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**SIZE EFFECTS IN LEAD TELLURIDE
THIN FILMS AND THERMOELECTRIC
PROPERTIES**

The influence of thickness d on thermoelectric properties (the Seebeck coefficient S , electric conductivity σ , the Hall coefficient R_H , charge carrier mobility μ_H) of films $d = 8 - 170$ nm in thickness, prepared by vacuum evaporation of $PbTe$ crystals with lead excess onto (001) KCl substrates coated with Al_2O_3 layer has been studied. It has been established that films with $d < 75$ nm possess hole conductivity, and at $d > 75$ nm carrier transport is determined by n -type charge carriers. The inversion of conductivity sign close to $d \approx 75$ nm is attributed to a change in thermodynamic equilibrium conditions in the films as compared to crystal, as well as to material evaporation and condensation features. Oscillations on the d -dependences of the kinetic coefficients of films with p -type conductivity are attributable to quantization of the hole gas of carriers. Calculation of oscillation period Δd using a model of infinitely deep rectangular potential well is in good agreement with the experimentally determined Δd value. For n -type conductivity films the values of kinetic coefficients increase with increase in d , which points to manifestation of a classical size effect.

Key words: thin film, classical and quantum size effect, thickness.

Introduction

The IV-VI semiconductor compounds are widely used in thermoelectricity, optoelectronics, infrared technology and other fields of science and engineering [1-4]. Lead telluride ($PbTe$) is well known as one of the best materials for thermoelectric (TE) generators operated in medium temperature range [2, 3].

Considerable improvement of TE figure of merit in superlattices based on IV-VI semiconductors [5-8] earlier predicted theoretically [5], arouses interest in studying thermoelectric properties of $PbTe$ in the thin-film state.

One of the main tasks of nanophysics and nanotechnologies is development of methods for preparation and study of material properties in the low-dimensional state (quantum wells, quantum wires, quantum dots). In the thin-film state the size of a sample in one direction is considerably smaller than in the other two directions. Considerable impact on the transport properties of $2D$ -structures can be produced by size effects, namely classical (ClSE) which can be observed in the case when the mean free path of charge carriers is comparable to film thickness d , and quantum (QSE), which is manifested when film thickness becomes comparable to de Broglie wavelength value [9].

In a number of works (see, for instance, [10-16]) for lead chalcogenide films (PbS , $PbSe$, $PbTe$) prepared by vacuum evaporation of a blend with different concentration of charge carriers of both n - and p -type (from $\sim 10^{18}$ to 10^{20} cm^{-3}) the authors observed the oscillatory behaviour of the dependences of TE properties (the Seebeck coefficient S , electric conductivity σ , Hall charge carrier mobility μ_H and TE power $P = S^2\sigma$) on the film thickness d , attributing this phenomenon to

manifestation of QSE. The increase in monotonic components of σ and μ_H versus thickness, discovered in *PbSe* films prepared from crystals of stoichiometric *p-PbSe*, was attributed by the authors of [17] to manifestation of CISE due to increased contribution of diffused carriers scattering on interfaces with a reduced d . The results obtained in [16, 17] have demonstrated that varying film thickness in small steps according to the value of d in a wide thickness range, one can study QSE and CISE on the same objects simultaneously.

The purpose of this work is to study size effects in the films prepared by vacuum evaporation onto (001) *KCl* substrates of *n-PbTe* crystals with lead excess (2 at.% *Pb*) and coated with Al_2O_3 layer. In [15], on the films prepared in a similar way, protected from interaction with air oxygen by *EuS* layer ~ 30 nm thick and having *n*-type conductivity, there were revealed thickness oscillations of the kinetic properties with the period $\Delta d \sim 100$ nm, though the theoretical calculation of Δd , with the use of a model of a rectangular well with infinitely high walls yielded much lower value, namely $\Delta d = 20$ nm. The observed discrepancy was attributed by the authors of [15] to a great deal of simplifications used in the model, as well as to insufficient number of thin-film samples with different values of d . The latter factor predetermined the arrangement of the present work.

As a result of research performed in this work, we have managed to establish the presence of *p*-type conductivity region in small thickness range, to discover the oscillatory behaviour of d -dependences of kinetic properties in this region, to determine the oscillation period practically corresponding to theoretically calculated one, as well as to observe manifestation of CISE in the thickness range with *n*-type conductivity.

Experimental procedure

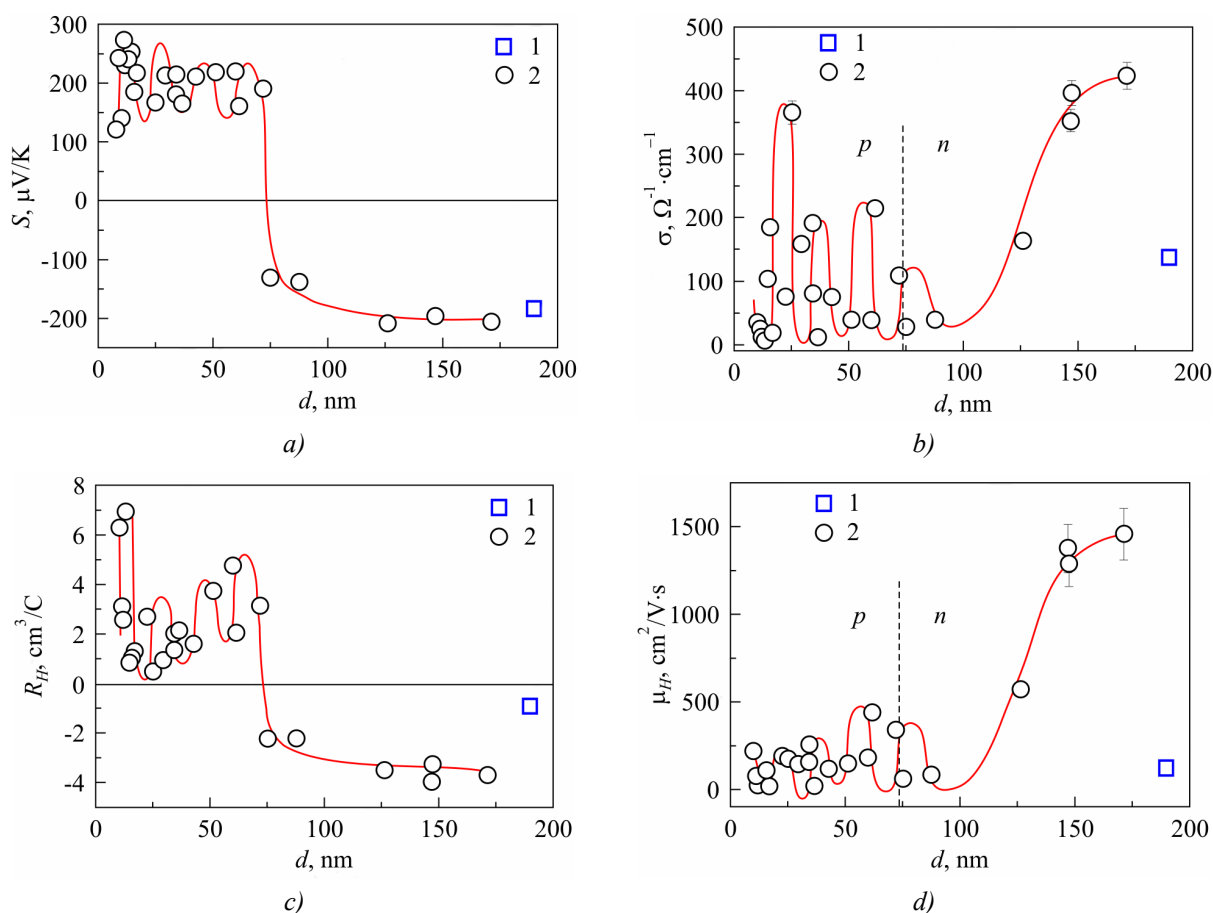
Epitaxial films *PbTe* of thickness $d = 8 - 170$ nm were prepared by vacuum evaporation ($\sim 10^{-5} - 10^{-6}$ Pa) of *PbTe<Pb>* crystals with lead excess (2 at.% *Pb*) with subsequent condensation onto fresh cleavages of (001) *KCl* at a temperature of (520 ± 10) K. The rate of material condensation was 0.5 – 1.0 nm/s. Film thickness d was controlled by means of a quartz resonator preliminarily calibrated with the aid of interferometer (for $d > 100$ nm) and small-angle *X*-ray diffraction method (for $d < 100$ nm). Electron-beam technique was used to deposit Al_2O_3 layer $\sim 10 - 15$ nm thick on top of the film. The wide-gap Al_2O_3 semiconductor, on the one hand, protected *PbTe<Pb>* films from oxidation and mechanical damages, and, on the other hand, served as a barrier layer whose contribution to conductivity was small. The electrical conductivity σ and the Hall coefficient R_H were measured by standard *dc* method with an error not exceeding ± 5 %. Indium was used for contacts. The Hall mobility of charge carriers μ_H was calculated by the formula $\mu_H = R_H \sigma$, and charge carrier concentration was determined on the assumption of one sort of charge carriers as $n = r/(e \cdot R_H)$, where the Hall factor $r = 1$. The measurements of S were done by compensation method with respect to copper in the plane of films to an accuracy of ± 3 %. The type of charge carriers was determined by the sign of R_H and S . The measurements were conducted on as-prepared samples at room temperature.

Results

The measurements have shown that *PbTe<Pb>* crystal, used as blend for preparation of films, possessed *n*-type conductivity (which is in agreement with the reported data [1]) and had the following electrophysical parameters: $n = 7 \cdot 10^{18} \text{ cm}^{-3}$, $S = -180 \text{ } \mu\text{V/K}$, $\sigma = 140 \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$, $\mu_H = 125 \text{ cm}^2/\text{V} \cdot \text{s}$. In passing to the thin-film state, *n*-type conductivity was observed only in the films of thickness $d \geq 75$ nm, and at lower thicknesses the conductivity sign changed for the opposite.

One of possible reasons for the appearance of *p*-type conductivity at $d \leq 75$ nm in *PbTe*<*Pb*> films can be a change in thermodynamic equilibrium conditions in the thin-film state as compared to the bulk crystal and, as a consequence, a change in equilibrium concentration of defects in the film. It can be also supposed that a change in conductivity type with a change in film thickness is determined by the specific features of crystals evaporation. In the course of heating *PbTe* is mainly evaporated in the form of *PbTe* molecules (dissociation energy of *PbTe* molecule 229.2 J/mole is much in excess of sublimation heat 224.6 J/mole), though apart from *PbTe* molecules, small amounts of lead or tellurium atoms can be present in the vapours [18]. Though the content of free *Te* in the vapours is small, during condensation this *Te* excess can be accumulated in the bulk of the deposited film and result in *p*-type conductivity. The impact of this factor will be the greatest with small film thicknesses. One should also take into account the possibility of partial reevaporation of lead excess during deposition on the substrates. In [15], with the use of the same blend material as in the present work, *p*-region was not observed. It is apparently due to the fact that the thickness (30 nm) and material (*EuS*) of protective coating on *PbTe* film differed from these values in the present work and better protected the film from oxidation. In [15, 19] it was established that the type of conductivity can be controlled by changing film thickness d and protective layer thickness d_{EuS} , namely the presence of *EuS* with $d_{EuS} > 30$ nm completely protects lead chalcogenide films from oxidation and retains *n*-type conductivity, and with $d_{EuS} < 30$ nm the inversion point of conductivity type is displaced toward the region of smaller thicknesses.

Fig. 1 gives d -dependences of S , σ , R_H and μ_H of *PbTe*<*Pb*> thin films obtained in the present work.



*Fig. 1. Thickness dependences of the Seebeck coefficient S (a), electric conductivity σ (b), the Hall coefficient R_H (c) and the Hall mobility μ_H (d): 1 – crystal *PbTe*<*Pb*>; 2 – films (001)*KCl*/*PbTe*<*Pb*>/*Al*₂*O*₃.*

From Fig. 1 it is seen that in the range of thicknesses corresponding to *p*-type conductivity in *PbTe*<*Pb*> films, there is a non-monotonous behaviour of S , σ , R_H and μ_H versus the thickness, namely the kinetic coefficients oscillate with increase in d . Note that positions of peaks on the dependences $S(d)$ and $R_H(d)$ coincide and correspond to the minima on the curves $\sigma(d)$ and $\mu_H(d)$ (Fig. 1). This, as well as the fact that σ , S and R_H were measured independently, confirms the reality of oscillations existence. The average distance between the peaks or minima (oscillation period) is $\Delta d = (16 \pm 2)$ nm. It should be noted that oscillation amplitudes on the dependences $S(d)$, $\sigma(d)$, $R_H(d)$ and $\mu_H(d)$ are rather large and reach 25 %, 100 %, 80 % and 80 %, respectively. With the increase in film thickness, the amplitude of d -oscillations of the kinetic coefficients is decreased.

We attribute the presence of oscillations on d -dependences of the kinetic properties of *p-PbTe*<*Pb*> films to the manifestation of QSE. Taking into account that *PbTe*<*Pb*> film is located between two isolators, namely the substrate (001) *KCl* and Al_2O_3 protective layer, the motion of charge carriers (here holes) in the direction normal to the plane of thin film, is restricted, which results in the quantization of the transverse component of hole quasi-pulse in this direction and the formation of transverse energy subbands. Carrier motion in the plane of a film is not quantized. Therefore, the structure (001) *KCl/PbTe*<*Pb*>/ Al_2O_3 can be approximately represented as a rectangular potential quantum well with infinitely high walls. In this case in the effective mass approximation the energy levels are written as [9]:

$$E = \frac{\hbar^2}{2m_z^*} \frac{\pi^2}{d^2} N^2 + \frac{\hbar^2 k_x^2}{2m_x^*} + \frac{\hbar^2 k_y^2}{2m_y^*}, \quad (1)$$

where m_z^* is the effective mass along the direction normal to quantum well, k_x , k_y and m_x^* , m_y^* are the wave vector and effective mass components, respectively, with charge carrier motion parallel to quantum well. With a change of d by the value equal to half de Broglie wavelength, $\lambda_F/2$ (λ_F is de Broglie wavelength on the Fermi level), N subbands will consecutively cross the Fermi level ε_F , which will involve a stepwise change in the density of states. Density of states oscillations lead to transport properties oscillations. The oscillation period values Δd and N can be determined using the following expressions [9]:

$$\Delta d = \frac{\lambda_F}{2} = \frac{h}{\sqrt{8m_z^* \varepsilon_F}}, \quad (2)$$

$$N = \frac{k_F d}{\pi} = \frac{d}{\lambda_F / 2} = \frac{d \sqrt{8m_z^* \varepsilon_F}}{h}. \quad (3)$$

It can be readily shown [14] that the thickness d_1 whereby the first subband crosses the Fermi level ($E_1 = \varepsilon_F$) is equal to $d_1 = h/\sqrt{8m_z^* \varepsilon_F} = \Delta d$, i.e. is nothing but oscillation period. So, to determine Δd , there is no need to measure transport properties of films in a wide thickness range, it is enough to determine experimentally the first extremum on d -dependences of properties which will yield the most precise value of Δd .

For the investigated structures (001) *KCl/PbTe*<*Pb*>/ Al_2O_3 with regard to known values of the effective mass of holes in *p-PbTe* (the transverse and longitudinal components of the effective mass $m_t^* = 0.022 m_0$, $m_l^* = 0.31 m_0$, respectively) [1] and the value ε_F determined by the average concentration of holes ($p = 3.8 \cdot 10^{18} \text{ cm}^{-3}$) in the area with *p*-type conductivity ($d < 75$ nm), the oscillation period was calculated from formula (2) that made $\Delta d = (17 \pm 2)$ nm. The resulting value of Δd is in very good agreement with the experimentally determined average distance between the

adjacent maxima on d -dependences of S , R_H , σ and μ_H , as well as with the position of the first extremum in p -region ($d_l = 14 \pm 1$ nm) (Fig. 1).

Quantum thickness oscillations of the kinetic properties become pronounced at room temperature, though according to theoretical models the oscillations can be distinctly pronounced only at low temperatures [20]. The fact of observation of quantum size effect can point to sufficiently high degree of structural perfection of films and/or the impact of other factor.

In n - $PbTe\langle Pb \rangle$ films (with $d > 75$ nm) higher values of σ and μ_H were obtained than in $PbTe\langle Pb \rangle$ crystal from which the films were prepared, which can testify to a higher structural perfection of films as compared to crystal.

When analyzing the kinetic coefficients behaviour versus the thickness of films with n -type conductivity ($d > 75$ nm) it is seen (Fig. 1) that, with increase in d , the monotonous component of S , σ and μ_H is increased and gradually reaches saturation. Such behaviour of S , σ and μ_H with thickness points to the existence of classical size effect (CISE).

Conclusions

Vacuum evaporation technique of $PbTe$ crystals with lead excess and subsequent condensation on (001) KCl substrates was used to prepare $PbTe\langle Pb \rangle$ thin films of thickness $d = 8 - 170$ nm. A change of p -type conductivity for n -type with $PbTe$ layer thickness $d \approx 75$ nm was established. It is supposed that conductivity sign inversion can be due to a change in thermodynamic equilibrium conditions in $2D$ -state as compared to the bulk crystal, peculiarities of evaporation and condensation processes or to insufficient thickness of Al_2O_3 protective coating.

It is shown that in the range of thickness $d \leq 75$ nm there are thickness oscillations of the Seebeck coefficient, the Hall coefficient, electric conductivity and mobility of holes with the period $\Delta d = (16 \pm 2)$ nm, which is related to quantization of hole energy spectrum and manifestation of quantum size effect. Theoretical calculation of quantum oscillation period with the use of a model of infinitely deep rectangular potential well is in good agreement with the experimentally determined Δd value.

Analysis of the monotonous components of transport coefficient dependences on the thickness of films with n -type conductivity ($d \geq 75$ nm) has shown that the values of the Seebeck coefficient, electric conductivity and electron mobility are increased with thickness increase and gradually reach saturation, which is related to manifestation of a classical size effect.

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