

Improved quantitative chemical analyses of Cu(In,Ga)Se₂ solar cells performed by STEM/EDXS

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In recent years researchers have paid much attention to Cu(In,Ga)Se₂ (CIGS) thin-film solar cells with Zn(O,S) buffer layers due to their high photovoltaic conversion efficiency [1] and non-toxic buffer layers. The solar-cell efficiency is significantly influenced by the chemical composition of each layer in the device, particularly the CIGS absorber and the Zn(O,S) buffer. Thus, it is of great importance to determine accurately the local stoichiometry of these layers in the final device. Scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDXS) is a powerful technique for quantitative analysis of the local chemical composition with high spatial resolution. However, even for thin TEM specimens the accuracy of quantitative STEM/EDXS composition analyses can be severely affected by X-ray absorption and other effects. X-ray absorption is particularly influenced by the composition and local thickness of the TEM specimen, and these two parameters are generally unknown. Due to significant quantification errors for EDXS analyses of CIGS solar cells only intensities of X-ray lines are usually given in the literature [2, 3].

In this work, the influence of the local sample thickness on quantitative STEM/EDXS was studied for CIGS solar cells with Zn(O,S) buffer layers and ZnO:Al window layers. For this purpose, a multi-layer stack of sputtered Zn_{0.5}O_{0.5} / Zn_{0.5}O_{0.35}S_{0.15} / Zn_{0.5}O_{0.25}S_{0.25} / Zn_{0.5}O_{0.2}S_{0.3} / Zn_{0.5}S_{0.5} layers on a Si wafer was utilized as a reference in addition to the CIGS solar cells. Cross-sectional TEM lamellae with homogeneous thickness and wedge-shape specimens were prepared from the Zn(O,S) multilayers and solar-cell stacks, respectively, by focused ion beam (FIB) milling with a Thermo Fisher dual-beam Helios G4 FX microscope. To avoid the influence of Cu stray X-rays on EDXS quantification results, it is important to attach CIGS lamellae to Cu-free lift-out grids during FIB preparation of TEM lamellae. STEM imaging and EDXS analyses were performed using a FEI Tecnai Osiris microscope operated at 200 kV, which is equipped with a SuperX EDXS detector system comprising four Si-drift detectors. Quantification of the EDXS raw data was carried out by the Bruker Esprit software version 2.1 using the thin-foil approximation [4].

Figure 1a shows a cross-section high-angle annular dark-field (HAADF) STEM image of the Zn(O,S) multilayer stack on Si where the nominal S/O concentration ratio increases from the bottom layer to the top layer. An element-concentration profile (see Figure 1b) of the region marked by an arrow was obtained by applying the thin-foil approximation for the evaluation of the EDXS data. The determined S concentration in each layer agrees well with the nominal value, while the O concentration is lower and the Zn concentration is higher than the correct stoichiometry owing to the thickness-dependent absorption of the low-energy O- K_{α} X-rays. X-ray absorption of oxygen was taken into account in the composition profile shown in Figure 1c. The lamella thickness was adapted to obtain the correct stoichiometry for ZnO with known composition and a ZnO material density of 5.61 g/cm^3 . The absorption-corrected composition profile in Figure 1c shows that the measured composition of each layer is consistent with its nominal value within an error limit of $\pm 2 \text{ at.}\%$. This indicates that the X-ray absorption in Zn(O,S) layers with different S/O concentration ratios can be properly taken into account by the absorption correction on the basis of the ZnO layer, if the local thickness does not significantly change. Furthermore, it can be deduced that in a multilayer system including a ZnO layer as in CIGS solar cells, the X-ray absorption of oxygen in all the O-containing layers can be corrected by the use of the ZnO layer. On the contrary, the thickness-dependent absorption of O X-rays can be exploited to determine the local thickness of the TEM sample. In addition, the correct stoichiometry of the Zn(O,S) layers can also be achieved by an iterative method.

Figure 2a shows a top-view secondary-electron scanning electron microscopy (SE-SEM) image of a wedge-shaped TEM sample of the CIGS solar cell, which shows a wedge angle of 25° . A cross-section HAADF STEM image of this wedge-shaped sample is depicted in Figure 2b, where the local sample thickness is well known as a function of the distances from the thin wedge edge. The thickness-dependent quantified EDXS line profile along the arrow is shown in Figure 2c. In thick regions ($> 100 \text{ nm}$), the evaluated concentration of each element agrees well with the integral chemical composition of $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$ (i.e. 24 at.% Cu, 18 at.% In, 8 at.% Ga, 50 at.% Se) as determined by X-ray fluorescence. However, in thin regions ($< 100 \text{ nm}$) the determined Se concentration is much lower, the In slightly lower, and the Cu much higher than the nominal value. This artifact may result from a preferred Se and In evaporation compared to that of Cu and Ga during ion-beam milling [5], likely to be related to the different vapor pressures of these elements ($\text{Se} > \text{In} > \text{Ga} > \text{Cu}$) in CIGS, which in practice cannot completely be prevented. Besides, the existence of O indicates the oxidation of the TEM lamella. The influence of element evaporation and sample oxidation is more pronounced in thin regions, because these effects generally occur at the sample surface. Thus, it is important to use lower ion-beam energy and smaller ion currents, and to keep the sample temperature for FIB milling as low as possible by using sample cooling stage. Also, the TEM sample should be stored under O-free conditions.

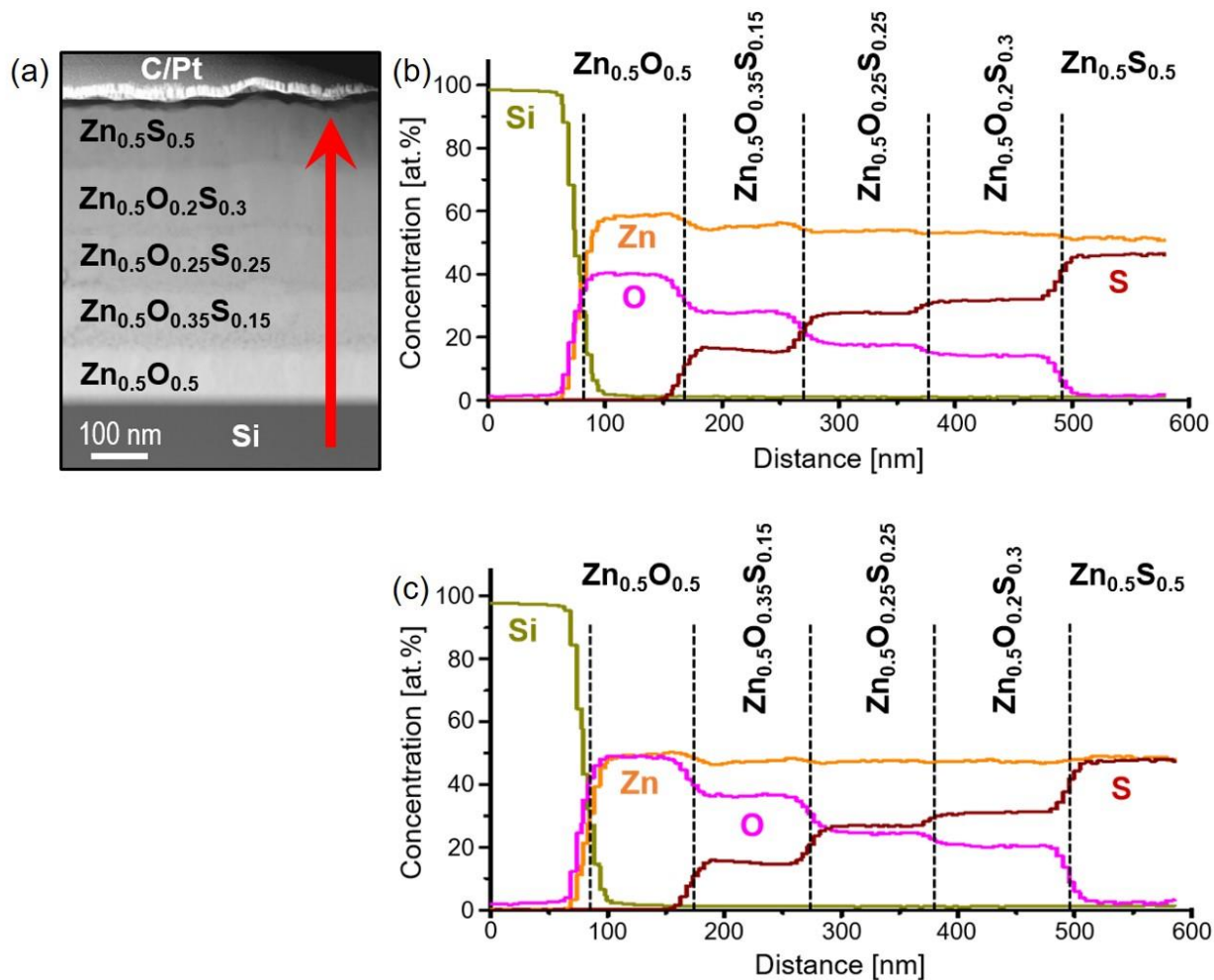


Figure 1. (a) Cross-section HAADF STEM image of a stack of sputtered Zn(O,S) layers with different S/O concentration ratios on a Si substrate coated with a carbon and platinum layer on top. An EDXS line profile was acquired along the arrow. The element concentrations of the quantified EDXS line profiles are shown in (b) without and (c) with absorption correction.

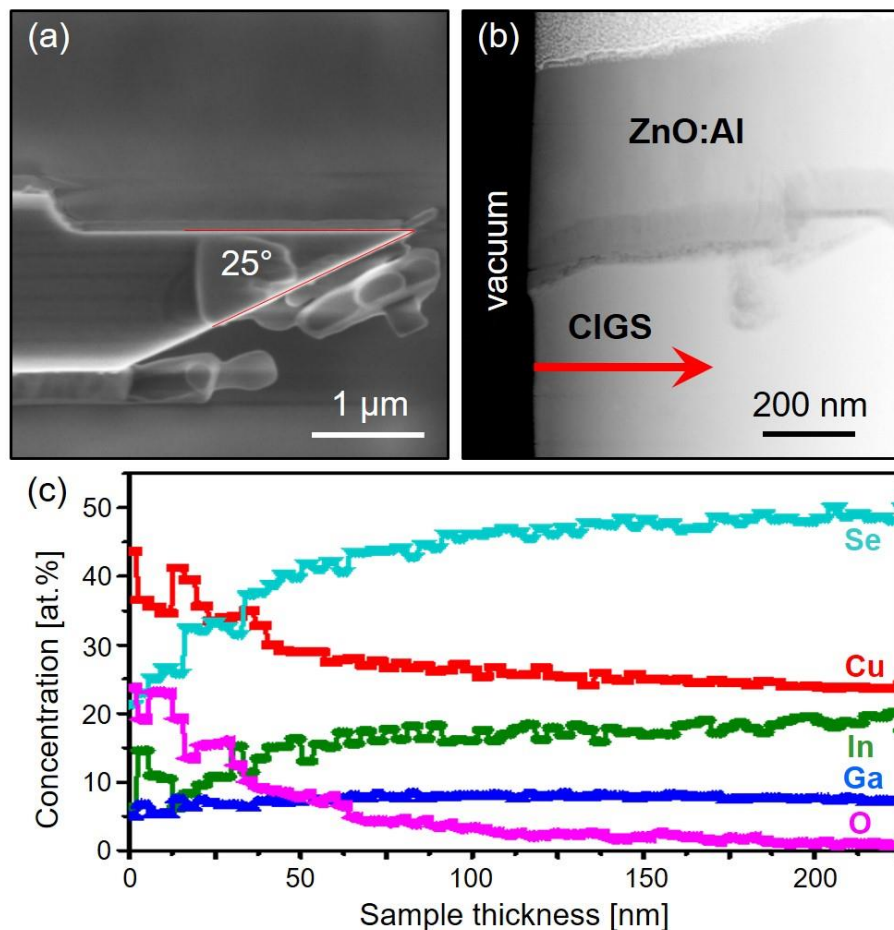


Figure 2. (a) Top-view SE-SEM image and (b) cross-section HAADF STEM image of a wedge-shaped TEM lamella of a CIGS solar cell. (c) Quantified EDXS line profile of the CIGS layer obtained as a function of the local sample thickness along the red arrow in (b).

References

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