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Technology for Obtaining $Cu_2ZnSnSe_4$ Thin Films

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***Abstract*. $Cu_2ZnSnSe_4$ thin films were obtained by sequential deposition of basic elements (Sn, Se, Zn, Cu) on a glass substrate. The thickness of each layer was selected to achieve 2:1:1:4 stoichiometric ratio for copper, zinc, tin and selenium, respectively. To obtain compound $Cu_2ZnSnSe_4$ samples were annealed at temperature range of 150^0C to 400^0C. Surface of samples were investigated using scanning electron microscope. Analysis of chemical composition and x-ray diffractometry was performed before and after annealing of samples.**

***Keywords* – semiconductor, $Cu_2ZnSnSe_4$, thermal annealing.**

I INTRODUCTION

Copper zinc tin selenide $Cu_2ZnSnSe_4$ (CZTSe) is among perspective materials for solar energy harvesting due to its optical and electrical properties. $Cu_2ZnSnSe_4$ has a narrow bandgap, high absorption and long-term stability. From the ecological point of view it is important that $Cu_2ZnSnSe_4$ is a non-toxic («Cd-free») material because of the lack of heavy metals in it. It consists of widespread and therefore relatively cheap elements. Still, efficiency of material is low and it is necessary to invest in further research to optimize technological processes of $Cu_2ZnSnSe_4$ production.

The aim of the research was to obtain $Cu_2ZnSnSe_4$ compound by sequential sputtering on glass substrate and annealing the samples afterwards. Influence of annealing temperature on forming of compound was investigated as well as influence of layer sputtering sequence on optical and electrical properties of $Cu_2ZnSnSe_4$ samples.

II MATERIALS AND METHODS

A. *Synthesis of $Cu_2ZnSnSe_4$ (CZTSe) films*

To provide interaction between the initial compounds (copper selenide, zinc and tin) most effective technology for obtaining thin films was selected. CZTSe films were obtained on glass substrate using vacuum evaporation system EMC 150T ES (Quorum Technologies Ltd.), which is a combined system with interchangeable inserts for sputter coating or carbon/metal evaporation.

For application of selenium (Se) thermal evaporation method was used. Thickness of applied layers was controlled by quartz resonator while evaporation rate was maintained in required range by regulating current in evaporator. Evaporator is a metallic plate shaped as boat which contains selenium tablets.

Evaporation time was 10 minutes. Cu, Zn and Sn were applied by magnetron sputtering device EMC 150T ES (Quorum Technologies Ltd). The effect of compound application sequence was studied and optimal parameters were selected on the basis of experimental data (Table 1). Table 1 shows the sequence of sputtered layers as well as thickness of each layer.

TABLE 1.

Layer N^0	Compound	Layer thickness (mm)
1.	Cu	20
2.	Zn	20
3.	Sn	30
4.	Se	360
5.	Sn	60
6.	Cu	30
7.	Se	800
8.	Zn	25
9.	Cu	45

To determine the optimal conditions for obtaining $Cu_2ZnSnSe_4$, samples were annealed in furnace at different temperatures. Temperature was varied from 150^0C to 400^0C by step of 50^0C. It was investigated if there is a correlation between annealing temperature and formation of compound $Cu_2ZnSnSe_4$.

B. *Methods of investigation*

Surface of thin films was investigated, using scanning electron microscope (SEM) TESCAN-VEGA LMU II. Investigation of thin films structure was performed on x-ray difractometer SmartLab RIGAKU with Cu-Kα radiation (λ = 1.543 Å) operated at an acceleration voltage of 40 kV and an emission current of 150 mA. Bragg - Brentano focusing optic wavelength with a primary monochromator was used.

The phase structure analysis of films was performed by comparing distances between crystal lattice planes of samples with those of etalon samples according to JCPDS data. Relative intensity of x-ray diffractogram (XRD) peaks was also compared to etalon samples.

To acquire precise values of crystal lattice constant, Nelson-Riley extrapolation method was applied. Linear approximation of obtained values was carried out with a method of least squares.

III RESULTS AND DISCUSSION

Figures 1 and 2 show SEM images of $Cu_2ZnSnSe_4$ films annealed at different temperatures. At annealing temperature of 200^0C film has a finely dispersed structure. With a temperature growth, an increase of crystallite size can be observed (Fig.1).

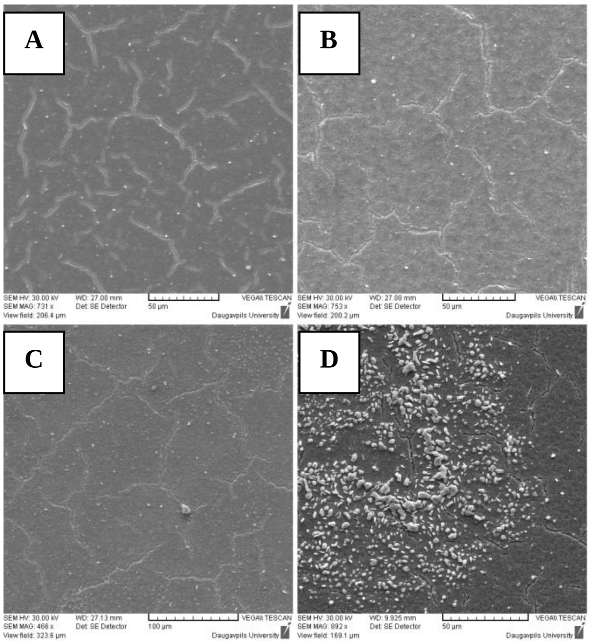

Fig. 1. SEM images of $Cu_2ZnSnSe_4$ films annealed at a) 250 ^{0}C; b) 300^0C; c) 350^0C; d) 400^0C.

Structural analysis of crystallites of the sample annealed at 400^0C (Fig.1,d) showed that they consist of copper oxide. That means that further increase of annealing temperature is not recommended because of increase of metal oxide in sample. Besides, in the annealing process amount of Se in sample decreases due to its evaporation.

Investigation of thin films structure was performed on x-ray difractometer. Since the multi-layer structures were evaporated on glass substrates coated with an ITO layer, there are peaks corresponding to In_2O_3 on all XRD patterns. In samples annealed at 250^0C, the required CZTSe compound wasn't obtained. In that case thin films are composed of CuSe, ZnSe and SnSe. At annealing temperature of 300^0C CZTSe compound appears and peaks relevant to simple selenides CuSe, ZnSe and SnSe disappear. When increasing temperature to 350^0C, improvement of CZTSe crystalline structure is observed. Further increase of temperature to 400^0C, Cu_8O peaks appears on XRD pattern together with CZTSe peaks.

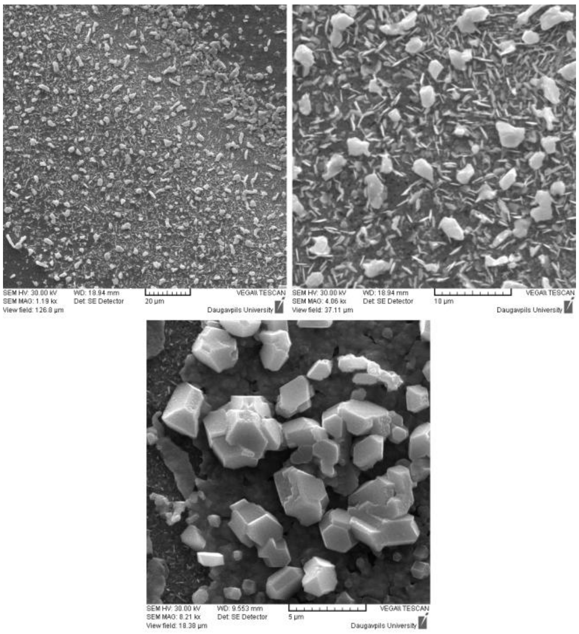

Fig. 2. SEM images of CZTSe film annealed at 400^0C at different scale.

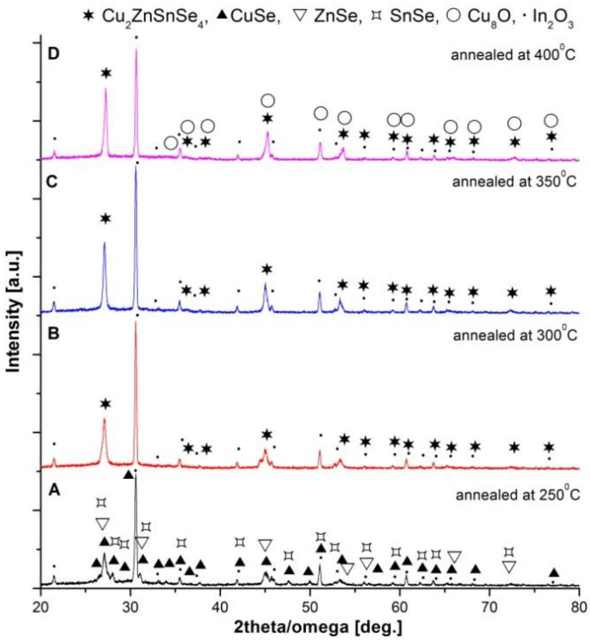

Fig. 3. X-ray diffractometry data of $Cu_2ZnSnSe_4$ films annealed at: a) 250 ^{0}C; b) 300^0C; c) 350^0C; d) 400^0C.

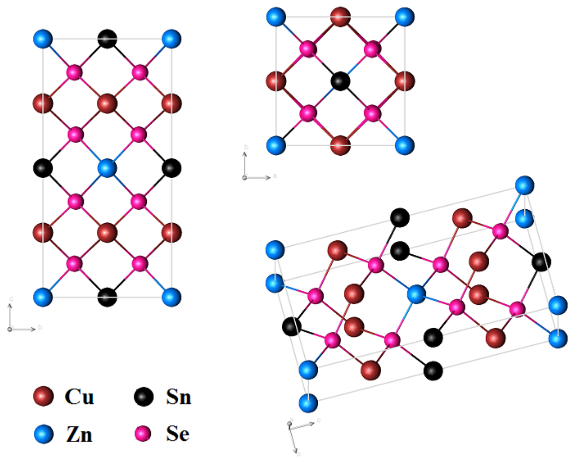

Fig. 4. Structure of $Cu_2ZnSnSe_4$ crystal lattice according to x-ray diffractometry data of thin film annealed at 350 ^{0}C.

From the experimental data it was concluded that optimal conditions for annealing of compounds is temperature of 300 - 350^{0}C for 30 minutes.

IV CONCLUSION

Method for obtaining $Cu_2ZnSnSe_4$ compound was developed. Potential of obtaining extra-pure thin films using thermal and magnetron sputtering was investigated. Surface morphology and structure of $Cu_2ZnSnSe_4$ films was explores after annealing at different temperatures. Minimal temperature of transition from amorphous to crystalline phase was determined.

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