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DEPENDENCES OF THERMOELECTRIC PROPERTIES ON THE THICKNESS OF THIN FILMS OF INDIUM DOPED LEAD TELLURIDE

Dependences of thermoelectric properties (the Seebeck coefficient S, the electric conductivity σ, the Hall coefficient R_H, the carrier mobility μ and the thermoelectric power $P = S^2 \cdot \sigma$) on the thickness d (d = 10 – 255 nm) of thin films prepared by vacuum evaporation of indium-doped PbTe crystals and subsequent condensation on (111) BaF_2 substrates were obtained. With decreasing thickness of films to d ≈ 40 nm, there is n- to p-type inversion of conduction which is related to a change in thermodynamic equilibrium conditions and partial re-evaporation of lead and/or indium atoms. Extremes were found on the thickness dependences of properties at d_1 ≈ 20 nm which is indicative of hole gas quantization. In the range of thicknesses with n-type conduction there is a smooth change in thermoelectric properties with thickness which testifies to manifestation of classical size effect and is sufficiently well described in the framework of the Fuchs-Sondheimer theory.
Key words: lead telluride, thin film, thickness, size effect.

Introduction

The advancement of nanophysics and nanotechnologies calls attention to the development of methods for preparation of low-dimensional structures with the assigned characteristics and to the investigation of their properties. It is known that in low-dimensional state, for instance, in thin films, one can observe size effects. Classical size effect is due to diffusion carrier scattering on film interfaces and is manifested in the case when film thickness *d* is comparable to mean free path length of charge carriers. Quantum size effect results from quantization of carrier energy spectrum and is observed when *d* value becomes comparable to de Broglie wavelength λ_F [1]. When using thin films for practical purposes, account must be taken of the size effects that can result in fundamental changes of material properties.

IV-VI-class semiconductors refer to materials that are widely used in thermoelectricity [2, 3]. Lead telluride has recommended itself as the most efficient material for thermal generators working in the range of medium temperatures (from room temperature to $870 \div 920$ K) [4]. Doping is known to change over a wide range the thermoelectric (TE) properties of material (conduction type, carrier concentration and mobility, etc). As the donor dopants for *PbTe*, use is made of iodine, chlorine, indium and bismuth impurities [5]. It was established [5] that

introduction of indium into *PbTe* crystal lattice yields uniform-carrier concentration crystals with stable properties and low sensitivity to the influence of uncontrolled defects and impurities. Such properties of indium-doped *PbTe*, attractive from a practical point of view, are generally attributable to the existence of a quasi-local impurity level located above the bottom of conduction band and stabilization of the Fermi level at that level [5]. It was shown [6] that introduction of a considerable amount of InTe impurity (up to ~ 6 mol.%) into *PbTe* does not lead to changes in the law of carrier dispersion in conduction band, and that on doping of *PbTe* with In impurity up to ~ 2 at.%, the shape and orientation of the Fermi surface, as well as the value of carrier effective mass remain the same as in the undoped *PbTe* [7].

It was shown [8-13] that in lead chalcogenide films grown by vacuum evaporation of crystals with subsequent condensation on (001) *KCl* substrates there is an oscillating behavior of the kinetic properties with film thickness, attributable by the authors to quantum size effects. In *PbSe* films, there was increase in the electric conductivity and carrier mobility with film thickness, which testified to manifestation of classical size effects [12, 14], and when studying *PbSe* films doped with chlorine the authors of [15] came to conclusion on the overlapping of classical and quantum size effects.

To study size effects, it is important to use structurally perfect films. Small difference in lattice periods and close values of dilatation coefficients of *PbTe* and *BaF₂* make (111) *BaF₂* cleavages most suitable substrates for preparation of structurally perfect *PbTe* films [16]. As far as we know, size effects in *PbTe* thin films doped with indium donor impurity and grown on (111) *BaF₂* substrates have not been investigated by studying transport phenomena.

The purpose of this work is to establish the influence of thickness *d* of films grown by vacuum evaporation of *PbTe* crystals doped with indium and deposited on (111) *BaF₂* cleavages on their thermoelectric properties.

Experimental procedure

The films were prepared by vacuum evaporation (~10^{-5}-10^{-6} Pa) of *PbTe* crystals doped with 1 mol. % *InTe* with subsequent deposition on fresh (111) *BaF₂* cleavages maintained at a temperature of (600 ± 10) K. Film thicknesses varied within $d = 10 – 255$ nm. On top of the films, a protective layer of *BaF₂* was deposited by an electron-beam method to protect the film from oxidation and mechanical damages. Film thickness was measured by means of a precalibrated quartz resonator. The Seebeck coefficient *S* was measured by compensation method with respect to copper in the film plane with an error not exceeding ± 3 %. The electric conductivity σ and the Hall coefficient R_H were measured by standard *dc* method to an accuracy of ± 5 %. The Hall mobility μ_H was calculated as $\mu_H = R_H \cdot \sigma$, the TE power value – by formula $P = S^2 \cdot \sigma$. The measurements were performed on as-prepared samples. In the measurements, crystal was shaped as a parallelepiped of size 10x2x3 mm, and the films of thickness *d* had the form of a double Hall cross.

The surface morphology and chemical composition of the resulting films was controlled by

electron-probe microanalysis using a scanning electron microscope JSM-6390 LV (Jeol, Japan) with a system of energy-dispersive spectrometer X-Max^{n} 50 (Oxford Inst., Great Britain) at accelerating voltage 10 kV.

Results

The results of S and R_H measurement have shown that crystal of which the films were prepared was of n-conduction type and had electron concentration $n = 3.0 \cdot 10^{18}$ cm^{-3}. The low value of n with a considerable content of indium impurity, as mentioned above, is attributable to the Fermi level stabilization on a quasi-local donor level [5].

Studies by electron-probe microanalysis method in the mode of scanning along the film surface and in the mode of probing by the surface points have shown that *PbTe<InTe>* films possess high degree of homogeneity on a microlevel, i.e. the distribution of (*Pb*, *Te*, *In*) elements in the film from one analyzed part to another does not vary within the accuracy of the method. Study on the surface of the films in the mode of secondary electrons (resolution 10 nm) has shown that grain structure in the films is not apparent, the surface is uniform and defects (agglomerates, pores, cracks, etc.) are not observed on the surface. Thus, high homogeneity degree and low sensitivity to the presence of defects are typical not only of the bulk *PbTe<InTe>* crystals [5], but also of the films.

Dependences of S, R_H, σ, μ_H, as well as P on the thickness of *PbTe* layer at room temperature are given in Fig. 1, where the values of crystal kinetic coefficients are marked by black squares, those of thin films – by white circles.

Measurements of S and R_H have shown that with increasing the thickness of films, there is *n*- to *p*-type inversion at $d \approx 40$ nm (dashed line in Fig. 1 corresponds to the boundary between the areas with *p*-and *n*-type conduction). Possible reason for the appearance of *p*-type conduction can be a change in thermodynamic equilibrium conditions in the thin-film state as compared to crystal. One should also take into account the possibility of partial reevaporation of indium or lead atoms at condensation on the substrates.

Note that in *PbTe* films under study with thicknesses $d \approx 100\text{-}255$ nm the values of S and R_H practically coincide with S and R_H of polycrystal. At the same time, the electric conductivity and carrier mobility in the films are almost three times higher than σ and μ_H of the initial charge (Fig. 1), which indicates to a higher degree of structural perfection of films as compared to crystal. As a result, in the film state one can reach the value of thermoelectric power $P = S^2 \cdot \sigma = 16.5 \cdot 10^{-4}$ W/K^{2}m which is more than three times as large as the P of the initial crystal.

As is evident from Fig. 1, for films with *p*-type conduction for $d_1 = (20 \pm 2)$ nm on the thickness dependences of S and R_H there are maxima that correspond to minima on the dependences $\sigma(d)$, $\mu_H(d)$ and $P(d)$. In the area with *n*-type conduction ($d > 40$ nm) there are also extremes on the *d*-dependences of the kinetic coefficients at $d = (50 \pm 4)$ nm. With larger

thicknesses ($d > 50$ nm) TE properties change monotonically with film thickness, namely S, σ, μ_H, P and smoothly increased, and R_H is decreased.

Note that in [12], like in the present work, extremes were observed on d-dependences of TE properties of *PbSe* films in *p*-type conduction area at $d = 10$ nm, which was attributable by the authors to manifestation of quantum size effect for carrier hole gas and explained by intersection of the first hole subband of the Fermi level. In the present paper, the observed extreme in the area of *p*-type conduction films can be also related to size quantization of carrier energy spectrum. If a layer of *PbTe<InTe>* is represented as a rectangular potential well with infinitely high walls arranged between isolating BaF_2 layers, one of which is a single-crystal substrate, and the other – protective coating, in such a well carrier motion is limited, which leads to quasi-pulse quantization and formation of transverse energy subbands. The number of carrier-filled subbands N varies stepwise, and when film thickness is increased by the value equal to half de Broglie wavelength, a new subband intersects the Fermi level and contributes to conduction. The thickness whereby the first subband ($N = 1$) intersects the Fermi level can be written as [12]:

$$d_1 = \frac{h}{\sqrt{8m_\perp^* \varepsilon_F}}, \qquad (1)$$

where h is the Planck constant, $m_\perp^*$ is effective mass along the direction perpendicular to quantum well, ε_F is the Fermi energy. The period of quantum oscillations Δd is also determined by formula (1) [17], i.e. it completely coincides with the value of d_1. In a number of works it was shown (see, for instance [12, 13, 17]) that for precise determination of quantum oscillation period it is sufficient to fix the first extreme on the film thickness dependences of the kinetic properties.

Let us determine thickness d_1 in *PbTe* films under study. In the calculation, we shall use the value of ε_F found by the average hole concentration in the films with hole conduction $p = 2.7 \cdot 10^{18}$ cm^{-3} with regard to the transverse and longitudinal components of effective mass $m_\perp^* = 0.022$ m$_0$, $m_\parallel^* = 0.31$ m$_0$ [18]. Calculation by formula (1) yielded the value of $d_1 = (21 \pm 2)$ nm, which is in good agreement with the position of the first extreme in the region with *p*-type conduction ($d_1 = 20 \pm 2$ nm) (Fig. 1).

A similar calculation of oscillation period was performed for *n*-type films, i.e. in the area with $d > 40$ nm. As the input parameters, use was made of the values of effective masses $m_\perp^* = 0.024$ m$_0$, $m_\parallel^* = 0.24$ m$_0$ [18] for electrons in *PbTe* and the value of ε_F calculated by the Hall coefficient values in the thick films. As a result of calculation, the value of oscillation period was $\Delta d = (20 \pm 2)$ nm.

It can be supposed that the extremes observed at $d \approx 50$ nm on the dependences $S(d)$, $R_H(d)$, $\sigma(d)$, $\mu_H(d)$ and $P(d)$ correspond to intersection of the Fermi level by the energy subband. Smooth variation of the kinetic coefficients with thickness for films with $d > 50$ nm can be related to manifestation of classical size effect. Due to the fact that the electron gas in films under study was degenerate, an attempt was made to describe the thickness dependences of transport properties using the Fuchs-Sondheimer theory for metals [19]. The theory is concerned with a
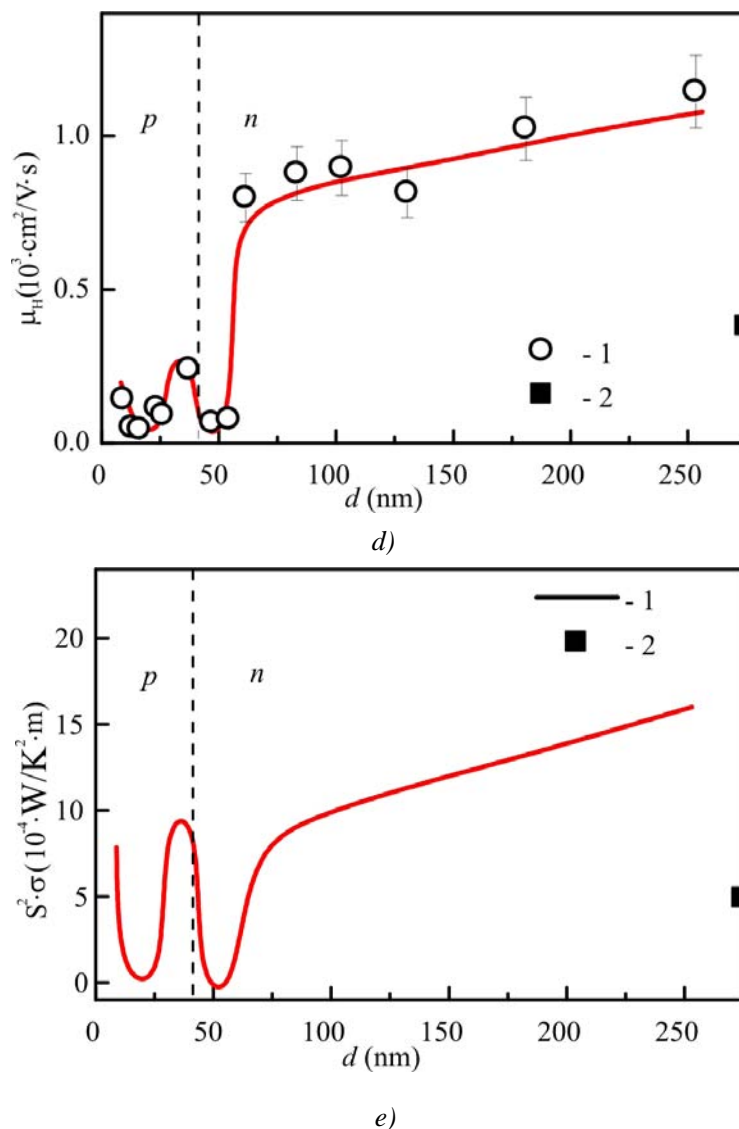
a)

b)

c)

d)

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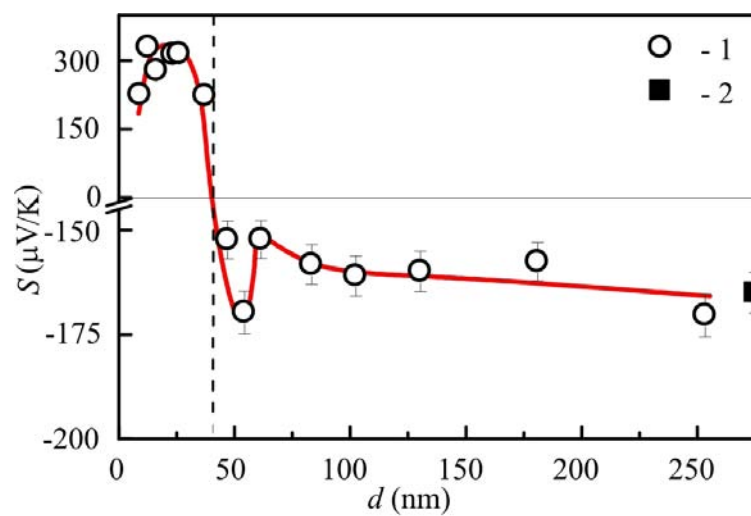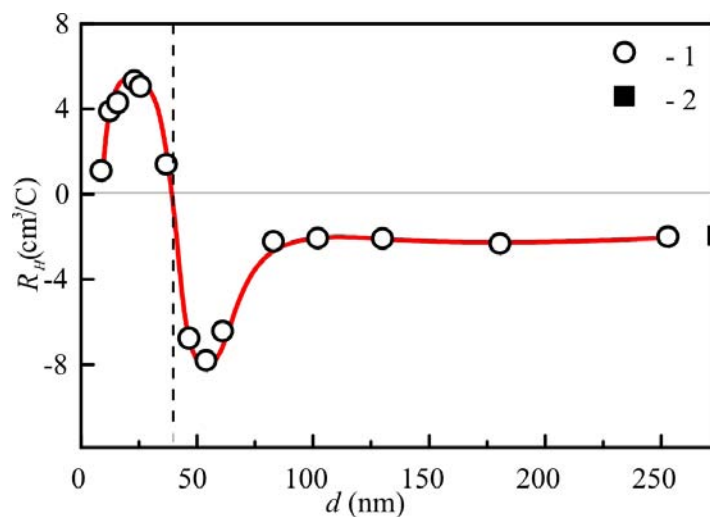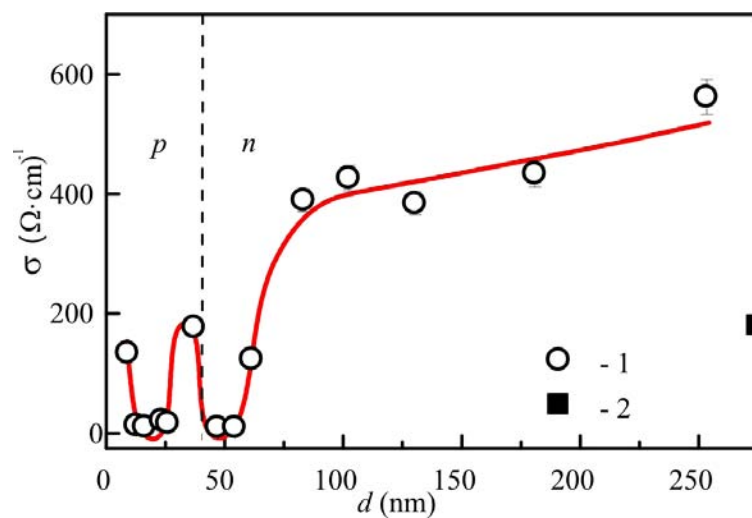
Fig. 1. Dependences of the Seebeck coefficient S (a), the Hall coefficient R_H (b), the electric conductivity σ (c), the Hall carrier mobility μ_H (d) and the thermoelectric power $P = S^2 \cdot \sigma$ (e) on the thickness of PbTe<InTe> films in the structure (111)BaF$_2$/PbTe<InTe>/BaF$_2$: 1 – PbTe<InTe> films; 2 – PbTe<InTe> crystal.

metal having a spherical Fermi surface and isotropic carrier mean free path *l*.

A specularity parameter *p* is introduced which characterizes the share of carriers elastically reflected from the film interfaces. The value of *p* can lie in the range from 1 (fully specular reflection) to 0 (fully diffuse reflection). With a fully specular reflection, classical size effect will be not apparent. In the theory it is assumed that *l* and *p* do not depend on the thickness, and *p* is a constant which is equal for both surfaces and does not depend on the trajectory and the angle of carrier incidence on the surface.

If the films are not too thin (*d* ~ *l*), then according to the Fuchs-Sondheimer theory, the expression for electric conductivity of metal plate of thickness *d* can be written as follows [19, 20]:

$$\sigma_d = \frac{\sigma_\infty}{1 + \frac{3}{8}(1-p)\frac{l}{d}}, \qquad (2)$$

where σ_∞ is the value of electric conductivity for a sample with infinitely large thickness.

Based on the Fuchs-Sondheimer theory, Mayer [21] obtained the expression for the Seebeck coefficient S of metallic plate as a function of its thickness. In the approximation of not very thin films ($d \sim l$), S is written as [21]:

$$S = S_\infty \left(1 - \frac{3}{8}(1-p)\frac{l}{d}\frac{U}{1+U}\right), \qquad (3)$$

where S_∞ is the S value of a film with infinitely large thickness, parameter $U = \left(\frac{\partial \ln l}{\partial \ln E}\right)_{E=\varepsilon_F}$ characterizes the energy dependence of mean free path, and with a quadratic dispersion law $U = 2$ [22].

In the framework of the Fuchs-Sondheimer theory, subject to condition $d \sim l$, the Hall coefficient is practically unvaried with thickness ($R_H = R_{H\infty}$, where $R_{H\infty}$ is the Hall coefficient of a film with infinitely large thickness) [22]. With regard to the fact that carrier mobility is a product of σ and R_H, dependence of μ on d, provided $d \sim l$, is determined by dependence $\sigma(d)$, i.e. it can be written as:

$$\mu_d = \frac{\mu_\infty}{1 + \frac{3}{8}(1-p)\frac{l}{d}}, \qquad (4)$$

where μ_∞ is the mobility of a film with infinitely large thickness.

With the aid of software package MatLAB 6.5, by varying the values of p and l, conditions were determined (the values of l and p), whereby there is the best fit of theoretical curves $\sigma(d)$, $S(d)$ and $\mu_H(d)$ to the respective experimental data. As a criterion of the best coincidence between the calculated and experimental curves, a root-mean-square deviation ε was chosen. Calculation was made for the films with thicknesses $d > 55$ nm, where one can observe gradual increase of the electric conductivity, the Seebeck coefficient and the mobility with thickness. Fig. 2 shows the results of theoretical calculation of dependences $\sigma(d)$, $S(d)$ and $\mu_H(d)$ in the framework of the Fuchs-Sondheimer theory (continuous line) and experimental data (white circles).

It is seen that the experimental dependences $\sigma(d)$, $S(d)$ and $\mu_H(d)$ can be fairly well described in the framework of the Fuchs-Sondheimer theory, considering the case of not very thin films. As the input parameters, the values of $\sigma_\infty = 565$ (Ohm · cm)$^{-1}$, $\mu_\infty = 1150$ cm^2/V·s and $S_\infty = -170$ µV/K were used corresponding to the kinetic coefficients of the thickest film under study. The lowest value of ε in the calculation of dependences $\sigma(d)$, $S(d)$ and $\mu_H(d)$ was achieved with specularity parameters $p = 0.64$, 0.87 and 0.75 and the electron mean free path lengths $l = 470$ nm, 400 nm and 410 nm, respectively. The spread in the values of p can be due to a small number of experimental points and/or considerable number of simplifications

used in the calculation. Nevertheless, averaging of specularity parameter values determined from the dependences σ(*d*), *S*(*d*) and μ_H(*d*) yields rather high value of $< p > = 0.75$ which points to preferably specular reflection of electrons from the film interfaces.
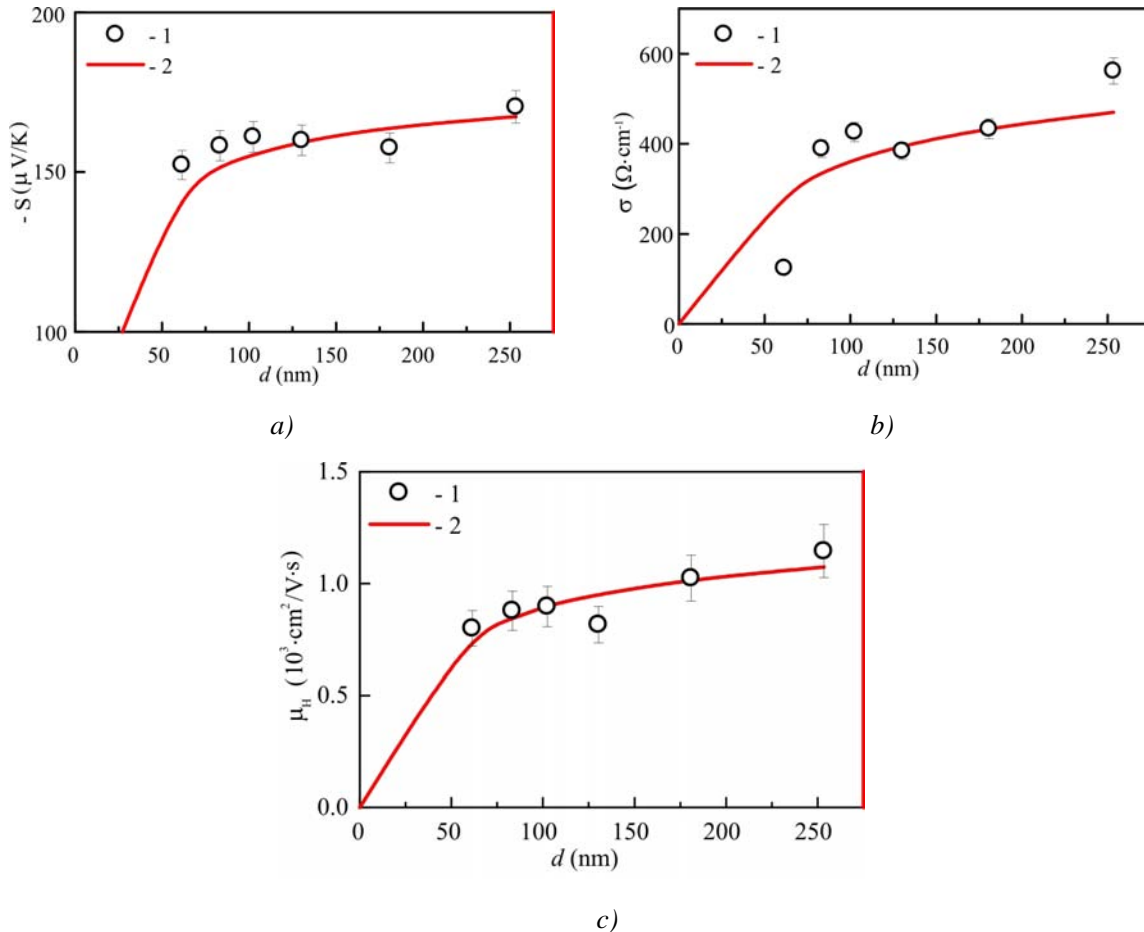

a)   *b)*

c)

Fig. 2. The Seebeck coefficient S (a), the electric conductivity σ (b) and the
electron mobility μ_H (c) in the structure (111)BaF$_2$/PbTe<InTe>/BaF$_2$: 1 – PbTe<InTe> films;
2 – theoretical calculation in the framework of the Fuchs-Sondheimer theory.

In [12], for *PbSe* films in the calculation of *σ(d)* dependence in the framework of the Fuchs-Sondheimer theory the value of *p* = 0.57 was obtained that proved to be lower than in the present work. The difference in *p* values for lead chalcogenide films grown on different substrates (*KCl* and *BaF$_2$*) is attributable to different location of atoms (lead and chalcogen) in crystallographic planes (001) and (111). As long as lead chalcogenides have the structure of *NaCl* type [18], with the growth of film in [001] orientation on *KCl* substrates [12], on the interfaces in (001) plane the atoms of components (lead and chalcogen) are arranged in staggered rows, and with the growth of film in [111] orientation, i.e. on *BaF$_2$* substrates, like in this paper, (111) plane consists of one sort of atoms (either lead atoms or chalcogen atoms only). Obviously, several sorts of atoms available on (001) surface result in a more considerable diffuse scattering than in the films with [111] orientation, where only one sort of atoms contributes to scattering.

Conclusions

1. Vacuum evaporation of *PbTe* crystals doped with 1 mol. % InTe with subsequent condensation on (111) *BaF*$_2$ substrates was used to obtain films of thickness d = 10-255 nm.

2. With decreasing film thickness to $d \approx 40$ nm, there is $n \to p$ type inversion of conduction. It is supposed that the effect observed can be due to a change in thermodynamic equilibrium conditions in the thin film as compared to the bulk crystal and due to partial reevaporation of indium and/or lead atoms.

3. The films possess high degree of homogeneity, and the grain structure in the films is not manifested, which is of interest from practical standpoint.

4. The dependences of the electric conductivity σ, the Hall mobility μ_H, the Hall coefficient R_H, the Seebeck coefficient S and the thermoelectric power $P = S^2 \cdot \sigma$ on the thickness of films are of nonmonotonic nature. In the range of thicknesses of *p*-type films there are extremes on the thickness dependences of all properties at $d_1 = (20 \pm 2)$ nm that are attributable to quantum size effect.

5. The increase in S, σ and μ_H with film thickness in the range with *n*-type conduction indicates the manifestation of classical size effect. Theoretical calculation of the dependences σ(d), $S(d)$ and $\mu_H(d)$ in the framework of the Fuchs-Sondheimer and Mayer theories is in rather good agreement with the experimental data.

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