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Structure and Electrical Properties of Thin Films of Pure and Bismuth-Doped Lead Telluride

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The electrical properties of thin films obtained by deposition in vacuum of the pair of PbTe on the substrates of polyamide tape and PbTe:Bi on fresh cleavages of (0001) mica-muscovite under different processing conditions, as well as at their subsequent exposure to air, were studied. The high temporal stability of the films on air was revealed.

Keywords: Lead telluride, Doping, Thin films, Thermoelectric properties.

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1. INTRODUCTION

Lead telluride is an effective thermoelectric material for the medium-temperature range of 500-750 K and sources and sensors of the infrared radiation of the optical spectrum [1]. Intense interest to the films and nanostructures is conditioned by the possibility to influence on the parameters by the technological factors of the growing process [2-3]. However, the problem of temporal stability of the electrical parameters remains completely unsolved. Thus, in particular, a layer of p-type conduction is rapidly formed on the condensate surface during contact with oxygen, and, as the previous works have shown [4], it is impossible to obtain a stable material of n-type based on pure lead telluride. To our opinion, this question can be solved by doping of the main matrix.

In the present work we study the structure features and behavior of the electrical parameters in thin films of pure and bismuth-doped PbTe.

2. EXPERIMENTAL TECHNIQUE

Films for the investigation were obtained from the vapor phase by the method of open evaporation in vacuum. Pure PbTe was deposited on the substrates of polyamide tape, and doped one – on fresh cleavages of (0001) mica-muscovite. Evaporator temperature during deposition was T_E = 970 K, and substrate temperature T_S = 420-470 K. Film thickness was specified by the deposition time in the range of 10-90 min and measured using the microinterferometer MII-4.

Measurement of the electrical parameters of films was performed on air at room temperatures in constant magnetic fields. Measured sample had four Hall and two current contacts. As ohmic contacts we have used silver films. Current passing through the samples was equal to ~ 100-1000 μA. Magnetic field was perpendicular to the film surface at the field induction of 1,5 T.

A series of measurements was carried out for each sample in certain time up to one year.

Structure of the condensate was investigated by the atomic-force microscopy (AFM) methods. Measurements are realized in the central part of the samples using series silicon probes NSG-11.

3. INVESTIGATION RESULTS

AFM images and profilograms of nanostructures are represented in Fig. 1. It is seen that the obtained condensates consist of nanosized crystallites of pyramidal shape. Average sizes of crystallites for thin films in the perpendicular to the surface direction are equal to ~ 15 nm, and in the lateral direction – ~ 80 nm (see Fig. 1B) and are much less than for thick films with the following sizes: ~ 80-140 nm and ~ 300-500 nm, respectively (Fig. 1A,C). We have also to note that thick films on mica cleavages are characterized by flatter apexes (Fig. 1C) than films on polyamide (Fig. 1A).

Dependences of the resistivity, Hall coefficient, and charge currier mobility of the structures with different thickness on the exposure time on air are illustrated in Fig. 2. It is seen that electroconductivity σ of thin films (Fig. 2a, curves 1, 3) much higher than of thick ones (Fig. 2a, curves 2, 4). In this case, conductivity of PbTe films slightly increases with the exposure time (Fig. 2a, curves 3, 4), and of doped ones – decreases for thin films (Fig. 2a, curve 1), and remains almost constant for thick ones (Fig. 2a, curve 2). Hall concentration of charge curriers for pure and doped structures differs in both behavior and type of the main charge carriers. Non-doped PbTe structures had p-type conductivity, and carrier concentration increased with the exposure time on air. Doped samples had n-type conductivity and dropping behavior of the dependence of the carrier concentration on the exposure time (Fig. 2b, curves 1, 2). Such behavior of Hall concentration of the carriers can be explained by acceptor action of oxygen. Carrier mobility for thin films on the initial stages of exposure is higher than for thick ones (see Fig. 2c, curves 1, 2 and curves 3, 4, respectively). In this case, if carrier mobility slightly decreases with the time (Fig. 2c, curves 1, 3), then for thick films it has the tendency to increase (Fig. 2c, curves 2, 4).

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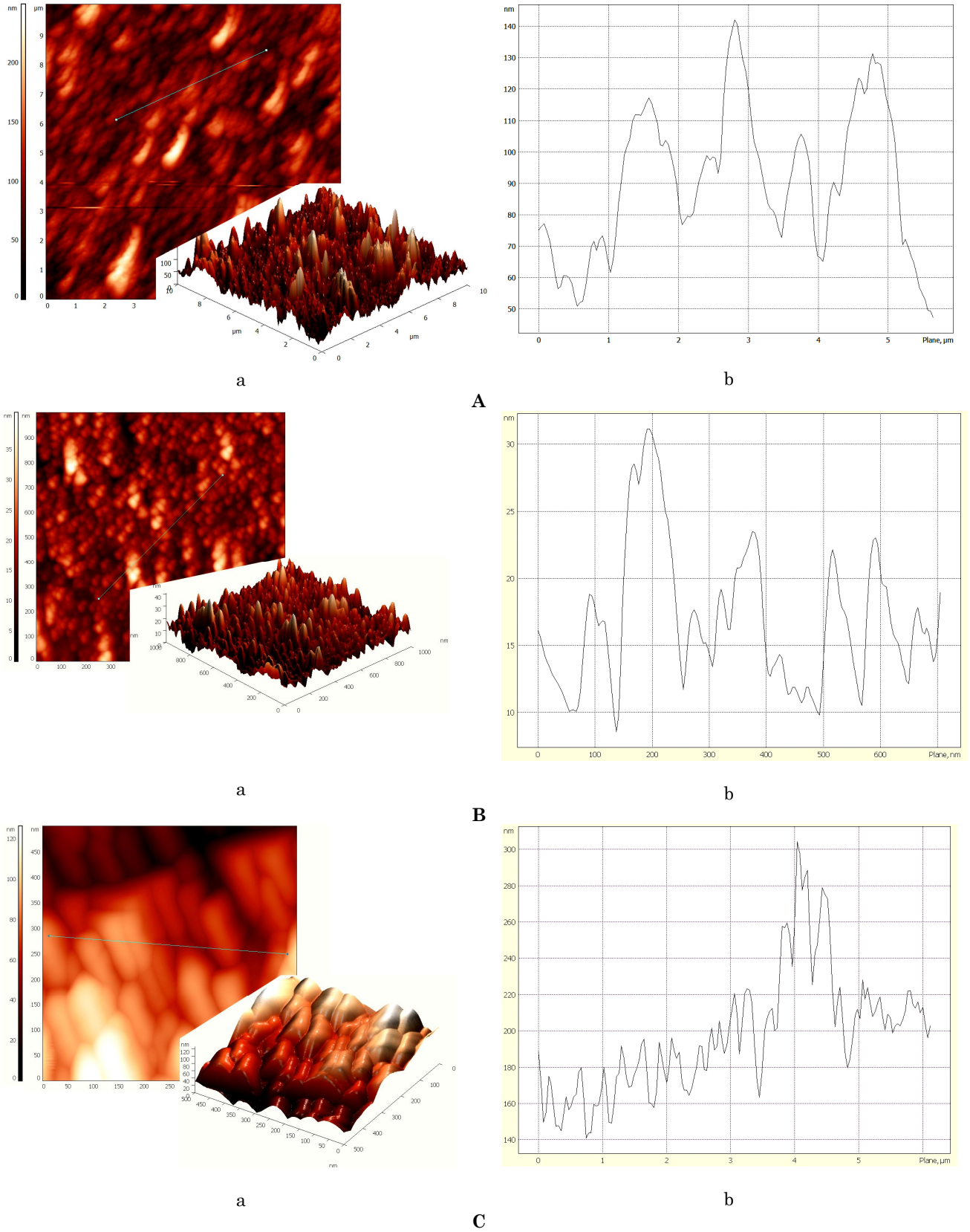

Fig. 1 – AFM images (a) and profilograms (b) of PbTe nanostructures on polyamide (A) and PbTe:Bi on cleavages of (0001) mica-muscovite (B, C). Evaporation temperature is $T_E = 970$ K, deposition temperature is $T_S = 420$ K, deposition time t: min – 30 (A), 5 (B), 30 (C)

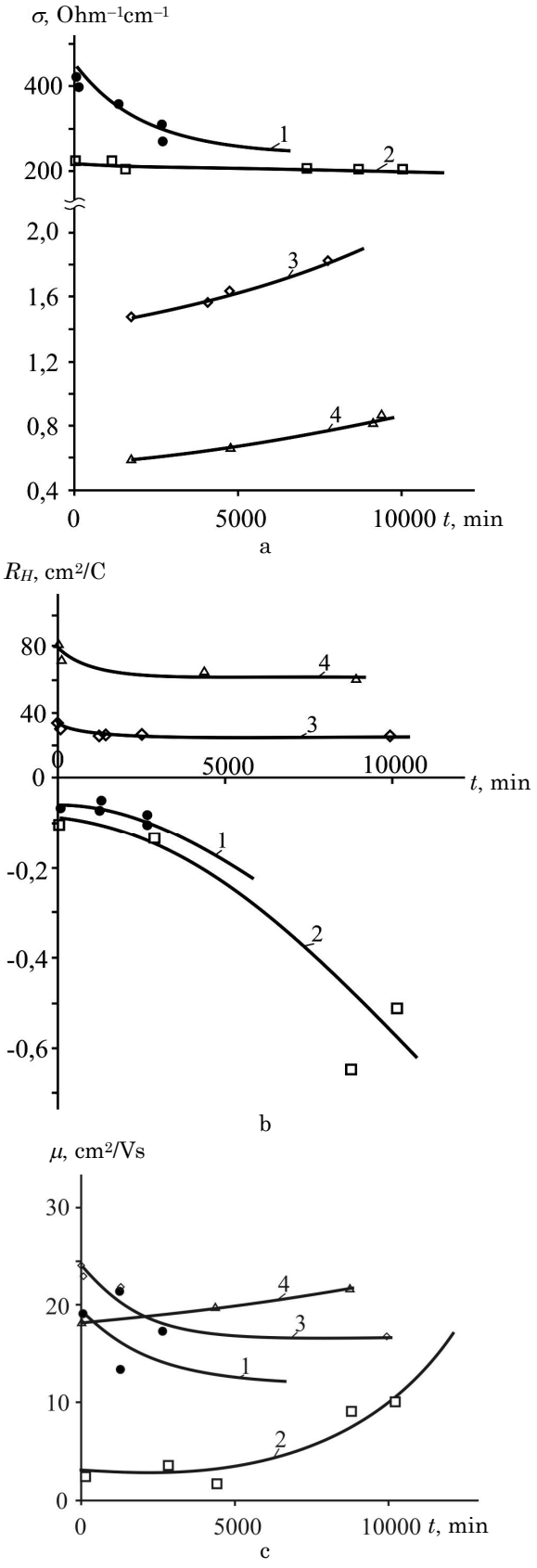

Fig. 2 – Dependences of the conductivity σ (a), Hall coefficient R_H (b), and charge carrier mobility μ (c) on the exposure time on air for PbTe:Bi films of different thickness d, μm: ● (1) – 0,08; □ (2) – 1,08, and PbTe films with thickness d, μm: ◊ (3) – 0,08; Δ (4) – 0,3

In Fig. 3 we represent the thickness dependences of the electrical parameters of the films. As seen, they differ in both the modulus and behavior: conductivity of doped films is 3 orders more than of pure ones (Fig. 3a). This is connected with high concentration of electrons in doped material which also 3 times exceeds the concentration of holes in non-doped PbTe structures (Fig. 3b).

Thickness dependences of the conductivity and carrier mobility have non-monotonic behavior with clear minimum (at the thickness of 0,2 μm) for pure films and maximum (at 0,3 μm) for doped ones (Fig. 3c).

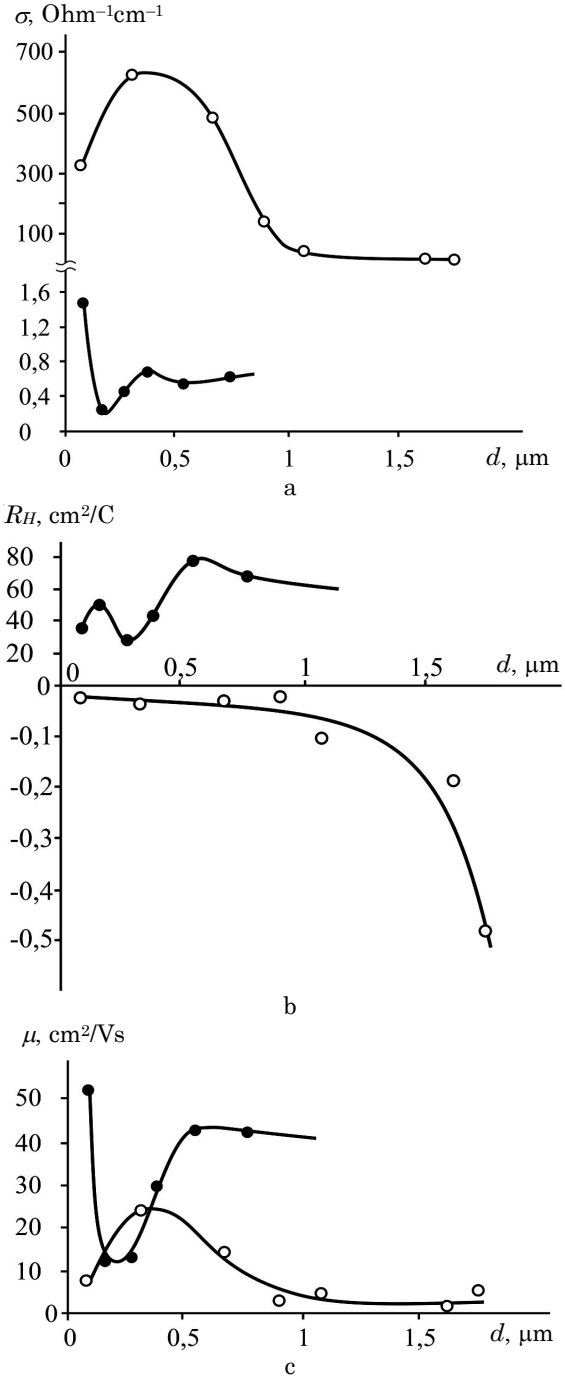

Fig. 3 – Dependences of the conductivity (a), Hall coefficient (b), and charge carrier mobility (c) on the film thickness: PbTe (●) and PbTe:Bi (○).

4. ANALYSIS OF THE INVESTIGATION RESULTS

Bismuth doping conditions an active donor action in lead telluride which is manifested in considerable increase in the concentration of electrons up to ~ 10^{20} cm^{-3} (Fig. 3c; Table 2). We note that in pure PbTe films it, as a rule, is in the range of 10^{17}-10^{18} cm^{-3} [7]. Remembering that bismuth in PbTe can display amphoteric properties, which consist in the fact that substitution lead in a cation sublattice ($Bi^{3+} \rightarrow Bi^{+}_{Pb}$) is a donor, and in an anion one ($Bi^{3-} \rightarrow Bi^{-}_{Te}$) – is an acceptor, one can state that in our case the first doping mechanism dominates.

Obtained complex behavior of the dependences of the electrical parameters on the exposure time on air (Fig. 2) can be explained by the influence of, at least, three primary processes which take place in the samples during interaction with atmospheric oxygen. Firstly, this is the process of oxygen adsorption by free film surface and formation of charged acceptor centers (O^{2-} is very active during first minutes and even a day depending on the initial carrier concentration and ideality of the film structure) at exposure on air. Secondly, the process of oxygen diffusion inside the film material is more effective in polycrystalline samples, where there are many intercrystalline sublayers which form additional high-speed diffusion paths. And, thirdly, diffusion process of donor centers (in the first place, internodal lead ions Pb^{+}_{i}, Pb^{2+}_{i}) to the film surface.

Estimation of the influence of oxygen on the electrical properties of the structures is performed based on the two-layer Petritz model [5]. According to the model, thin film is represented consisted of two layers: near-surface (I) (thickness d_p, charge carrier concentration n_p, mobility μ_p, conductivity σ_p, and Hall coefficient R_p) and volume (II) which is characterized by the same values d_n, n_n, μ_n, σ_n, R_n connected parallel. The film thickness is $d = d_p + d_n$.

If volume layer is of n-type, and surface region is of p-type, connection between the coefficient R_H and resistivity ρ is determined by the formula [6]:

$$R_H = \mu_p \rho - e\frac{n_b \mu_n d_b}{d}\left[\mu_n + \mu_p\right]\rho^2 . \qquad (1)$$

If volume layer is of p-type, and surface region is of p-type, connection between the coefficient R_H and resistivity ρ is determined by the formula [6]:

$$R_H = \mu_p \rho . \qquad (2)$$

Typical dependences of the Hall coefficient on the resistivity $R_H = f(\rho)$ for films of different thickness are represented in Fig. 4.

Table 1 – Values of the surface mobility (μ_s) of charge carriers of as-grown PbTe films of different thickness (d)

d, nm	μ_s, cm^2/Vs
80	50,8
300	50,1
540	42,6
760	38,0

Table 2 – Parameters of the near-surface layer and volume of PbTe:Bi films on mica cleavages

Thin structures	
d_p, μm	0,03
d, μm	0,08
μ_p, cm^2/Vs	15
μ_n, cm^2/Vs	31
n_n, cm^{-3}	1 10^{20}
Thick structures	
d_p, μm	0,2
d, μm	1,08
μ_p, cm^2/Vs	2
μ_n, cm^2/Vs	5,4
n_n, cm^{-3}	1 10^{20}

Dependences of the Hall coefficient on the resistivity have linear piece on the initial stages of interaction with oxygen (up to two days of exposure) (Fig. 4) that gave the possibility to estimate the value of the surface mobility of charge carriers for the films of different thickness (Tables 1, 2).

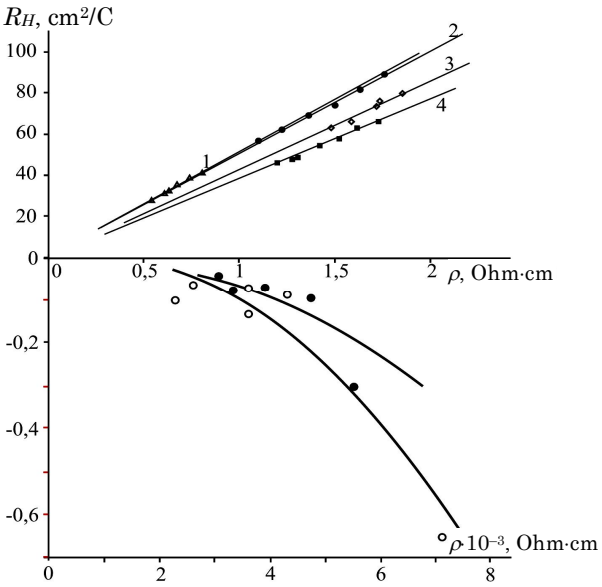

Fig. 4 – Dependence of the Hall coefficient on the resistivity for PbTe films obtained on polyamide substrates (film thickness d, μm: 1 – 0,08; 2 – 0,3; 3 – 0,54; 4 – 0,76), and for thin (d = 0,08 μm) (●) and thick (d = 1,08 μm) (○) PbTe:Bi films on mica cleavages. Dots are the experiment; solid lines are the calculations by the formulas (1) and (2), respectively.

Thus, exposure and annealing in air of doped n-PbTe:Bi films do not significantly influence the change in the carrier concentration and do not lead to the change in the conductivity type from n- to p- (Fig. 2b, curves 1, 2), as it takes place for non-doped thinfilm material [7]. Moreover, Hall mobility of charge carriers of thin films is some times (10-15) more than of thick ones (see Fig. 2c, curves 1, 2), and oxygen leads to the changes in the electrical parameters in insignificant (0,03-0,2 μm) near-surface layer only (Table 2). Analyzing the obtained experimental results for doped films (Fig. 2, 4) and taking into account small thickness of the near-surface layer (Table 2) obtained from calculations, one can suggest that for thin condensate oxygen, in fact,

does not enter into crystal lattice being localized on the surface. For thick films oxygen also does not lead to the considerable changes in the electrical parameters (see Fig. 2) because of high concentration of electrons which can not be compensated by acceptor centers. In whole, influence of the near-surface layer on the thermoelectrical properties of n-PbTe:Bi films is insignificant that provides high stability of the material at its exposure on air.

For thick pure p-PbTe films exposure on air conditions the formation due to oxygen of additional acceptor center that is the reason of increase in the concentration of main carriers (Fig. 2b, curves 3, 4) and increase in the value of conductivity (Fig. 2a, curves 3, 4).

As for the thickness dependences of the electrical parameters of both pure and doped lead telluride films which have the tendency to oscillations (Fig. 3), they can be explained by the quantum-size effects [8, 9]. Thus, in particular, if consider the studied PbTe/polyamide and PbTe:Bi/mica structures to be a quantum well of the "dielectric-semiconductor-dielectric" type with high walls, then increase in the well width on the value of Fermi half-wave leads to the appearance of new filled subzone and jump of the density of states of charge carriers that is the reason of the observed oscillation of the electrical parameters (Fig. 3).

5. CONCLUSIONS

1. Thermoelectrical properties of PbTe and PbTe:Bi thin films on the film thickness and exposure time on air are investigated.

2. Within the two-layer Petritz model, dependences of the Hall coefficient on the resistivity are analyzed; and thickness of the near-surface layer and surface electrical parameters are determined.

3. Bismuth-doped thin-film PbTe:Bi material with stable on air electrical parameters is obtained.

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