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Report:

It is the aim of this project to study the nanostructure of Cu(In,Ga)Se₂ (CIGS) thin film solar cells with different Cu content and different Cu history using extended X-ray absorption fine structure spectroscopy (EXAFS) in order to better understand the correlation between preparation conditions and device performance.

High efficiency CIGS solar cells are typically Cu-poor with a Cu/III = Cu/(In+Ga) ratio between 0.8 and 0.9 [1]. However, the material has usually passed through a Cu-rich intermediate stage during deposition as shown schematically in Figure 1 [2]. This is known to be highly beneficial for the microstructure and the electrical properties of the CIGS absorber layer and thus for the overall efficiency of the solar cell. However, the mechanisms of this improvement are not yet fully understood. Recent EXAFS studies comparing powders and thin films suggest that also the CIGS nanostructure is influenced by the Cu content and the

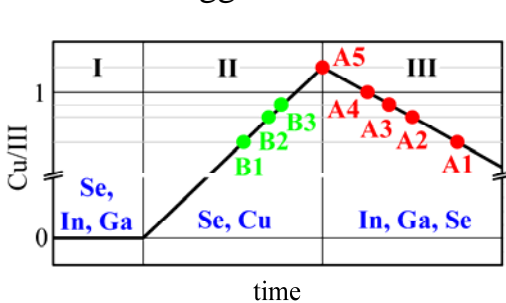


Figure 1: Schematic of the three-stage co-evaporation process with the elements deposited given in blue and the samples A1-A5 and B1-B3 indicated in red and green, respectively.

Cu history of the material but the grain size distribution and the presence of alkali elements may also have an influence on local structural parameters [3].

Therefore, a total of sixteen different CIGS absorber layers were studied in this experiment. Samples A1 to A5 have all passed through the Cu-rich stage but differ with respect to their final Cu/III ratio as shown in Figure 1. In contrast, samples B1 to B3 have the same final Cu content as samples A1 to A3 but have never passed through the Cu-rich stage. Another six thin films were prepared in the same way as A1 and A3 except that the

alkali supply from the glass was suppressed. Samples C1 and C3 therefore do not contain any alkali elements while samples D1 and D3 and E1 and E3 were further subjected to a post deposition treatment with Na and K. Comparing these samples thus allows to determine the influence of the final Cu content, the Cu-rich intermediate stage and the presence of alkali elements during or after film growth on the CIGS nanostructure. Additionally, two CIGS thin films studied previously [3] were remeasured as a check for consistency.

Spectra of the Ga and In K-edges (10.367 and 27.940 keV, respectively) were recorded in fluorescence mode at a sample temperature of approximately 25 K to minimize thermally induced disorder and to resolve subtle differences in the bond length variation of the different samples. Measurements of the Cu K-edge (8.979 keV) were omitted since the Cu-Se structural parameters were shown to be insensitive to the Cu content and the preparation conditions for CIGS powders and thin films previously studied [3]. To facilitate good thermal contact between the CIGS thin films and the sample holder, the films were lifted off the glass substrate prior to the measurements and were mounted on small Al disks using a graphite-containing epoxy. Spectra were recorded up to a photoelectron wave-number k of approximately 16 \AA^{-1} .

As an example, Figure 2 plots the spectra recorded at the In K-edge for the samples A1, B1 and A4 (see also Figure 1). Obviously, the peak height is smaller for the samples with lower Cu content (A1 and B1) corresponding to an increase of the bond length variation and thus to an increase of structural disorder. In contrast, there is basically no difference between the sample that passed through the Cu-rich stage (A1) and the sample that did not (B1) contrary to our previous hypothesis [3]. A detailed analysis of all spectra measured at the Ga and In K-edge is currently under way using the IFEFFIT software package [4] and the computer code FEFF9 [5]. It yields the element-specific Ga-Se and In-Se average bond length and bond length variation depending on the final Cu content, the Cu history and the presence of alkali elements during or after thin film growth. These results provide unique insight into the correlation between preparation conditions and CIGS nanostructure and will help to fully exploit the potential of high efficiency CIGS thin film solar cells.

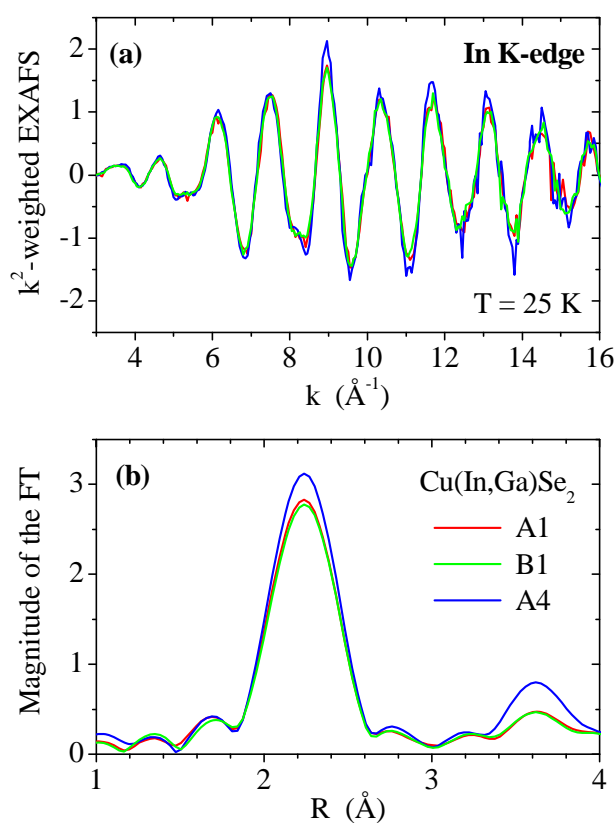


Figure 2: (a) k^2 -weighted EXAFS spectra and (b) magnitude of the Fourier transformation (FT) measured at the In K-edge of three different CIGS thin film absorbers.

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