ESRF	**Experiment title:** Spatially resolved composition and structure of $Cu(In,Ga)Se_2$ thin film solar cells	**Experiment number**: MA-2216
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Report:

It was the aim of this project to investigate lateral and depth-dependent inhomogeneities in the composition and structure of $Cu(In,Ga)Se_2$ (CIGS) based thin film solar cells using X-ray fluorescence (XRF) and X-ray diffraction (XRD) measurements with high spatial resolution. To that end, thin cross section lamellas of complete solar cells that were prepared under different process conditions were studied at ID16B-NA (XRF) and ID13 (XRD). Correlating these results with other structural, electrical and optical measurements performed at the same samples will contribute significantly to a more comprehensive understanding of these devices and will help to exploit their full potential.

A typical CIGS thin film solar cell consists of a glass substrate, a Mo back contact, the polycrystalline CIGS absorber layer, a CdS buffer layer, and a transparent ZnO front contact as shown in Figure 1. A total of 20 different solar cells was studied. For 15 of these solar cells, the CIGS absorber layer was fabricated by selenization of a metallic Cu-In-Ga precursor. Different parameters of this sequential process were varied including the Ga content of the precursor and the temperature for selenization. These process conditions are expected to influence the morphology and Ga profile of the resulting absorber layer and thus the device performance. Additionally, 5 solar cells were studied where the CIGS absorber had been formed by co-evaporation of all elements which is an alternative method of fabrication. Again, different process conditions were applied.

In order to facilitate XRF and XRD measurements with high spatial resolution, thin cross section lamellas were prepared from the complete solar cells using a focused ion beam

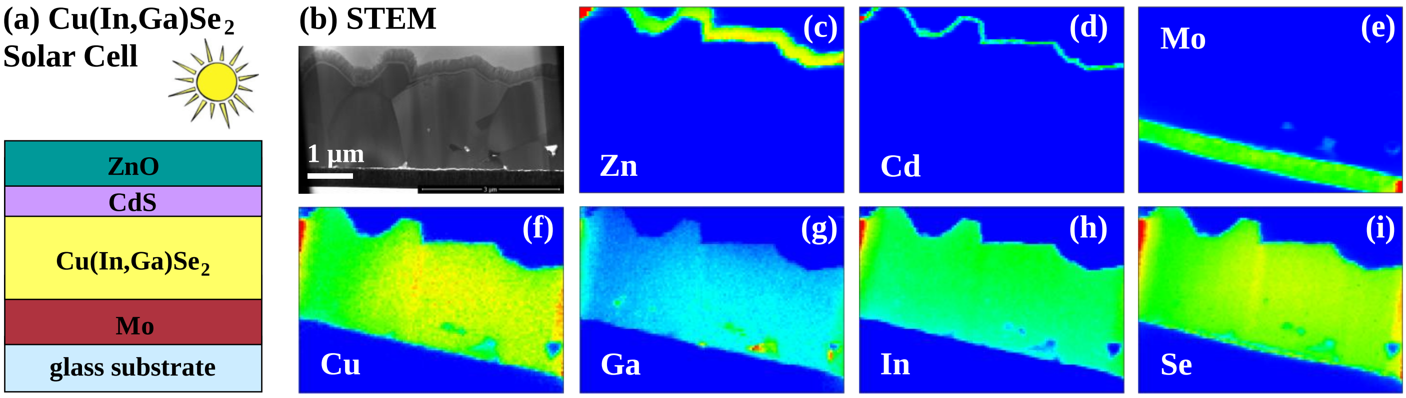

Figure 1: *(a) Schematic of the typical layer sequence of CIGS thin film solar cells, (b) STEM image of a 120 nm thick cross section lamella and (c) – (i) elemental XRF maps collected at 29.3 keV at ID16B-NA.*

system. The thicknesses of these lamellas were between 100 and 300 nm, which represents the optimal compromise between mechanical stability and count rate on the one hand, and minimal averaging in the direction of the beam on the other hand. Given the typical grain sizes of 0.5 to 1 µm, this also allows us to study the composition and structure of individual CIGS grains in the absorber layer. Figure 1 shows a scanning transmission electron microscopy (STEM) image of one of the lamellas where the different layers and CIGS grains are clearly visible. Lamellas were mounted on Ni grids to avoid erroneous Cu signals in the XRF spectra.

XRF measurements were performed at 29.3 keV in pink beam operation mode. The high beam energy enables the detection of fluorescence K-lines for all elements of interest, ranging from Cu to In, which significantly improves the quantitative determination of the sample composition. A bovine liver reference and a CIGS solar cell with known integral composition were measured as calibration samples. The spot size was 40 to 70 and 70 to 100 nm in the horizontal and vertical direction, respectively. This enables the study not only of individual CIGS grains but also of grain boundaries and interfaces like that between the CIGS absorber and the Mo back contact.

As an example, Figure 1 presents elemental XRF maps collected with a step size of 50 nm. All elements can easily be assigned to the different layers of the solar cell as seen in the STEM image. However, Se is also present in the back contact layer whereas Cu, In and Ga are confined to the absorber layer. This provides direct evidence for the formation of a Mo-Se layer at the CIGS/Mo interface. Relating the Cu, Ga and In signals to each other yields the depth dependent absorber composition for the different CIGS grains of the lamella. Lateral inhomogeneities in the Ga profile and variations of the Cu content at grain boundaries are particularly interesting as they directly affect the electrical properties of the material and thus the efficiency of the solar cell.

A detailed analysis of all samples measured is currently under way using the PyMca software [1]. The results can be correlated with other structural, electrical and optical measurements including the XRD investigations performed at ID13 [2]. This will contribute to a more comprehensive understanding of these thin film solar cells and will point out optimized preparation conditions to further increase their conversion efficiency.

[1] V. A. Solé *et al.*, Spectrochimica Acta B 62, 63 (2007).
[2] See Experimental Report for ID13 beamtime of MA-2216.