of impurities and the formation of secondary phases. Particularly in the latter case, the growth conditions controlling the composition of CZTSe based solar cells are critical in order to avoid formation of detrimental secondary phases, namely ZnSe, Cu_{2-x}Se and Cu₂SnSe₃.

In this work, the role of the p-n junction and grain boundaries (GB) in CIGSe thin-films will be presented. Furthermore, in CZTSe thin-films the formation of secondary phases and the effect of CZTSe GBs and CZTSe/ZnSe phase boundaries on cell performance will be discussed.

We applied correlative transmission electron microscopy (TEM) and atom probe tomography (APT) studies for microstructure and compositional analyses of internal interfaces at the atomic scale. With APT it is possible to determine composition of selected regions, such as grain and phase boundaries, precipitates, etc.

The APT experimental findings for CIGS thin-films show that the absorber surface is generally Cu-depleted and Cd-enriched (CdS acts as buffer layer). This observation is a strong indication for the existence of an inverted p-n junction within the first layers of the CIGS absorber layer [1,2]. Na and O impurities are detected at the CdS/CIGS interface, as well (**Figure 1**). Furthermore, we detect Na also at CIGS GBs as well as in the grain interior [3].

APT and TEM measurements of Cu-rich and Cu-poor CZTSe thin-films prepared by co-evaporation exhibit a heterogeneous microstructure and a fine network of ZnSe. Secondary phases, especially Cu_{2-x}Se and Cu₂SnSe₃, which we detect as well, can lead to non-working devices. Therefore, the growth recipe was improved by an additional KCN etching before annealing. This will lead to working devices, where the efficiency strongly depends on absorber composition [4]. Nevertheless, we still detect a complex, nano-sized network of CZTS and ZnSe domains for the final absorber layers (**Figure 2**). In addition, we detect nano-precipitates being present with a small volume fraction, where the composition cannot be assigned to any of the known equilibrium phases [5]. Moreover, we discuss possible effects on cell performance originating from the decoration of alkali metals at CZTSe GBs and CZTSe/ZnSe phase boundaries. In conclusion, we show how APT can help to explore novel phases in such complex multicomponent systems, which can be the starting point for further theoretical investigations.

References:

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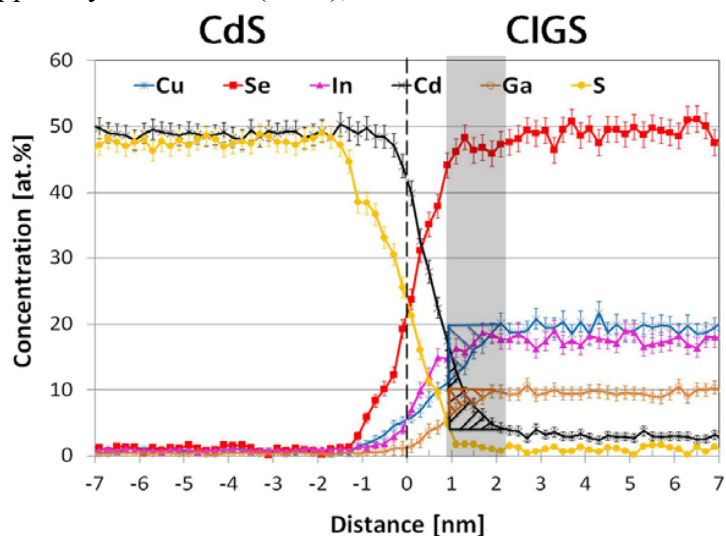


Figure 1. Proximity histogram across the CdS/CIGS interface.

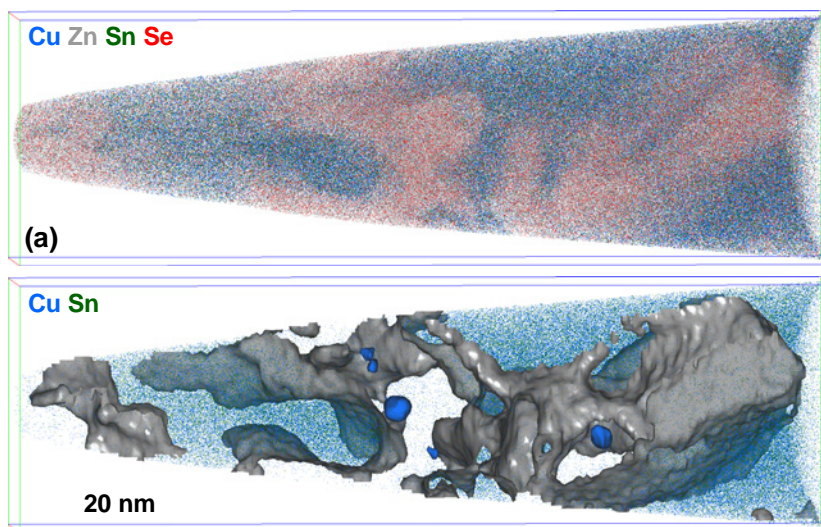


Figure 2. (a) Three-dimensional elemental map of Cu (blue), Zn (grey), Sn (green), and Se (red); (b) only Cu and Sn displayed as well as iso-concentration surface of 32.5 at. % Zn (grey) and 7.0 at. % Cu (blue). Volume size for (a) and (b) is 62 x 66 x 219 nm³. I & II represent CZTSe regions, III & IV ZnSe