

## Combined SEM microscopic and spectroscopic study of selenization of thin metallic films

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Polycrystalline CuInSe<sub>2</sub> and CuInS<sub>2</sub> are the most widely investigated materials for thin film solar cell application. Currently electrical conversion efficiency approaching 20% has been demonstrated for Cu(InGa)Se<sub>2</sub> [1]. The feasibility of replacing of In in CuInSe<sub>2</sub> (CuInS<sub>2</sub>) with Zn and Sn enables the production of quaternary Cu<sub>2</sub>ZnSnSe<sub>4</sub> (Cu<sub>2</sub>ZnSnS<sub>4</sub>) and to avoid the use of very expensive In with limited resources in solar cells.

The precursor copper–indium alloy films (Cu/In=0.88) were deposited by magnetron co-sputtering of elemental Cu and In. The stacked precursor Sn-Zn-Cu films were sequentially deposited by vacuum evaporation of precursor metals or their selenides in different ratios of Cu to Zn, Zn to Sn and Cu to (Zn+Sn). As substrate Mo coated soda lime glass plates were used in both cases. The precursor films were annealed with elemental selenium in temperature range between 175°C and 470°C. The duration of the selenization was between 0.33 and 5 hours.

The study focuses on the investigation of influence of post-treatments on the structure, morphology and composition of different selenized films. SEM based methods were used as major in this study. If the identification of chemical nature of formed multiphase materials was needed the SEM based microscopic methods were combined with spectroscopic investigations. Evolution of the surface morphology and the crystalline structure of the precursor and the selenized films were analyzed by the high resolution scanning electron microscope (HR-SEM) Zeiss ULTRA 55 equipped with the In-Lens SE detector for topographic imaging and energy, angle selective backscattered detector (EsB) for compositional contrast. The chemical composition and the distribution of components in films were determined using an SEM integrated energy dispersive x-ray (EDX) and microbeam x-ray fluorescence (XRF) analysis (diameter of X-ray spot 10 μm). The phase composition of films was studied by micro-Raman spectroscopy using the incident laser light with the wavelength of 532 nm focused on samples within a spot of 1 μm in diameter and by X-ray diffraction (XRD) using Cu Kα as X-ray source in a Bragg-Brentano geometry.

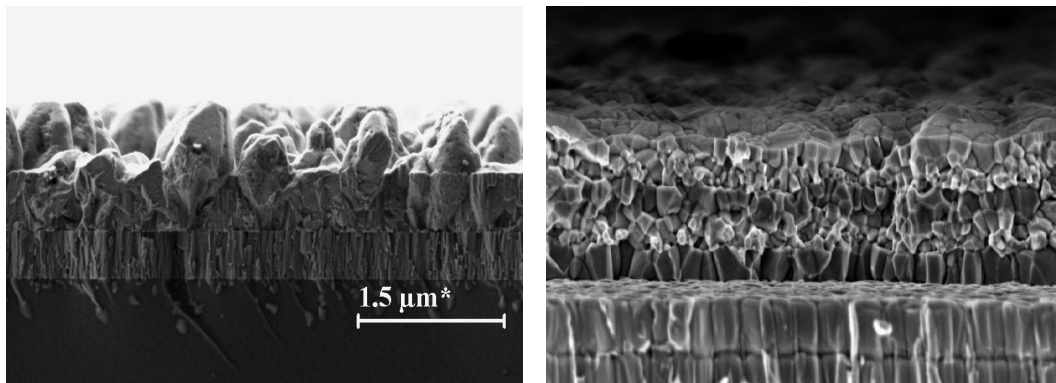
It is shown that co-sputtering of Cu-In layers leads to rough layers with a bi-layer structure of the surface in which island-type CuIn<sub>2</sub> crystals are formed in a small-crystalline copper-rich Cu<sub>11</sub>In<sub>9</sub> matrix layer (fig. 1). The diffusion Cu from the bulk of the layer to the surface at low temperatures of selenization (up to 300°C) leads to the formation of different binary copper selenides. The selenization of In proceeds at higher temperatures and CuInSe<sub>2</sub> formation could be described as a reaction of different binary selenides. The combination of SEM, EDX, XRF, micro-Raman, and XRD studies allows us to show that CuInSe<sub>2</sub> films formed at temperatures higher than 420°C are homogeneous and in single-phase composition with a preferred orientation of crystals along the (112) plane.

The morphology and the structure of precursor Sn-Zn-Cu films depend on the sequence of deposited layers (fig. 2). It is shown that the pathway to form the Cu<sub>2</sub>ZnSnSe<sub>4</sub> under the pressure of elemental Se and the phase composition of selenized films depend on the temperature of selenization. Selenization begins with the formation of binary Cuselenides

on the surface of layers (fig. 3), with the composition varying with the temperature of selenization. The selenization of Sn-Zn-Cu films at temperatures higher than 375°C results always in multiphase films that consist of high quality  $\text{Cu}_2\text{ZnSnSe}_4$  crystals with a size of about 2  $\mu\text{m}$  and of a separate phase of ZnSe. ZnSe phase formed at lower temperatures was amorphous and was not detectable by XRD but well seen on SEM images (fig.4). Selenization at higher temperatures lead to the formation of well-crystalline ZnSe that was easily detected by XRD analyse.

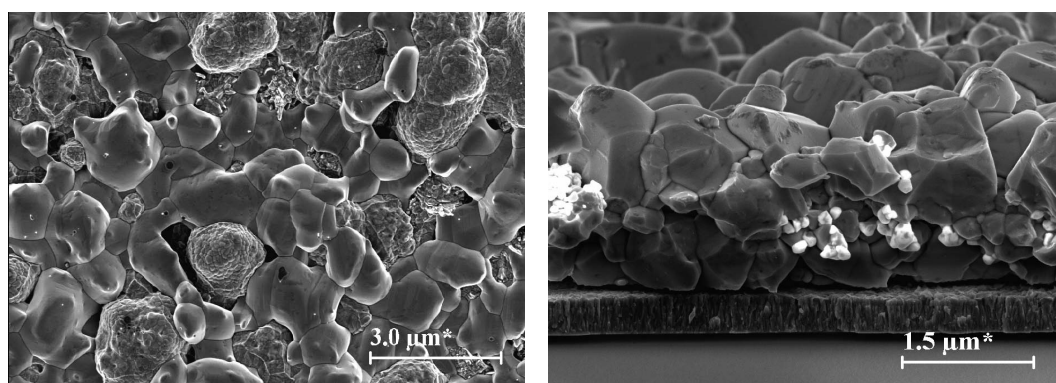
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**Figure 1.** Cross-section of precursor Cu-In layer. The formation of crystals in two different crystalline structure and chemical nature is well seen [1]

**Figure 2.** Cross-section of sequential precursor layer 2x(Zn- Cu/ Sn)



**Figure 3.** Surface of selenized at 320°C Cu-Sn-Zn layer. The out-diffusion of Cu and formation of separate phase of CuSe on the surface is well seen [2]

**Figure 4.** Cross-section of selenized at 420°C  $\text{Cu}_2\text{ZnSnSe}_4$  layer. The formation additionally to  $\text{Cu}_2\text{ZnSnSe}_4$  of separate phase of ZnSe phase is well seen.