

## The elemental composition, topography and wettability of $Pb_{0.25}Sn_{1.75}S_2$ thin films

**Abstract.** *PbSnS thin films were prepared by hot-wall vacuum evaporation (HWVE) and effect of substrate temperature on structural and surface morphological properties was thoroughly investigated by means of Rutherford backscattering spectroscopy, atomic force microscopy and water contact angle techniques, respectively.*

**Streszczenie.** *Cienkie warstwy PbSnS były wytwarzane metodą naparowania (HWVE). Badano wpływ temperatury podłoża na właściwości warstwy metodą spektroskopii Rutherforda i mikroskopem sił atomowych. (Struktura i and wsiąkliwość cienkich warstw  $Pb_{0.25}Sn_{1.75}S_2$ ).*

**Keywords:** PbSnS films; elemental composition; atomic force microscopy; Contact angle measurement.

**Słowa kluczowe:** cienkie warstwy PbSnS; skład pierwiastków; mikroskopia sił atomowych; pomiary kąta zwilżania.

### Introduction

Most of the present global energy production is accomplished by burning fossil fuels. However, the inherent problems associated with the use of fossil fuels such as their limited availability and the environmental issues force mankind to look for new, more sustainable long-term energy solutions to provide the future energy supply. One of the most powerful alternatives for future large-scale electricity production is photovoltaics, that is, the conversion of sunlight directly into electricity.

Solar cell energetic demands new direct band gap materials instead of current dominant technology based on Si, Cu(In,Ga)Se<sub>2</sub> and CdTe because of indirect band gap of crystalline silicon, high toxicity of cadmium and strong limitation of indium in nature.

In the presented paper we report the properties of thin films of lead tin sulfide (PbSnS). Both PbS (band gap 0.37 eV) [1] and SnS (band gap 1.3 eV) [2] are promising materials in photovoltaic, infrared detection and other optoelectronic devices. These two binary compounds have been extensively studied by many research groups. However, Sn<sub>1-x</sub>Pb<sub>x</sub>S is only rarely described in literature [3] and there is no detailed report on the surface structural behavior with respect to growth temperature.

Hot wall vacuum deposition method (HWVD) has been used for thin IV-VI films deposition for some decades [4]. The method showed high efficiency and economy because it is concerned with the film growth under conditions close to thermodynamic equilibrium and with a minimum loss of material [5]. HWVD has contributed significantly to the growth of high quality epitaxial thin films with smooth surfaces.

### Experimental details

The proper amounts of the elements of 99.999% purity Pb, Sn and S were used to prepare the solid solution initial ingots of bulk material. The mixture is sealed under  $1.3 \cdot 10^{-1}$  Pa vacuum in quartz tube. It was placed vertically in an electric furnace and kept at 450°C for 7 days and after that at 700°C for 10 days. In order to avoid explosions due to the sulfur vapour pressure, the tube was heated slowly (25°C/h). Then the product was grounded and mixed in an agate mortar, sealed in a silica glass tube and reheated at 700°C for 10 days. Crushed powder was used as the raw material for the HWVD the PbSnS thin films onto glass substrates. The chamber pressure was about  $1.3 \cdot 10^{-3}$  Pa. Walls temperature and deposition time were constant 590°C and 30 min, respectively, during deposition process, while the substrate temperature was varied from 268°C to

361°C. The substrate temperature was measured using a Chromel–Alumel thermocouple in contact with substrate surface. Comparisons were drawn in terms of the structure, the elemental composition, the surface morphology and the surface wettability of the semiconductor films.

The Rutherford backscattering technique (RBS) was employed for the investigation of target composition and for depth profiling of components in prepared structures. The energy of He<sup>+</sup> ions was 2.0 MeV, and the scattering, entry and escape angles were 160°, 0°; and 20°, respectively. The energy resolution of the analyzing system was 15 keV. Concentration profiles of components were evaluated using the RUMP code computer simulation.

The surface morphology, crystalline structure and the grain size of thin films were investigated and analyzed using atomic force microscopy (AFM). Atomic force microscopy study of samples was performed using NT-206 microscope (“Microtestmashines”) in the contact mode with silicon cantilever tips CSC21 (“MicroMash”). Roughness values in this paper refer to the average surface roughness values,  $R_a$ , calculated from the AFM surface topographic data. Contact angle (CA) measurement was based on the sessile-drop method described in [6] (Fig. 1). The wetting agent was doubly distilled water.

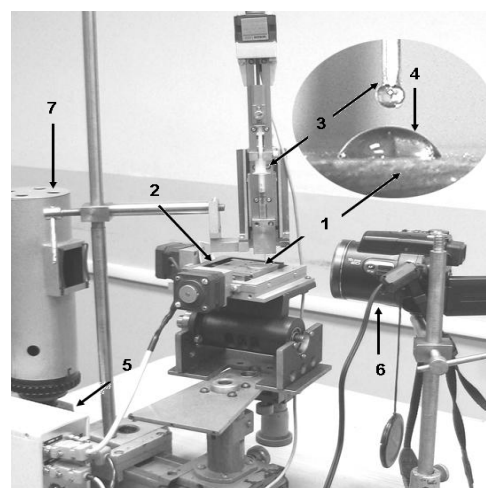


Fig.1. Equipment for contact angle measurements: 1 – sample; 2 – device of positioning of the sample; 3 – syringe; 4 – water drop; 5 – block of electronics; 6 – digital camera; 7 – source of monochromatic light

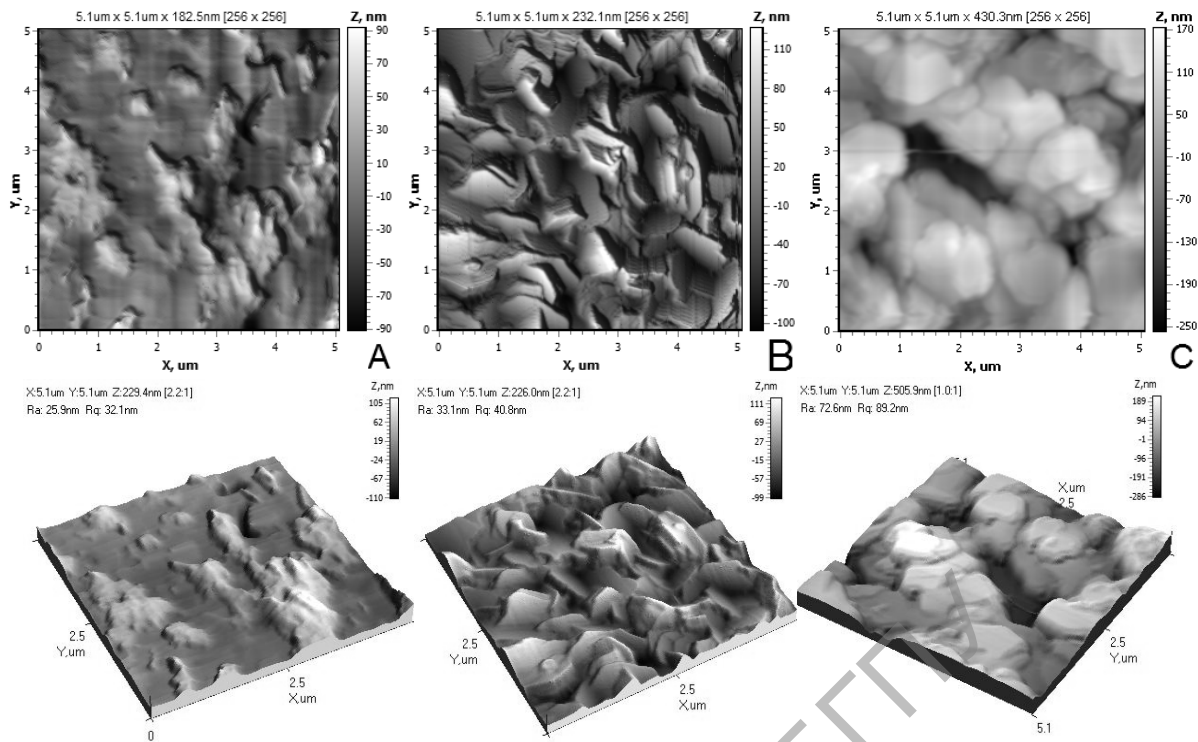


Fig.2. AFM-images of the surface of three different samples (2 and 3 dimensional): (A)  $T_{sub}=268^{\circ}\text{C}$ , (B)  $T_{sub}=330^{\circ}\text{C}$ , (C)  $T_{sub}=361^{\circ}\text{C}$

### Results and discussion

RBS spectra of PbSnS film deposited at  $T_{sub}=330^{\circ}\text{C}$  is shown in Figs. 3 and 4 presents the depth distribution of indicated components in the same (Fig. 3) sample. The data are obtained using the RUMP code simulation. The backscattered energy is nonlinearly connected with depth scale, which starts from the surface for each element at a specific backscattered energy. The surface and the interface lead to the edges in the spectrum.

According to experimental data, the PbSnS films are 0.83-1.68 microns thick (at different temperatures) (Table). With the increase of the substrate temperature, the thickness of film increases too. The films consist of 6.8-10.4 at.% lead, 36.6-44 at.% tin and 48-53 at.% sulphur (Table). Profiles of distribution of elements show that the obtained films are homogeneous. These data indicate that noticeable amount of lead, tin and sulphur (0.1 at.%) is at the depth which is more than  $0.5\ \mu\text{m}$  deeper under interface. This means that during HWVD process the atoms: Pb, Sn and S penetrate deeply into the glass. The thickness of an intermediate layer also increases from 0.48 microns to above 1.65 microns with the increase of the substrate temperature. As appears from spectra, the substrate includes silicon, oxygen and calcium. One can observe outdiffusion of elements of a substrate (Si, O, Ca) into the coating.

Table. The characteristics of the PbSnS thin films

Sample	№1	№2	№3	
$T_{sub}, ^{\circ}\text{C}$	268	330	361	
The concentration of elements in the top layer (thickness about 100 nm), at.%	Pb	10.4	7	8.6
	Sn	36.6	40	43.4
	S	53	53	48
Thickness PbSnS, $\mu\text{m}$	0.83	1.12	1.68	
Thickness of intermediate layer, $\mu\text{m}$	0.48	0.71	>1.65	
$R_a$ , nm	25.8	33.1	72.6	
CA, degrees	70.7	100.7	112.0	

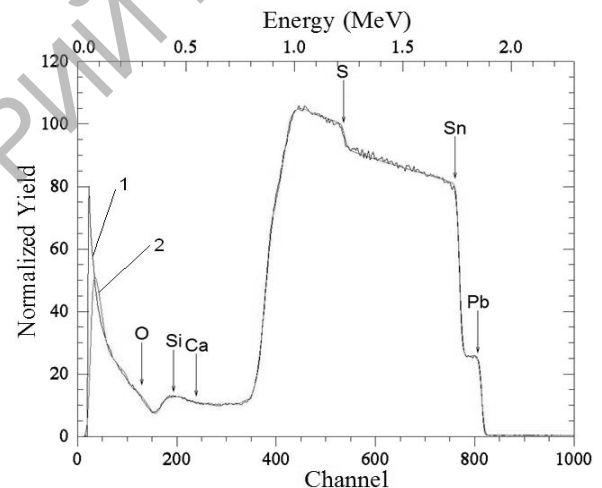


Fig.3. 2.0 MeV  $^4\text{He}$  RBS spectra from PbSnS film deposited at  $T_{sub}=330^{\circ}\text{C}$ : 1 – experimental data, 2 – simulation

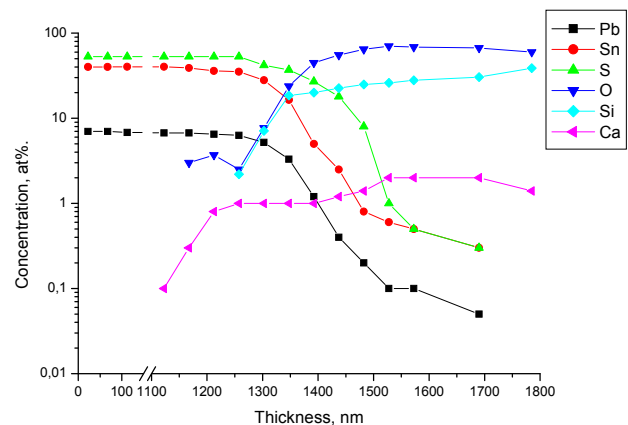


Fig.4. Relative content of species in PbSnS film deposited at  $T_{sub}=330^{\circ}\text{C}$



Fig.5. Water drop on the surface of PbSnS thin films (A)  $T_{sub}=268^{\circ}\text{C}$ , (B)  $T_{sub}=330^{\circ}\text{C}$ , (C)  $T_{sub}=361^{\circ}\text{C}$

The surface topography of PbSnS thin films was characterized using the AFM operated in contact mode. Fig. 2 shows a typical large area ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) topography image. The AFM studies showed that the increase in temperature of a substrate was accompanied by a cardinal change of structure of a surface and growth of the average surface roughness of PbSnS films (from 25.8 nm to 72.6 nm.) (Table). It is clear from the AFM-images (Fig. 2.A) that at the substrate temperature  $268\ ^{\circ}\text{C}$  the surface of the PbSnS films is smooth with irregular blurred hill shape granules and voids. With the increase of the substrate temperature, the voids disappear and the number of granules on the surface of the films increased. For the films deposited at the substrate temperatures  $330^{\circ}\text{C}$  granules fill the entire PbSnS surface. These granules are grown randomly with irregular shapes and sizes. It also appears that the grown granules are loosely packed together and form a highly rough surface. The average grain size, evaluated using a standard statistical averaging technique, is about  $1.4 \times 0.8 \times 0.2\ \mu\text{m}$ . Dot-like features were observed over large areas of the PbSnS films prepared at  $361\ ^{\circ}\text{C}$  as depicted in Fig. 2C. It shows a flat, uniform and dense grain structure. These microstructures with an average diameter of  $1\ \mu\text{m}$  and height of 90 nm are subdivided into layers. They are always parallel to the substrate surface. For this case, the particles were distributed homogeneously on the surfaces and a difference in number and size with increasing substrate temperatures is observed.

An empirical diagnostic method for evaluation of thin film solar cell absorbers is the measurement of water contact angle on its surface. Lokhande et al. [7] reported that the presence of local inhomogeneities, chemical composition and surface morphology in CIS film is directly related to the surface water contact angle, which in fact has a direct relation with solar absorption.

As it is seen from the wettability test results surfaces reveal hydrophobic behavior at temperatures  $330^{\circ}\text{C}$  and  $361^{\circ}\text{C}$  (Table, Fig. 5). Water contact angle increases from  $70.7^{\circ}$  to  $112.0^{\circ}$ . This situation is attributed to change in chemical composition, grain size and surface roughness of the PbSnS films.

We consider that reduction in the value of water contact angle result from reduction in the surface energy. Therefore we are going to conduct further experiments in respect of the surface energy of thin films PbSnS.

Our measurements for surface water contact angle are in good agreement to that reported by Lokhande et al. [7].

## Conclusions

The PbSnS films prepared at different temperatures are 0.83-1.68 microns thick. With the increase of the substrate

temperature, the thickness of film increases too. They consist of 7-10.4 at.% lead, 36.6-44 at.% tin and 48-53 at.% sulphur. Profiles of distribution of elements show that the obtained films are homogeneous. As appears from spectra, the substrate includes silicon, oxygen and calcium. Mutual diffusion of elements of a substrate (Si, O, Ca) and from films (Pb, Sn, S) has been found out. The thickness of an intermediate layer also increases from 0.48 microns to above 1.65 microns with the increase of the substrate temperature.

The AFM studies show that the increase in temperature of a substrate was accompanied by a cardinal change of structure of a surface and the growth of the average surface roughness of PbSnS films, and their CA parameter. Surfaces reveal hydrophobic behavior at temperatures  $330^{\circ}\text{C}$  and  $361^{\circ}\text{C}$ .

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