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THERMOELECTRIC PROPERTIES OF THIN FILMS BASED ON PURE AND DOPED LEAD TELLURIDE

The influence of technological factors of production, namely the time and temperature of deposition, on the surface morphology and the thermoelectric properties of thin films based on pure lead telluride and bismuth- doped PbTe:Bi with the content of bismuth 1 at. % (n-type) and $Pb_{17}Ag_2Te_{20}$ (p-type) compounds is investigated. The films were obtained in vacuum at different temperatures on fresh chips (0001) of mica-muscovite. It has been established that samples of PbTe: Bi with thickness of 0.3-0.5 μm have maximum thermoelectric power. It reaches 25μW/K^{2}cm, which is much higher than that of pure lead telluride. For p-type films based on $Pb_{17}Ag_2Te_{20}$ compounds the thermoelectric power is much lower, despite the high values of the Seebeck coefficient, due to low conductivity values.

Key words: thin film, lead telluride, doping, thermoelectric properties.

Introduction

Films based on lead telluride are promising for the creation on their basis of active elements of micro and optoelectronics: detectors and infrared sources of optical spectrum [1], thermoelectric energy converters [2, 3]. The properties of thin polycrystalline films are strongly dependent on the surface morphology and electronic processes occurring at interphase boundaries [4 – 7]. The problem of obtaining films with predetermined properties and ensuring the stability of their electrical parameters in time is still relevant and unresolved. Moreover, when the films are exposed to air, due to the acceptor effect of oxygen, a layer rich in *p*-type carriers is formed on the surface, which prevents from obtaining a stable *n*-type material based on pure lead telluride [8, 9].

Doping of main matrix with donor impurities yields stable in time *n*-type material based on lead telluride [8]. For *p*-type material, complex compounds based on *PbAgTe* can be used.

The purpose of the work is to obtain stable in time films based on *PbTe* deposited on fresh chips (0001) of mica-muscovite and to study the influence of technological factors of production on the surface morphology of the films and their thermoelectric properties.

Experimental procedure

Films to be studied were obtained by vapour deposition of pre-synthesized *PbTe*, *PbTe*:*Bi*, $Pb_{17}Ag_2Te_{20}$ material in vacuum on the substrates of fresh chips (0001) of mica-muscovite. The temperature of the evaporator was T_{ev} = 600 °C, and the temperature of substrates varied in the range of T_s=150 – 250 °C. The temperature of the films was set by deposition time within (20 – 2100) °C and measured by microinterferometer MII-4.

Measurement of the electrical and thermoelectric parameters of films was made in air at room temperatures in permanent magnetic fields on the designed automated installation, which provides measuring electrical parameters, as well as recording and primary processing of data, with the possibility of plotting 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 directed perpendicular to the surface of films at 1.5 T induction.

The resulting samples were studied by methods of atomic force microscopy (AFM) on a Nanoscope 3a Dimension 3000 (Digital Instruments USA) in periodic contact mode. Measurements were made in the central part of the samples using serial silicon probes NSG-11 with a nominal radius of curvature to 10 nm (NT0MDT, Russia). According to the results of AFM studies, in addition to the surface morphology, the size of individual nanocrystals in the lateral direction and their height were determined by the watershed method using the Gwyddion program.

Surface morphology of films

Analysis of the results of AFM studies (Figs. 1 – 3) allows establishing certain common factors in the formation of epitaxial nanostructures, depending on their thickness and substrate temperatures. Thus, for instance, low deposition temperatures $T_s = 150$ °C contribute to formation of nanocrystals with a predominance of growth rate in the tangential direction to substrate surface. This is indicated by the fact that their linear dimensions in the plane of the substrate azimuth exceed considerably the dimensions in the normal to surface direction. The rise in growth temperature to $T_s = 200$ °C leads to formation of more homogeneous nanocrystals both in the form and linear dimensions in the lateral and normal directions to substrate surface (Fig. 1, Table). Thus, for films based on pure lead telluride the dimensions of crystallites in the lateral and normal directions are commensurate, for *Bi*-doped films the predominance of lateral dimensions remains, though much less pronounced. For *PbAgTe* films there are many coarse grains with flat tops (Fig. 3). A further rise in the deposition temperature leads to the formation of new growth stages on nanocrystals.

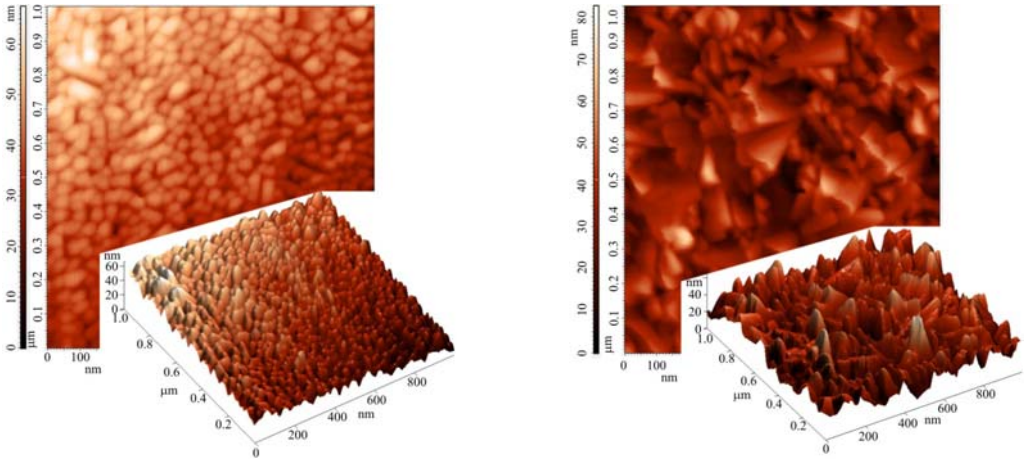
Table

Technological conditions of deposition and main morphological characteristics of resulting films. Evaporation temperature is 600 °C, deposition temperature is 200 °C.

Compound	Deposition time, s	Thickness (*d*), nm	Horizontal diameter of grains (*D*), nm	Average height of grains (*H*), nm	Average roughness (*Sa*), nm
PbTe	600	810	39	51.5	8.43
PbTe	445	540	24	26.2	5.57
PbTe	150	270	31	39.3	3.79
PbTe:Bi	300	320	45	16.2	1.81
PbTe:Bi	900	670	97	47.1	2.21
PbTe:Bi	1800	1620	107	60.3	3.12
$Pb_{17}Ag_2Te_{20}$	60	405	150	13.7	1.23
$Pb_{17}Ag_2Te_{20}$	35	270	100	14.1	1.86

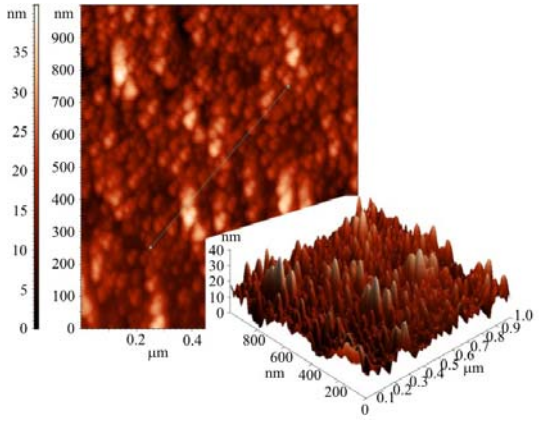
Interesting is the dependence of the morphology of epitaxial structures on their thickness. For thin films based on pure *PbTe*, the formation of nanostructures with rounded faces and without a clear cut (Fig. 1a) is characteristic. With the increase in the time of deposition and, accordingly, the thickness of the condensate to ~ 1 microns, the growth of well-formed nanocrystals of different heights 20 – 80 nm (Fig. 1b) with linear dimensions at the base up to 100 nm takes place. For the *PbTe:Bi* films, the resulting structures consist of nanosized pyramidal form crystallites. The average size of crystallites perpendicular to the direction of the surface is ~ 50 nm, and in the lateral ~ 100 nm (Fig. 2, Table 1). Thin films based on

$Pb_{17}Ag_2Te_{20}$ compounds are characterized by rather homogeneous crystallites with rounded faces and flat tops, the sizes in the normal direction are rather small ~ 14 nm. As the film thickness increases to ~ 0.5 μm, the structure of the films becomes heterogeneous, with the predominance of grains in the form of flat cut pyramids of height of ~ 5 nm with a base of 300 – 500 nm, on the background of which there are single grains of height ~ 20 nm with sharp tops and a base of 80 – 100 nm. In this case, the average surface roughness is several times lower than for pure *PbTe* films and is 1 – 2 nm.



a) *b)*

Fig. 1. AFM image of the surface of PbTe films on chips (0001) of mica-muscovite, thickness: nm – 270 (a), 810 (b).



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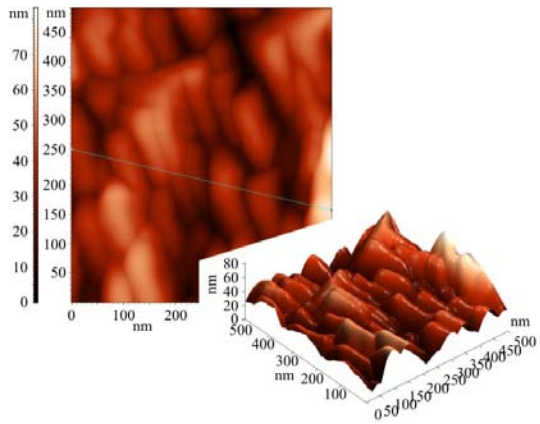

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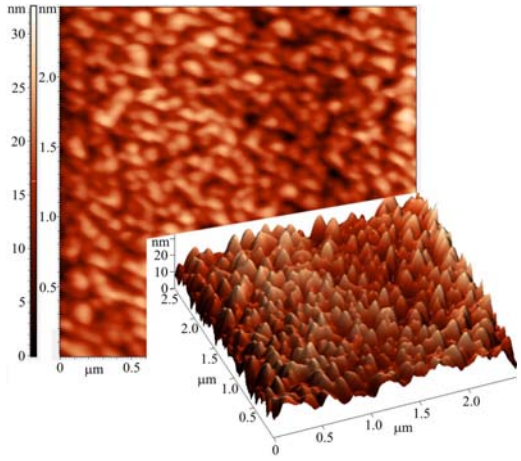
Fig. 2. AFM image of the surface of PbTe:Bi films on chips (0001) of mica-muscovite, thickness d: nm – 320 (a), 1620 (b).



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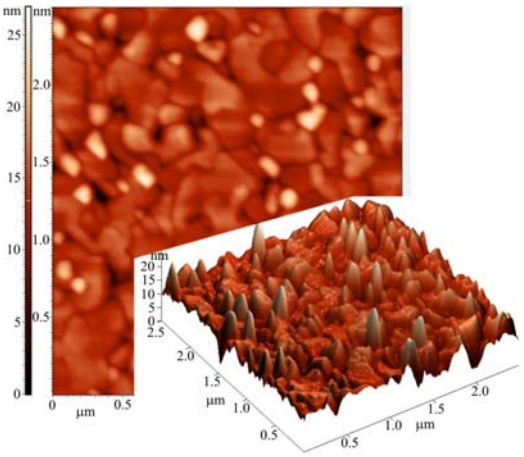

b)

Fig. 3. AFM image of the surface of $Pb_{17}Ag_2Te_{20}$ films on chips (0001) of mica-muscovite, thickness d: nm – 270 (a), 405 (b).

Analysis of thermoelectric properties of the films

The resulting dependences of the electric conductivity σ and the Hall concentration of current carriers $n_{H,}$ the Seebeck coefficient S and the thermoelectric figure of merit $S^2\sigma$ on the film thickness are represented in Fig. 4.

From the previous works it can be concluded that deposition temperature has a significant impact on the thermoelectric parameters of material under study. For films based on pure lead telluride the electric conductivity, the Hall concentration of charge carriers and the thermoelectric power increase with a rise in deposition temperature, and the thermoelectric power has a clear peak at deposition temperature 200 ^{o}C. With a further rise in the temperature of the substrate, the growth rate increases more than twice to reach 2.25 nm/s (Fig. 2), and the thermoelectric parameters somewhat degrade. The thermoelectric power of films based on pure lead telluride is relatively low and reaches the maximum 6.2 μW/K^{2}cm at thicknesses close to 400 nm. To increase the thermoelectric power, 1 at. % of bismuth doping impurity was introduced into lead telluride. Taking into account clear peak of thermoelectric power, subsequent studies versus the thickness of doped condensate were conducted for samples obtained at T_s = 200 ^{o}C.

Introduction of bismuth doping impurity somewhat reduced deposition rate to 0.85 nm/s, but

thermoelectric parameters of such samples are much better.

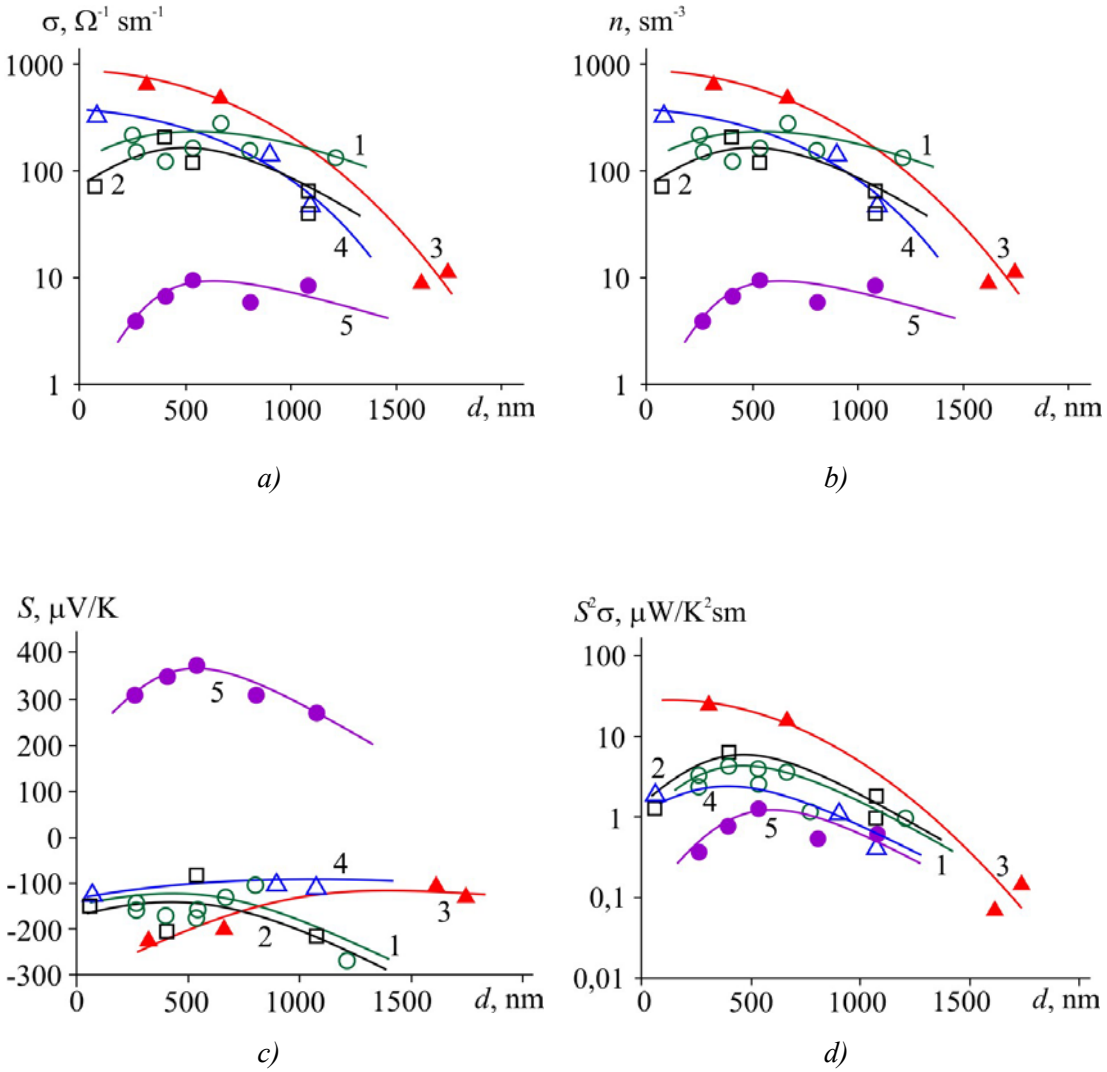

Fig. 4. Dependences of the electric conductivity σ(a), the Hall concentration n (b), the Seebeck coefficient (c) and the thermoelectric power $S^2\sigma$ (d) on the thickness of films obtained on fresh chips of mica. 1,○ – PbTe films obtained at Ts = 200 °C; 2, □ – PbTe films obtained at Ts = 250 °C; 3,▲ – PbTe:Bi films obtained at Ts = 200 °C; 4,△ - PbTe:Bi films obtained at Ts = 150 °C; 5,● – $Pb_{17}Ag_2Te_{20}$ films obtained at Ts = 200 °C.

Specifically, bismuth doping resulted in the increase of the Hall concentration of charge carriers by more than an order of magnitude, the increase in the electric conductivity by more than three times with practically unvaried Seebeck coefficient, which made it possible to achieve a significant increase in thermoelectric power up to 25 μV/K. One should also note the thickness dependence of thermoelectric power which demonstrates a clear peak at thicknesses close to 320 – 400 nm. The growth of thermoelectric figure of merit is due to improvement of structural perfection of films (Fig. 5), which leads to reduction of scattering effect at grain boundaries and considerable increase in the electric conductivity. With rather small thicknesses, the role of carrier scattering on the surface of film is increased and the conductivity is considerably reduced.

For the films of p-type $Pb_{17}Ag_2Te_{20}$ such high values of thermoelectric power could not be

reached, despite the sufficiently high Seebeck coefficient values of 300 – 400 μV/K, because of low electric conductivity to 10 $\Omega^{-1}cm^{-1}$.

The thickness dependence of thermoelectric power also demonstrates a clear peak with the thicknesses close to 500 nm, which is related to essential change of film structure at these thicknesses.

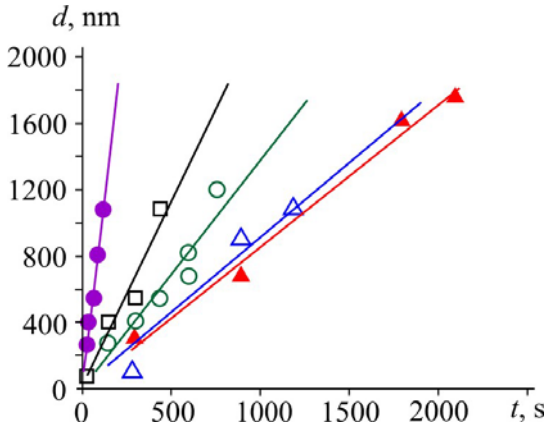

Fig. 5 Dependence of film thickness on deposition time. ○ – PbTe films obtained at Ts = 200 °C;□ – PbTe films obtained at T_s = 250 °C; ▲ – PbTe:Bi films obtained at Ts = 200 °C; Δ – PbTe:Bi films obtained at T_s = 150 °C; ● – $Pb_{17}Ag_2Te_{20}$ films obtained at T_s = 200 °C.

Conclusions

1. The effect of technological factors on the structure, surface morphology and thermoelectric properties of vapour phase thin films based on pure and bismuth-doped lead telluride *PbTe:Bi* and $Pb_{17}Ag_2Te_{20}$ compounds obtained by vapour phase methods on mica substrates is investigated.
2. It is established that *PbTe:Bi* samples with the content of *Bi* 1 at. % and a thickness close to 320 – 400 nm have maximum thermoelectric power 25 μW/K^2cm which is much better than that of pure tin telluride. For films based on $Pb_{17}Ag_2Te_{20}$ the peak of thermoelectric characteristics is observed at somewhat larger thickness – close to 500 nm.
3. It is shown that thin films based on *PbTe* have improved thermoelectric parameters as compared to the bulk samples.

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