Oscillations of Thermoelectric Parameters of PbTe:Bi Nanofilms on Glass-Ceramic

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There were investigated the thickness (d) dependences of thermoelectric (TE) parameters (concentration n, mobility μ, conductivity σ, Seebeck coefficient S, and thermoelectric power $S^2\sigma$) for bismuth-doped n-PbTe nanostructures containing 2 at.% Bi grown from the vapor phase on glass-ceramic. Nonmonotonous change of d-dependences for the studied parameters was explained by the quantization of the energy spectrum of electron gas in quantum well of the glass-ceramic/n-PbTe:Bi structure. On the basis of this assumption for these structures the theoretical d-dependences of the corresponding TE parameters were built and compared with the experimental dependences.

Keywords: Lead telluride, Bismuth, Glass-ceramic, Nanostructures, Quantum-size effects.

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1. INTRODUCTION

Lead telluride is a well-known thermoelectric material in the middle temperature range [1]. As previous investigations have shown [2, 3], bismuth-doped PbTe has high and stable value of carrier concentration. This allows to obtain time-constant values of the Seebeck coefficient (S), electrical (σ) and thermal (χ) conductivities, and thermoelectric Q-factor $Z = S^2\sigma/\chi$. Growth of the impurity (Bi) concentration in PbTe leads to the decrease in its thermal conductivity and increase in the electrical conductivity (due to the increase in the electron concentration of carriers) [2-5].

Ability of nanostructured materials to increase the thermoelectric (TE) Q-factor is of intense interest [6, 7]. Decrease in the material dimension creates conditions for the quantum-size effect which leads to the increase in the density of states near the Fermi energy. This allows to preserve a sufficiently high electrical conductivity σ at comparatively low Fermi energy E_F, at which high values of the Seebeck coefficient S take place. Tangible influence of quantum effects on the TE characteristics is possible only under the condition that structure dimension in the direction of restriction is comparable with the the Broglie wavelength of carriers. The given condition, in particular, is fulfilled for the structures in the form of potential wells [8-12].

The aim of the present work is the investigation of the behavior features of TE parameters on the thickness of bismuth-doped nanostructures of n-type lead telluride deposited on glass-ceramic substrates.

2. EXPERIMENTAL TECHNIQUE

Samples for investigation were grown from the vapor phase by the open evaporation method in vacuum on glass-ceramic substrates. Evaporator temperature during deposition was $T_e = 700°C$ and substrate temperature was equal to $T_s = 200°C$.

Material for the growth was synthesized by alloying of high-purity Pb, Bi, and Te (99,99% of the main component) in vacuum up to $\sim 10^{-1}$ Pa quartz ampoules and cooling in the mode of switched off oven. Percentage of the components was chosen based on calculation that Bi substitutes lead atoms due to of its donor action in Pb sublattice: 50% – Te, 48% – Pb, Bi – 2%.

Measurements of the electrical parameters were performed on air at room temperature during 10 min after growth. Measured sample had four Hall and two current contacts. Silver films were used as ohmic contacts. The value of current passing through the samples was equal to 1 mA or 2 mA.

Hall mobility was calculated as $\mu = R_H\sigma$. The Hall constant R_H was determined by measurement of the transverse potential difference in magnetic field with induction of 1,4 T perpendicular directed to the structure surface. All samples had n-type conductivity.

3. INVESTIGATION RESULTS

As seen from Fig. 1, experimental dependences of the TE coefficients on the thickness of PbTe:Bi nanostructures on glass-ceramic at room temperature are characterized by non-monotonous behavior. Here, concentration achieves the maximum value of $3,82 \cdot 10^{20}$ cm^{-3} at the thickness of $d_{макс} = 121$ nm. Increase in the thickness of condensate leads to the decrease in the value of electron concentration: at $d = 221$ nm $n = 1,05 \cdot 10^{20}$ cm^{-3}, and at $d = 341$ nm – $n = 2,6 \cdot 10^{19}$ cm^{-3}. The value of $n = 1,82 \cdot 10^{20}$ cm^{-3} (Fig. 1a) corresponds to the thickness of $d = 101$ nm which is less than the maximum thickness.

On the thickness dependence of the mobility of main carrier three maximums and three minimums are fixed (Fig. 1b). d-dependence of the Seebeck coefficient is characterized by five absolute values of the extreme points: two maximums and three minimums (Fig. 1c). Three maximums and three minimums are revealed on the dependence $\sigma(d)$ (Fig. 1d).

The power coefficient $P = S^2\sigma$ calculated based on the obtained values of $\sigma(d)$ and $S(d)$ (Fig. 1c and Fig. 1d) as the function of thickness is also described by three maximums and three minimums (Fig. 1e).
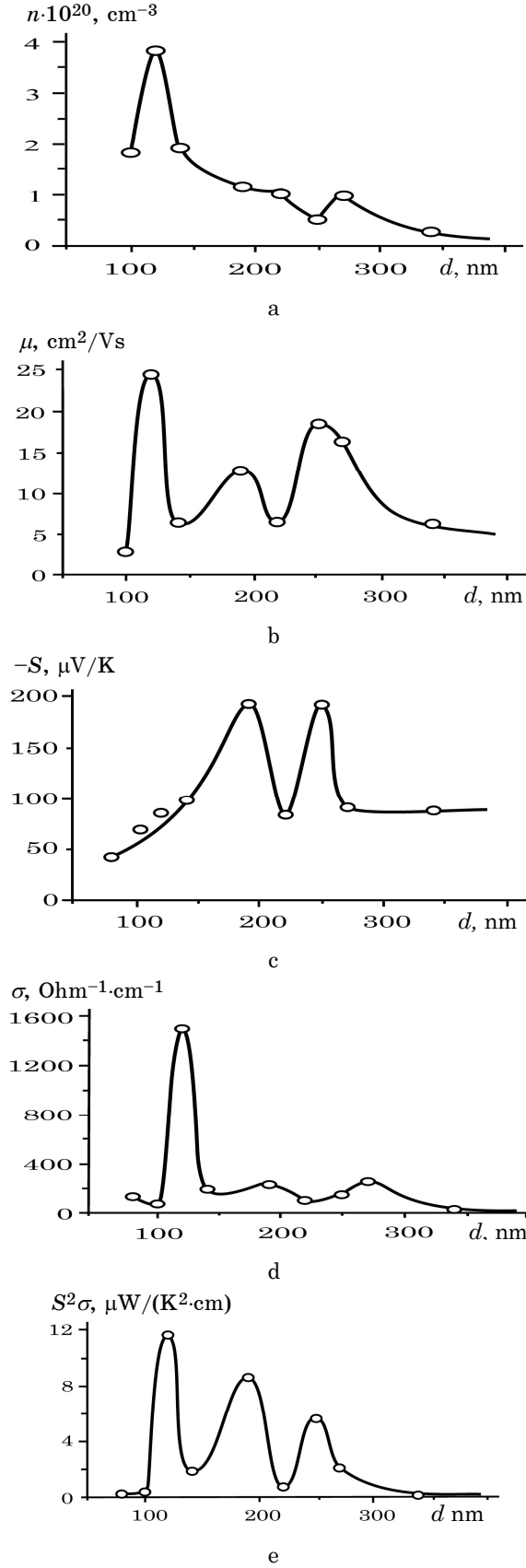
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Fig. 1 – Dependence of the concentration n (a), mobility μ (b), Seebeck coefficient S (c), conductivity σ (d), and thermoelectric power $S^2\sigma$ (e) on the thickness of PbTe:Bi nanostructures on glass-ceramic at $T = 300$ K

4. DISCUSSION OF THE RESULTS

Based on the experimental dependences (see Fig. 1) which demonstrate non-monotonous oscillating behavior of the change in the TE coefficients with the change in the condensate thickness, it is natural to assume that such behavior is conditioned by the energy quantization of carriers due to the restriction of their motion in potential well. Increase in the well width on the value of Fermi half-wave leads to the appearance of new filled sub-band below the Fermi energy. At the width of filling of new zone, a jump is observed in the density of states that leads to the oscillating behavior.

For quantum well (QW) with high walls, electrons are confined along the oz-direction, and along the x- and y-directions electrons move freely. Electron wave function and energy eigenvalues under the condition of parabolicity of energy bands are determined by the following expressions [13]

$$\psi = \left(\frac{2}{\Omega}\right)^{\frac{1}{2}} \exp(ik_x x + jk_y y) \sin\left(\frac{n\pi z}{d}\right), \qquad (1)$$

$$E = \frac{\pi^2\hbar^2}{2m_z^* d^2} n^2 + \frac{\hbar^2 k^2}{2m_p^*}, \qquad (2)$$

where $k^2 = k_x^2 + k_y^2$; m_z^* is the effective electron mass along the direction of restriction; $m_p^* = \sqrt{m_x^* m_y^*}$; m_x^*, m_y^* are the effective electron masses along the ox and oy axes; Ω is the total volume of the layer; d is the well width; n is the quantum number which takes values of natural numbers.

A number of quantized levels which lie below the specified energy is defined by the first part of (2)

$$E_n = \frac{\pi^2\hbar^2}{2m_z^* d^2} n^2. \qquad (3)$$

Substituting the value of the Fermi energy into (3), it is possible to find the width d at which the specified number of levels n lie below the Fermi level. Difference between values of this width for two nearest levels determines the oscillation period Δd which will be equal to the width $d_{\min}$, at which bottom of the lowest sub-band coincides with energy E_F. Thus, it follows from (3)

$$\Delta d = d_{\min} = \frac{\lambda_F}{2} = \frac{h}{\sqrt{8m_z^* E_F}}. \qquad (4)$$

As seen from (4), change in the value of the Fermi level leads to the change in the oscillation period. The value of the Fermi energy can be expressed through the well width d and carrier concentration in the conduction band [14]

$$E_F = \varepsilon_1 \frac{(n_0 + 1)(2n_0 + 1)}{6} + \frac{\pi\hbar^2}{m^*}\frac{n_e}{n_0} d, \qquad (5)$$

where ε_1 is the first quantized level which is defined by formula (3) when $n = 1$; $n_0 = [(E_F/\varepsilon_1)^{1/2}]$ is the integer part of $(E_F/\varepsilon_1)^{1/2}$; m^* is the effective mass of carriers; n_e is the electron concentration.

If Fermi level coincides with the band bottom n_0, then $E_F(d_0) = \varepsilon_1 n_0^2$. At such widths $(E_F(d_0)/\varepsilon_1)^{1/2}$ is the integer number. Substituting this value into (5), for d_{n0} we obtain

$$d_{n_0} = d_0 n_0 \left[1 - \varepsilon_1 \frac{(n_0+1)(2n_0+1)}{6n_0^2} \right]^{1/3}, \qquad (6)$$

where $d_0 = (\pi/2n_e)^{1/3}$. Number n_0 at the given width d is found as an integer part of the result of the solution of (6) with respect to n_0 when $d_{n0} = d$.

Influence of the level of bismuth-doping of PbTe on the Fermi energy can be estimated by the corresponding change in the effective mass in (5) based on the empirical formula obtained as a result of approximation of the experimental dependence of the effective mass on the electron concentration [15]:

$$\frac{m^*}{m_0} = 0{,}111 \cdot 10^{-6} \cdot n_e^{\frac{1}{3}}, \qquad (7)$$

where m_0 is the electron mass; n_e is the electron concentration in cm^{-3} units.

Thus, substitution of the integer part of the solution of equation (6) with respect to n_0 when $d_{n0} = d$, as well as the obtained from (7) effective mass m^* into (5) gives the possibility to build the dependence $E_F(d)$. In Fig. 2 we present the dependence of the Fermi energy in $k_B T$ units on the QW width in the experimentally studied range of 50-400 nm in the approximation of constant electron concentration ($n_e = 4{,}5 \cdot 10^{18}$ cm^{-3}) of bulk sample. As seen from the figure, the given dependence has non-monotonous decaying character. At thicknesses larger than 300 nm $E_F(d)$ achieves saturation that is close to E_F in a bulk sample. Increase in the QW width leads to the decrease in the position of Fermi level (Fig. 2), and, according to (4), to the increase in the oscillation period of the d-dependences of TE parameters. Constant value of the oscillation period Δd in the range of QW widths of $d > 300$ nm is the result of the attainment of saturation by $E_F(d)$ at the mentioned thicknesses.
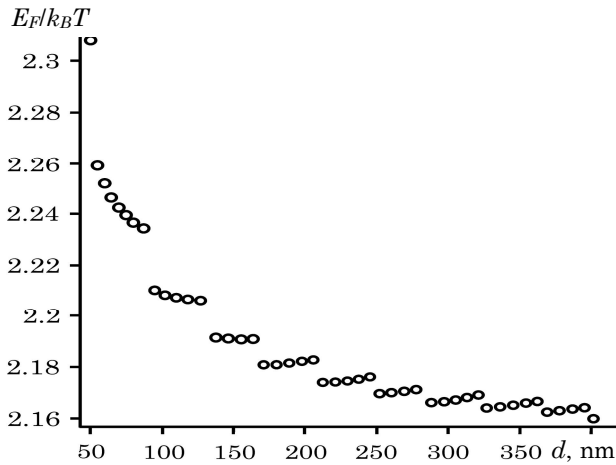
$E_F/k_B T$

Fig. 2 – Calculated values of the Fermi energy versus the QW width in PbTe:Bi at $n_e = 4{,}5 \cdot 10^{18}$ cm^{-3}, $m^* = 0{,}18\, m_0$

Taking into account a directly proportional dependence of the perpendicular component of effective mass

on the energy [14], near the Fermi energy correlation between m_z^* and d will have the same behavior as $E_F(d)$. In Fig. 3 we represent the dependence $m_z^*(d)$ built by the formula [14]

$$m_z^* = m_{z0}^* \left(1 + 2E_F / \varepsilon_g \right), \qquad (8)$$

where m_{z0}^* and ε_g are the z-component of the effective mass at small concentrations and band gap of PbTe, respectively. It is seen that increase in the concentration of n-type carriers in the conduction zone of PbTe leads to the increase in the z-component of their effective mass ($m_{z0}^* = 0{,}024\, m_0$, $m_z^* \approx 0{,}032$).
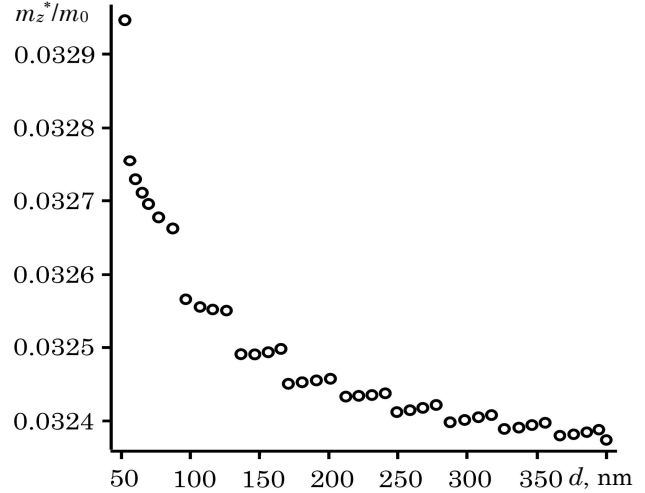
m_z^*/m_0

Fig. 3 – Calculated values of the component of the effective mass m_z^* in units of electron mass m$_0$ versus the QW width of PbTe:Bi at $n_e = 4{,}5 \cdot 10^{18}$ cm^{-3}

In the case of QW, TE transport coefficients can be obtained from Boltzmann equations which are written in assumption that electron distribution function in a stationary state remains constant and can be changed only at the expense of external forces and fields. Then, system of electrons returns to the equilibrium state due to different relaxation processes with characteristic relaxation times. For quasi-two-dimensional system we can write [16]

$$\sigma = \frac{e^2}{T} \Gamma^1, \qquad (9)$$

$$S = \frac{E_F}{eT} + \frac{1}{eT} \frac{\Gamma^2}{\Gamma^1}, \qquad (10)$$

where σ is the electrical conductivity; S is the Seebeck coefficient; E_F is the Fermi energy; e is the electron charge; T is the absolute temperature.

Transport coefficient Γ is determined by the semi-classical approach, according to which particles are restricted in single-dimensional box. In this case, temperature gradient and electric field are directed along the ox-axis. Then

$$\Gamma^1 = -\zeta^{(0)}, \qquad (11)$$

$$\Gamma^2 = \zeta^{(1)}, \qquad (12)$$

where

$$\zeta^{(s)} = \frac{2T}{\pi a}\sqrt{\frac{m_y^*}{m_x^*}}\frac{1}{\hbar^2}\sum_{n=1}^{E_n \le E_F}\int_0^{\infty} E^s \tau \varepsilon (\frac{\partial f}{\partial \varepsilon})d\varepsilon . \qquad (13)$$

Here f is the Fermi distribution function; $\varepsilon = E - E_n$; τ is the relaxation time which in the case of scattering on acoustic phonons does not depend on the energy [17] ($\tau = \tau_0$), therefore, it can be taken out of the integral. Based on this condition, expressions for Seebeck coefficient S and electrical conductivity σ can be written as

$$S = \frac{k_B}{e}\left[\frac{E_F}{k_B T} - \frac{A_1 + A_2}{A_3}\right], \qquad (14)$$

$$\sigma = \frac{1}{2\pi d}\frac{2k_B T}{\hbar^2}\sqrt{\frac{m_x^*}{m_y^*}}e^2 \tau_0 A_3 , \qquad (15)$$

where

$$A_1 = \left(\sum_{n=1}^{E_n \le E_F}\int_0^{\infty} x^2\left(-\frac{\partial f_n}{\partial x}\right)\right), \qquad (16)$$

$$A_2 = \left(\sum_{n=1}^{E_n \le E_F}E'\int_0^{\infty} x\left(-\frac{\partial f_n}{\partial x}\right)dx\right), \qquad (17)$$

$$A_3 = \left(\sum_{n=1}^{E_n \le E_F}\int_0^{\infty} x\left(-\frac{\partial f_n}{\partial x}\right)dx\right). \qquad (18)$$

Fermi distribution function has the known form

$$f_n = \frac{1}{e^{x-\eta_n}+1} , \qquad (19)$$

where $x = \varepsilon/(k_B T)$ is the decreased energy of a charge; $\eta_n = \xi - E'_n$. Here $\xi = E_F/(k_B T)$ and $E'_n = E_n/(k_B T)$; k_B is the Boltzmann constant.

Relaxation time in (15) can be estimated based on the mobility μ of n-type carriers in a bulk sample [18]

$$\mu = e\tau_0 / m^* . \qquad (20)$$

Estimation of the mobility μ of n-type carriers for PbTe crystals depending on the content of doping Bi impurity in the range from 0 to 1 at.% at temperature of 300 K is carried out in [19] based on the calculation of the Hall coefficient. Approximation of the corresponding experimental points gives values of the mobility of n-type carriers of $\mu = 200$ cm^2/(Vs) at Bi content of 2 at.%. Substitution of this mobility value, as well as the effective mass estimated by formula (7), into (20) gives the value of relation time of $\tau_0 = 5, 64 \cdot 10^{-14}$ s.

Accounting of the d-dependence of the Fermi energy (Fig. 2) in formulas (14)-(19), as well as d-dependence of the z-component of the effective mass (Fig. 3) in correlations (16)-(19) allowed to obtain the corresponding dependences of the Seebeck coefficient S and electrical conductivity σ on the QW width of PbTe:Bi.

As seen from formula (3), a number of levels below the Fermi energy is determined by the d-dependences of the effective mass and E_F itself, as well as by the well width d. Calculation procedure took into account both the change in the Fermi energy and change in the number of levels below it at the change in the well width. Also, it was assumed that $m_x^* = m_y^*$ in calculations of electrical conductivity by formula (15).
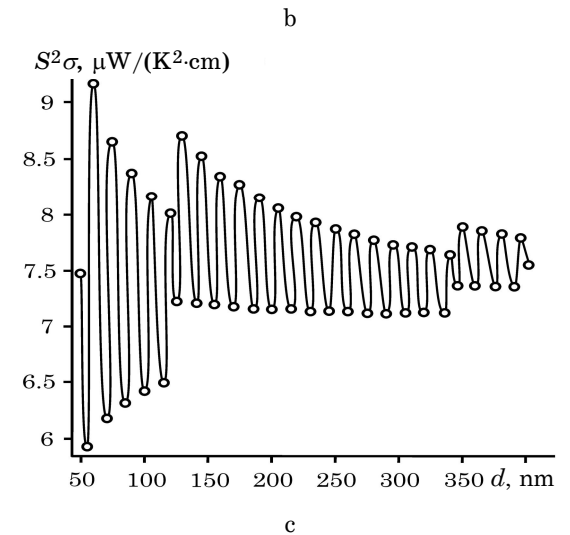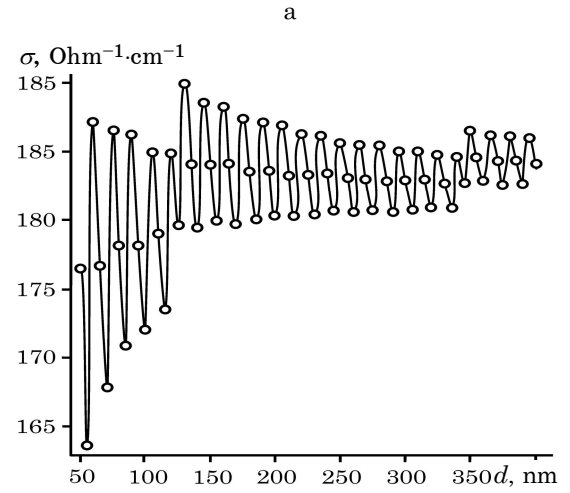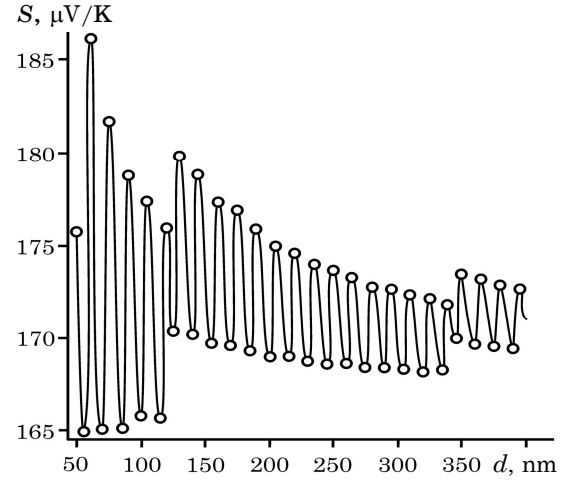

Fig. 4 – Theoretical dependences of the Seebeck coefficient S (a), electrical conductivity σ (b), and TE coefficient of the power $S^2\sigma$ (c) on the QW width of PbTe:Bi in the model of infinitely deep potential at $T = 300$ K

When using the above described theoretical model for the description of the behavior of TE coefficients in PbTe:Bi nanostructures at 300 K, QW width within the theoretical model is considered to be equal to the width of condensate in the experimental dependences of the corresponding parameters (Fig. 1). Obtained dependences of TE coefficients on the QW width of PbTe:Bi are characterized by non-monotonous oscillation behavior (Fig. 4). Here, calculated values (Fig. 4) agree well with the corresponding values in experimental dependences (see Fig. 1).

Comparing the experimental and theoretical dependences of TE coefficients (Fig. 1c, d, e and Fig. 4), except good agreement in value and oscillation behavior, one can note that oscillation amplitude in theoretical dependences of the corresponding coefficients is slightly less than the experimental one. Thus, if in experimental d-dependence of the Seebeck coefficient it is equal to ~ 100 μV/K (Fig. 1c), then in the theoretical – ~22 μV/K (Fig. 4a). Taking into account that measurement of TE parameters of nanostructures is performed on air and their surface is not protected from oxygen action, oxide dielectric layer can be formed on the surface. This leads to the situation that thickness of conduction part of the condensate is less than its total thickness on the value of oxide layer. In this case, width range in the model of potential well with high walls should be shifted to the left on the value of an external layer at the condensate surface. As seen from Fig. 4, decrease in the well width leads to the increase in the oscillation amplitude. Thus, shift of the studied range toward the region of less QW widths will lead to the growth of oscillation amplitude which in this case can be agreed with the experimental one. In the present work such shift was not carried out because of the complexity of estimation of the value of oxide layer on the nanostructure surface.

As to the electrical conductivity, its anomalously high value at the thickness of ~ 120 nm (Fig. 1d) is fixed in experimental d-dependence and is not observed in the corresponding theoretical dependence (Fig. 4b). Firstly, shift of the investigated range to the left on the value of external dielectric layer can lead to the appearance of the experimentally revealed peak in theoretical dependence $\sigma(d)$. On the other hand, the revealed anomalous value of electrical conductivity can be explained by the processes of self-ordering. In any case, such growth is described by only one experimental point and requires additional confirmation. When calculating the electrical conductivity, we have used the value of relaxation time calculated by formula (20) based on the value of mobility of n-type carriers in a bulk sample [18, 19]. It is seen from Fig. 1b that experimentally obtained Hall mobility of carriers is anomalously low in comparison

with its analogue in a bulk sample [19]. We explain this fact by the influence of non-monocrystalline structure which leads to the decrease in the Hall coefficient R_H and, consequently, the Hall mobility ($\mu = R_H \sigma$). Since calculation of TE parameters took place in the approximation of constant concentration of a bulk sample, the mobility value for the calculation of relaxation time also was taken from the experimental data of measurement of TE parameters of PbTe:Bi crystals [19].

Thus, theoretically calculated dependence of the TE power coefficient on the well width (Fig. 4c) describes sufficiently well its experimental equivalent (Fig. 1e). The fact that the maximum experimental value of the coefficient $S^2\sigma$ (12 μW/(K²cm)) slightly exceeds the corresponding theoretical value (9,2 μW/(K²cm)) is connected with the presence of high value of the electrical conductivity at $d \approx 120$ nm. Moreover, excess of the experimental oscillation amplitude of all three TE coefficients of their theoretical analogue is explained by less number of measurement points in comparison with model calculation.

5. CONCLUSIONS

1. Analysis of the experimental dependences of the concentration, mobility, Seebeck coefficient, conductivity, and TE power on the thickness of PbTe:Bi nanostructures on glass-ceramic at 300 K is carried out in the present work. It is revealed that these dependences are characterized by non-monotonous oscillation behavior.

2. Dependences of the Fermi energy and the effective mass on the QW width are calculated within the model of QW with infinitely high walls. Behavior of the change in the oscillation period of the density of states with the growth of the well width is investigated based on the mentioned dependences.

3. d-dependences of the Seebeck coefficient, electrical conductivity, and TE power coefficient are built on the basis of correlations between the Fermi energy and effective mass of carriers and the well width. As shown, obtained theoretical d-dependences of the TE coefficients agree well with the experimental ones.

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