

Analysis of the Elemental Composition of $\text{Cu}_2\text{ZnSnSe}_4$ Films by the PIXE and μ -PIXE Methods

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(Received 23 March 2014; published online 20 June 2014)

By X-ray characteristic radiation induced by focused proton beam, the distribution of compound components over the area of $\text{Cu}_2\text{ZnSnSe}_4$ (μ -PIXE) films is investigated and their elemental composition (PIXE) is determined. Nuclear scanning microprobe with the proton beam energy of 1.5 MeV and the transverse dimension of the probe of $4 \times 4 \mu\text{m}^2$ was used for the method realization. Films of four-component compound were obtained under different physical and technological deposition modes by the thermal co-evaporation of the components using electron-beam gun. Sodium glass with molybdenum sublayer heated to 400 °C was used as the substrate. As a result of investigations it was established that the distribution of elements over the film area is homogeneous and their composition is determined by physical and technological conditions of preparation.

Keywords: Elemental composition, $\text{Cu}_2\text{ZnSnSe}_4$ film, PIXE, μ -PIXE techniques.

PACS numbers: 68.37.Hk, 78.66.Hf, 81.15.Ef

1. INTRODUCTION

Four-component $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) compound is currently considered as an alternative to traditional absorbing layers of high-efficiency thin-film solar cells, such as CuInSe_2 (CIS), $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) and CdTe . This is conditioned by the compound band gap, which is close to the optimal one for the transformation of solar energy and equal to $E_g = 1.0$ eV, by high light absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$), p -type electrical conduction of the material, large lifetime of charge carriers, and sufficiently high their mobility as well [1-2]. In contrast to other semiconductors, which are used today as absorbing layers of film photoconverters, this compound does not contain rare and environmentally dangerous metals; the elements entering its composition are widespread in the Earth's crust, and their extraction cost is low [3-4]. Together with this, production of the films of four-component CZTSe compound is connected with certain difficulties, since its components have substantially different values of the vapor pressure and homogeneity region is rather narrow [1]. As a result, obtained layers often contain some phases with different band gaps [5-7].

At present, film-like CZTSe compound is obtained by several methods, such as magnetron batch sputtering, electrical deposition of Cu, Zn, Sn precursors with their further annealing in Se atmosphere, spray pyrolysis, thermal co-evaporation of the components, etc. [1-2, 5-9]. Here, method of thermal co-evaporation of the compound components is one of the most acceptable, since it allows to control the composition of the obtained films in a wide range of values. Together with this, the influence of the physical and technological conditions of preparation on the film composition during their deposition by this method has been studied insufficiently.

2. INVESTIGATION TECHNIQUE

CZTSe films were obtained by the method of co-evaporation of the compound components (Cu, Zn, Sn and Se)

using electron-beam gun; here Se was evaporated thermally in order to obtain high deposition rate. Chemical composition of the samples was controlled by the deposition rate and time, which were governed by the device SQC310C (Inficon Inc., USA), in which quartz crystal with golden coating was used. Calculated composition of the obtained films is given in Table 1. Condensation was performed on the cleaned sodium-containing glass substrates with conducting Mo sublayer of the thickness of 1 μm . During deposition substrate temperature was maintained at 400 °C. Condensation time was equal to 2 hours. Technique of the condensate preparation is described in detail in [10-11].

Table 1 – Physical and technological conditions of film preparation

Sample number	Thickness, μm	Cu/(Zn + Sn)	Zn/Sn	Notes
1161	1.25	0.8	1.2	stoichiometric
1156	1.9	0.47	1.69	Cu depleted, Zn enriched
1152	1.75	0.84	0.51	Cu, Zn depleted
1157	2.25	1.22	1.23	Cu, Zn enriched

Morphology of the film surface was investigated by the scanning microscopy.

To determine the elemental composition of the samples, we have used microanalytical accelerating complex based on compact electrostatic accelerator "Sokil" with the proton beam energy up to 2 MeV (Institute of Applied Physics NASU, Sumy). The complex is equipped by analytical channels of the analysis of nuclear reactions, ionic luminescence, Rutherford backward scattering (RBS) with magnetic spectrometer and nuclear scanning microprobe with detectors of the secondary electron emission, semiconductor detector of the characteristic X-ray radiation and charge-particle detector [12].

X-ray characteristic radiation induced by a proton beam was used for the analysis of the film composition [13-14]. Here, total spectra from some surface regions of the samples were taken (PIXE), whose point scanning was performed later by a microbeam (μ -PIXE). Usually, a film region of the size of $200 \times 200 \mu\text{m}$ was scanned, the transverse size of the probe was equal to $4 \times 4 \mu\text{m}^2$, charge $Q = 4 \times 10^{-10} \text{ C/pixel}$, raster 50×50 pixels, scanning step $4 \mu\text{m}$, proton energy was $E_p = 1.5 \text{ MeV}$. Here, by pixel we mean the stationary position of the probe during discrete scanning. Features of the focusing and scanning system of the microanalytical accelerating complex are described in [11].

As a result of the study, we have obtained the distribution maps of the elements entering to the compound composition over the sample area and established the elemental composition of the condensates in some film regions. Processing of the PIXE spectra was carried out using the GUPIX program. For the transition from the mass concentration to the atomic one (C_i) we have used the standard expression given in [15].

The RBS method was also applied for the determination of the elemental composition of the films [13-14]. In this case, primary proton beam fell normally on the target; the angle between primary beam direction and scattering direction was equal to 135° . Magnetic spectrometer with silicon charge-particle detector was used as the detecting system. Processing of the RBS spectra was performed by the SIMNRA and DVBS programs.

3. EXPERIMENTAL PART

Electron microscope images of the surface of CZTSe films obtained at different pressures of the components are illustrated in Fig. 1.

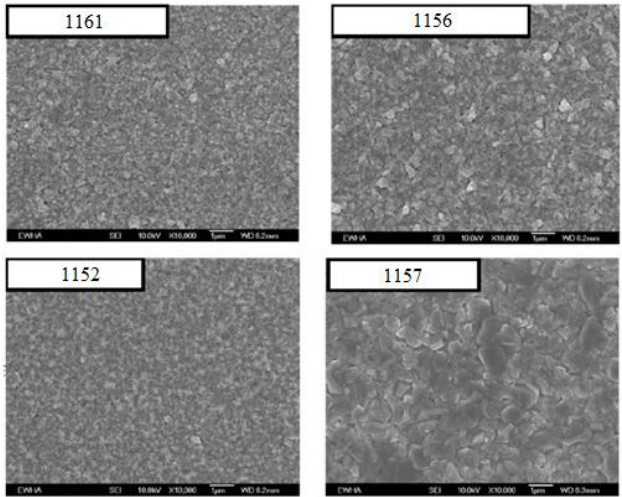


Fig. 1 – Electron microscope image of the CZTSe film surface

The films had polycrystalline structure with the grain size of $0.1\text{-}1 \mu\text{m}$. It was shown earlier by the X-ray diffractometry and Raman spectroscopy methods that condensates were virtually single-phase and mainly contained only CZTSe compound [11].

Typical total PIXE spectra (in the logarithmic scale) obtained from two arbitrary surface regions of CZTSe film (sample 1152) after irradiation by a proton beam are represented in Fig. 2. As seen from the figure, only

lines from the compound components (Cu, Zn, Sn, Se) are registered in the spectra, as well as from the conducting Mo sublayer.

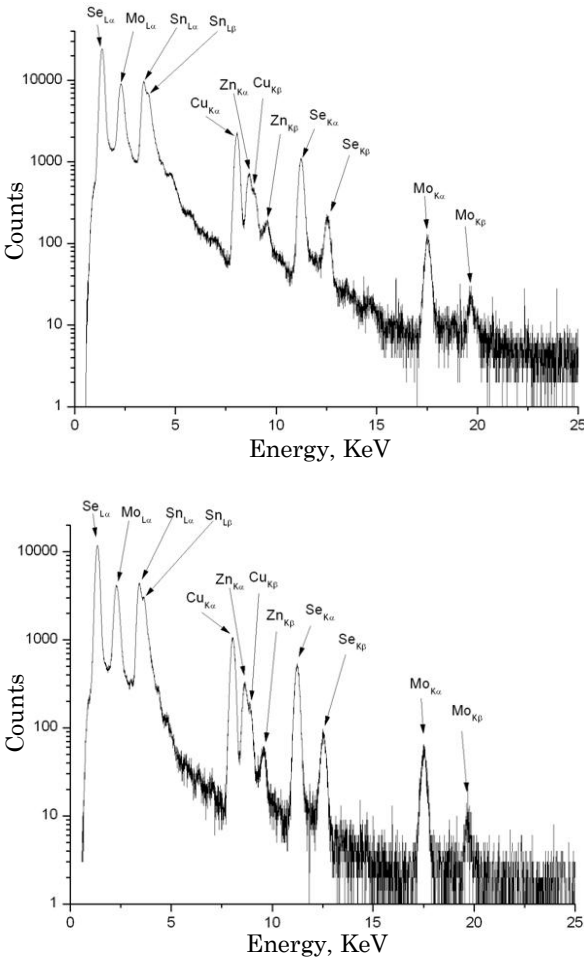


Fig. 2 – Total PIXE spectra obtained from CZTSe film (sample 1152) induced by a proton beam: region 1 (a), region 2 (b)

Processing of the experimental PIXE spectra allowed to define the mass concentrations of the constituent elements of CZTSe films. The corresponding results for a set of the samples obtained at different physical and technological conditions of condensation are presented in Table 2. Using these results, we later obtained the atomic concentration of the components in the samples and their ratio which determines the compound stoichiometry. The averaged calculation data is also given in Table 2. As it was already indicated, the measurements were performed in some points of the samples surface; and here we should note that with the method accuracy the changes in the composition of the solid solution over the film surface have not been revealed.

Table 2 – Analysis results of the elemental composition of the samples by the PIXE method

Sample No	Cu, wt. %	Zn, wt. %	Sn, wt. %	Se, (at.) %	Cu/(Zn+Sn)	Zn/Sn
1161	19.45	12.41	54.24	13.91	0.74	0.89
1156	16.81	17.57	52.52	13.11	0.55	1.34
1152	22.11	7.44	51.66	18.79	0.84	0.40
1157	18.03	17.70	47.91	16.36	0.53	1.08

As seen from the comparison of the data of Table 1 and Table 2, film composition was determined by the physical and technological conditions of deposition and slightly differed from the calculated one.

Typical distribution maps of the elements over the surface of the studied sample for the region of CZTSe film, in which the PIXE spectrum was taken, are illustrated in Fig. 3. Here on a scale near the maps we have shown the yield in each pixel of a number of quanta of the characteristic X-ray radiation induced by a focused proton beam in the energy range conforming to the K_α -peak of the corresponding element in the spectrum (see Fig. 3). It is established that difference in the yields of the characteristic X-ray radiation in each pixel is on the level of statistical straggling; therefore, one can state that distribution of the compound components over the film surface is sufficiently uniform.

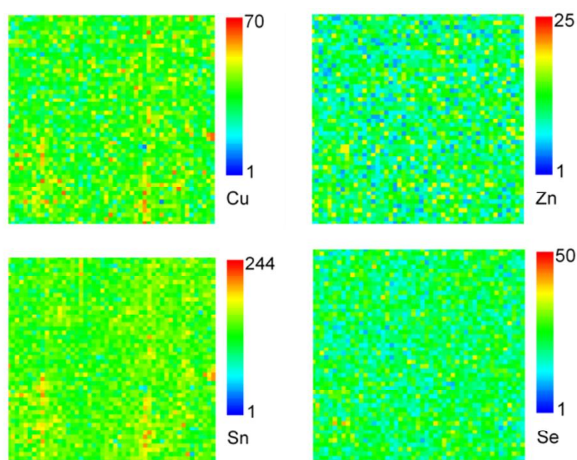


Fig. 3 – Distribution maps of Cu, Zn, Sn, Se over the surface region of CZTSe film of the size of $200 \times 200 \mu\text{m}$, scanning step is $4 \mu\text{m}$ (sample 1152)

In order to increase the reliability of the obtained results in the study of the elemental composition of CZTSe films, we have tried to apply the RBS proton method. The typical scattering spectra from the condensates are represented in Fig. 4.

As seen from Fig. 4, peaks from copper, tin, zinc and selenium in the RBS spectra, as well as in the work [2], are superimposed with each other. This did not allow to determine the elemental composition of the condensates with the necessary accuracy by the given method and

plot the distribution of the elements over the layer thickness, as we have done earlier for ZnS films [16]. However, analysis of the RBS spectra allowed to calculate the film thickness. The corresponding results are represented in Table 1.

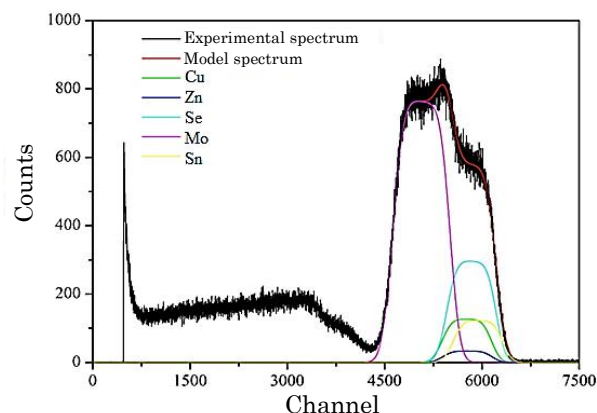


Fig. 4 – Energy RBS proton spectra from the sample 1152. The dashed line is the spectrum simulation

4. CONCLUSIONS

1. Investigation of CZTSe film samples obtained by co-evaporation of the components is performed by the PIXE and μ -PIXE methods.

2. Distribution maps of the elements entering the compound composition over the surface area are plotted and elemental composition of the films depending on the deposition conditions is determined.

3. It is shown that distribution of the elements over the film area is uniform and film composition is defined by the physical and technological conditions of deposition and differs slightly from the calculated one.

4. We failed to determine the elemental composition of CZTSe films by the RBS method because of the overlapping of the peaks of the elements entering the compound composition.

ACKNOWLEDGEMENTS

This work has been performed under the financial support of the State Agency of Ukraine on Science, Innovations and Informatization and the Ministry of Education and Science of Ukraine (Grant M/56, Project No 0113U000131).

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