ФИЗИКА

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СТРУКТУРНЫЕ СВОЙСТВА ТОНКИХ ПЛЕНОК $Pb_{1-x}Sn_xTe$, ПОЛУЧЕННЫХ МЕТОДОМ «ГОРЯЧЕЙ СТЕНКИ»

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STRUCTURAL PROPERTIES OF $Pb_{1-x}Sn_xTe$ THIN FILMS PREPARED BY THE "HOT WALL" METHOD

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Исследованы кристаллическая микроструктура, химический состав и морфология тонких пленок $Pb_{1-x}Sn_xTe$ ($0{,}05 \le x \le 0{,}80$), полученных на стеклянных подложках методом «горячей стенки». Рентгеноструктурные исследования показали, что пленки были однофазными и имели кубическую структуру. Постоянная решетки пленок в зависимости от состава изменялась по закону Вегарда. Полученные пленки были гомогенными с воспроизводимым составом. Микроструктура пленок состояла из плотноупакованных зерен размером 0,3–4,0 мкм, выращенных перпендикулярно плоскости подложки.

***Ключевые слова**: теллурид свинца-олова, метод «горячей стенки», поликристаллические пленки, кристаллическая структура, параметр решетки, химический состав.*

In this paper, crystalline microstructure, chemical composition and morphology of $Pb_{1-x}Sn_xTe$ thin films with the composition range of $0{,}05 \le x \le 0{,}80$ prepared by the "hot wall" method on glass substrates were investigated. The X-ray diffraction studies showed a polycrystalline single phase cubic crystalline structure with the dependence of the lattice constant on composition x with a linear behavior described by the Vegard's law. The energy dispersive analysis showed that the obtained films are homogeneous and the compositions of the films are reproducible. Scanning electron microscopy revealed the thin films microstructure consisted of densely packed crystals with dimensions of 0,3–4,0 μm and crystallite growth direction is perpendicular to substrate plane.

Keywords: *lead tin telluride, "hot wall" method, polycrystalline films, crystalline structure, lattice parameter, chemical composition.*

Introduction

Lead tin telluride ($Pb_{1-x}Sn_xTe$) ternary solid solution is a narrow gap semiconductor with a rock salt crystalline structure that has been investigated for many decades and applied in the fabrication of mid-infrared photodetectors and diode lasers, for which it is easily possible to vary the wavelength by adjusting the composition of the solid solution [1]–[4]. A proper technique of growing of high-quality $Pb_{1-x}Sn_xTe$ single crystalline films is a key aspect of the manufacturing of high-performance devices [5]. $Pb_{1-x}Sn_xTe$ alloy layers for the practical applications are grown by diffusion, hot-wall epitaxy, liquid-phase epitaxy, as well as molecular beam epitaxy [6]–[9] on glass, BaF_2, Si(100) and Si(111) (with CaF_2 or BaF_2 buffer layers) substrates [2], [10]–[12], allowing to compensate the lattice mismatch and thermal expansion coefficient differences. Preparing of $Pb_{1-x}Sn_xTe$ thin films with strictly controlled composition is, in general, problematic because of the controlling of Te due to its low vapor pressure [13]. Moreover, the crystalline quality of $Pb_{1-x}Sn_xTe$ thin films is an important subject during the fabrication of infrared detectors, because their physical properties depend significantly on the crystallinity, structural and chemical lattice imperfections [1]. The conductivity types and the carrier concentrations of undoped PbTe and $Pb_{1-x}Sn_xTe$ crystal layers strongly depend on the non-stoichiometry of the crystals [13], [14]. The conductivity types of undoped PbTe and $Pb_{1-x}Sn_xTe$ grown by the Bridgman method without application of vapor pressure are usually *p*-type [5], 13], but the conversion the conductivity type is achievable using annealing [5]. A prospective direction in the field is the fabrication of polycrystalline $Pb_{1-x}Sn_xTe$ films with fine nm-sized grain [15], [16], which would be beneficial for the efficiency of optoelectronic and thermoelectric systems [17], [18]. On the other hand, the surface morphology of the lead chalcogenide-based films can be modified on the micro- and nanoscale using dry etching techniques [19]. The aim of the present work was to develop hot wall deposition regimes for stable high-quality polycrystalline $Pb_{1-x}Sn_xTe$

($0{,}05 \le x \le 0{,}80$) thin films on glass substrates and to investigate microstructure properties.

1 Experimental details

Polycrystalline $Pb_{1-x}Sn_xTe$ ($0{,}05 \le x \le 0{,}80$) films were grown using hot wall deposition (HWD) on Corning 7059 glass substrates according to a well-established technique as follows [14], [15]. Initially, high purity (99,999%) mixtures of constituent elements (Pb, Sn, and Te) in stoichiometric proportions (with an accuracy of 0,5 mg) were sealed into silica tubes at the pressure of 10^{-3} Torr. The evacuated tubes were then placed into an electric furnace and kept at 450°C for 7 days and after that at 700°C for 10 days. The tubes were gradually cooled with a cooling rate of about 20°C/h to room temperature in order to obtain polycrystalline $Pb_{1-x}Sn_xTe$ compounds [20]. The main feature of the HWD system is the heated linear quartz tube of 1,2 cm diameter, which was placed inside the vacuum chamber and served to enclose and direct the vapor from the source to the substrate. The quartz tube was kept at ~600°C and was loaded with $Pb_{1-x}Sn_xTe$ powder, so that $Pb_{1-x}Sn_xTe$ films were deposited on chemically cleaned glass plates with substrate temperature varied from 230 to 340°C. The pressure in the chamber was about 10^{-5} Torr during the evaporation. The deposition duration varied from 10 min to 50 min in order to obtain thin films in wide range of thicknesses. The evaluated thickness varied from 0,7 to 4.0 μm.

Morphology of the films was studied with scanning electron microscopy (SEM) using JEOL JSM-6400 and Supra 40 Carl Zeiss microscopes. Crystalline structure and the phase composition of the $Pb_{1-x}Sn_xTe$ films were investigated by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with CuK_α ($\lambda = 1{,}54056$ Å) radiation. The angle 2θ was measured in the range from 15° to 100° with a step of 0,01°. The observed phases were determined by comparing the *d*-spacing with the Joint Committee on Powder Diffraction Standard (JCPDS) data files. Local elemental composition of the films was determined from energy dispersive X-ray (EDX) data, using AN 10000 EDX spectrometer mounted in the Stereoscan-360 electron microscope with and INCAx-act Oxford Instruments EDX spectrometer in the Supra 40 electron microscope.

2 Structural properties of the films

The influence of substrate temperature on the phase formation and crystalline structure of the $Pb_{1-x}Sn_xTe$ thin films were studied by X-ray diffraction. The XRD spectra of hot wall deposited layers showed that all the films exhibited polycrystalline nature, supporting the visual SEM data. The thin film powder patterns matched the powder target pattern satisfactorily and indicated the absence of any binary phases. Some minor differences in the relative intensities between the powder target and experimental patterns could be attributed to some minor texturing of the films. All the thin films exhibited a strong (200) peak representing the preferable orientation. The spectrum also showed other peaks in addition to the (200) peak. The most intensive peaks corresponds to (220), (400) and (420) orientations. Typical XRD spectra for $Pb_{0.70}Sn_{0.30}Te$, $Pb_{0.40}Sn_{0.60}Te$, and $Pb_{0.05}Sn_{0.95}Te$ thin films on glass substrates are shown in Figure 2.1.

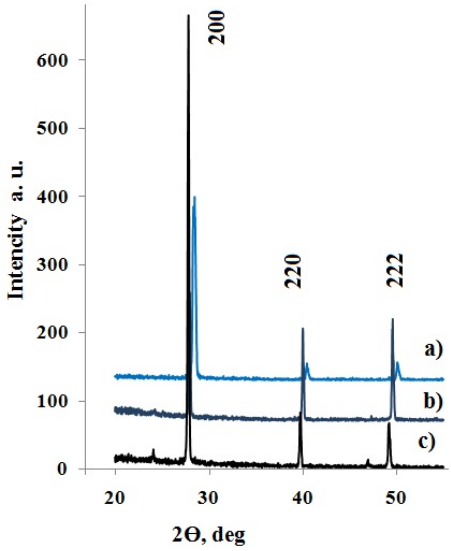

Figure 2.1 – Typical XRD spectra for $Pb_{0.70}Sn_{0.30}Te$, $Pb_{0.40}Sn_{0.60}Te$, and $Pb_{0.05}Sn_{0.95}Te$ thin films on glass substrates

All the deposited $Pb_{1-x}Sn_xTe$ films showed a single phase cubic structure (space group O5h-Fm3m). The lattice constant was evaluated using the standard equation for a cubic crystal structure (Table 2.1).

Table 2.1 – Characteristics of the $Pb_{1-x}Sn_xTe$ thin films

Mole Fraction	Composition, at. %			Lattice parameter, Å	$T_{Sub.}$, °C	D, nm
	Pb	Sn	Te			
$Pb_{0.05}Sn_{0.95}Te$	2,26	46,6	51,14	6,311 ± 0,002	338	45
$Pb_{0.10}Sn_{0.90}Te$	4,52	44,79	50,69	6,322 ± 0,002	335	95
$Pb_{0.15}Sn_{0.85}Te$	7,87	41,72	50,41	6,330 ± 0,002	340	105
$Pb_{0.20}Sn_{0.80}Te$	9,77	37,75	52,47	6,343 ± 0,002	335	145
$Pb_{0.40}Sn_{0.60}Te$	22,14	25,36	52,5	6,370 ± 0,002	335	90
$Pb_{0.55}Sn_{0.45}Te$	26,31	21,85	51,85	6,404 ± 0,002	340	105
$Pb_{0.70}Sn_{0.30}Te$	35,59	13,67	50,74	6,419 ± 0,002	330	110
$Pb_{0.80}Sn_{0.20}Te$	42,39	7,79	49,82	6,422 ± 0,002	290	95

The evaluated interplanar spacing (*d*-values) and the lattice parameters of SnTe films (a = 6,304± ±0,002 Å) and PbTe films (a = 6,450±0,002 Å) are in agreement with the standard JCPDS data (cards No. 46-1210 and No. 78-1905, respectively). The similar behavior was also observed [21] for the vacuum-evaporated PbTe, SnTe and $Pb_{1-x}Sn_xTe$ films with varying substrate temperature. A linear relationship between the lattice parameter (a) and the composition of the $Pb_{1-x}Sn_xTe$ solid solution was established in the least squares approximation to be as follows:

$$a = 0{,}167x + 6{,}305 \text{ Å}. \quad (2.1)$$

Figure 2.2 shows the dependence of $Pb_{1-x}Sn_xTe$ thin film lattice parameters on the atomic composition.

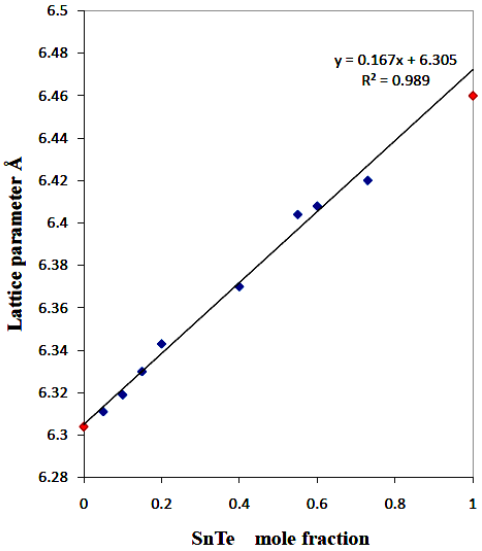

Figure 2.2 – Dependence of $Pb_{1-x}Sn_xTe$ thin film lattice parameters on the composition

The value of the lattice parameter gradually increases from PbTe to SnTe in agreement with the published data on lead tin telluride alloy bulk materials, where there was reported similar linear dependence of lattice constant on composition in $Pb_{1-x}Sn_xTe$ alloys with tellurium excess according to Vegard's law [22], [23].

To calculate the mean grain size in thin films we used the Debye – Scherrer formula:

$$D = \frac{K\lambda}{B\cos\theta}. \quad (2.2)$$

Where D is the grain size, B is a broadening of peak intensity at half maximum (FWHM) in radian, λ is the X-ray wavelength used (Cu Kα = 1,54056 Å), θ is the Bragg angle and K is a dimensionless constant that may range from 0,89 to 1,39 depending on the specific geometry of the scattering objects. For a perfect two-dimensional lattice, where every point on the lattice emits a spherical wave, numerical calculations yield the lower bound of 0,89 for K. A cubic three-dimensional crystal is best described by K = 0,94 [24]. The crystal size found by X-ray analysis is determined by the smallest crystallites through the entire thickness of the film where SEM image does not reflect the grain size calculation based on X-ray data [25]. On the other hand, SEM images may not have the capability to reveal crystalline film substructures [26].

3 Chemical composition of the films

The physical properties of $Pb_{1-x}Sn_xTe$ thin films, obviously, are strongly influenced by the elemental composition; therefore it is crucially to control the latter. The energy dispersive analysis of all the as-deposited films showed that the obtained films are homogeneous and the compositions of the films are reproducible in the framework of the HWD technique. Figure 3.1 shows a typical EDX spectra for the obtained $Pb_{1-x}Sn_xTe$ thin films with different composition ($Pb_{0.70}Sn_{0.30}Te$, $Pb_{0.40}Sn_{0.60}Te$, and $Pb_{0.05}Sn_{0.95}Te$) measured using AN 10000 EDX spectrometer in the 1–6 keV range with the designation of the respective peaks of lead, tin and tellurium.

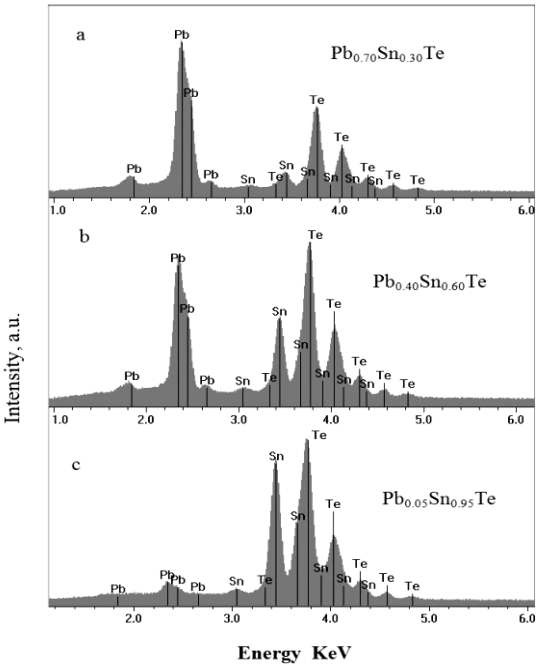

Figure 3.1 – EDX spectra for $Pb_{0.70}Sn_{0.30}Te$ (a), $Pb_{0.40}Sn_{0.60}Te$ (b) and $Pb_{0.05}Sn_{0.95}Te$ (c) films

From the numerical calculations, EDX showed a deviation from the stoichiometric composition towards the excess tellurium (Table 2.1).

4 Morphological properties of the films

SEM studies of the cross-sections of as-deposited $Pb_{1-x}Sn_xTe$ films on glass substrates demonstrated that the films had a strongly pronounced columnar structure with the crystal lateral dimensions of 0,3–4,0 μm and with densely packed crystals, with the films grown at higher temperature generally consisting of larger crystallites. The surface roughness for all the $Pb_{1-x}Sn_xTe$ films was 10–40 nm and the crystallites with distinct boundaries

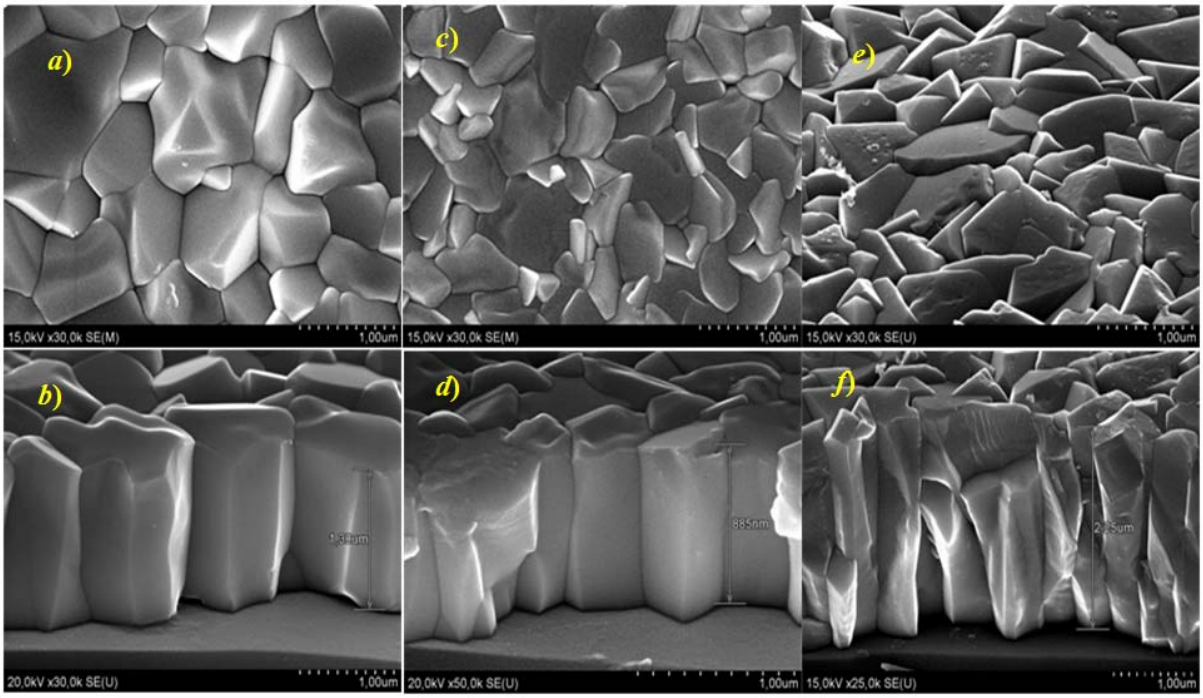

Figure 4.1 – SEM images of the surface morphology and cross-sections of $Pb_{0.70}Sn_{0.30}Te$ (*a*, *b*), $Pb_{0.55}Sn_{0.45}Te$ (*c*, *d*) and $Pb_{0.05}Sn_{0.95}Te$ (*e*, *f*) thin films on glass substrates

were clearly observed. Typical SEM images of the surface and cross-sections on the example of $Pb_{0.70}Sn_{0.30}Te$, $Pb_{0.55}Sn_{0.45}Te$ and $Pb_{0.05}Sn_{0.95}Te$ films are shown in Figure 4.1.

SEM studies also demonstrated that the thickness of the layers depends on growth conditions. The increase in substrate temperature at constant deposition time leads to the increase in the film thickness. The temperature dependence of films thickness could be explained by the availability of thermal energy for nucleation at different substrate temperatures which in turn increases with the increasing substrate temperature. The fact that the crystals are densely connected to each other is essential for the development of device structures with *p-n*-junctions based on polycrystalline $Pb_{1-x}Sn_xTe$ films. The overall density of the films is of critical importance, since it would prevent the diffusion of atoms during the growth of the other material layers during the fabrication of electronic devices.

Conclusions

Lead tin telluride films $Pb_XSn_{1-X}Te$ with the composition range of $0{,}05 \le x \le 0{,}80$ were successfully deposited at different substrate temperatures from 230ºC to 340ºC by hot wall vacuum deposition of bulk material onto glass substrates. X-ray diffraction measurements showed that the grown $Pb_XSn_{1-X}Te$ films have a cubic crystal structure and demonstrated the lattice constant dependence on composition *x* with linear behavior according to the Vegard's law. The energy dispersive analysis showed the homogeneous characteristic of the obtained films. The compositions of the films are reproducible. SEM morphology and cross sections revealed the thin films microstructure consisted of pinhole free and densely packed columnar grains and crystallite growth direction is perpendicular to substrate plane.

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