



Structural Properties of the Sn_xS_y Films Obtained by the Thermal Vacuum Co-evaporation

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The present work deals with the study of the structural properties of the Sn_xS_y thin films deposited by the closed-spaced vacuum co-evaporation (CSVCE) method. Calculation of temperature dependencies of the sulfur and tin vapor pressures allows to estimate growth conditions of the films with the stoichiometric composition. The effect of growth conditions on surface morphology and structural properties of Sn_xS_y films were studied. Surface morphology of obtained films was determined by the scanning electron microscope (SEM-102E). Structural investigations of the films were performed with the X-ray diffraction (XRD) method. The analysis of chemical composition of the layers was carried out by the scanning electron microscope by energy dispersive X-ray (EDAX) spectroscopy. Influence of the substrate temperature on chemical composition of thin films and their structural characteristics was also investigated.

Keywords: Thin Films, Sn_xS_y , Co-evaporation, Surface morphology, X-ray diffraction, Crystal structure.

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1. INTRODUCTION

The usage of solar energy is the progressive way to overcome global energy crisis. Among widely known modern methods of conversion of solar energy into electricity the photoelectric with the application of semiconductor solar cells (SC) based on heterojunction is the most effective one [1].

A set of demands is placed on the base-layer materials of highly effective thin films SC. Namely, optimal band gap for converting solar energy $E_g = (1.0-1.5)$ eV, p-type conductivity, substantial lifetime ($\tau = 7.5 \cdot 10^{-7}$ sm²·V⁻¹) and mobility of free carriers ($\mu = 21$ cm²/V·s), also it should be a direct band gap material with high photonic absorption coefficient ($\sim 10^5$ cm⁻¹) [2-4]. Such materials as GaAs, CdTe, CuInSe₂ (CIS), CuIn_{1-x}Ga_xSe₂ (CIGS) fulfill above mentioned requirements. Unfortunately, these compounds include rare (In, Ga) or toxic (Cd) elements, this complicates use of their materials in creation of large – scale terrestrial thin film solar cells [2].

This led to the search for new economic semiconductor materials for third generation SC [5]. Today SnS could be considered as the perspective material for thin film SC. This is presupposed by the fact that it fully meets demands to highly effective SE, possess bang gap $E_g = 1.36$ eV, and includes no toxic or rare elements [6]. Besides of that, the SnS, Sn₂S₃ and SnS₂ compounds with different band gaps and conductivity type could be formed within sulfur-tin system [7]. This gives an opportunity to create heterojunctions SC based on the, n - SnS₂/p - SnS [8].

Nevertheless today record efficiency of SnS based laboratory SC is only 2.46 % [9]. This is due to difficulties in obtaining films SnS with optimized properties and ineffectiveness of the construction of converters [10].

Properties of thin films Sn_xS_y were studied in various works [11-15]. Several different techniques have been successfully employed in SnS thin films deposition, such as spray pyrolysis [5,16], chemical deposition

[17], pulsed chemical vapor deposition (P-CVD) [18], electrochemical deposition [19], pulsed electrochemical deposition [20], atomic layers deposition [21], sulfurization of Sn [22], thermal vacuum evaporation [3,6,11-15,23-25], hot wall vacuum deposition method [7,12]. It was showed that with the changing of the growth method or growth parameters it is possible to obtain both single-phase films SnS, Sn₂S₃, SnS₂ and layers including several phases.

In order to use Sn_xS_y as a SC base layer it is necessary to obtain thin films with controllable and predefined optical and electrophysical characteristics, which in their turn are defined by their crystal structure. However, currently there are only few works dealing with the study of the influence of growth conditions on the phase composition and structural characteristics of films, deposited by close-spaced vacuum co-evaporation (CSVCE).

2. EXPERIMENTAL DETAILS

Thin films Sn_xS_y were obtained on ultrasonically cleaned glass substrates in vacuum chamber under interstitial gas pressure not higher than $5 \cdot 10^{-3}$ Pa. The CSVCE was used as growth method due to necessity to obtain films with small deviation from stoichiometry, in conditions close to thermodynamic equilibrium. For this purpose a system for co-evaporation of sulfur and tin was created and approbated. This evaporation system is presented at Fig.1.

The temperature of sulfur evaporator was $T_{\text{S}_2} = 420$ K and for tin - $T_{\text{Sn}} = 1190$ K. Temperature of the substrate T_s was changed within range from 573 to 732 K. Deposition time was $t = 5$ min. Thickness of the obtained layers was estimated by the SEM from the cross-section of samples.

Surface morphology of the films was investigated by a scanning electron microscope (SEM-102E).

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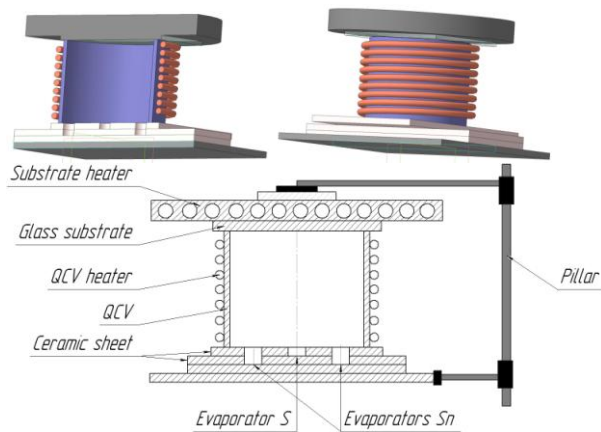


Fig. 1 – Scheme and 3D model of the system closed-spaced vacuum co-evaporation of sulfur and tin

The chemical composition of the films was estimated by X-ray radiation energy-dispersive analysis (EDAX). Hereby calculation of concentration was performed in at least 5 points on the sample’s surface with the averaging of results. The following formula was used to convert mass concentration to atomic concentration:

$$C_i(\% \text{ at}) = \frac{C_i(\% \text{ mas})}{A_i \left(\sum_{i=1}^n \frac{C_i(\% \text{ mas})}{A_i} \right)} \quad (1)$$

where A_i – atomic weight of the i -element ($A_S = 23.066$; $A_{Sn} = 118.71$), C_i – atomic and mass concentrations of the i -element. To estimate the deviation from stoichiometry, correlation C_S/C_{Sn} was used.

Structural analysis of the Sn_xS_y films was performed by XRD. The samples were studied by the X-ray diffractometer DRON 4-07 in the Ni-filtered K_α radiation of a Cu anode in the range of diffraction angles 2θ from 20° to 80° .

Lattice constant of the materials of films was defined with the use of well-known equation [26].

3. RESULTS AND DISCUSSION

The difficulty in obtaining films Sn_xS_y with vacuum methods could be explained by the incongruent dissociation of the compound during evaporation and great difference in vapor pressure of components of the compound Sn and S [27,28]. That is why to obtain Sn_xS_y thin films of a defined composition by vacuum evaporation, it is very important to calculate the vapor pressure of sulfur and tin. This gives possibility to estimate optimal evaporation temperatures at which it is possible to obtain the material with the close to stoichiometry composition. Correspondent calculations were carried out according to a standard formula [29]:

$$\log P = A + BT^{-1} \quad (2)$$

where P – pressure (Pa), A , B – constants (S_2 : $A = 10.07$; $B = 4928.53$; Sn: $A = 6.036$; $B = -15710$), T – temperature (K).

Correspondent coefficients A , B were taken from the reference literature [29] or were calculated by approximation of the experimental data [30].

Results of calculation of the pressure of sulfur and tin at different evaporation temperatures are presented at Fig. 2.

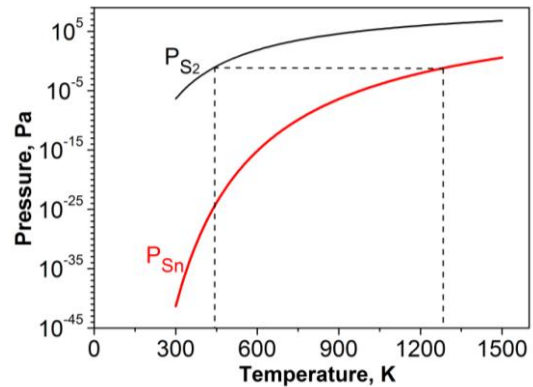


Fig. 2 – The temperature dependence of the vapor pressure of S_2 and Sn on (the dotted lines show optimal temperatures, which allow to obtain similar vapor pressure of the components during their co-evaporation)

It was determined that, optimal temperatures for sublimation of the components at the vapor pressure of S_2 and Sn $P = 0.1$ Pa is $T_{S_2} = 420$ K and $T_{Sn} = 1190$ K. This temperature regimes were used to obtain Sn_xS_y films.

Surface morphology of the films, obtained at different temperatures of the substrate, is presented at Fig. 3. SEM picture show that thin layers are polycrystalline and consist of platelet-shaped grains.

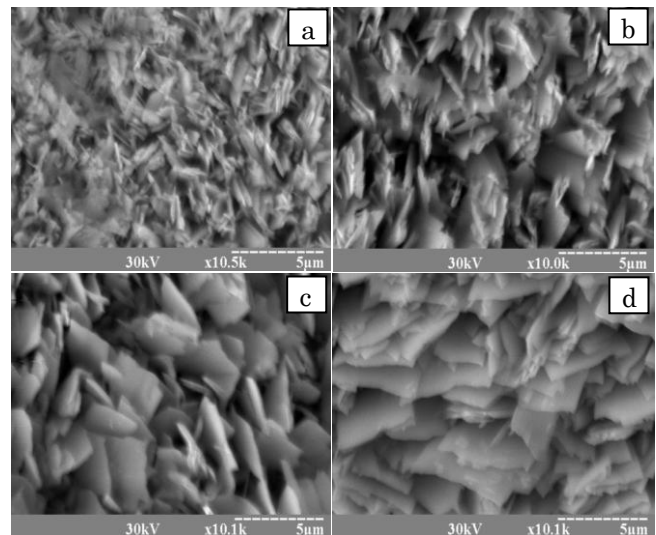


Fig. 3 – SEM images of Sn_xS_y films, obtained at different T_s , K: 573 (a), 623 (b), 673 (c), 723 (d)

Thickness of the grains was about 300 nm. It was observed a tendency of increasing in size of platelet-shaped crystals from 0.7 μm to 4.2 μm with the increasing of the temperature of the substrate from 573 K to 732 K.

Thickness of the Sn_xS_y films was estimated from SEM picture of the samples cross-section (Fig. 4) and it was about $d = 6 \mu\text{m}$.

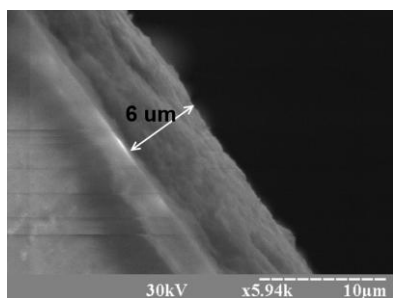


Fig. 4 – Typical cross-section of the film Sn_xS_y obtained at $T_s = 673$ K

To define the influence of substrate temperature on stoichiometry of the Sn_xS_y films, obtained by closed-spaced vacuum co-evaporation, their chemical composition was investigated by X-ray microanalysis. The EDAX spectrums of the samples are shown at Fig. 5.

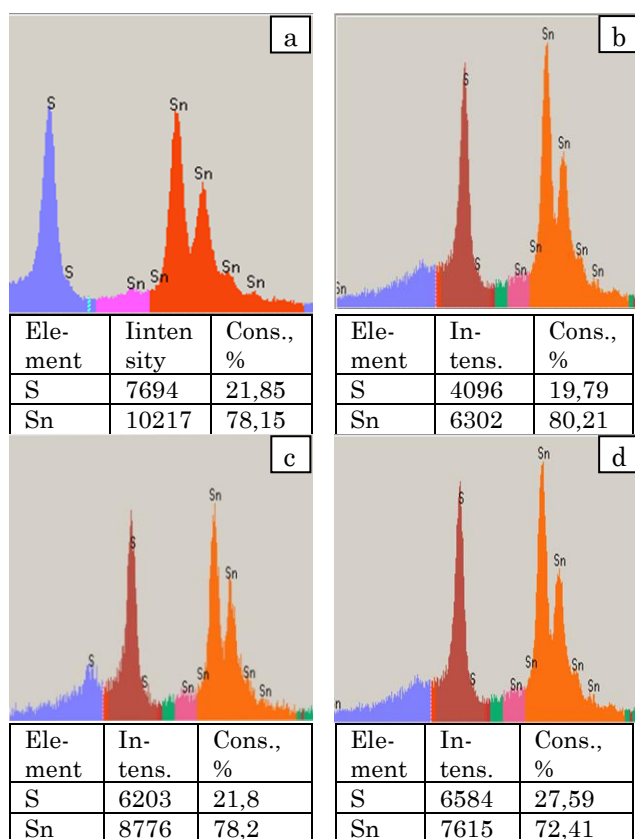


Fig. 5 –EDAX spectrum of the Sn_xS_y films, obtained at different substrate temperatures T_s , K: 573 (a), 623 (b), 673 (c), 723 (d)

The Fig. 5 shows that at the spectrum there are only lines of components of the compound. The lines from uncontrolled impurities were not observed. Analysis of the films showed homogenous composition on the whole surface. To define stoichiometry of the films mass concentrations of components were converted into atomic ones and there ration was calculated. Results of the calculation are presented in Table 1.

As the results of the investigation of film composition by EDAX method (Fig. 6) proved, these films in general are slightly tin-rich. Hereby with the change of substrate temperature, composition of films was chang-

ing within the limits $\gamma = C_s/C_{\text{Sn}} = 1.03 - 1.41$. It was determined that stoichiometry of films was becoming better when condensation conditions were close to thermodynamic equilibrium. The most stoichiometric samples $\gamma = C_{\text{Sn}}/C_s = 0.96$ were obtained at $T_s = 573$ K.

Table 1 – Stoichiometry of the Sn_xS_y films

T_s , K	mas.% S	mas. % Sn	at. % S	at.% Sn	C_{Sn}/C_s	C_s/C_{Sn}
573	21.85	78.15	50.86	49.13	0.96	1.03
623	19.79	80.21	47.73	52.26	1.09	0.91
673	21.8	78.20	50.78	49.21	0.96	1.03
723	27.59	72.41	58.51	41.48	0.70	1.41

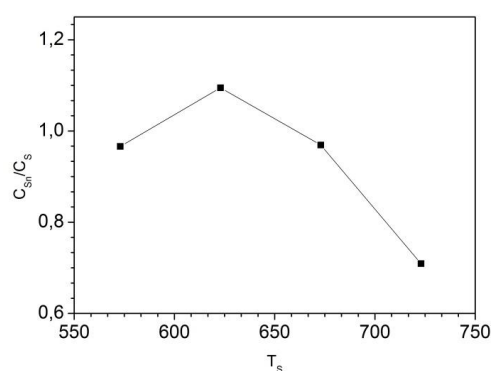


Fig. 6 – Influence of the substrate temperature on the composition of films

The X-ray patterns of the Sn_xS_y films deposited at different substrate temperature presented on Fig. 7.

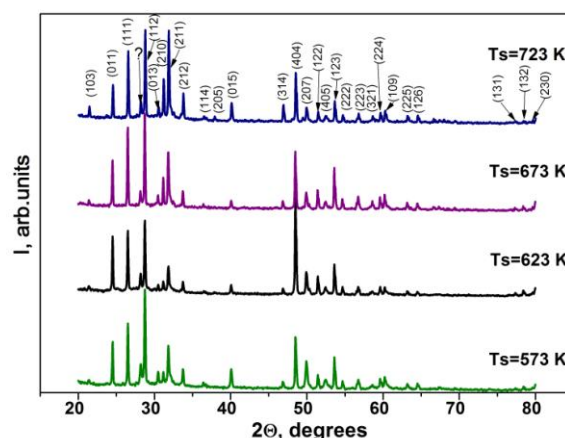


Fig.7 – XRD patterns of the films obtained at different substrate temperature

At XRD patterns a range of peaks, which were identified by us as returns from crystallographic planes (103), (011), (111), (112) and other orthorhombic phase were observed. Positions of this peaks coincides with the JCPDS data for Sn_2S_3 (card No 75-2183), that is not fully understandable, as according to EDAX, correlation of atomic concentrations of tin and sulfur is about 1, that corresponds to compound SnS . Calculated pa-

rameters of the crystal lattice of the material made up $a = 0.88741 - 0.89129 \text{ }\mu\text{m}$, $b = 0.37525-0.37568 \text{ }\mu\text{m}$, $c = 1.40209-1.40948 \text{ }\mu\text{m}$.

As XRD analysis show, with the increase of substrate temperature, peaks (210), (211), (212), (314) increase their intensity. That proves the change of the quality of samples texture.

4. CONCLUSION

1. The work deals with creation and approbation of the system for deposition Sn_xS_y films by closed-spaced vacuum co-evaporation of elements of a compound. Calculated vapor pressures and evaporation temperatures of sulfur and tin allows to provide deposition of thin layers of stoichiometric composition.

2. Analysis of surface morphology and structure of deposited films depending on the substrate tempera-

ture was performed. It was proved that obtained layers consist of platelet-shaped grains about $300 \text{ }\mu\text{m}$ thickness. There was observed increasing in size of crystals from $0.7 \text{ }\mu\text{m}$ to $4.2 \text{ }\mu\text{m}$ with the increasing in the substrate temperature.

3. Chemical composition of the obtained layers depended on the substrate temperature and changed in the range from $\gamma = C_{\text{S}}/C_{\text{Sn}} = 1.03$ to 1.41 . Hereby their stoichiometry was becoming better when condensation conditions were close thermodynamic equilibrium. The most stoichiometric samples ($\gamma = C_{\text{Sn}}/C_{\text{S}} = 0.96$) were obtained at $T_s = 573 \text{ K}$.

4 All obtained films were single-phase and had orthorhombic structure with following parameters of the crystal lattice $a = 0.88741 - 0.89129 \text{ }\mu\text{m}$, $b = 0.37525-0.37568 \text{ }\mu\text{m}$, $c = 1.40209-1.40948 \text{ }\mu\text{m}$.

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