

## Linking Microstructure and Local Chemistry in Cu(In,Ga)Se<sub>2</sub> Thin-Film Solar Cells

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Cu(In,Ga)Se<sub>2</sub> (CIGSe) is one of the strongest candidates for thin-film photovoltaic applications with its high power conversion efficiencies up to 21.7% at laboratory scales [1]. In our study we focus on the microstructural evolution of structural defects, which may influence the electronic properties locally and limit the device efficiencies in polycrystalline CIGSe absorber layers.

During the growth of the CIGSe absorber layers, using a three-stage co-evaporation process, samples pass through a Cu-rich phase at the end of the second stage [2]. It is known that this intermediate Cu-rich stage is needed for defect annihilation [3,4]. A crystal structure transformation from a hexagonal to tetragonal chalcopyrite lattice also occurs in the second stage [3]. If these transformations are fast non-thermal-equilibrium transformations, planar faults form in the material.

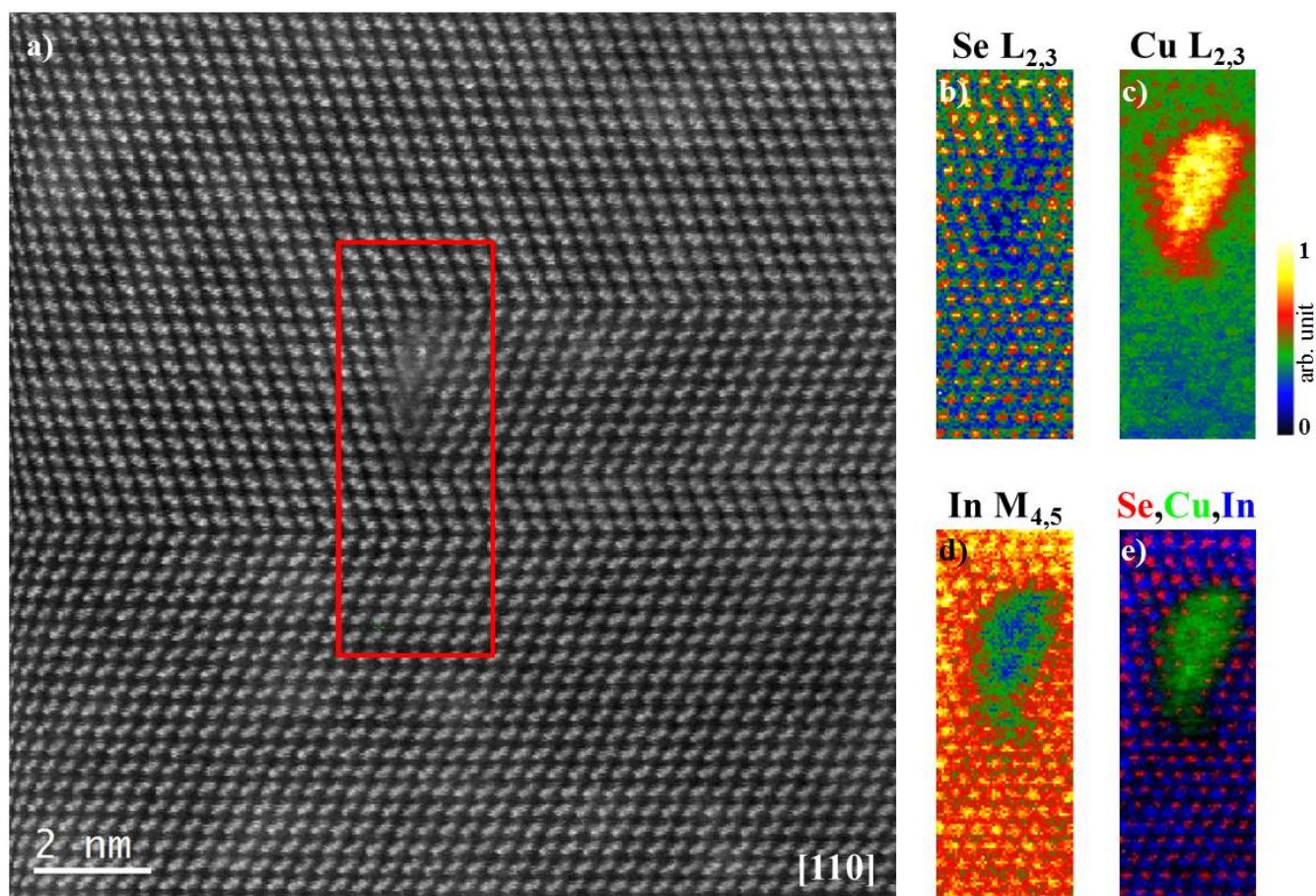
We prepared two Cu-poor CIGSe samples. The first sample (A) was produced by interrupting the growth process before it reaches the Cu-rich composition at the end of the second growth stage. The second sample (B) was grown by fully completing the three-stage co-evaporation process. The microstructure of the CIGSe thin film was analysed in depth and defect concentrations were determined by bright field (BF) and low angle annular dark field (LAADF) imaging using scanning transmission electron microscopy (STEM). The atomic structure and local chemistry of individual defects, like twin boundaries, stacking faults and dislocations, as well as of grain boundaries were studied in detail using high-resolution STEM in combination with electron energy loss spectroscopy (EELS).

BF and LAADF STEM analyses showed large grains with low defect concentrations in sample B, whereas smaller grains with high defect concentrations were observed in sample A. The reason for these differences is the lack of the Cu-rich stage and recrystallization in the interrupted-process sample A. HR-STEM and EELS analysis showed striking chemical characteristics for a number of observed individual defects. The {112} twin planes, which often extend across the entire grain, exhibit homogeneous elemental distributions, which possibly do not affect the electrical properties [5]. However, at grain boundaries and complex defects we found Cu enrichment in correlation with In depletion. The local chemical change in these regions may alter the electronic properties.

A Cu-segregated complex defect is shown in [110] projection in Figure 1. The segregation process apparently creates high local strain, which is subsequently relaxed via twin boundary formation in the chalcopyrite structure. Se-cation terminated twin boundaries are formed at {112} planes. This contribution on the CIGSe thin-film solar cells' growth process provides detailed information on the microstructural evolution, the defect formation and accompanied local compositional changes with the objective to further improve solar-cell performance via microstructure control.

## References:

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**Figure 1.** (a) HAADF image of a complex defect twin boundary association. (b), (c), (d) elemental distribution maps extracted from the spectrum image acquired, showing Se, Cu and In maps, respectively. (e) Color-coded combination of the elemental maps.