The Influence of the Size Effects on the Termoelectric Properties of PbTe Thin Films

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Based on the Boltzmann kinetic equation, the boundary problem of calculating the conductivity and Seebeck coefficient for a film with a rectangular cross section is solved. The mirror-diffuse mechanism of reflection of charge carriers from the film surfaces is considered. The calculations are performed for different thicknesses of n-PbTe semiconductor. For the model of a quantum rectangular well with a flat bottom and infinitely high walls, the value of the Seebeck coefficient S was calculated for n-PbTe. The quantum and classical size effects are experimentally investigated. The transition from the oscillating to monotonic dependences of the thermoelectric parameters of nanostructures based on n-PbTe is proved.

Keywords: Classical size effects, Quantum size effects, Thin film, Lead telluride, Thermoelectric properties.

1. INTRODUCTION

Lead telluride belongs to IV-VI semiconductors, which are widely used in semiconductor technology. PbTe is a narrow-band semiconductor; therefore, it is suitable for the use in infrared lasers, optical detectors, as well as a thermoelectric material for the middle temperature range (500-750) [1-4]. The transition to a thin film causes the appearance of new size effects.

Today, the problems of calculating the conductivity of thin films are particularly relevant in connection with the rapid development of micro- and nanoelectronics. Moreover, the needs of modern society in new energy sources accompany the rapid development of thermoelectric materials science.

In the last decade, a new direction in thermoelectric materials science is associated with the use of structures, whose sizes are in the nanometer range. A decrease in the dimension leads to the manifestation of quantum size effects, which are exhibited in oscillations of thermoelectric parameters with changing thickness. This makes it possible to determine the optimal thickness with the best thermoelectric quality factor. And, thus, to obtain modern devices, which efficiently convert heat into electricity.

In this paper, the implementation of quantum and classical size effects in thin films based on PbTe on mica substrates is considered. Moreover, the impact of these effects on the thickness dependences of the kinetic parameters of the films is investigated.

For most semiconductors at room temperature, the free paths l are from 10 nm to 1000 nm, and the characteristic de Broglie wavelength λ at this temperature is about 10 nm [5, 6]. For the manifestation of size quantization, the film thickness D should be of the order of the carrier de Broglie wavelength λ [7]. Moreover, we have to note that for the observation of the quantum size effect, the charge carriers in the film should be degenerate [8]. The classical size effects should be taken into account at $\lambda << D << l$ [9]. In other words, there is the possibility to study the quantum and classical size effects on the same object – a thin film of lead telluride, as well as for PbSe [10]. The purpose of this work is to consider these effects for PbTe.

In [6], the theoretical basis for calculating quantum size effects for the kinetic coefficients of n-PbTe quantum wells based on the Boltzmann kinetic equation is considered. The authors believed that the Fermi energy does not depend on the film thickness. We took into account this dependence, as well as different approximations for the calculations in [11].

The non-local transport for PbTe quantum wells was proved in [12, 13]. The authors showed the pronounced non-locality of the resistance and magnetoresistance in the microstructure of PbTe on BaF$_2$. The effect of surface scattering of charge carriers on the conductivity of thin wires is considered in [14].

In our previous work [15], the influence of classical size effects on the thermoelectric properties of n-PbTe thin films versus the film thickness was experimentally and theoretically revealed. The mirror-diffuse mechanism of reflection of current carriers from the film surfaces is considered and the non-locality of the conductivity and Seebeck coefficient is taken into account.

2. EXPERIMENTAL

The films of 40-1215 nm thick were obtained for the study by deposition of vapor of the synthesized n-PbTe in vacuum on the substrates of mica-muscovite fresh cleavages (0001). The evaporator temperature was equal to $T_E = 870$ K and the substrate temperature – $T_S = 470$ K. The film thickness was set by the deposition time within 15 s-10 min and measured using a microinterferometer MII-4 by the digital image processing method.

Measurements of the electrical parameters of the films were performed in air at room temperatures in constant magnetic fields on the developed automated device, which provides both the measurement of the electrical parameters and data recording and processing with the ability to construct graphs of time and temperature dependences.

Schematic representation of the thin film model for the mirror-diffuse mechanism of carrier reflection from the film surfaces is shown in Fig. 1. The dependences of the integral values of the electrical conductivity G and the Seebeck coefficient S_{xx} on the thickness D for n-PbTe films are illustrated in Fig. 2 and Fig. 3.
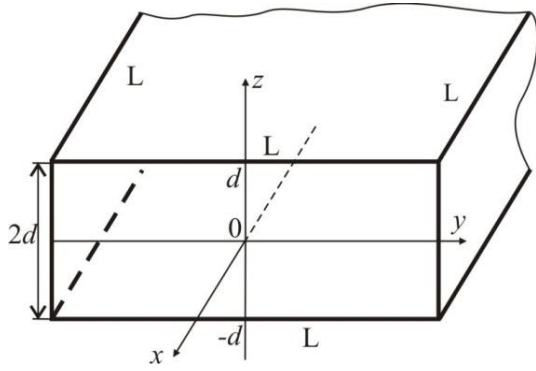
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Fig. 1 – The schematic representation of the thin film model for the mirror-diffuse mechanism of carrier reflection from the film surfaces
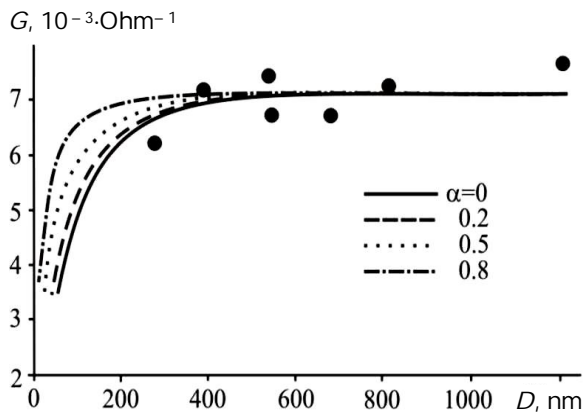

Fig. 2 – Dependence of the integral conductivity G versus the n-PbTe film thickness on mica-muscovite fresh cleavages (0001) for different values of α. The dots are the experiment; the lines are the calculation according to the quasi-classical approximation model
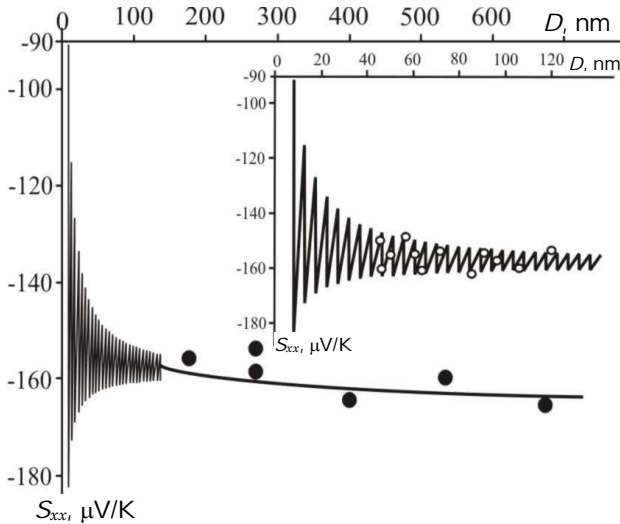

Fig. 3 – Dependence of the Seebeck coefficient S on the n-PbTe film thickness on mica-muscovite fresh cleavages (0001). The dots are the experiment and the solid lines are the calculation according to the quasi-classical approximation model and in the case of quantization of the carrier energy spectrum

The theoretical calculation for the description of the behavior of the dependences $G(D)$ and $S_{xx}(D)$ was carried out using the tools of Maple 18.

3. THEORETICAL MODEL

Let the quantization of the carrier energy spectrum is realized in the films at certain thicknesses. If the z axis is directed along the normal to the film, then the conduction electrons will execute free motion with a parabolic dispersion law along the x and y axes (in the film plane), and the motion along the z axis will be limited to the film surface [4]. As a model of the film potential, as usual, we take a rectangular well with a flat bottom and infinitely high walls [11].

It is possible to analytically determine the values of the thicknesses D_{n0}, at which the Fermi level coincides with the bottom of the n_0-th subzone, as well as to compare $E_F(D_{n0})$ with the value of the Fermi level $E_F(\infty)$ for a massive sample [4]

$$E_F\left(D_{n_0}\right) = E_F\left(\infty\right)\left[\frac{3}{2} - \frac{(n_0+1)(2n_0+1)}{4n_0^2}\right]^{-2/3} \quad (1)$$

$$n_0 = 2,3,4,\ldots$$

$$E_F\left(\infty\right) = \frac{\hbar^2}{2m_n}\left(3\pi^2 n_{el}\right)^{2/3}, \quad (2)$$

n_{el} is the carrier concentration and $m_n = \left(m_\perp^2 m_z\right)^{1/3}$, $m_\perp$ is the transverse effective electron mass (in the film plane $m_x = m_y = m_\perp$), m_z is the longitudinal effective electron mass (along the z axis).

For D_{n0}, we obtain [4]

$$D_{n_0} = D_0 n_0 \left(\frac{m_\perp}{m_z}\right)^{1/3}\left[1 - \frac{(n_0+1)(2n_0+1)}{6n_0^2}\right]^{1/3}, \quad (3)$$

$$D_0 = \left(\pi/2n_{el}\right)^{1/3}. \quad (4)$$

The intermediate value of $E_F(D)$ between D_{n0} and D_{n0+1} is determined as

$$E_F\left(D\right) = B_{n_0}\varepsilon_1 + \frac{\pi\hbar^2}{m_\perp}\frac{n_{el}}{n_0}D, \quad (5)$$

where $D_{n_0} < D < D_{n_0+1}$, $\varepsilon_1 = \frac{\hbar^2}{2m_z}\left(\frac{\pi}{D}\right)^2$ is the energy of the first occupied sublayer, B_{n0} are the coefficients which are defined by the formula

$$B_{n_0} = \frac{(n_0+1)(2n_0+1)}{6}. \quad (6)$$

Let us consider a degenerate electron gas. We take into account that for a case of scattering in sufficiently thin films by acoustic phonons, the relaxation time does not depend on energy [16]. In this case, on the basis of the Boltzmann kinetic equation, the Seebeck coefficient is determined as [6]:

$$S_{xx} = \frac{k_B}{e}[\xi\left(D\right) - \frac{A_1\left(D\right)+A_2\left(D\right)}{A_3\left(D\right)}], \quad (7)$$

where

$$A_1 = \sum_{n=1}^{n_{max}(D)} \int_0^\infty x^2 (-\frac{\partial f_n}{\partial x}) dx =$$

$$= \sum_{n=1}^{n_{max}(D)} \int_0^\infty x^2 \frac{e^{x-\left[\xi(d)-\varepsilon_1'(D)n^2\right]}}{\left(e^{x-\left[\xi(D)-\varepsilon_1'(D)n^2\right]}+1\right)^2} dx, \quad (8)$$

$$A_2 = (\sum_{n=1}^{n_{max}(D)} \varepsilon_1'(D) n^2 \int_0^\infty x(-\frac{\partial f_n}{\partial x}) dx) =$$

$$= \sum_{n=1}^{n_{max}(D)} \varepsilon_1' n^2 \int_0^\infty x \frac{e^{x-\left[\xi(D)-\varepsilon_1'(D)n^2\right]}}{\left(e^{x-\left[\xi(D)-\varepsilon_1'(D)n^2\right]}+1\right)^2} dx, \quad (9)$$

$$A_3 = (\sum_{n=1}^{n_{max}(D)} \int_0^\infty x(-\frac{\partial f_n}{\partial x}) dx) =$$

$$= \sum_{n=1}^{n_{max}(D)} \int_0^\infty x \frac{e^{x-\left[\xi(D)-\varepsilon_1'(D)n^2\right]}}{\left(e^{x-\left[\xi(D)-\varepsilon_1'(D)n^2\right]}+1\right)^2} dx. \quad (10)$$

Here $f_n = (e^{x-\eta_n}-1)^{-1}$ is the Fermi distribution function, $x = \varepsilon/k_B T$ is the dimensionless carrier energy, $\eta_n = \xi - \varepsilon_n'$, $\xi(D) = E_F(D)/k_B T$ and $\varepsilon_1' = \varepsilon_1/k_B T$, $\varepsilon_1(D) = \frac{\pi^2 \hbar^2}{2m_z^* D^2}$, k_B is the Boltzmann constant, $n(D)_{max} = \left[\left(\frac{\xi(D)}{\varepsilon_1'(D)}\right)^{1/2}\right]$ is the integer part in square brackets.

In the decomposition of (7) by the Poisson summation formula [17, 18], we derive

$$S_{xx} = -\frac{k_B}{e}\left\{\frac{(\pi^2/3)k_B T\left[\delta_F - \frac{1}{2} + \sum_{l=1}^\infty \frac{\sin(2\pi l\delta_F)}{\pi l}\right]}{\left[E_F\left(\frac{2}{3}\delta_F - \frac{1}{2}\right) + \frac{\varepsilon_1}{2}\sum_{l=1}^\infty \frac{\sin(2\pi l\delta_F)}{(\pi l)^3} - \varepsilon_1\sum_{l=1}^\infty \frac{\cos(2\pi l\delta_F)}{(\pi l)^2}\right]}\right\}, \quad (11)$$

where $\delta_F = \left(\frac{E_F}{\varepsilon_1}\right)^{1/2}$, $\varepsilon_1 = \frac{\hbar^2}{2m_z}\left(\frac{\pi}{D}\right)^2$.

When neglecting the de Broglie wavelength (the film thickness is less than the carrier free path $D < l$), it is necessary to take into account the classical size effects. The theoretical basis for calculating the film parameters was presented in our previous work [15]. A thin film with a rectangular cross-section is considered. We will assume that the film length is much larger than the film thickness ($L \gg 2d$). The schematic representation of the film model is illustrated in Fig. 1. It is believed that carrier scattering occurs only from the upper and lower film boundaries. The calculations are performed for a semiconductor with a quadratic dispersion law taking into account the anisotropy of effective masses ($m_\perp$, m_z). An electric field is applied along the x-axis direction to the ends of the film. The coordinate system is selected as shown in Fig. 1.

When the film thickness $D = 2d$ is comparable or less than the carrier free path ($D \le l$), a significant nonlocality in the relationship between E and j appears. To describe this nonlocality, it is necessary to know the non-equilibrium distribution function of carriers [19]:

$$f(r, p, t) = f_0(\varepsilon) + f_1(r, p, t), \quad (12)$$

where f_1 is the deviation of the distribution function f from the equilibrium Fermi distribution function f_0

$$f_0(\varepsilon) = \left(\exp\left[(\varepsilon - \mu)/k_B T\right] + 1\right)^{-1}, \quad (13)$$

where μ is the chemical potential, T is the film temperature, k_B is the Boltzmann constant.

An external electric field acting on the carriers causes the occurrence of current and electrical conductivity in the film interior. Due to the boundary conditions, the nonlocality of the conductivity $\sigma = \sigma(z)$ is manifested. We introduce the concept of integral conductivity

$$G = \int_{-d}^d \sigma(z) dz. \quad (14)$$

By solving the Boltzmann kinetic equation in the relaxation time approximation for the stationary state [15], we obtain the following expression for the integral conductivity along the x-axis of the film:

$$G = \frac{e^2 (k_B T)^2}{\pi^2 \hbar^3 v^2} \int_{-\mu^*}^\infty d\eta \left[1 - \exp\left(-\frac{q}{\sqrt{\eta + \mu^*}}\right)\right] \ln\left(1 + e^{-\eta}\right), \quad (15)$$

where $\mu^* = \mu/k_B T$ is the dimensionless chemical potential, $q = d/l$ is the dimensionless film half-width, $v = 1/\tau$, l is the electron mean free path,

$$l = \sqrt{\frac{k_B T}{m_z}}\tau. \quad (16)$$

We assume that the relaxation time τ does not depend on the energy (for sufficiently thin films, this corresponds to the acoustic-phonon scattering mechanis). The value of τ can be estimated by the experimental value of the carrier mobility μ_d [20],

$$\tau = \frac{\mu_d m_z}{e}. \quad (17)$$

Due to the boundary conditions, the nonlocality of the thermoelectric coefficient $\beta = \beta(z)$ is manifested. Therefore, we introduce the integral thermoelectric coefficient

$$B = \int_{-d}^d \beta(z) dz. \quad (18)$$

The thermoelectric current is determined by the integral coefficient B

$$I_{th} = B\Delta T = B\frac{\partial T}{\partial x} L, \quad (19)$$

where $\Delta T = \frac{\partial T}{\partial x} L$, L is the film length. Then

$$B = \frac{ek_B}{\pi^2 \hbar^3 v^2}(k_B T)^2 \int_{-\mu^*}^\infty \left[1 - \exp\left(-\frac{q}{\sqrt{\eta + \mu^*}}\right)\right] \times$$
$$\times \left[\frac{\eta}{e^\eta + 1} + 2\sum_{n=0}^\infty \frac{(-1)^n}{(1+n)^2} e^{-(n+1)\eta}\right] d\eta. \quad (20)$$

The film thermoemf is equal to B-to-G ratio

$$S_x = -B/G . \qquad (21)$$

Thus,

$$S_{xx} = -\frac{k_B}{e} \frac{\int\limits_{-\mu^*}^{\infty}\left[1-\exp\left(-\frac{q}{\sqrt{\eta+\mu^*}}\right)\right]}{\int\limits_{-\mu^*}^{\infty}\left[1-\exp\left(-\frac{q}{\sqrt{\eta+\mu^*}}\right)\right]\ln\left(1+e^{-\eta}\right)d\eta} \times$$

$$\times\left[\frac{\eta}{e^{\eta}+1}+2\sum_{n=0}^{\infty}\frac{(-1)^n}{(1+n)^2}e^{-(n+1)\eta}\right]d\eta . \qquad (22)$$

We note that the relation between the film thickness D and the carrier free path l is considered arbitrary.

For the case of a mixed mirror-diffuse reflection, it is necessary to make a replacement in the obtained formulas obtained for G, B and S_{xx}

$$\exp\left(-\frac{q}{\sqrt{\eta+\mu^*}}\right) \rightarrow \frac{1-\alpha}{\left(1-\alpha e^{\frac{-2q}{\sqrt{\eta+\mu^*}}}\right)}\exp\left(-\frac{q}{\sqrt{\eta+\mu^*}}\right) , \quad (23)$$

where α is the mirror reflection coefficient (probability of mirror reflection), $0 \le \alpha \le 1$. At $\alpha = 0$, we have diffuse reflection; at $\alpha = 1$ – purely mirror reflection; $0 < \alpha < 1$ – is the mixed mirror-diffuse reflection. The case of a bulk film is realized at $d \to \infty$, as well as at $\alpha \to 1$.

4. ANALYSIS OF THE ELECTRICAL PROPERTIES

In Fig. 2 we illustrate the theoretical curve for the integral conductivity of the films of different thickness and experimental data. As seen, with increasing film thickness D, the conductivity increases essentially with attainment of saturation at $D \approx 400$ nm. In this case, the size effects, which become insignificant with increasing thickness, have a significant influence.

The values of the carrier effective masses in n-PbTe and electron mobility in bulk crystals were used as the initial parameters. The parameters given in Table 1 were utilized in the calculation. The determined value of the dimensionless Fermi energy for the obtained curves (see Fig. 2, Fig. 3) was equal to $\mu^* = 2$. That is, the electron gas in the films will be degenerate.

The theoretically calculated curves correspond to the experimentally obtained results. The mismatch may be due to the fact that grain boundary scattering was not taken into account in this model, as well as the acceptor action of oxygen, which significantly affects the electrical parameters of the films [21]. Moreover, the difference between the two film/substrate and film/air surfaces is not taken into consideration. In our previous work [15], we presented data for lead telluride synthesized from materials of higher purity. In the previous material, the conductivity is less due to the absence of contamination which can induce additional conductivity. However, the coincidence between the experiment and the theory is worse, since a greater effect of oxygen is manifested.

Table 1 – Parameters used in the calculation of the thermoelectric characteristics of n-PbTe films [23, 24]

μ, cm²/V·s	T, K	$m_\perp$, kg	m_z, kg	n_{el}, cm⁻³
1700	300	0.024 m_0	0.24 m_0	0.97·10¹⁸

m_0 is the real electron mass

The carrier mean free path l calculated according to the formulas (16)-(17), for thin films based on n-PbTe is equal to ~ 45 nm.

The integral conductivity was also calculated for different values of the mirror reflection coefficient α (see Fig. 2). As seen, the curve with $\alpha = 0$ describes best the experiment. That is, for these films, the mechanism of completely diffuse scattering is realized due to the fact that the film surface is imperfect and can have nano-sized crystallites on the surface [22].

As seen from the analysis of the curves in Fig. 3, all curves coincide, since there is a macroscopic asymptotic behavior. That is, thick films acquire the properties of a bulk sample.

Fig. 3 illustrates the result of calculating the dependence S_{xx} by the formulas (11) and (22). The parameters used for the calculation are given in Table 1. For these samples, an oscillatory behavior is observed in the range of thicknesses less than 100 nm. As known, an increase in the well width by the value of Fermi half-wave leads to the appearance of a new occupied subband below the Fermi energy. At the occupation width of a new band, there is a jump in the density of states that leads to an oscillatory behavior, which can be observed in figures. The oscillation period is ~ 5 nm. However, a small number of experimental points in the range of thicknesses less than 40 nm does not allow to speak about the full coincidence of the theory with the experiment. As seen from Fig. 3, the oscillation amplitude is large for films of small thicknesses of ~ 20 nm.

With increasing thickness, the amplitude gradually decreases, and at a certain thickness it should be close to zero. So, we obtain a monotonic change in the transport coefficients. In this case, the quantization of the energy spectrum is eliminated and the classical regularities will be fulfilled.

For films of larger thickness, the theory for the quasi-classical approximation model is used. There is a monotonic increase in the absolute value of the thermosemf with increasing film thickness. For films of thicknesses > 500 nm, the curve is saturated. That is, the films will have the properties of a bulk sample.

5. CONCLUSIONS

1. The integral conductivity and the Seebeck coefficient for a film with a rectangular cross-section versus its thickness are determined based on the Boltzmann kinetic equation.

2. The mirror-diffuse mechanism of carrier reflection from the film surfaces is considered. The calculation is performed for n-PbTe semiconductor.

3. The comparison of the theoretical calculations with the experiment is carried out for vapor-phase condensates based on PbTe. It is shown that theoretical results satisfactorily describe experimental data.

4. An oscillatory behavior of the quantum size dependences of thermoemf is shown for n-PbTe nanostructures.

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