HRSEM Study of Sn-Zn-Cu Film Formation

Semiconductor Films Produced by Selenization of Precursors

The formation of CuInSe$_2$ and Cu$_2$ZnSnSe$_4$ thin films in the process of selenization precursor films was studied in use of combined microscopic (HRSEM) and spectroscopic (micro-XRF, EDS, micro-Raman and XRD) methods. Results of investigations allowed showing that the pathway of formation of CuInSe$_2$ and Cu$_2$ZnSnSe$_4$ thin films is similar but there are several differences in the phase composition of the final product that has to be taken into account in the practical use of developed materials.

Introduction

Materials science is a hybrid entity coupling fundamental research with engineering application of the end-product. Following this, material science is aiming to the improvement or development of new materials and to the establishment of relationship between the composition, structure and properties of developed materials. One of the most popular instruments in materials science research is scanning electron microscopy (SEM). There have been remarkable developments in SEM technology during the recent years, driven in part by the need to investigate smaller and more complex objects with higher resolution. With newly developed detectors, the use of SEM is contributed as a powerful tool in both, the characterization and identification of materials [1]. At the same time the use of SEM as the only method in materials characterization has several limitations and combination of SEM investigations with some spectroscopic methods could give additional very valuable information for materials scientists [2].

Chalcopyrite and kestrite polycrystalline semiconductors (CuInSe$_2$ (CIS), Cu$_2$ZnSnSe$_4$ (CZTS) have been extensively studied due to their excellent optoelectronic properties for solar cells formation. These materials are characterized by a suitable band gap, a high absorption coefficient that exceeds 105 cm$^{-1}$ and good stability [3, 4]. Several techniques have been reported for the growth of chalcopyrite and kestrite polycrystalline films, such as metal-organic vapor phase epitaxy, molecular beam epitaxy, chemical spray, flash evaporation, coevaporation, synthesis from the melt, chemical deposition and electrodeposition.
The two-stage process of the chalcogenization of precursor layers of different origin in elemental selenium and sulphur vapor has shown a promise of low-cost and large-scale production of films with photovoltaic applications quality [5, 6].

**Experimental**

The precursor alloy films for CIS were deposited by magnetron co-sputtering of elemental Cu and In. The stacked precursor Sn-Zn-Cu and stacked binary ZnSe-SnSe$_2$-CuSe films were sequentially deposited by vacuum evaporation 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 540°C. The duration of the selenization was between 0.16 and 5 hours.

SEM based methods were used as major to study the influence of precursor composition and post-treatments on the structure, morphology and composition of different precursor CuInSe$_2$ and Cu$_2$ZnSnSe$_4$ films. 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 micro-beam X-ray fluorescence (XRF) analysis (diameter of X-ray spot 10 μm). If the precise chemical identification of formed multiphase materials was needed, the SEM based microscopic methods were combined with different spectroscopic investigations. The phase composition of films was studied by Horiba’s LabRam HR high resolution spectrometer, equipped with a multichannel detection system in the backscattering configuration using the incident laser light with the wavelength of 532 nm focused on samples within a spot of 1 μm in diameter and/or by X-ray
diffraction (XRD) using Cu Kα as X-ray source in a Bragg-Brentano geometry [7].

**Formation of CuInSe$_2$ Films**

Co-sputtering of Cu-In leads to the formation of layers with a bi-layer structure of the surface in which island-type CuIn$_2$ (34.3 at % Cu, 65.7 at % In by EDS) crystals are formed in a small-crystalline copper-rich Cu$_{11}$In$_9$ (50.6 at % Cu, 49.4 at % In by EDS) matrix layer (fig. 1). The diffusion of Cu from the bulk of the layer to the surface at low temperatures of selenization (up to 300°C) leads to the formation of binary copper selenides on the surface. The selenization of In proceeds at higher temperatures and CuInSe$_2$ 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$_2$ films formed at temperatures higher than 420°C are homogeneous and in single-phase composition (fig. 2) with a preferred orientation of crystals along the (112) plane.

**Formation of Cu$_2$ZnSnSe$_4$ Films**

The morphology and the structure of precursor stacked Sn-Zn-Cu films depend on the sequence of deposited layers. The pathway of formation of Cu$_2$ZnSnSe$_4$ in selenization process is similar to the pathway of formation of CuInSe$_2$. Selenization begins with the formation of binary copper selenides on the surface of formed layers, with the composition varying with the temperature of selenization (fig. 3, 4). In difference of formation of CuInSe$_2$ the formation of Cu$_2$ZnSnSe$_4$ the selenization of Sn-Zn-Cu films at temperatures higher than 375°C results always in multiphase films that consist of high quality Cu$_2$ZnSnSe$_4$ crystals with a size of about 2 μm and of a separate phase of ZnSe. Formed ZnSe phase was as rule amorphous and was not detectable by XRD (fig. 4) but was easy detectable in Raman spectra and well seen on SEM images (fig. 5).

**Conclusions**

The pathways to form the CuInSe$_2$ phase during selenization of co-sputtered Cu-In alloy films and the Cu$_2$ZnSnSe$_4$ phase from sequential Sn-Zn-Cu films under pressure of elemental Se are kinetically controlled and the phase composition of selenized films depends on temperature of selenization. The important role of Cu out-diffusion at temperatures less than 300°C in CuInSe$_2$ and Cu$_2$ZnSnSe$_4$ phases' formation mechanism and kinetics is confirmed. The selenization at high temperatures (higher than 420°C) results in high quality dense chalcopyrite CuInSe$_2$. 
films with a preferred orientation of the crystals in the (112) direction. In difference the selenization of Sn-Zn-Cu films at temperatures higher than 375°C results always in multiphase films that consist of high quality Cu$_2$ZnSnSe$_4$ crystals and of separate phase of ZnSe.

**Acknowledges**
This research was financially supported by Estonian Ministry of Higher Education and Science (project T099) and by ESF (projects G-8147 and G-7595).

**References**

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