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Size effects in thin n–PbTe films

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The effect of the film thickness d on the Seebeck coefficient S, the Hall coefficient R_H, electrical conductivity σ, charge carrier mobility μ_H and thermoelectric power factor $S^2 \cdot \sigma$ of thin films (d = 7–235 nm) prepared by thermal evaporation of n–-type PbTe polycrystals doped with InTe in vacuum onto (001)KCl substrates was investigated. It was established that at $d \approx 20$ nm, an inversion of the conductivity type ($p \rightarrow n$) occurs, which is attributed to a change in the thermodynamic equilibrium conditions in films as compared with bulk crystals and\or to partial re-evaporation of In atoms. In the thickness range $d < 20$ nm, extrema in the d-dependences of the properties are detected at $d \approx 13$ nm, and at $d > 20$ nm, the thickness dependences of the properties exhibit an oscillatory behavior with the period $\Delta d \approx 12$ nm. The observed oscillatory character of the thickness dependences of the kinetic coefficients is attributed to the manifestation of quantum size effects. The theoretical $S(d)$ dependence calculated in the approximation of size quantization taking into account d-dependences of the Fermi energy and a number of subbands is in good agreement with the experimental one with regard to the oscillation period.

Keywords: lead telluride, indium, thin film, thickness, thermoelectric properties, quantum size effect.

Исследовано влияние толщины d на значения коэффициента Зеебека S, коэффициента Холла R_H, электропроводности σ, подвижности носителей заряда μ_H и термоэлектрической мощности $S^2 \cdot \sigma$ тонких пленок (d = 7–235 нм), полученных методом термического испарения в вакууме на подложки (001)KCl поликристаллов PbTe, легированных InTe, с n-типом проводимости. Установлено, что при $d \approx 20$ нм имеет место инверсия типа проводимости ($p \rightarrow n$), что связывается с изменением условий термодинамического равновесия в пленках и/или с частичным реиспарением атомов In. В области $d < 20$ нм обнаружен экстремум на d-зависимостях свойств при $d \approx 13$ нм, а при $d > 20$ нм наблюдается осциллирующий характер изменения свойств с толщиной с периодом $\Delta d \approx 12$ нм. Наблюдаемый осциллирующий характер толщинных зависимостей кинетических коэффициентов связывается с проявлением квантовых размерных эффектов. Расчет зависимости $S(d)$ в приближении размерного квантования при учете d-зависимости энергии Ферми и нескольких подзон совпадает с экспериментальной по величине периода осцилляций.

Розмірні ефекти в тонких плівках n–PbTe. *С.І.Меньшикова, О.І.Рогачова, О.Ю.Сіпатов, Є.М.Зубарєв.*

Досліджено вплив товщини d на значення коефіцієнта Зеєбека S, коефіцієнта Холла R_H, електропровідності σ, рухливості носіїв заряду μ_H та термоелектричної потужності $S^2 \cdot \sigma$ тонких плівок (d = 7–235 нм), які були отримані методом термічного випаровування у вакуумі на підкладки (001)KCl полікристалів PbTe, легованих InTe, з n-типом провідності. Встановлено, що при $d \approx 20$ нм має місце інверсія типу провідності ($p \rightarrow n$), що пов'язується зі зміною умов термодинамічної рівноваги в плівках та/або з частковим ревипаровуванням атомів In. В області $d < 20$ нм виявлено екстремум на d-залеж-

ностях властивостей при $d \approx 13$ нм, а при $d > 20$ нм спостерігається осцилюючий характер зміни властивостей з товщиною з періодом $\Delta d \approx 12$ нм. Осцилюючий характер товщинних залежностей кінетичних коефіцієнтів пов'язується з проявом квантових розмірних ефектів. Розрахунок залежності $S(d)$ у наближенні розмірного квантування з урахуванням d-залежності енергії Фермі та декількох підзон співпадає з експериментальною за величиною періоду осциляцій.

1. Introduction

In structures, where charge carrier motion is confined in one, two or three directions (thin films, quantum wires, and quantum dots, respectively) and dimensions of structures in those directions are comparable with the de Broglie wavelength λ_F, quantum size effects (QSE) can be observed [1]. The manifestation of such effects can significantly change kinetic properties of a material in a low-dimensional state in comparison with bulk crystal.

One of the manifestations of size quantization of energy spectrum in thin films is an oscillatory behavior of the dependences of kinetic properties on film thickness with period Δd equal to a half of the de Broglie wavelength $\lambda_F/2$. In metals, charge is mainly transferred by carriers with high energies (of the order of the Fermi energy), for which λ_F are comparable to interatomic distances. This complicates the observation of the thickness oscillations of kinetic properties. From this point of view semimetals and semiconducting materials are more convenient objects, because the λ_F values for them are much larger than for metals and it facilitates experimental studying of QSE. For the first time, quantum oscillations of galvanomagnetic properties were observed in thin bismuth films [2]. Starting from the 2000's, a series of studies on quantum oscillations in IV–VI thin films, in particular lead telluride films, have been carried out [3–9].

Lead telluride (PbTe) belongs to well-known thermoelectric (TE) materials; it is also applied in many other fields of science and technology [10, 11]. With a view to controlling its properties, type and concentration of charge carriers, PbTe is usually doped with donor and acceptor impurities [10]. Indium is a well-known donor dopant, which makes it possible to obtain PbTe samples with a spatially uniform charge carrier concentration and stable properties [12]. A small effective mass in the direction perpendicular to the film surface and a high charge carrier mobility indicate that PbTe is a convenient object for studying QSE by investigating transport phenomena.

The goal of the present work is to reveal the effect of the film thickness d on the galvanomagnetic and TE properties of films obtained by thermal evaporation of n–PbTe crystals in vacuum with subsequent deposition onto (001)KCl substrates.

2. Experimental

n–PbTe films with thicknesses $d = 7$–235 nm were grown by thermal evaporation of PbTe crystals doped with 1 mol.% InTe (PbTe<InTe>) in vacuum (~10^{-5}–10^{-6} Pa) with subsequent deposition onto freshly cleaved (001)KCl substrates. Using electron-beam epitaxy, the films were covered by a 15 nm thick BaF_2 layer with a view to protecting the film surface from oxidation and mechanical damage. The condensation rate was 0.5–1.0 nm/s. The film thickness d was controlled using a quartz resonator, which was preliminary calibrated with the help of an interferometer MII-4 (for $d > 100$ nm) and the small angle X-ray scattering method (for $d < 100$ nm).

The Hall coefficient R_H and electrical conductivity σ were measured using a conventional dc method with an error not exceeding ±5 %. The Hall charge carrier mobility μ_H was calculated as $\mu_H = R_H \cdot \sigma$. The in-plane Seebeck coefficient S was measured using a compensation technique relative to copper with an accuracy of ±3 %. On the basis of the measured values of S and σ, thermoelectric power factor was calculated as $P = S^2 \cdot \sigma$. The measurements were carried out on freshly prepared films at room temperature. The type of dominant charge carriers was determined from the sign of R_H and S. The measurements of R_H and S showed that the PbTe<InTe> crystal used as the initial material for thin film preparation exhibited electron conductivity with charge carrier concentration = $3.0 \cdot 10^{18}$ cm^{-3}.

Electron microscopy characterization of films was performed using a transmission electron microscope PEM-U at accelerating voltage of 100 kV. For electron microscopy investigations films were separated by dissolving substrates in distilled water and then fished out on a copper grid. The structure of films was investigated by diffraction

contrast in a bright-field imaging mode. Electron microscopy characterization was carried out on two-layer structures PbTe<InTe>/BaF_2.

Theoretical calculations describing the oscillatory dependence of the Seebeck coefficient on the film thickness were performed using software package Maple 15.

3. Results and discussion

The electron microscopy study of the films showed that both PbTe on (001)KCl substrate and the protective BaF_2 layer on the film surface grow epitaxially in a (001) orientation. In microdiffraction patterns for films with thicknesses in the range of d = 7–50 nm, reflections indicating diffraction by two structures were seen. The results of indexing of the patterns showed that these reflections correspond to PbTe and BaF_2. No reflections corresponding to any other phases were observed.

In Fig. 1, the room-temperature d-dependences of galvanomagnetic and TE properties for thin film structures (001)KCl/PbTe<InTe>/BaF_2 are presented. It is seen in the figure that at thicknesses d < 20 nm, the films exhibit p-type conductivity, whereas at larger thicknesses — n-type, like in the initial crystal. It can be suggested that one of the causes of the appearance of hole conductivity at small thicknesses is a change in thermodynamic equilibrium conditions in the thin film state as compared with the bulk crystal, and, as a result, a change in equilibrium concentration and type of defects. Another factor leading to the change in the conductivity sign can be re-evaporation (at least partial) of indium atoms, which are donor dopants, in the process of the material deposition on the substrate. Note, however, that for PbTe films grown by thermal evaporation in vacuum and deposition on (001)KCl substrates of n–PbTe crystals, exhibiting electron type of conductivity not due to doping with InTe, but rather due to introducing excess lead, in the range of small thicknesses (up to $d \approx 75$ nm), the change in the conductivity sign from n- to p- was also observed [9]. That is why the first cause (a change in thermodynamic equilibrium conditions in thin films) seems to be more grounded, although purely qualitative.

It is seen in Fig. 1 that in the p-type conductivity region, in all curves: $S(d)$, $R_H(d)$, $\mu_H(d)$ and $S^2 \cdot \sigma(d)$, extrema are observed at the film thickness d_1 = (13±1) nm.

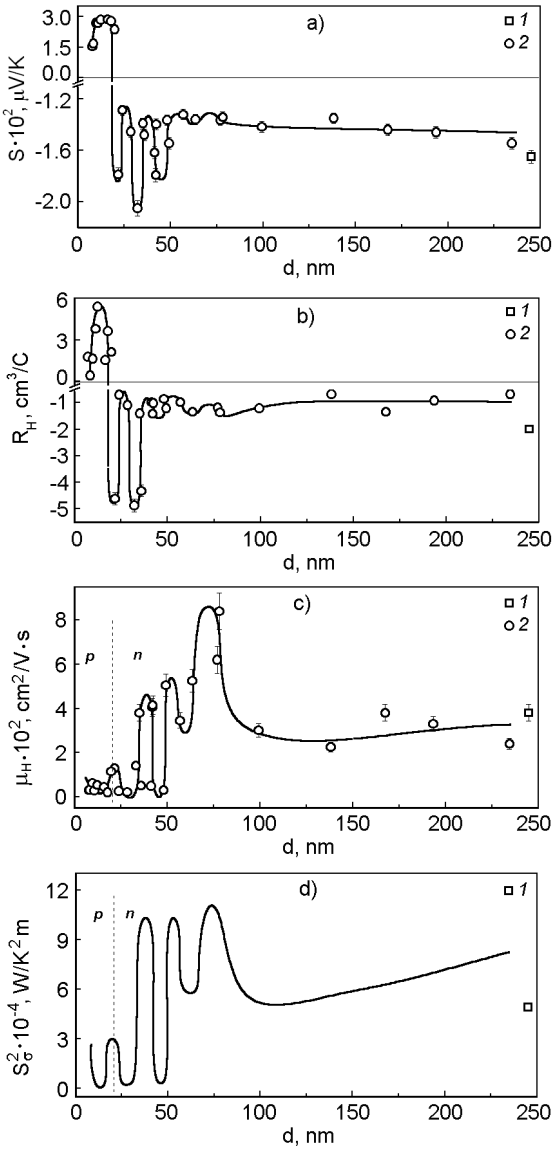

Fig. 1. The thickness dependences of the Seebeck coefficient S (a), the Hall coefficient R_H (b), the Hall mobility of charge carriers μ_H (c), and thermoelectric power factor $S^2 \cdot \sigma(d)$:
1 — PbTe<InTe> crystal;
2 — (001)KCl/PbTe<InTe>/BaF_2 films.

In the thickness range corresponding to n-type conductivity (d > 20 nm), all d-dependences have an oscillatory character, and the average distance between two maxima or two minima is Δd = (12±1) nm. It should also be noted that for the $S(d)$ and $R_H(d)$ dependences, the positions of corresponding extrema (maxima and minima) practically coincide, whereas maxima in the $\mu_H(d)$ and $S^2 \cdot \sigma(d)$ curves correspond to minima in the $S(d)$ and $R_H(d)$ dependences and vice versa (Fig. 1). The oscillatory behavior of the $S(d)$

and $R_H(d)$ dependences with amplitudes reaching 80 %, is observed for $d <$ ~60 nm (Fig. 1a and 1b), while at larger d the oscillation amplitude decreases and eventually the kinetic coefficients practically cease to change under further increase in thickness. Let us note that the Seebeck coefficient, the Hall coefficient and electrical conductivity were measured independently, although on the same samples. Thus, the fact that in all curves the oscillation period is practically the same represents another argument in favor of the existence of such oscillations.

One can see in Fig. 1d that the dependence of thermoelectric power factor $S^2 \cdot \sigma$ on the film thickness also exhibits an oscillatory behavior, besides in films one can obtain values of $S^2 \cdot \sigma$ more than twice as high as for the crystal used as the initial material for the thin film preparation. Note that σ and μ_H in the films with thicknesses $d > 20$ nm were also higher than in the polycrystal (Fig. 1c), which, in accordance with the results of electron microscopy study, is connected with a monocrystalline structure of the films.

The presence of the extrema in the p-region at $d_1 \approx (13 \pm 1)$ nm and thickness oscillations in the region of n-type conductivity can be connected with the quantization of hole and electron gas of carriers.

If the PbTe<InTe> film is assumed to be a rectangular potential well with infinitely high walls formed by (001)KCl and BaF_2 insulating layers, the carrier motion in such potential well will be confined by the well width, which will lead to the quantization of the transverse component of quasi-momentum of charge carriers in the given direction and the formation of transverse energy subbands. The charge carrier motion in other directions is not quantized. In the effective mass approximation, assuming that charge carriers in a quantum well occupy the lowest subband [13] and assuming a parabolic dispersion law, the energy of charge carriers in the potential well can be expressed as [1]:

$$E = \frac{\hbar^2}{2m^*_\perp}\frac{\pi^2}{d^2} + \frac{\hbar^2 k_x^2}{2m_x^*} + \frac{\hbar^2 k_y^2}{2m_y^*}, \qquad (1)$$

where n is the quantum number ($n = 1, 2, 3, \ldots$), $m^*_\perp$ is the effective mass along the direction perpendicular to the quantum well, k_x, k_y and m_x^*, m_y^* are the components of the wave vector and effective mass, respectively, for charge carrier motion parallel to the quantum well. As d increases, the number of occupied energy subbands N in the two-dimensional system changes in a jump-like fashion, and every time the increase in thickness d equals a half of the de Broglie wavelength, a new subband drops below the Fermi level ε_F and a new wave function starts to make contribution to the density of states, which leads to a sharp growth in charge carrier concentration. Within an individual energy subband the concentration n first grows, reaches its maximum and then decreases [14]. The relationship between d and N accounts for oscillations in the transport properties and the appearance of QSE.

Within the framework of such model the quantum oscillation period Δd and the number of energy subbands N can be calculated as follows [1, 15]:

$$\Delta d = \frac{\lambda_F}{2} = \frac{h}{\sqrt{8 m^*_\perp \varepsilon_F}}, \qquad (2)$$

$$N = \frac{k_F d}{\pi} = \frac{d}{\lambda_F / 2} = \frac{d\sqrt{8 m^*_\perp \varepsilon_F}}{h}. \qquad (3)$$

The thickness d_1 at which the first subband crosses the Fermi level ($E_1 = \varepsilon_F$) is calculated as $d_1 = \frac{h}{\sqrt{8 m^*_\perp \varepsilon_F}}$, which coincides with the value of Δd (Eq.(2)). Thus, it follows that one can determine the quantum oscillation period with a high of accuracy from the position of the first extremum in the thickness dependences.

For films exhibiting hole conductivity ($d <$ 20 nm), the value of Δd calculated theoretically using Eq.(2) and substituting the Fermi energy value ε_F determined on the basis of the mean hole concentration $p = 4.3 \cdot 10^{18}$ cm^{-3} and values of the longitudinal and transverse components of effective mass for p–PbTe, $m^*_\perp = 0.022 m_0$, $m^*_\parallel = 0.31 m_0$ [11], was $\Delta d =$ (16±2) nm, which is in good agreement with the position of the first extremum observed in the thickness dependences.

For the n-type conductivity region ($d >$ 20 nm), Δd calculated using the values of $m^*_\perp = 0.024 m_0$. $m^*_\parallel = 0.24 m_0$ for n-PbTe [11] and the mean electron concentration $n = 5.2 \cdot 10^{18}$ cm^3, was equal to $\Delta d = (14 \pm 1)$ nm,

which is close to the experimentally observed average distance between extrema $\Delta d = (12\pm1)$ nm (Fig. 1).

As was mentioned above, to estimate the effect of size quantization on the properties of thin films, it is assumed that charge carriers occupy only the lowest subband. The authors of [16, 17] took into account the contribution to kinetic coefficients by a number of energy subbands, besides they assumed that the relaxation time did not depend on energy. In such a case the Seebeck coefficient for a two-dimensional system can be presented as:

$$S = \frac{1}{eT}\left(\varepsilon_F - \frac{\sum_{n=1}^{E_n<\varepsilon_F}\int_0 E\varepsilon\left(\frac{\partial f}{\partial\varepsilon}\right)d\varepsilon}{\sum_{n=1}^{E_n<\varepsilon_F}\int_0 \varepsilon\left(\frac{\partial f}{\partial\varepsilon}\right)d\varepsilon}\right), \quad (4)$$

where f is the Fermi distribution function, $\varepsilon = E - E_n$, and $E_n = \frac{\pi^2\hbar^2}{2m_\perp^* d^2}N^2\}$. The Seebeck coefficient S can be rewritten as in the following way:

$$S = \frac{k_B}{e}[\xi - \frac{\beta+\gamma}{\alpha}], \quad (5)$$

$$\alpha = \sum_{n=1}^{E_n\le\varepsilon_F}\left(\ln(1+e^{bn^2-\xi}) - bn^2 + \xi\right),$$

$$\beta = b\cdot\sum_{n=1}^{E_n\le\varepsilon_F} n^2\cdot\left(\ln(1+e^{bn^2-\xi}) - bn^2 + \xi\right),$$

$$\gamma = \sum_{n=1}^{E_n\le\varepsilon_F}\left(2\cdot di\,\log(1+e^{bn^2-\xi}) + (bn^2-\xi)^2 + \frac{\pi^2}{3}\right),$$

where $b = \frac{1}{k_B T}\frac{\pi^2\hbar}{2m_\perp^* d^2}$, $\xi = \varepsilon_F/k_B T$, k_B is the Boltzmann constant. In this case, the summation is made over several subbands. It is important to note that in Eq. (5) it is assumed that the value of ε_F does not depend on thickness.

The assumption about the constancy of the Fermi energy value under changing d is a simplification used in the model on which equation (5) is based. In [14] it was shown that the value of ε_F must oscillate with changing film thickness. A rigorous expression for ε_F for 2D-degenerate electron gas

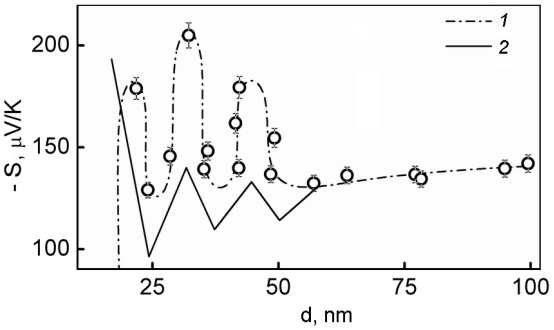

Fig. 2. The thickness dependence of the Seebeck coefficient S for thin films PbTe<InTe>: 1 — experiment; 2 — theoretical calculations of QSE in accordance with [16, 18].

with a given electron concentration taking into account size quantization as a function of d and the number of discrete filled levels N in the quantum well was obtained in [18]:

$$\varepsilon_F = \varepsilon_F^0\cdot\frac{4}{3}\left[\frac{d}{\lambda_F N} + \frac{\lambda_F^2(N+1)(2N+1)}{32\quad d^2}\right], \quad (6)$$

where ε_F^0 is the Fermi energy in the crystal volume where size quantization is negligible. Equation (6) is true when the condition $E_N \le \varepsilon_F \le E_{N+1}$, where N is the maximum number of the subband located below the Fermi energy, is fulfilled. The number of subbands depends on d and $epslon_F$ according to the following equation:

$$N = \frac{d\sqrt{8m_\perp^*\varepsilon_F(d)}}{\hbar}.$$

Within the framework of the model [16] and taking into consideration equation (5) and the assumption regarding the dependence of ε_F on thickness (6), we calculated the dependence $S(d)$ in the range of $d \approx 20$–60 nm, which is shown in Fig. 2 as the solid line. As is seen in Fig. 2, the Seebeck coefficient oscillates with amplitude decreasing as d increases and with the period $\Delta d = (13\pm1)$ nm, which is close to the experimentally determined value of $\Delta d = (12\pm1)$ nm. However, the calculated values of S are significantly lower than those determined experimentally. Such discrepancy is probably connected with a number of simplifying assumptions used when constructing the theoretical curve $S(d)$ (independence of the relaxation time of energy and its dependence on the film thickness only, the assumption that electrons occupy only the lowest subband, etc.). As initial parameters in our calculations we used the values of effective

masses in n–PbTe and the value of ε_F^0 determined for the mean electron concentration $n = 4.8 \cdot 10^{18}$ cm^{-3} in the thickness range $d \approx 20$–60 nm.

It is known that the possibility of observing QSE to a great extent depends on temperature: thermal broadening k_BT of energy subbands must be small in comparison with the distance between the subbands ΔE [19], i.e. the condition $k_BT < \Delta E$ must be fulfilled. The value of ΔE between the states with the lowest energies in neighboring subbands is determined as $\Delta E = \frac{h^2}{8m_\perp^* d^2}(2N+1)$ [1]. The film thickness at which QSE can be observed at room temperature for $N = 1$, can be estimated using the following inequality $d^2 < \frac{3}{8}\frac{h^2}{m_\perp^* k_B T}$. Substituting the value of the effective mass for n-PbTe ($m_\perp^* = 0.024 m_0$ [11]) into the inequality, we obtain $d < 43$ nm. It means that at room temperature it is possible to experimentally observe QSE in films with thicknesses d less than ~43 nm. And indeed, the oscillatory behavior of the thickness dependences of S and R_H is observed at thicknesses $d <$ ~60 nm (Fig. 1), which is in good agreement with the calculated thickness at which QSE can be observed at room temperature.

4. Conclusions

It is established that thin films grown by thermal evaporation in vacuum of n–PbTe crystals doped with 1 mol.% of InTe, exhibit p-type conductivity at thicknesses $d < 20$ nm, and n-type conductivity at $d > 20$ nm. The appearance of hole conductivity at small thicknesses d is attributed to a change in the thermodynamic equilibrium conditions in thin films as compared with the bulk crystal and/or to partial re-evaporation of indium atoms in the process of deposition. In the p-type conductivity region, in the d-dependences of the Seebeck coefficient, the Hall coefficient and charge carrier mobility, extrema are observed at $d = 13$ nm, while in the films exhibiting electron conductivity the thickness dependences of properties have an oscillatory character. The observed effects are attributed to quantization of energy spectrum of hole and electron gases. The experimentally determined oscillation periods are in good agreement with those calculated theoretically within the framework of the model of a rectangular potential well with infinitely high walls. The theoretically calculated $S(d)$ dependence in the thickness range $d \approx 20$–60 nm, based on the assumption of the size quantization and taking into account the contributions by several subbands and the $\varepsilon_F(d)$ dependence, is in good agreement with the experimental one as far as the oscillation period is concerned, although theoretical values of S are lower than experimentally observed ones.

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