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QUANTUM-SIZE OSCILLATION EFFECTS OF THERMOELECTRIC PARAMETERS IN LEAD CHALCOGENIDES NANOSTRUCTURES

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On the basis of the theoretical model of a quantum well (QW) with infinitely high walls, we study the thermoelectric parameters depending on the thickness of the layer of nanostructures IV–VI (PbS, PbSe, PbTe) in the approximation of changing Fermi energy. It is shown that the dependences of the Seebeck coefficient, electrical conductivity, and thermoelectric power factor on the well width for nanofilms of lead chalcogenides are in good agreement with the experimental data. This proves the correctness of the used model.

Keywords: lead chalcogenides, nanostructures, quantum-size effects.

1. Introduction

In the previous work [1] on the basis of theoretical models of a quantum well (QW) with infinitely high walls, we investigated the dependences of the Seebeck coefficient S on the layer thickness of nanostructures IV-VI in the approximation of constant Fermi energy. It was shown that both the experimentally and theoretically obtained dependences of the Seebeck coefficient S on the width of the quantum well with infinitely high walls for structures based on compounds PbS, PbSe, PbTe, and SnTe are characterized by breaks with a certain period. Based on the experimentally determined oscillation period Δd of the thickness dependences of the Seebeck coefficient, the values of Fermi energy in QW structures of compounds IV–VI were determined and used to construct the corresponding theoretical size dependence of the Seebeck coefficient.

This work is a continuation of work [1]. Here, we present the calculation results and the analysis of the size dependences of the Seebeck coefficient, electrical conductivity, and thermoelectric power coefficient in the approximation of variable Fermi energy.

The ability of nanostructured materials to improve the thermoelectric (TE) Q-factor has received an increasing attention [2]. Reducing the dimension of the material creates conditions for the quantum size effect, which leads to an increase in the density of states near the Fermi energy $E_{\rm F}$. This allows one to maintain the high electrical conductivity σ and a sufficient asymmetry of a number of filled and unfilled states and makes it possible to obtain a high Seebeck coefficient S [2]. The tangible influence of quantum effects on the thermoelectric properties is possible only if the size of a structure in the direction of confinement is comparable with the de Broglie wavelength of carriers. This condition holds, in particular, for structures in the form of quantum wells [3–5].

The aim of this work was the theoretical explanation of the behavior of a number of thermoelectric (TE) parameters on the width of quantum wells (QW) for lead chalcogenides (PbS, PbSe, PbTe) [3–5].

2. Theoretical Model

For a quantum well (QW) with high walls, electrons are limited in the direction OZ, and their movement is free in the OX- and OY-directions. The electronic wave function and the energy eigenvalue, provided by parabolic energy bands, are defined by the expressions [6]:

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

$$E = \frac{\pi^2\hbar^2}{2m_z^* d^2} n^2 + \frac{\hbar^2 k^2}{2m_p^*}. \tag{2}$$

Here, $k^2 = k_x^2 + k_y^2$, m_z^* is the effective mass of an electron along the direction of limitation; $m_p^* = \sqrt{m_x^* m_y^*}$ and m_x^*, m_y^* are the effective masses of an electron along the axes OX and OY, Ω is the total volume of

the layer, d is the well width, and n is a quantum number, which takes integer values.

The number of quantized levels that are below a given energy is defined by the first part of (2):

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

Substituting the value of Fermi energy ($E_{\rm F}$) in (3), we can find the width d such that there is a specified number of levels n below the Fermi level. The difference between the values of this width for the next two levels will determine the period of oscillations Δd, which is equal to the width d_{min}, where the bottom of the lowest subband coincides with the energy $E_{\rm F}$. Thus, relation (3) yields

$$\Delta d = d_{\rm min} = \frac{\lambda_{\rm F}}{2} = \frac{h}{\sqrt{8m_z^* E_{\rm F}}}. \tag{4}$$

From (4), we can see that a change of the Fermi level leads to a change of the oscillation period. The Fermi energy can be expressed through the well width (d) and the concentration of carriers in the conduction band [7]:

$$E_{\rm F} = \varepsilon_1 \frac{(n_0+1)(2n_0+1)}{6} + \frac{\pi\hbar^2}{m^*}\frac{n_{\rm el}}{n_0} d. \tag{5}$$

Here, ε_1 is the first quantized level, which is determined by formula (3), when n=1; $n_0 = [(E_{\rm F}/\varepsilon_1)^{1/2}]$ is the integer part of the number $(E_{\rm F}/\varepsilon_1)^{1/2}$; m^* is the effective mass of carriers, which is defined as $m^* = (m_\perp^2 m_\parallel)^{1/3}$ [7]; and $n_{\rm el}$ is the electron concentration.

If the Fermi level coincides with the bottom of the band n_0, then $E_{\rm F}(d_0) = \varepsilon_1 n_0^2$. At such width, $(E_{\rm F}(d_0)/\varepsilon_1)^{1/2}$ is an integer. Substituting this value in (5), we obtain

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

where $d_0 = (\pi/2n_{\rm el})^{1/3}$. The number n_0 at a given width d is the integer part of the solution of Eq. (6) relatively to n_0, when $d_{n_0} = d$.

Thus, the substitution of the integer part from the solution of Eq. (6) relatively to n_0, when $d_{n_0} = d$, in (5) makes it possible to build the ratio $E_{\rm F}(d)$. Based on the directly proportional dependence of the perpendicular component of the effective mass on the energy [7]

$$m_z^* = m_{z0}^* (1 + 2E_{\rm F}/\varepsilon_g), \tag{7}$$

where m_z^* and ε_g are the z-component of the effective mass at low concentrations and the bandgap, it can be argued that the ratio of m_z^* and d near the Fermi energy has the same character as $E_{\rm F}(d)$.

In the case of a quantum well, the thermoelectric transport coefficients can be obtained from the Boltzmann equation, which is written under the assumption that the electron distribution function in the steady state is stable and may be changed only by the action of external forces and fields. Then the system of electrons comes back to the equilibrium due to various relaxation processes with characteristic relaxation times. For a quasitwo-dimensional system, we can write [8]

$$\sigma = \frac{e^2}{T}\Gamma^1, \tag{8}$$

$$S = \frac{E_{\rm F}}{eT} + \frac{1}{eT}\frac{\Gamma^2}{\Gamma^1}, \tag{9}$$

where σ is the conductivity, S is the Seebeck coefficient, $E_{\rm F}$ is the Fermi energy, e is the electron charge, and T is the absolute temperature.

The transport coefficient Γ is defined by the semiclassical approach, whereby particles are limited in a potential well. The temperature gradient and the electric field are directed along the axis OX. Then

$$\Gamma^1 = -\zeta^{(0)}, \tag{10}$$

$$\Gamma^2 = \zeta^{(1)}, \tag{11}$$

where

$$\zeta^{(s)} = \frac{2T}{\pi a}\sqrt{\frac{m_y^*}{m_x^*}}\frac{1}{\hbar^2}\sum_{n=1}^{E_n \le E_{\rm F}} \int_0^\infty E^s \tau\varepsilon \left(\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon. \tag{12}$$

Here, f is the Fermi distribution function, $\varepsilon = E - E_n$, and τ is the relaxation time, which in the case of the scattering on acoustic phonons is independent of the energy [8] ($\tau = \tau_0$), so it can be taken outside the integral.

Under this condition, the expressions for the Seebeck coefficient S and the electrical conductivity σ can be written as

$$S = \frac{k_{\rm B}}{e}\left[\frac{E_{\rm F}}{k_{\rm B}T} - \frac{A_1 + A_2}{A_3}\right], \tag{13}$$

$$\sigma = \frac{1}{2\pi d}\frac{2kT}{\hbar^2}\sqrt{\frac{m_x^*}{m_y^*}}e^2\tau_0 A_3, \tag{14}$$

where

$$A_1 = \left(\sum_{n=1}^{En\le E_F}\int_0^\infty x^2\left(-\frac{\partial f_n}{\partial x}\right)dx\right), \tag{15}$$

$$A_2 = \left(\sum_{n=1}^{En\le E_F} E'\int_0^\infty x\left(-\frac{\partial f_n}{\partial x}\right)dx\right), \tag{16}$$

$$A_3 = \left(\sum_{n=1}^{En\le E_F}\int_0^\infty x\left(-\frac{\partial f_n}{\partial x}\right)dx\right). \tag{17}$$

The Fermi distribution function has the well-known form

$$f_n = \frac{1}{e^{x-\eta_n}+1}, \tag{18}$$

where $x = \varepsilon/k_BT$ is the reduced carrier energy, and $\eta_n = = \xi - E_n'$. Here, $\xi = E_F/k_BT$, $E_n' = E_n/k_BT$, and k_B is the Boltzmann constant.

The relaxation time in (15) can be estimated, by basing on the mobility μ of n-type carriers in the bulk samples [9]:

$$\mu = e\tau_0/m. \tag{19}$$

3. Results and Discussion

Based on the experimental dependences [3–5], which show a nonmonotonic oscillatory character of the change of the TE parameters with changing the thickness of the condensate (Fig. 1), it is natural to assume that such behavior is due to the quantization of energy carriers under the restriction of their movement in the potential well.

Increasing the well width by the value of Fermi half-wave leads to the appearance of a new subband below the Fermi energy. At the filling width of the new band in the density of states, the jumpis observed, which leads to the oscillatory behavior.

The account for the d-dependence of the Fermi energy (Fig. 2) in formulas (13)–(18) and the z-component of the effective mass in the ratios (16)–(19) allowed us to obtain the corresponding dependences of the Seebeck coefficient S and the electrical conductivity σ on the well width for nanofilms of lead chalcogenides (Fig. 3, *a,b*). Formula (3) shows that

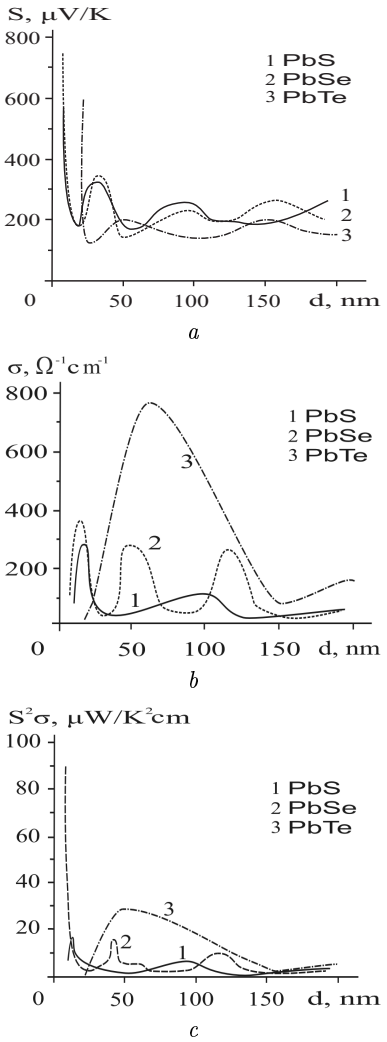

Fig. 1. Experimental dependences of the Seebeck coefficient S (*a*), electric conductivity σ (*b*), and TE power factor $S^2\sigma$ (*c*) on the thickness of the nanofilms of PbS, PbSe, and PbTe on the substrate of KCl covered with a layer of EuS, at $T = 300$ K [3–5]

the number of levels below the Fermi energy is determined by the d-dependence of the effective mass and actually by E_F, as well as by the well width d. The calculations take into account a change of the Fermi energy and a change of the number of levels below it, depending on the well width. Calculating the electrical conductivity σ by (14), it was assumed that $m_x^* = m_y^*$. In the theoretical model, the quantum well width was considered to be equal to the thickness of the condensate in the experimental dependences of

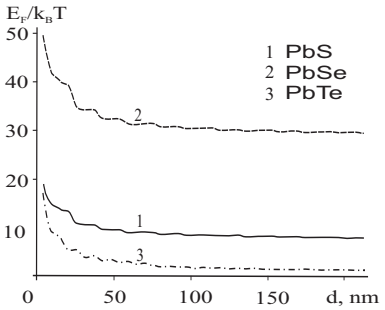

Fig. 2. Calculated values of the Fermi energy E_F in units of k_BT versus the QW width for PbS, PbSe, and PbTe at $T = 300$ K

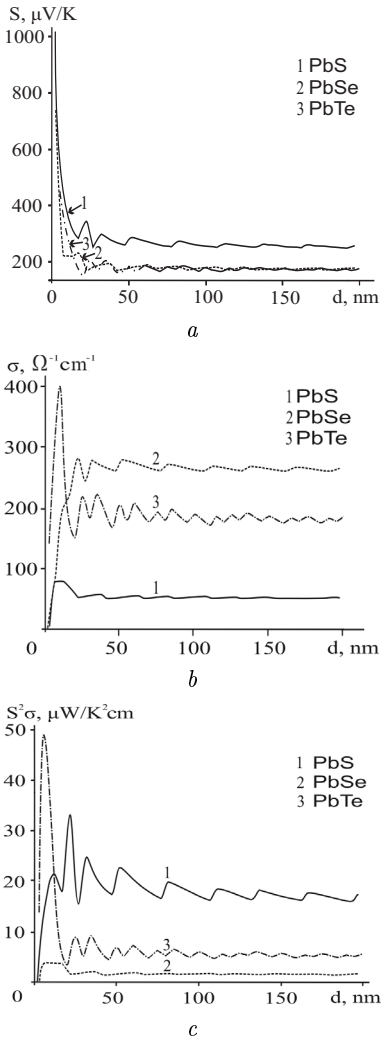

Fig. 3. Theoretical dependences of the Seebeck coefficient S (*a*), electric conductivity σ (*b*), and TE power factor $S^2\sigma$ (*c*) on the QW width for films of PbS (*1*), PbSe (*2*), PbTe (*3*) in the model of infinitely deep potential well at $T = 300$ K

relevant parameters. The calculation was carried out in the approximation of constant concentration and carrier mobility across all the range of well widths. The values of the last were selected based on relevant experimental measurements (table, according to the data in Fig. 1). The resulting dependences of TE coefficients on the width of lead chalcogenides QW are characterized by a nonmonotonic oscillating behavior (Figs. 2 and 3).

The dependences of TE parameters on the well width for films of various compounds of lead chalcogenides are distinguished by the average value of TE parameters throughout the studied range of thicknesses, as well as by the sizes and the positions of extrema (Fig. 3). However, the characters of changes of the curves are identical. So, for all structures at the small values of well width (less than 20 nm), the high values of Seebeck coefficient and the very low values of conductivity are revealed. Increasing the well width leads to a decrease of the value of Seebeck coefficient and to increase of the value of electrical conductivity. Thus, all these dependences go to saturation. Note that this character of the change of theoretical curves (Fig. 3) is fully consistent with the experimental data (Fig. 1) [3–5], which proves the correctness of the chosen calculation model.

As is seen from relation (4), the period of oscillations is inversely proportional to the value of Fermi energy. The descending character of the Fermi energy (Fig. 2) indicates that the period of oscillations of d-dependences for TE parameters increases with the well width (Fig. 3). The lowest average Fermi energy was obtained for lead telluride (Fig. 2, curve *3*). Therefore, PbTe should be characterized by the largest average period Δd of oscillations, which is also fully confirmed by experiment (Fig. 1, curve *3*) [3–5].

Figure 3 shows the d-dependences of the thermoelectric power factor $S^2\sigma$. In general, we can say that the maximum values of $S^2\sigma$ are smaller than the ex-

Mobility of carriers (μ) and the concentration (n) for films of n-type lead chalcogenides, which were used in the calculations of thermoelectric coefficients

	PbS	PbSe	PbTe
μ, cm^2/Vs	70	200	1096
n, cm^{-3}	2.5×10^{18}	4×10^{18}	0.72×10^{18}

perimental ones (Fig. 1, *c*) [10]. Only for compound PbTe, the maximum value of $S^2\sigma$ is higher than experimental, but this value corresponds to a very small well width, for which no experiment was carried out. On the one hand, the cause of this mismatch may be neglecting the limited height of the potential barrier. On the other hand, the presence of additional experimental factors along with the phenomenon of quantum size effect can influence the oscillation amplitude of *d*-dependences of thermoelectric characteristics.

Taking the limited height of potential barriers into account and the calculation of the thermal conductivities for lead chalcogenides nanostructures for the determination of the *d*-dependences of the thermoelectric Q-factors for relevant structures, will be accomplished in our subsequent works.

4. Summary

Within the model of a quantum well (QW) with infinitely high walls, we have presented the expressions for the dependences of the Fermi energy and the effective mass on the QW width. On this basis, the character of change of the oscillation period for the density of states with increasing the well width is determined.

We have calculated and built the dependences of the Seebeck coefficient, electrical conductivity, and thermoelectric power factor for the nanofilms of lead chalcogenides on their thickness. It is shown that the resulting character of oscillations of their profiles is in good agreement with the experimental data.

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КВАНТОВО-РОЗМІРНІ ОСЦИЛЯЦІЙНІ ЕФЕКТИ ТЕРМОЕЛЕКТРИЧНИХ ПАРАМЕТРІВ У НАНОСТРУКТУРАХ ХАЛЬКОГЕНІДІВ СВИНЦЮ

Р е з ю м е

На основі теоретичної моделі квантової ями (КЯ) з нескінченно високими стінками було досліджено термоелектричні параметри залежно від товщини шару наноструктур IV–VI (PbS, PbSe, PbTe) в наближенні змінної енергії Фермі. Було показано, що залежності коефіцієнта Зеєбека, електропровідності і термоелектричного коефіцієнта потужності від ширини ями для наноплівок халькогенідів свинцю добре узгоджуються з експериментальними даними, що доводить коректність використаної моделі.