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THERMOELECTRIC PROPERTIES OF $PbTe$-Bi_2Te_3 SOLID SOLUTION THIN FILMS

Thermoelectric properties of films based on $PbTe$-Bi_2Te_3 solid solutions of different composition prepared by vapour condensation in open vacuum on glass-ceramic and mica substrates have been investigated. Based on the two-layer Petritz model, thermoelectric parameters of near-surface layers have been determined. It is shown that thin films on (0001) fresh cleavages of muscovite mica containing ~ 1 mol. % Bi_2Te_3 are characterized by maximum values of thermoelectric power ~ 95 μW/K^2cm.

Key words: thin films, lead telluride, solid solutions, thermoelectric properties.

Introduction

Lead telluride is an efficient thermoelectric material for medium-temperature region (500 – 750) K [1-4]. Thin-film material expands considerably the limits of its practical application. Owing to the size and surface effects, the thermoelectric parameters of a condensate are significantly different from those of bulk analog. Despite the large number of publications [5-7], the problem of surface effect on the entire set of thermoelectric parameters of thin films based on lead chalcogenides remains unsolved. Moreover, on their exposure to the air, due to acceptor oxygen effect, a layer rich in *p*-type carriers is formed on the surface [7]. So, attempts to obtain *n*-type thin-film material based on pure lead telluride with stable thermoelectric parameters often fail. Earlier it had been revealed that doping of *PbTe* with V group elements, in particular, *Bi*, yields a condensate with high values of thermoelectric power [8].

This paper studies the regularities of change in thermoelectric parameters of films based on $PbTe$-Bi_2Te_3 solid solutions of different composition, obtained from vapour phase on glass-ceramic and mica substrates, as a function of their thickness.

Experimental procedure

Films for investigation were obtained by vacuum deposition of synthesized material vapour onto (0001) fresh cleavages of muscovite mica and glass-ceramic substrates. The elaborated construction of vacuum sectional heaters yielded vapour-phase structures both of different thickness (d) at given deposition temperature T_s, and of equal thickness at different deposition temperatures in a single technological cycle without vacuum system depressurization [9]. The evaporator temperature during deposition was T_e= 970 K, and substrate temperature T_s = 470 K. Film thickness was assigned by deposition time within 15 – 75 s and measured by means of MII-4 microinterferometer. For evaporation, use was made of a pre-synthesized material, namely $PbTe$-Bi_2Te_3 solid solutions with 1, 3 and 5 mol.% Bi_2Te_3.

The electric parameters of films were measured in the air at room temperatures in constant magnetic fields on the elaborated automated plant providing the processes of electric parameter measurement, as well as recording and primary processing of data with the possibility of constructing the plots of time and temperature dependences. The measured sample had four Hall and two current contacts. Silver films were used as ohmic contacts. Current through the samples was ≈ 1 mA. Magnetic field was applied perpendicular to the surface of films at induction of 1.5 T.

The obtained samples were investigated using a Digital Instruments Dimension 300 Atomic Force Microscope (AFM) and Nanoscope 3a controller in periodic contact mode. The measurements were performed in the centre of the samples using serial silicone probes NSG-11 with a nominal radius of edge rounding to 10 nm (NT-MDT, Russia). According to the results of AFM investigations of vapour-phase condensates, the surface morphology and its profilograms were determined.

The results of AFM investigations and the thickness dependences of electric conductivity (σ), the Seebeck coefficient (S) and thermoelectric power ($S^2\sigma$) for $PbTe$-Bi_2Te_3 films are shown in Figs. 1 – 4.

Research results and their analysis

Introduction of Bi_2Te_3 causes active donor effect in lead telluride which is manifested in considerable growth of electron concentration up to ~10^{10} cm^{-3}. The latter is due to the fact that in n-$PbTe$-Bi_2Te_3 solid solution bismuth with configuration of valence electrons $6s^26p^3$ substitutes lead with configuration of valence electrons $6s^26p^2$, in the cation sublattice lead telluride is an active donor ($Bi^{3+} \rightarrow Bi^{1+}_{Pb}$). Films prepared on mica substrates are characterized by high values of electric conductivity (σ) which with Bi_2Te_3 content 3 mol.% reaches the values over 1.3 10^3 Ω^{-1}cm^{-1}, and the Seebeck coefficient (S) and thermoelectric power ($S^2\sigma$) in this case are 120 μV/K and 17 μW/K^{2}cm, respectively. Films of one percent composition (~1 mol.% Bi_2Te_3), despite their considerably lower electric conductivity ($\sigma \approx 300\ \Omega^{-1}$cm^{-1}), are characterized by considerable thermoelectric power that reaches $S^2\sigma \approx 95$ μW/K^{2}cm owing to high values of the Seebeck coefficient ($S > 600$ μV/K). Films prepared on glass-ceramic substrates have lower values of electric conductivity σ = (150 – 300) Ω^{-1}cm^{-1} and the Seebeck coefficient S = (100 – 400) μV/K, providing thermoelectric power $S^2\sigma \approx 23$ μW/K^{2}cm.

It is seen from Fig. 1 that with increase in condensate thickness d, both on mica cleavages and on glass ceramics, irrespective of composition, conductivity (σ) increases with saturation at $d \approx 1$ μm. In this case of considerable importance are surface effects which become marginal with increasing thickness.

It is known that on exposure of films to the air, a layer rich in p-type carriers is formed on the surface due to acceptor oxygen effect [5]. To estimate the effect of near-surface layer on the electric properties of the films, the two-layer Petritz model has been used [10]. A thin film in this model consists of two layers: near-surface (I) (surface charge region) of thickness d_s, with charge carrier concentration n_s, and their mobility μ_s, and bulk (II), which is characterized by similar values: d_b, n_b, μ_b connected in parallel. The film thickness is $d = d_s + d_b$. In this case according to [10]:

$$\sigma = \frac{\sigma_s d_s + \sigma_b d_b}{d}; \tag{1}$$

$$R = \frac{R_s \sigma_s^2 d_s + R_b \sigma_b^2 d_b}{\left(\sigma_s d_s + \sigma_b d_b\right)^2} d; \tag{2}$$

$$\mu = \sigma R = \frac{\sigma_s{}^2 d_s R_s + \sigma_b{}^2 d_b R_b}{\sigma_s d_s + \sigma_b d_b}. \tag{3}$$

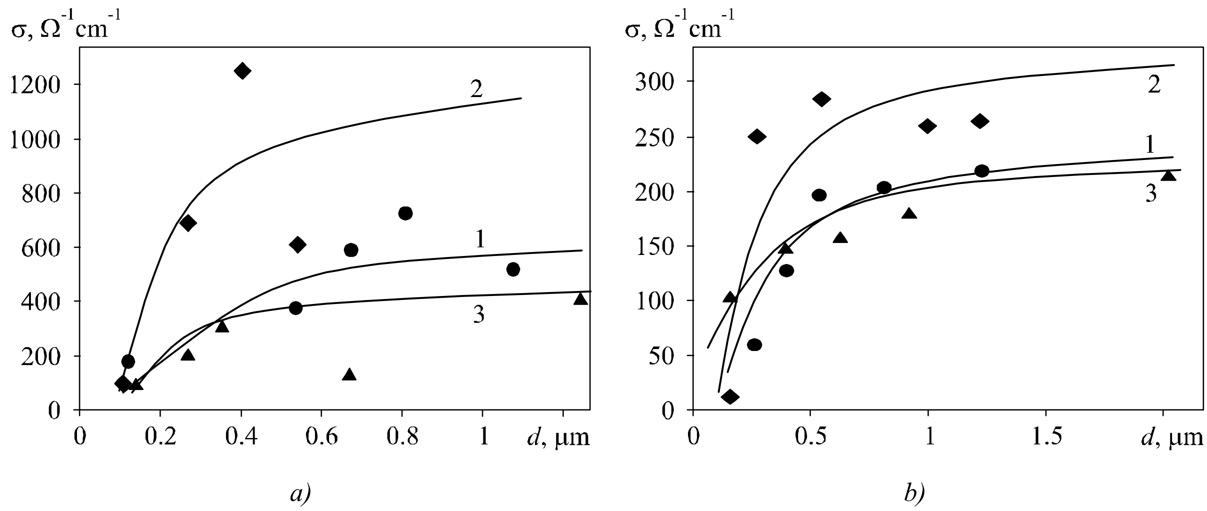


Fig. 1. Dependences of electric conductivity (σ) on thickness (d) of PbTe-Bi$_2$Te$_3$ films with Bi$_2$Te$_3$ content mol.%: (●, 1) – 5; (■, 2) – 3; (▲, 3) – 1, on mica (a) and glass-ceramic (b) substrates. Dots – experiment, solid lines – calculations according to the Petritz model.

Under the condition of known experimental values σ, R, μ and bulk σ_b, R_b, μ_b and d values, from the relations (1) – (3) one can estimate the near-surface layer parameters σ_s, R_s, μ_s, respectively.

The calculated thermoelectric parameters of near-surface layers estimated according to the Petritz model are given in the Table. The theoretical curves describe adequately the experimental results (Fig. 1 – 3) with certain values of near-surface thermoelectric parameters d_s, σ_s, S_s, $S^2\sigma_s$ (Table).

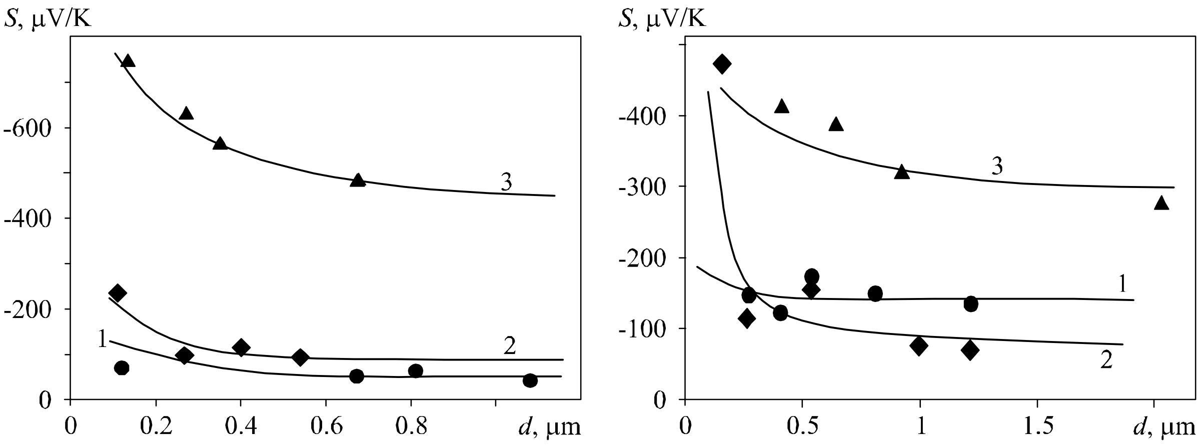
The near-surface layer thickness (d_s) (Table) is practically independent of composition, and is somewhat higher for films prepared on glass-ceramic substrates, which is attributable to their lower structural perfection as compared to samples on mica (Fig. 4).

Table

Thermoelectric parameter values of the near-surface layer (s) and volume (b) for PbTe-Bi$_2$Te$_3$ films of different composition, calculated according to the two-layer Petritz model

Substrate type	Mica			Glass ceramics		
Bi$_2$Te$_3$ content Parameters	5 mol.%.	3 mol.%.	1 mol.%.	5 mol.%.	3 mol.%.	1 mol.%.
d_s, μm	0.14	0.11	0.12	0.18	0.15	0.18
σ_s, Ω^{-1}cm^{-1}	170	70	20	30	12	110
σ_b, Ω^{-1}cm^{-1}	650	1200	500	250	350	230
S_s, μV/K	–70	–330	–959	–170	–600	–470
S_b, μV/K	–54	–90	–454	–145	–90	–304
$S^2\sigma_s$, μW/K^{2}cm	0.8	7.6	18.4	0.9	4.3	22.3
$S^2\sigma_b$, μW/K^{2}cm	1.9	9.7	103.1	5.1	2.8	21.3

The Seebeck coeffcient increases considerably to the values of 450 – 800 μV/K with reduction in film thickness (Fig. 2) which can caused by decreasing concentration of major carriers due to oxygen effect. For thick films (d > 700 nm), it is virtually independent of thickness (Fig. 2).

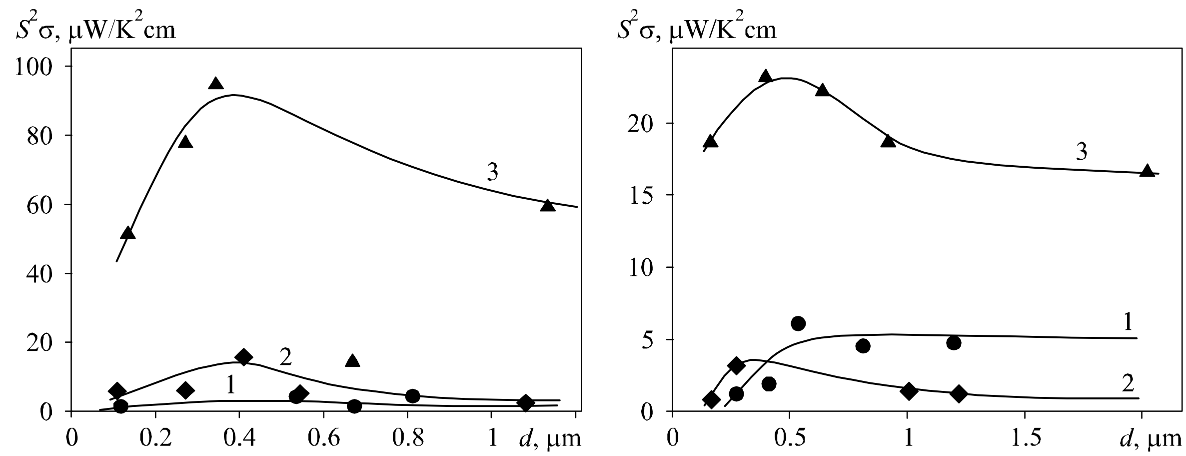


a) *b)*

Fig. 2. Dependences of the Seebeck coefficient (S) on thickness (d) of $PbTe$-Bi_2Te_3 films with Bi_2Te_3 content mol.%: (●, 1) – 5; (■, 2) – 3; (▲, 3) – 1, on mica (a) and glass-ceramic (b) substrates. Dots – experiment, solid lines – calculations according to the Petritz model.

Despite the high values of the Seebeck coefficient (S_s) in the near-surface layer, the thermoelectric power ($S_s^2\sigma_s$) near the surface of the majority of samples is considerably lower than in the bulk due to a drastic decrease in electric conductivity (σ_s) (Table). Electric conductivity of the near-surface layers (σ_s) is much lower than in the bulk (σ_b) (Table, Fig. 1) due to the influence of two factors: reduced concentration of major carriers caused by oxygen effect and their diffused scattering by the film surface (Fig. 4).

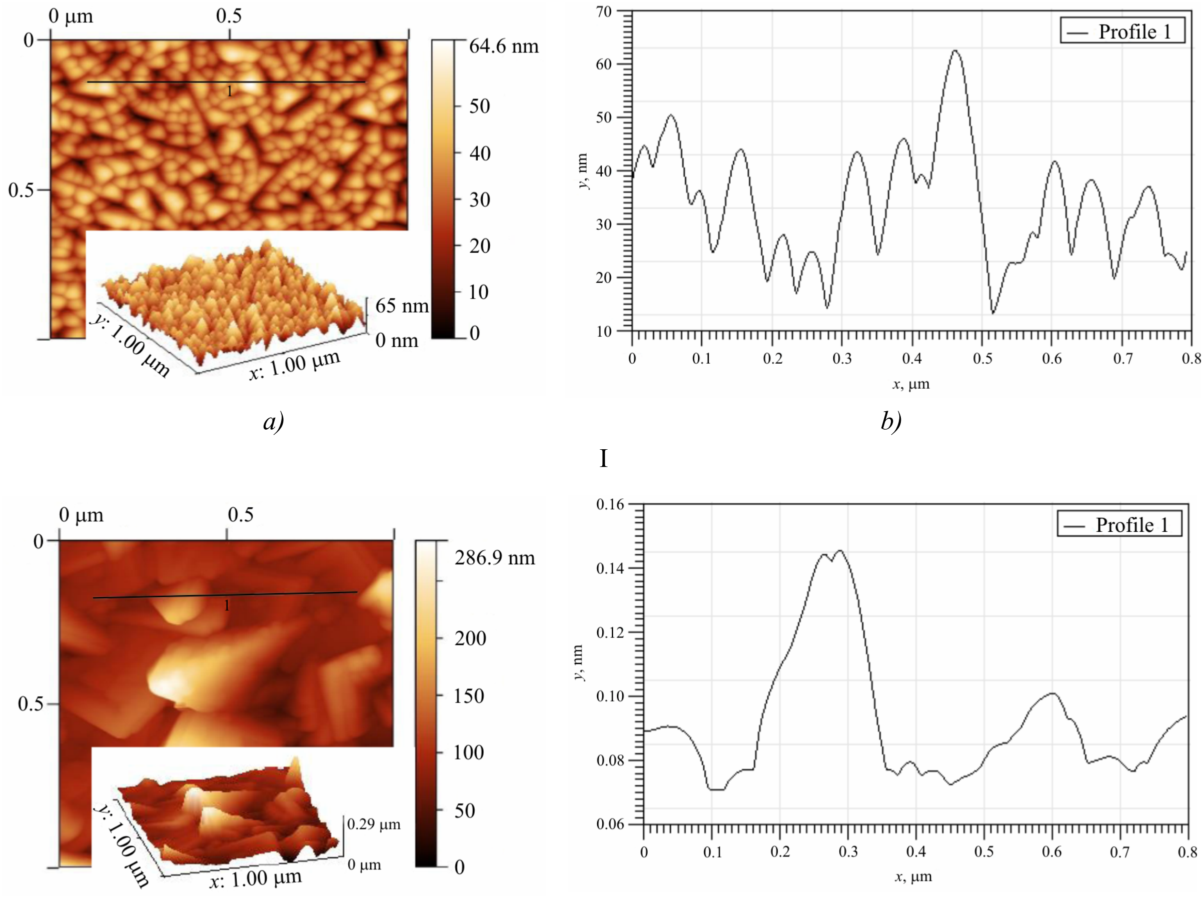
Thus, high values of electric conductivity (σ) combined with considerable value of the Seebeck coefficient (S_s) and thermoelctric power ($S^2\sigma$) of films based on $PbTe$-Bi_2Te_3 solid solutions with Bi_2Te_3 content 1 mol.% (Figs. 1 – 3 – curves 3) yielded stable in time *n*-type thermoelectric material, which is promising for use in thin-film micromodules for thermoelectric power conversion.



a) *b)*

Fig. 3. Dependences of thermoelectric power ($S^2\sigma$) on the thickness (d) of $PbTe$-Bi_2Te_3 films with Bi_2Te_3 content mol.%: (●, 1) – 5; (■, 2) – 3; (▲, 3) – 1, on mica (a) and glass-ceramic (b) substrates.

Fourfold thermoelectric power values of condensate on mica (~ 100 μW/K^{2}cm) compared to glass ceramics (~ 23 μW/K^{2}cm) for $PbTe$-Bi_2Te_3 solid solutions with ~ 1 mol.% Bi_2Te_3 are due to their structural state (Fig. 4). Better developed and ordered intergrain architecture of condensate nanocrystallites on mica cleavages (Fig. 4 – I) compared to glass ceramics (Fig. 4 – II) is the reason for efficient throttling of charge carriers on potential barriers, which accounts for considerable growth of the Seebeck coefficient (Table).



a) *b)*

I

c) *d)*

II

Fig. 4. 2D and 3D – ASM images (a) and profilographs (b) of the surface of vapour-phase condensates of $PbTe$-(1 mol.%)Bi_2Te_3 solid solutions deposited on fresh (0001) cleavage of muscovite mica (I) and glass ceramics (II): evaporation temperature T_e = 700 K, deposition temperature T_s = 470 K, deposition time 75 s.

It should be also noted that with increase in Bi_2Te_3 content in $PbTe$-Bi_2Te_3 solid solution condensates both on (0001) cleavages of muscovite mica and glass ceramics, the thermoelectric power of near-surface layers is reduced.

Conclusions

1. Thermoelectric properties of vapour phase thin films based on $PbTe$-Bi_2Te_3 solid solutions of different composition, deposited on glass-ceramic substrates and (0001) cleavages of muscovite mica have been investigated.
2. Using the two-layer Petritz model, the thermoelectric parameters of near-surface layer have been determined whose values are affected by atmospheric oxygen.
3. It has been shown that thin-film material based on $PbTe$-Bi_2Te_3 solid solutions with 1 mol.% Bi_2Te_3 has improved thermoelectric parameters on (0001) cleavages of muscovite mica.

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