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ELECTRICAL PROPERTIES OF HOT WALL DEPOSITED PbTe–SnTe THIN FILMS

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Polycrystalline $Pb_{1-x}Sn_xTe$ ($0.0 \leq x \leq 1.0$) telluride alloys were synthesized by the direct fusion technique. Thin films of these materials were prepared by a hot wall deposition method on glass substrates at T_{sub} =230–330 °C and in a vacuum of about 10^{-5} Torr. The microstructure of the films was characterized by XRD, SEM, EDX and AES. The films showed a natural cubic structure. The thin films' microstructure consisted of densely packed grains with dimensions of 50–300 nm and crystallite growth direction is perpendicular to substrate plane. The as-grown $Pb_{1-x}Sn_xTe$ films showed p-type conductivity. Thermoelectric measurements of the films showed high values for the room-temperature Seebeck coefficient ranging, from 20 to 400 μV·K^{-1}, for SnTe to PbTe thin films, respectively. The conductivity of the films was in the range of $3 \cdot 10^1$–$1 \cdot 10^4$ Ω^{-1}·cm^{-1}.

Keywords: hot wall deposition, electrical properties, thin films.

1. Introduction

IV–VI compound semiconductors are potentially attractive materials for a variety of electronic applications: IR detectors and sources, thermoelectric converters, solar cells, memory units, spintronic devices, and others [1–4]. The fundamental characteristics of these compounds, in particular their narrow band gap, high dielectric permittivity, radiation hardness, high carrier mobility, and high bond ionicity, make them unique among compound semiconductors. The main characteristics of IV–VI compound solid solutions (band gap, spectral response, lattice parameter, thermal expansivity, and others) depend on their composition. An important issue in the synthesis and practical application of materials is a precise knowledge of the composition stability limits of solid solutions' dependence on temperature, as well as their physical characteristics' dependence on composition. The rocksalt-structure IV-VI semiconductor compounds such as PbTe and SnTe have small band gaps, high dielectric constants, and a variety of very unusual thermodynamic, vibrational, electronic, and infrared properties [4]. These narrow band-gap semiconductors have been of great interest for the last four decades for their fundamental physics and their application in infrared devices and thermoelectric materials. In fact, PbTe was one of the first materials studied by Ioffe and his colleagues in the middle of the 20th century when there was a revival of interest in thermoelectricity [1]. In addition, lead and tin containing materials in electronic devices would decrease the production costs, because they are cost effective, abundant in nature, and relatively less-toxic. Several methods have been used to deposit SnTe and PbTe films, including e-beam sputtering, spray pyrolysis, chemical and electrochemical deposition. However, most of these methods involve subsequent annealing to obtain the required quality of the films. In our continuing effort to prepare the

PbTe-SnTe semiconductor films, we have used a hot wall deposition (HWD) method. Among the various thin film deposition techniques, HWD has become a popular and reliable synthesis for film preparation [5–11]. In this method, a heated silica tube directs the evaporated source material towards the substrate. This deposition technology yields high quality thin films with smooth surfaces grown under conditions very close to a quasithermal equilibrium conditions. High quality electro-optic thin films of the different II–VI materials produced by this method didn't require the post-growth heat treatments [6, 7]. Here, we report for the first time on the preparation of $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ thin films by the hot wall deposition of bulk materials onto glass substrates at different physical parameters. The microstructure and electrical properties of the as-deposited thin films are also described. Our work shows that HWD processing is promising for the fabrication of PbTe–SnTe ternary compounds.

2. Experimental Details

Polycrystalline $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ $(0.0 \leq x \leq 1.0)$ alloys were synthesized by the fusion method. In this method, the reaction between the sulfur vapors and molten metals were allowed to take place gradually in evacuated silica tubes. High purity (99.999%) mixtures of constituent elements (Pb, Sn, and Te) in stoichiometric proportions (with an accuracy of $5{\cdot}10^{-4}$ g) were sealed into evacuated silica tubes at 10^{-3} Torr. The evacuated tube was then placed into 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 telluride vapor pressure, the tube was heated slowly. The tubes were gradually cooled with a cooling rate of about 20 °C h^{-1} to room temperature in order to obtain polycrystalline $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ compounds. The main feature of the hot wall deposition system is the heated linear quartz tube of 1.2 cm diameter, which served to enclose and direct the vapor from the source to the substrate. The quartz tube and substrates were heated independently. $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ films were deposited by keeping the quartz tube temperatures around 600 °C. Glass plates were chemically cleaned, rinsed with distilled water and blown dried with compressed air before deposition. Substrate temperature was varied from 230 to 330 °C. The substrate was held at a distance of about 1 mm above the open end of the quartz tube acting almost as a lid closing the tube with the help of a substrate holder heater. The pressure in the chamber was about 10^{-5} Torr during evaporation. Chromel–alumel thermocouples were used to measure the temperatures of the quartz tube and the substrate. The deposition time was varied from 10 min to 50 min in order to obtain thin films in a wide range of thicknesses. The crystal structure of $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ in both powder and thin film forms was investigated by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with CuK_α ($\lambda = 1.5405$ Å) radiation. The observed phases were determined by comparing the d-spacing with the Joint Committee on Powder Diffraction Standard (JCPDS) data files. Surface morphology and cross-section of films were investigated with scanning electron microscope (SEM) (Hitachi S-806). The elemental composition of the obtained films was determined from energy dispersive X-ray (EDX) data, using scanning electron microscope Stereoscan-360 with EDX spectrometer AN 10000 with an accuracy of about 2%. The depth profiling was done by Auger electron spectroscopy (AES) using a Perkin Elmer Physical Electronics model 590 with simultaneous sputter etching. The conductivity (σ) of the films was measured by the Van der Pouw method. The temperature range during the conductivity investigation was provided by a special cryostat from 80 to 450 K. Measurements of the conductivity temperature characteristics were carried out in vacuum of about $1{\cdot}10^{-3}$ Torr. The 'Leit-C' conductive carbon-based paste was used as electrical contacts to the films. The ohmic nature of the contacts was checked by recording the current–voltage characteristics. Thermoelectric properties (Seebeck coefficient) of the films were investigated at the room temperature. The temperature difference between the 'hot' and 'cold' ends of the probes was 25 K.

3. Results and discussion

3.1. Compositional and structural analysis

The physical properties of $Pb_{1-x}Sn_xTe$ thin films are influenced by the elemental composition and the substrate temperature. The characteristics of these layers were studied by the appropriate techniques and are discussed in the following sections. The as-deposited films were pinhole free, uniform and strongly adherent to the surface of the substrate. The evaluated thickness varied from 0.7 to 4.0 μm. The energy dispersive analysis of all as-deposited films showed that the obtained films are homogeneous and the compositions of the films are reproducible. This clearly shows that composition control can be easily achieved using HWD technique. The AES depth profile was used to study the concentration of elements present in the bulk of the as-grown $Pb_{1-x}Sn_xTe$ films. The data were obtained by sputtering an area of 10×10 μm^2 with energetic argon ions at a rate of 1000 Å/min. The AES depth profiles of the films reveal relatively uniform distribution of the components in the bulk of the films through the depth. This observation supports the XRD data, indicating uniform, single-phase thin film material. The chemical composition was determined by averaging the values from 5 different points on the surface of the same films. Elemental composition of the as-deposited $Pb_{1-x}Sn_xTe$ films has been confirmed by the AES method. The influence of the substrate temperature on the phase formation and crystalline structure of the $Pb_{1-x}Sn_xTe$ thin films was studied using XRD. The XRD spectra of the hot wall deposited layers showed that the films exhibited a polycrystalline nature (Fig. 1).

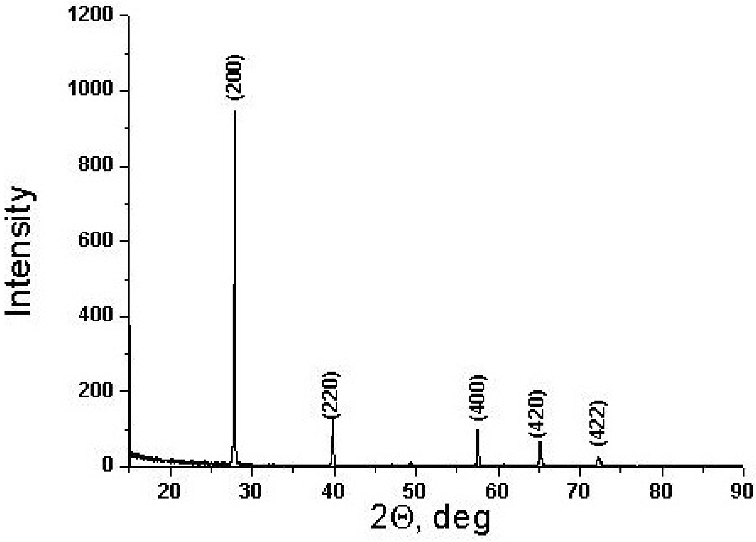

FIG. 1. Typical XRD spectrum of $Pb_{1-x}Sn_xTe$ films

The thin film powder patterns matched the powder target pattern satisfactorily and indicated the absence of binary phases. Differences in the relative intensities between the powder target and experimental patterns may be attributed to some texturing of the films. All 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 intense peaks correspond to (220), (400) and (420) orientations. As-deposited $Pb_{1-x}Sn_xTe$ thin films showed a single phase cubic structure (space group $O^5{}_{h-}F_{m3m}$). The cell parameter (a) was evaluated using the standard equation for a cubic crystal structure. The change of lattice parameters with substrate temperature is marginal. SEM studies of the as-deposited layers demonstrated that the surface topology of the films is dependent on the growth temperature. SEM cross-section image of the $\mathrm{Pb_{0.72}Sn_{0.28}Te}$ thin film on the glass substrate is shown in Fig. 2. The thin films microstructure consisted of densely packed grains with dimensions of 50–300 nm and crystallite growth direction is perpendicular to the substrate plane. A gradual change in growth of crystallites was observed with the increase of the substrate temperature. The films had a columnar structure with the lateral grain size in the range of tens of nanometers to several microns. The films grown at high temperature consisted of large crystallites. Scanning electron microscopy measurements showed that the surface roughness for all the $\mathrm{Pb_{1-x}Sn_xTe}$ films was 10–40 nm and the surface was characterized by crystallites with distinct boundaries. SEM studies demonstrated that the thickness of the layers depends on growth conditions. The increase in substrate temperature at constant deposition time leads to an increase in the film thickness. The temperature dependence of the film thickness could be explained by the availability of the thermal energy for a nucleation at different substrate temperatures, which in turn increases with increasing substrate temperature.

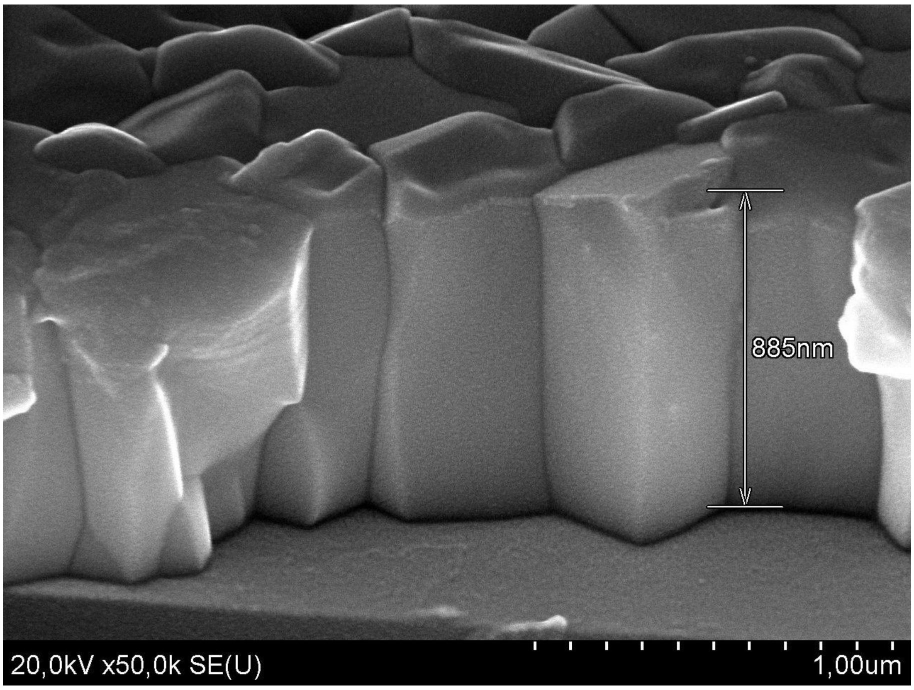

FIG. 2. SEM cross-section image of the $\mathrm{Pb_{0.72}Sn_{0.28}Te}$ thin film on glass

SEM images of the $\mathrm{Pb_{1-x}Sn_xTe}$ layers showed a densely packed microstructure free of pinholes. The grains are electrically well connected to each other, which is essential for the development of p-n junction. The density of the films is of critical importance, since it will prevent the diffusion of atoms during the growth of the other material layers for the production of electronic devices.

3.2. Electrical properties

The as-prepared films showed p-type electrical conductivity, which is confirmed by the thermoelectric probe measurement. The Seebeck coefficient and the conductivity of the $Pb_{1-x}Sn_xTe$ films was in the range of α =20–400 $\mu V \cdot K^{-1}$ and σ =$3 \cdot 10^1$–$1 \cdot 10^4$ $\Omega^{-1} \cdot cm^{-1}$ respectively, at room temperature depending on the concentration of Pb in the films. Fig. 3 shows the dependence of the Seebeck coefficient on the concentration of the lead atoms at room temperature.

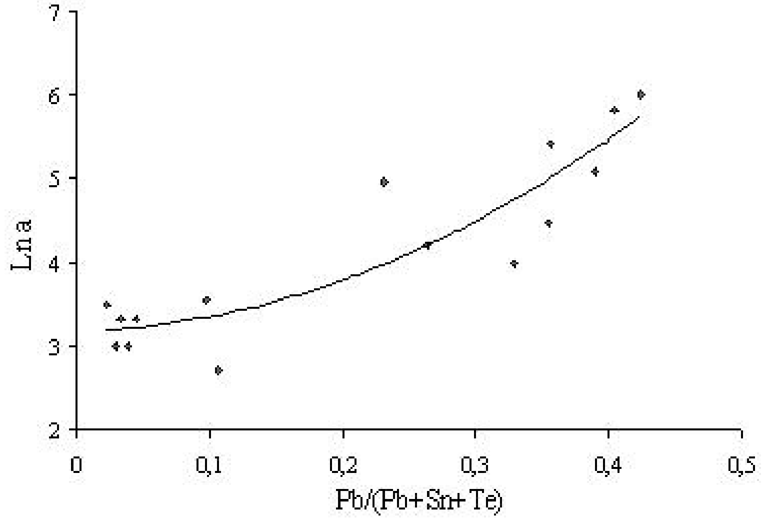

FIG. 3. Dependence of the Seebeck coefficient on lead concentration

Increasing of Pb concentration leads to an increase of the Seebeck coefficient. This coefficient is determined by various parameters of a material. In the case of a single-phase material with different kind of defects (or impurities), which produce both acceptor and donor energy levels in the band gap, the Seebeck coefficient can be written in the following form [12]:

$$\alpha = k_B \sigma^{-1} \left[\mu_n n \left(S + 5/2 - \ln n/N_c \right) - \mu_p p \left(S + 5/2 - \ln p/N_v \right) \right], \tag{1}$$

where μ_n, μ_p – mobility of carriers, σ – conductivity, S – charge carriers scattering mechanism, k_B – Boltzmann constant, n, p – charge carriers concentration, N_c, N_v – effective states density in the conduction band and in the valence band, respectively. As is seen from (1), the coefficient α is inversely proportional to the conductivity and directly proportional to the ratio between parameters determining the conductivity type. The increase of the Seebeck coefficient could be rationalized by both a decrease of the conductivity and by an increase in the holes mobility [13]. Increasing the lead concentration resulted in a decrease in the conductivity, as shown in Fig. 4.

The decrease of the conductivity could be explained by a decrease in the hole concentration in the films. The conductivity of the lead chalcogenides is independent of temperature at low temperatures [13]. The temperature dependence of the dark conductivity of the $Pb_XSn_{1-X}Te$ films is shown in Fig. 5.

As seen from Fig. 5, the conductivity does not vary appreciably from 90–190 K. Conductivity decreases by law $\sigma = T^{-n}$ with increasing temperature above 190 K. The decrease in conductivity can be explained by the decrease in the carrier mobility [13]. Conductivity begins to increase at temperatures above 300 K. It can be assumed that the thermal increase in conductivity (semiconductor conductivity) is due to the valence band-acceptor level transitions. Such

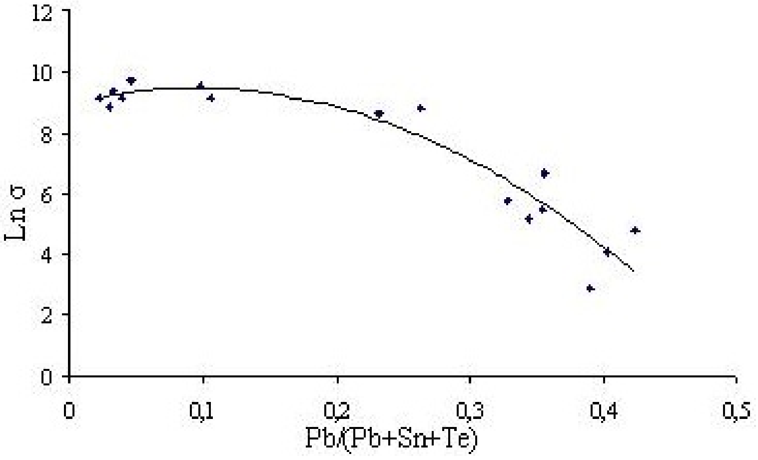

FIG. 4. Dependence of the film's electrical conductivity on lead concentration

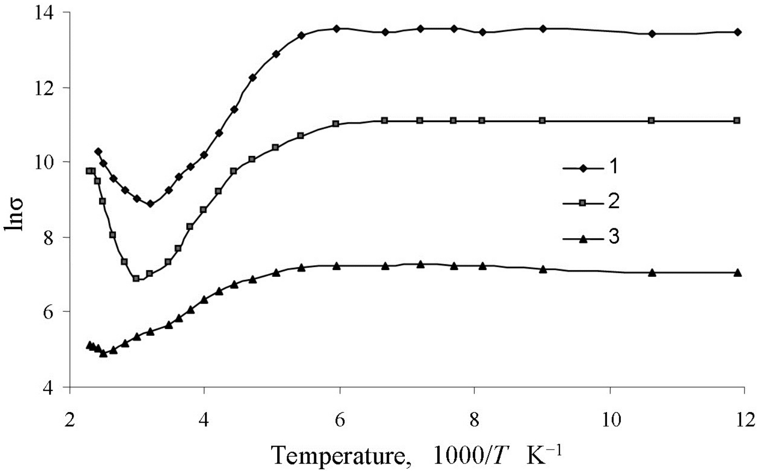

FIG. 5. Temperature dependence of the dark conductivity for films with different Pb concentration, at.%: 1 – 2.26; 2 – 23.14; 3 – 40.36

temperature dependence of conductivity is typical for all the investigated $Pb_{1-x}Sn_xTe$ films. The nature of the impurities responsible for the electrical properties requires further study.

4. Conclusions

Lead tin telluride films were deposited at different substrate temperatures from 230 °C to 330 °C by hot wall vacuum deposition of bulk material onto glass substrates. X-ray diffraction measurements showed that as-grown $Pb_{1-x}Sn_xTe$ films have a cubic crystal structure. With the increase of the substrate temperature, the crystal structure of the films remains unaffected and the change in lattice parameters is marginal. Using HWD, it is possible to produce layers of (Pb,Sn)Te mixed crystals, which are several microns thick, pinhole free conformal to the substrate, and which consist of densely packed columnar grains. The electrical measurements showed that as-grown $Pb_{1-x}Sn_xTe$ films were non-degenerate semiconductors of p-type conductivity. Increasing the lead concentration resulted in an increase of the Seebeck coefficient and in the decrease of electrical conductivity for as-grown thin films.

Acknowledgments

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