

In-situ observations of recrystallization in CuInSe₂ solar cells via STEM

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Cu(In,Ga)Se₂ (CIGS) solar cells have reached 22.6% efficiency, one of the highest in thin-film solar cells. High-performance CIGS absorber layers are produced by a three-stage co-evaporation technique: first In-Ga-Se is co-evaporated, second Cu-Se is co-evaporated until the [Cu]/([In]+[Ga]) ratio becomes >1, third In-Ga-Se is again co-evaporated until the [Cu]/([In]+[Ga]) ratio becomes <1. Typically, such three-stage processes involve an increase in the temperature from about 300–350°C in the first stage up to about 450–600°C in the second and third stages. It was reported that the Cu excess in the second stage is essential for recrystallization [1]. However, little has been known about how the atomic structures evolve during the recrystallization in the second stage.

In the present study, in-situ heating was performed and the structure changes were monitored in a scanning electron transmission microscope (STEM). Simultaneously the composition changes were monitored via electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX). We used a CuInSe₂ (CIS) system to avoid the more complicated Ga-induced gradient change. Equivalent to the second stage of the three-stage process for CIGS, Cu-Se (CS) was deposited on the CIS layer and then focused ion beam (FIB) was used to extract thin specimens for further in-situ STEM studies. The annular dark-field detector was used to integrate the signal from 30 to 71 mrad, including the outer portion of the bright field (BF) disk (30–49 mrad) and the low-angle annual dark-field (LAADF) signal (49–71 mrad). This was found to optimize the image contrast of the grain boundaries (GBs) and planar defects while retaining a strong EELS signal. The temperature was gradually increased in a rate of 10K/min with a pause of 6.5 min every 30K for EELS+EDX spectrum imaging. A longer pause of 82 min was taken at 395°C, followed by further heating towards 450°C.

Different phenomena were observed at different temperatures. Cu–In interdiffusion began above 155°C: starting from the CS/CIS interface Cu concentration in the CIS layer gradually increased, while in the CS layer In replaced some Cu forming CIS grains. Above 245°C, Cu diffusion along the GBs was observed. Above 335°C, clear grain recrystallization was observed and planar defects play an important role: the grains with high-density planar defects tend to be consumed by the grains without planar defects. This was consistently observed in all four sets of experiments we performed. A typical example is shown in Fig. 1. Simultaneous elemental maps show Cu accumulated at the migrating GB between the shrinking defected grain and the growing undefected grain. Above 335°C, Cu also replaced some In transforming some CIS grains to CS grains. The newly formed CS grains show a reconstructed Cu_{2-x}Se superlattice [2] aligned with the lattice of the surrounding CIS grains (Fig.2), suggesting a low-energy transformation mechanism between CIS and Cu_{2-x}Se. The Se concentration exhibits no clear change in the entire process. This recrystallization was however not observed using a CIS specimen without Cu-Se

layer, demonstrating the importance of excess Cu for recrystallization. The time-series images and elemental maps will be presented in videos and more details will be discussed in the conference [3].

References:

- [1] H Stange *et al.*, *Acta Materialia* **111** (2016) 377–384
 [2] W Qiu *et al.*, *The Journal of Chemical Physics*, **144** (2016) 194502
 [3] Research funded in part by the Helmholtz Virtual Institute “Microstructure Control for Thin- Film Solar Cells”, VH-VI–520 project.

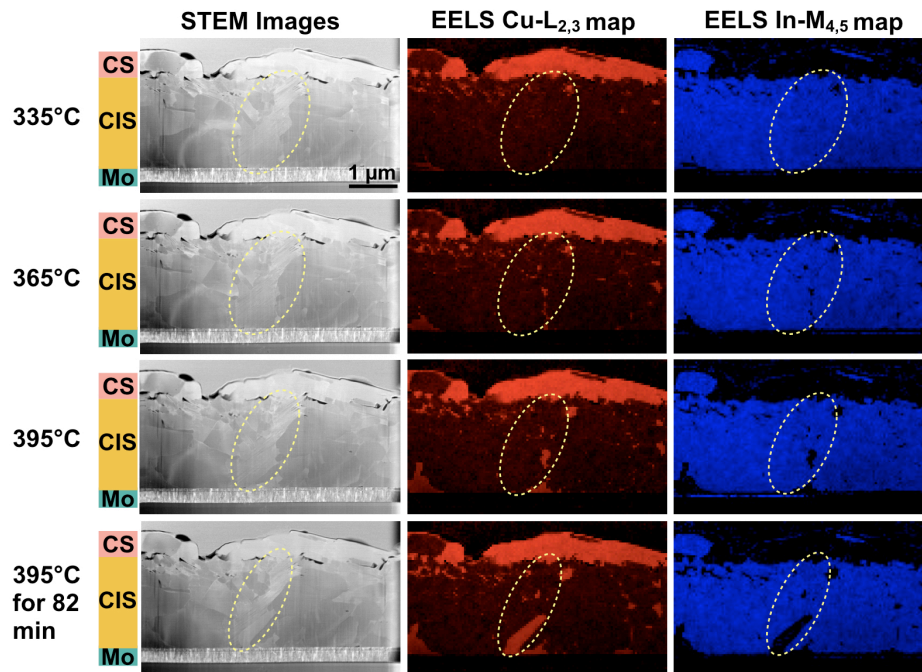


Figure. 1 Time-series STEM images and EELS elemental maps during in-situ heating. Above 335°C, the CIS grain with a high density of planar defects marked by yellow dashed ovals was consumed by the CIS grain on its right side that does not show planar defects. Cu gradually replaced some In forming CS grains, including the bottom part of the grain marked by yellow dashed ovals.

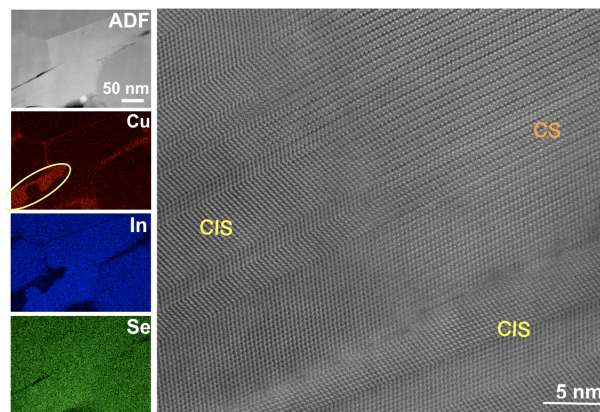


Figure. 2 Left: EELS mapping show Cu replaced In forming a CS grain (yellow oval). Right: atomic image showing a CS super-lattice meeting CIS with a high density of planar defects.