

Quantum Size Effects and Thermoelectric Transport in IV-VI – Based 2D-Structures

E.I. Rogacheva¹, and M.S. Dresselhaus²

¹National Technical University “Kharkov Polytechnic Institute”,
21 Frunze St., Kharkov 61002, UKRAINE ,

E-mail: rogacheva@kpi.kharkov.ua

²Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

Abstract

The present status of our studies on the observation of thickness oscillations of the thermoelectric and galvanomagnetic properties in IV-VI quantum wells (QWs) is reviewed. These oscillations are attributed to the quantum size effects (QSEs) due to electron or hole confinement in the QWs. The experimental values of the oscillation period are in good agreement with the results of the theoretical calculations using the effective mass approximation and a model of a rectangular potential well with infinitely high walls. The influence of various factors (carrier concentration, type of substrate, structural parameters, growth mechanism, etc.) on the observed oscillatory phenomena is analyzed. The effect of the size quantization on the thermoelectric power factor of thin film structures is considered.

Introduction

Electron confinement in low-dimensional structures leads to a radical change in physical properties of these systems as compared with bulk crystals and introduces new ways for controlling the properties of solids [1]. In QWs, charge carrier motion is confined in one direction, which results in the quantization of the electron quasi-momentum and energy spectrum in this direction. By now, the energy level structure of thin films and QWs has been determined by a number of experiments, mainly dealing with optical and tunneling techniques. Also sensitive to QSEs are the various transport properties, in particular thermoelectric (TE) properties. For thin film applications in thermoelectricity, it is necessary to take into account the QSEs, which can drastically change TE properties under thickness change. The interest in studying TE properties of 2D-structures has grown significantly since the possibility of a substantial increase in the TE figure of merit ZT in QWs and superlattices (SLs) under decreasing the QW width was predicted theoretically [2].

One of the possible manifestations of the QSEs in 2D-structures is an oscillatory behavior of the thickness dependences of the transport and thermodynamic properties due to the quantization of the energy spectrum [3]. Quantum oscillations in the transport properties of thin films with changing film thickness were observed for the first time in studies on semimetallic Bi films [4]. Metallic films are not very convenient objects for studying QSEs through transport property measurements because their Fermi wavelength λ_F and the oscillation period Δd are comparable to interatomic distances, which requires growing very thin films with a high degree of structural perfection.

Semiconductors, which have significantly lower charge carrier concentrations and, consequently, larger λ_F , represent more convenient systems for studying QSEs by measuring their transport properties [5]. By choosing an optimal set of parameters, one can create conditions for the experimental

studies of the oscillations even in rather thick films. However, up to now, the number of such investigations of semiconducting QWs has been very limited, which to all appearances is connected with the complexity of such studies. The authors of [6,7] observed oscillations in the d -dependences of the galvanomagnetic properties of InSb [6] and CdAs₂ [7] semiconducting thin films, and attributed their existence to quantization of electron spectrum.

IV-VI-based materials are well known as promising thermoelectrics [8]. A sufficiently small effective mass in the direction perpendicular to the direction of growth, with transport along the film surface, and a high charge carrier mobility make IV-VI compounds convenient materials for QSEs studies using transport properties. However, the available works were devoted mainly to the QSEs in space-charge accumulation or inversion [9,10] layers at the PbTe surface. Recently, interest in these compounds has grown due to the experimental observation of a substantial increase in ZT in IV-VI-based QWs and SLs [2,11,12] as compared with bulk crystals, which had been predicted earlier theoretically. All this stimulates further studies of the thermoelectric properties of IV-VI –based 2D-structures.

To realize conditions necessary for the observation of quantum oscillations, it is necessary to overcome a number of problems connected with the preparation of high-quality QWs. In the experimental study of the quantum oscillations in thin Bi films deposited on mica substrates [4], air played the role of one of the barriers, surrounding Bi QW, because at relatively low temperatures the transport properties of Bi layer exposed to air practically do not change. Unfortunately, oxygen in lead chalcogenides acts as an acceptor, causing the appearance of p -type charge carriers, whose presence can radically change the transport properties of crystals and thin films [13]. With decreasing film thickness d , a surface layer with p -type behavior becomes increasingly important in determining the thin film transport properties. However, until very recently the available results on the oxidation of IV-VI compound semiconductors were obtained for relatively thick ($d = 0.1-10 \mu\text{m}$) films, whereas there are practically no results yet available on nanosized film thicknesses. Our studies [14-16] of the effect of near surface oxidation on the transport properties of freshly prepared n -type IV-VI films on KCl and mica substrates showed that the appearance of an oxidized layer on the n -PbTe, n -PbSe and n -PbS freshly grown thin films surface in air at room temperature causes a strong d -dependences of the TE properties, including inversion of the dominant carrier sign from n to p at a certain critical thickness, depending on the chalcogenide species and carrier concentration. A two-carrier model for very thin films and a two-layer model for more thick films provide an explanation of the observed experimental dependences of the TE properties on the film

thickness [16]. It follows from the results obtained in those works that establishing the true thickness dependences of the TE properties of IV-VI QWs with a view toward revealing the physical effects occurring at a nanosize level, or controlling the properties of thin films, or using the films in TE and other devices is impossible without taking special measures for protecting the films from oxidation.

In the present paper, a review of the works of our research group on studying dependences of thermoelectric properties of IV-VI-based quantum wells on QW width with a view toward observing thickness oscillations is given.

Experimental details

IV-VI (PbTe, PbSe, PbS and SnTe) monocrystalline thin films were prepared by the thermal evaporation of IV-VI crystals from tungsten "boats" in an oil-free vacuum (10^{-5} – 10^{-6}) Pa and the subsequent deposition onto (001) KCl or (111) mica surface at (520 ± 10) K. For thin film preparation, we used only substrates of high quality, without steps. The condensation rate was $0.1 - 0.3$ nm/s. The film thickness and the condensation rate were controlled using a calibrated quartz resonator. The epitaxial growth and structure of the samples were studied by electron microscopy and electron diffractometry. Transport measurements were carried out on freshly grown epitaxial IV-VI thin films covered with a ~ 30 nm EuS or Al_2O_3 layers prepared by electron-beam evaporation. Being wide-gap semiconductors, these cover layers, on the one hand, protected the IV-VI thin layers from oxidation and, on the other hand, acted as barrier layers making a negligible contribution to the electrical conductivity. The Hall coefficient R_H and the conductivity σ were measured using a conventional dc method and a magnetic field of 0.8 T. Six ohmic contacts were prepared by soldering indium to the film surface. The error in the R_H and σ measurements did not exceed 5 %. The Hall mobility was calculated as $\mu_H = R_H \cdot \sigma$, and the electron concentration n was determined as $n = A/(R_H e)$, assuming the Hall factor A to be 1. The Seebeck coefficient S was measured relative to copper with an accuracy of ≈ 3 %.

Experimental results

It is known that lead chalcogenides grow by the Volmer-Weber mechanism on dielectric substrates, such as KCl, NaCl, etc., however the character of film overgrowth depends principally on the technological parameters of the growth. The results of our electron microscopy and electron diffraction studies showed that PbS, PbSe, PbTe, and SnTe thin films grow epitaxially on (001) KCl according to the vapor-crystal mechanism in the (001) orientation. The film growth starts with the formation of islands, which increase in size as d increases. At $d \sim 4 - 10$ nm, the films have a channel structure. Thin PbTe films grow on mica also epitaxially in an island like fashion predominantly in the (111) orientation [17]. SnTe and PbTe grow on one another in a layer-by-layer fashion. At the critical thickness of the growing layer $d_c \sim 2$ nm, misfit dislocations are introduced in the interface [18].

In Fig. 1, the thickness dependences of n , S , and σ for (001)KCl/PbS/EuS and (001)KCl/PbSe/EuS QWs are presented [19-21]. It should be noted that although σ , n , and

S were measured independently, all the dependences exhibited oscillatory behavior with similar oscillation periods, which allows us to draw a single curve through experimental points for both PbS and PbSe QWs. The positions of the first minimum in the $S(d)$ curve and the first maxima in $n(d)$ and $\sigma(d)$ curves correspond to $d = 17 \pm 3$ nm. The distances Δd between the two first extrema in the $\sigma(d)$, $S(d)$ and $n(d)$ curves are (30 ± 5) nm.

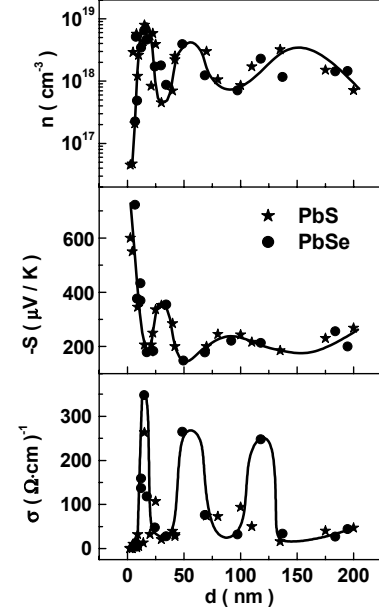


Figure 1. Room-temperature dependences of the charge carrier concentration n , Seebeck coefficient S , and electrical conductivity σ on PbS and PbSe layer thickness d in KCl/PbS/EuS and (001)KCl/PbSe/EuS quantum wells [20].

The simplest explanation of the oscillatory effect observed in Fig. 1 is in terms of the QSEs. The IV-VI layer sandwiched between two insulators - KCl and EuS, provides a QW within which carriers can be effectively confined. Such a system is a convenient object for investigation because it can be approximated as a rectangular potential QW with infinitely high walls. The theoretical model for this case is a simple one in comparison with that for a barrier of a finite width and height. This system is also convenient from the point of view of the transport properties measurement and interpretation, because the barrier does not practically contribute to the electrical conductivity.

Considering IV-VI layer to be confined between two infinitely high barriers provides a reflection in the propagating states of IV-VI film and the confinement of these states within the film. Localization in a well of atomic dimensions leads to a quantization of the transverse component of the wave vector k and formation of discrete energy states (subbands). The energy levels are given as

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

where d is the width of the quantum well, E_n are the discrete energy levels of the electron, n is the quantum number, indicating the subband number, k_x и k_y are the components of the electron wave vector in the direction parallel to the

well surface, and m_x , m_y , and m_z are the effective mass tensor components of the constant energy surfaces. A number of simplifying assumptions are made, specifically, assuming isotropic and parabolic carriers, a specular character for the carrier scattering, both barriers for the IV-VI quantum well to be identical and having infinite barrier heights, the absence of impurities and other defects.

The observed oscillatory dependences can be interpreted on the basis of quantum-mechanical notions about a gradual filling of lateral subbands with increasing d . As d increases, the number of populated subbands N changes in a step-like fashion as is expected for a 2D-system. Every time d increases by $\lambda_F/2$, where λ_F is the de Broglie wavelength at the Fermi level, an additional subband drops below ϵ_F , and contributes to electrical conduction. This interrelation between d and N leads to an oscillatory behavior in many physical properties and is the origin of the QSEs. The critical thickness d_1 , at which the first subband passes through the Fermi level ($E_1 = \epsilon_F$), can be estimated as $d_1 = h/\sqrt{8m_z\epsilon_F}$.

If we assume that a QW represents an ensemble of electrons with a fixed value of the chemical potential, corresponding to ϵ_F in thick films, then with changing d the electron concentration in the QW must oscillate relative to the constant value of ϵ_F . Within a single subband, n increases at first, then it reaches a maximum, after which n decreases. When the next subband (bottom of conduction band) intersects the Fermi level, a new wave function starts to contribute to the electron density and n increases again. Oscillations in the density of states must lead to oscillations in the charge carrier mobility, electrical conductivity, and Seebeck coefficient.

One can then make an order of magnitude estimate of Δd , which denotes an oscillation period, and N , which denotes the number of subbands contributing to conduction [3,5]:

$$\Delta d = \frac{\lambda_F}{2} = \frac{h}{\sqrt{8m_z^*\epsilon_F}} \quad (3)$$

$$N = \frac{k_F d}{\pi} = \frac{d}{\lambda_F/2} = \frac{d\sqrt{8m_z^*\epsilon_F}}{h}, \quad (4)$$

As is seen, an important parameter determining the oscillatory d -dependence of the transport properties is the charge carrier concentration (or ϵ_F), which determines Δd and the number of populated subbands N in Eqs. 3, 4. By increasing n , we can increase N and consequently the number of oscillations that are observed. One can see that $d_1 = \Delta d$, and from the position of the first extremum one can determine the oscillation period most precisely.

From the known effective masses of the electrons in n -PbSe ($m_t^*=0.04 m_0$, $m_l=0.07 m_0$) and PbS ($m_t^*=0.08 m_0$, $m_{in}=0.105 m_0$) [13] and by estimating ϵ_F from the average electron concentration in the films in Fig. 1 ($n \approx 1.5\text{-}2 \cdot 10^{18} \text{ cm}^{-3}$), the oscillation period can be estimated using Eq. 3, obtaining $\Delta d = 20 \pm 5 \text{ nm}$, which is in reasonable agreement with the experimentally measured position of the first extremum ($17 \pm 2 \text{ nm}$). The discrepancy between the experimentally determined Δd and the one calculated using Eq. 3 may be due to the oversimplifications of the model Eq. 1,3,4 based on. It should be also mentioned that surface

roughness and diffuse scattering of the carriers from the film surface usually complicate the observation of QSE and can lead to a change in Δd , to deviations from the $\lambda_F/2$ period, and even to their disappearance. The insufficient number of experimental points in the studied thickness range does not allow us to determine Δd precisely using the distances between the neighboring extrema.

Analogous studies conducted for PbTe thin films [20,22,23] also revealed the oscillatory behavior of thickness dependences of the transport properties. Investigation of films with different electron concentration n allowed us to establish correlation between Δd and n . For this purpose we studied three series of the PbTe-based QWs, in which PbTe layers were grown from the crystals of 1) stoichiometric PbTe, 2) PbTe with 2 at.% excess Pb relative to the ideal stoichiometry, 3) PbTe enriched in Pb and additionally doped with PbCl₂. The average electron concentrations in thick layers were $n = 1.5 \cdot 10^{18} \text{ cm}^{-3}$, $3.8 \cdot 10^{18} \text{ cm}^{-3}$, and $7 \cdot 10^{19} \text{ cm}^{-3}$, respectively. The films of series 1 and 2 were grown on KCl, whereas the films of series 3 were grown on mica.

In Fig. 2 a, the dependences of the galvanomagnetic and TE properties on the PbTe layer thickness d in KCl/PbTe/EuS structures of series 1 at room temperature are shown [22]. In the $S(d)$ and $R_H(d)$ curves, distinct minima at $d \sim 25\text{-}30 \text{ nm}$ and maxima at $d \sim 50 \text{ nm}$ are registered.

In Fig. 2,b, the d -dependences of n for the PbTe QWs of series 1 and 2 are presented. It is seen that with increasing n , a shift in the location of the n extrema to smaller values of d occurs. On the basis of the observed $S(d)$ and $\sigma(d)$ dependences, the d -dependences of the TE power factor $P = S^2\sigma$ are plotted for both series of QWs (Fig. 3,a). In the QWs of series 2 the maximum value of the power factor ($P_{\max} = 32.5 \cdot 10^{-4} \text{ W/m K}^2$) is higher than the maximum value of P ($P_{\max} = 29.2 \cdot 10^{-4} \text{ W/m K}^2$) observed in QWs of series 1. These maximum values of P exceed the highest values observed for bulk PbTe crystals [8] and are comparable to those observed in IV-VI-based SLs structures [2].

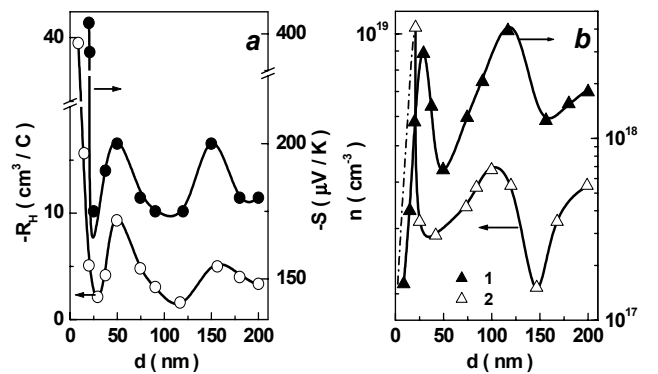


Figure 2. Room-temperature dependences of the Hall coefficient R_H (a), Seebeck coefficient S (a), and electron concentration n (b) on PbTe layer thickness d for KCl/PbTe/EuS QWs prepared from stoichiometric PbTe (a,b-1) and PbTe with 2 at.% excess Pb (b-2) [23]

In Fig. 4, the d -dependences of σ , S , R_H and P for the (111)mica/PbTe/Al₂O₃ QWs are presented. All dependences exhibit oscillatory behavior with $\Delta d = (20 \pm 2) \text{ nm}$. The positions of the first minimum in the $S(d)$ curve and the first

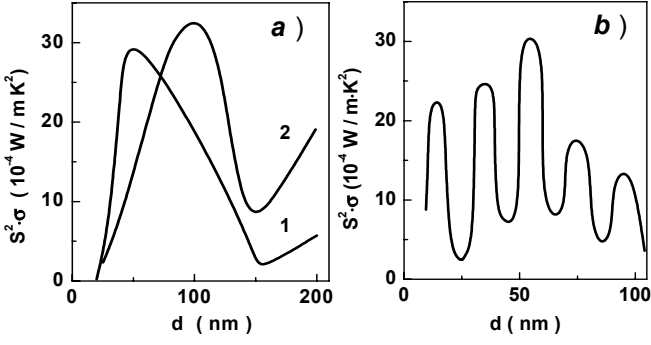


Figure 3. Room-temperature dependences of the thermoelectric power factor $P=S^2 \sigma$ on PbTe layer thickness d for (001)KCl/PbTe/EuS QWs (a) prepared from stoichiometric PbTe (1) and PbTe with 2 at.% excess Pb (2) [22], and for (111) mica/PbTe/Al₂O₃ QWs (b) prepared from PbTe doped with Pb and PbCl₂ (series 3). [23]

maxima in $n(d)$, $\sigma(d)$ and $\mu_H(d)$ curves correspond to $d = 14 \pm 2$ nm. The maximum value of the power factor ($P_{\max} \cong 30 \cdot 10^{-4} \text{ W/m K}^2$) does not exceed (Fig. 3,b) the ones attained for (001)KCl/PbTe/EuS QWs (Fig. 3,a) with lower n values. It is seen from Fig. 4 that with increasing d , a tendency to an increase in σ and n values and a decrease in R_H and S values are observed. To illustrate this tendency, the dotted lines are drawn through the points corresponding to the equilibrium positions of separate oscillations. The monotonic components of σ , R_H and S change with increasing d up to $d \sim 70$ nm and then level off, corresponding practically to σ , R_H and S values of the charge.

Knowing the effective masses of the electrons in n -PbTe ($m_t^* = 0.024 m_0$; $m_l^* = 0.24 m_0$ [13]) and having calculated the position of the Fermi level for the corresponding value of the charge carrier concentration [24], one can roughly estimate Δd using Eq. (3). If we assume $n \approx 1.5 \cdot 10^{18} \text{ cm}^{-3}$, $n \approx 3.8 \cdot 10^{18} \text{ cm}^{-3}$, and $7 \cdot 10^{19} \text{ cm}^{-3}$ (mean electron concentrations in thick films of series 1, 2 and 3 respectively), then we obtain $\Delta d \approx 32.5$, 20.0, and 15 nm, which is close to the values of d corresponding to the positions of the first extrema in d -dependences of TE properties. The experimentally observed Δd 's, which were determined as the distance between extrema of R_H , S , and n , are in good agreement with the calculated Δd values in mica/PbTe/Al₂O₃ structures (Fig. 4), but significantly exceed the calculated value for (001)KCl/PbTe/EuS structures.

In Fig. 5, the d -dependence of the Seebeck coefficient in SnTe thin films is presented. As is seen, S decreases in an oscillatory fashion with $\Delta d = 15 \pm 2$ nm [25].

SnTe belongs to IV-VI compounds, in which holes are dominant charge carriers. A specific feature of SnTe is its high concentration ($\sim 10^{20} - 10^{21} \text{ cm}^{-3}$) p -type charge carriers (light and heavy holes), caused by a significant deviation from stoichiometry [26]. For SnTe thin films, one can suggest two types of oscillations related to light and heavy holes. However, oscillations related to heavy holes are unlikely to be observed because of their small λ_F due to their large effective mass ($m_h^* = 3 m_0$) [26]. That is why one can suggest that QSEs are associated with the light holes, whose m_l^* is smaller and whose mobility is higher. The subband of

light holes is non-parabolic and the effective mass of the light holes is a function of p [26]. According to some experimental and theoretical results [27,28] in the range of $p = (2 - 8) \cdot 10^{20} \text{ cm}^{-3}$ (typical for SnTe thin films), the electrical-susceptibility effective mass m_s^* changes in the range of $m_s = (0.12 - 0.15) m_0$. Substituting the values of m_s^* and the longitudinal effective mass $m_l^* = 0.28 m_0$, in the equation $3/m_s^* = 2/m_t^* + 1/m_l^*$, which is correct for an ellipsoidal band, one can estimate the transverse effective mass: $m_t^* = (0.12 \pm 0.02) m_0$. According to data reported by different authors [26-28], in the above specified range of p , we obtain $\epsilon_F = 0.3 - 0.4$ eV. Substituting the values of m_t^* and ϵ_F in Eq. (3), we obtain $\Delta d_{\text{calc}} = 3 \pm 0.4$ nm, which is considerably lower than the experimental value $\Delta d = (15 \pm 2) \cdot \text{nm}$. The most probable explanation of the discrepancy between theory and experiment is an island-like growth mechanism complicating the study of QSEs in the range of small thicknesses ($d < 10$ nm), which is especially important in case of small oscillation period $\Delta d = \lambda_D/2$.

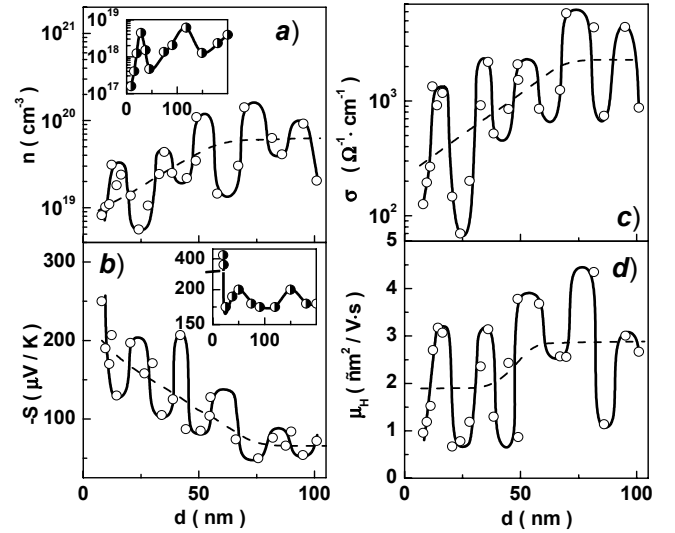


Figure 4. Room-temperature dependences of the electron concentration n (a), the Seebeck coefficient S (b), electrical conductivity σ (c), and charge carrier mobility μ_H (d) on the PbTe layer thickness d for mica/PbTe/Al₂O₃ quantum wells prepared from PbTe charge with $n = 1 \cdot 10^{20} \text{ cm}^{-3}$ [23]

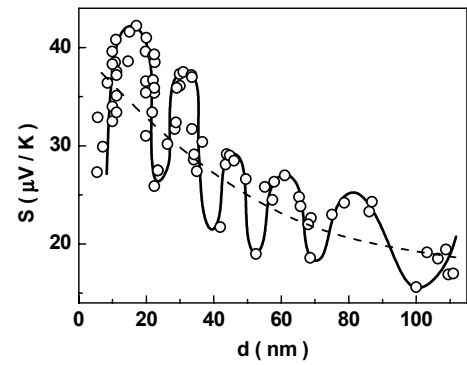


Figure 5. Room-temperature dependence of the Seebeck coefficient S on the SnTe layer thickness d in the range of $d = 5 - 110$ nm for (001)KCl/SnTe thin films [25].

Because of a small value of Δd , the first oscillations (from which one can determine Δd most precisely) are not observed. A high concentration of defects as a result of islands' merging in the process of formation of a continuous film also complicates the observation of all oscillations.

One can expect that if the barrier and QW layers grow on one another in a layer-by-layer fashion, the probability of the observation of size quantization in a separate QW will increase. PbTe and SnTe grow on one another in a layer-by-layer fashion [18]. That is why the dependences of the TE and galvanomagnetic properties of n -PbTe/ p -SnTe/ n -PbTe heterostructures on the SnTe QW width (d_{SnTe}) were studied (Fig. 6 a-d). The SnTe layer sandwiched between two barrier n -PbTe layers provides a QW, within which holes are effectively confined in the direction z perpendicular to the plane of the thin film. The thicknesses of the lower and upper PbTe layers were kept fixed ($d^1_{\text{PbTe}} \approx 40$ nm and $d^2_{\text{PbTe}} \approx 10$ nm), and d_{SnTe} was varied in the range 0.5-6.0 nm. All structures were covered with a ~ 25 nm thick EuS layer

It is seen (Fig. 6, a-d) that the d -dependences are distinctly non-monotonic: in the range of $d_{\text{SnTe}} = 2.8 \pm 0.2$ nm, all studied properties show maxima, while in the vicinity of $d_{\text{SnTe}} = 1.8 \pm 0.2$ nm and $d_{\text{SnTe}} = 4.7 \pm 0.2$ nm, they exhibit minima. In the range of $d_{\text{SnTe}} \equiv 0.5 - 1.8$ nm, with increasing d_{SnTe} , μ_{H} decreases, the absolute values of S and R_{H} , which exhibit a negative sign, decrease, and at $d_{\text{SnTe}} \equiv 1.8$ nm, a change in the dominant carrier sign from n to p is observed. The hole concentration in the SnTe layer is 2 to 3 orders of magnitude higher than the electron concentration in PbTe layers. As a result, even at small d_{SnTe} the conductivity in the QW layer is comparable with that in the barrier layer. With increasing d_{SnTe} , the contribution by the p -type carriers becomes more significant, which leads to a decrease in the absolute value of R_{H} and S and a subsequent inversion of the dominant carrier sign. Near $d_{\text{SnTe}} \equiv 1.8$ nm, the carrier sign changes back to negative, while μ_{H} , S , R_{H} and P increase until they reach their maximum values in the vicinity of $d_{\text{SnTe}} \equiv 2.8$ nm. Then μ , S , R_{H} , and P decrease up to $d_{\text{SnTe}} \equiv 4.8$ nm. At still larger d_{SnTe} μ , S , P increase, and R_{H} practically does not change. If we assume that the mean distance between minima ($\Delta d_{\text{exp}} = 2.9 \pm 0.3$ nm), which are observed in the $\mu_{\text{H}}(d)$, $R_{\text{H}}(d)$ and $S(d)$ dependences, corresponds to the period of oscillations, then the theoretically calculated Δd_{calc} and the experimental value Δd_{exp} are in good agreement.

In figure 6, a-d, we show with dotted lines the d -dependences of R_{H} , S , μ , and P theoretically calculated, without taking into account possible QSE, on the basis of a three-layer model, treating a n -PbTe/ p -SnTe/ n -PbTe heterostructure as conductors connected in a parallel fashion, each characterized by its specific electrophysical parameters [29]. As is seen, the theoretical curve lies above the experimental one, approaching the latter with increasing d_{SnTe} . The probable reason for such a discrepancy is the manifestation of the QSEs taking place in the SnTe QW.

One can estimate the critical thickness d_1 , at which the first subband passes through the Fermi level. Substituting $m_i^* = (0.12 \pm 0.02) m_0$, $N=1$, and $\varepsilon_{\text{F}} = 0.3-0.4$ eV, we obtain $d_1 = 3.1 \pm 0.6$ nm. However, a QW with infinitely high walls does not reflect what is usually observed in a real

semiconductor SL, and a change of the finite barrier height U_0 affects the energy spectrum of the charge carriers in a predictable way.²⁶ A decrease in U_0 must lead to a decrease in level energies at a fixed well width²⁶ and, accordingly, to a decrease in d_1 . For a precise determination of the barrier height, it is necessary to know the energy band diagram of

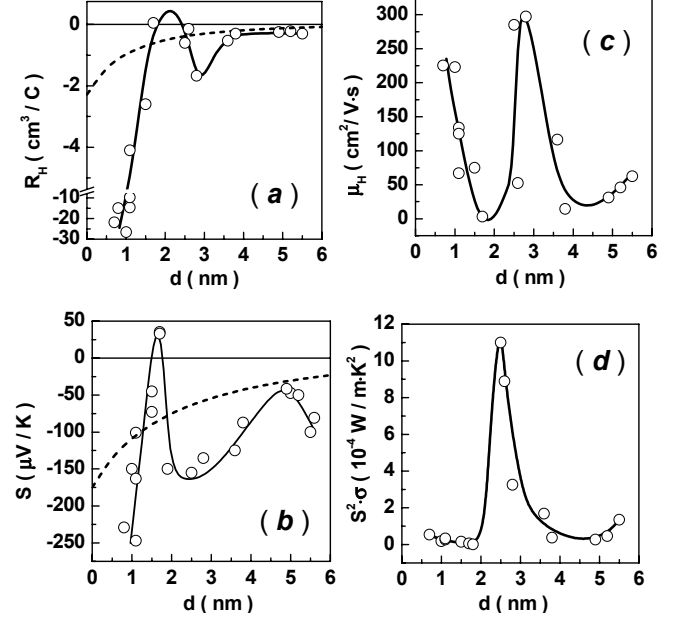


Figure 6. Room-temperature dependences of the Hall coefficient R_{H} (a), the Seebeck coefficient S (b), carrier mobility μ_{H} (c), and power factor $S^2\sigma$ (d) on the SnTe film thickness d in n -PbTe/ p -SnTe/ n -PbTe heterostructures [29].

the heterojunction, which requires a special investigation, both theoretical and experimental. At present, the precise shape of such a band diagram is not known, although the majority of authors are inclined to believe that PbTe and SnTe form SLs of the second type. Taking this assumption into account and using the values of the band gaps and Fermi energies for PbTe and SnTe, we have estimated the barrier height as $U_0 \equiv 0.6$ eV and we have calculated the critical width as $d_1 \equiv 1.8$ nm. This result shows that the minima in the properties curves at $d_{\text{SnTe}} \equiv 1.8$ and 4.7 nm with a high probability are associated with the first and second subband's dropping below ε_{F} . The experimental value of Δd and the position of extrema points are in good agreement with the results of the theoretical calculations, taking into account a finite barrier height. Such agreement is obtained to all appearances due to the fact that the studied heterostructures were grown in a layer-by-layer fashion which allowed us to study QSEs at small d 's.

Conclusions

The results of our works discussed in this paper provide the first experimental evidence for the existence of oscillations in the thickness dependences of the thermoelectric and galvanomagnetic properties of IV-VI QWs caused by size quantization of the electron (hole) energy spectrum. A convincing argument in favor of the interpretation of the data in terms of size quantization is a

good correspondence between experimentally determined and theoretically calculated values of the oscillation period, as well as the observed correlation between the energy band parameters and Δd .

It can be also concluded that under a sufficiently high carrier density and a sufficiently low m^* , the observation of a QSEs in the transport properties is quite possible for epitaxial films growing not only by the layer-by-layer growth mechanism but even in the island fashion. However, growth in the island fashion complicates determination of the oscillation period in case of small Δd values.

It is seen that the thickness oscillations of transport properties distinctly manifest themselves at room temperature, although in accordance with the commonly accepted theoretical views their observation is possible only at low temperatures. The fact that the QSE are observed at room temperature may imply, on the one hand, a rather high degree of structural perfection in the films, and, on the other hand, possible effects due to other factors.

The observed oscillatory character of the thickness dependences of the thermoelectric properties should be taken into account for 2D- structures applications in thermoelectricity.

References

1. Davies, J. H., The Physics of Low-Dimensional Semiconductors. An Introduction, Cambridge University Press (UA, 1998).
2. Dresselhaus, M. S. *et al*, Low Dimensional Thermoelectricity. In Semiconductors and Semimetals: Recent Trends in Thermoelectric Materials Research, ed. Tritt, T. M., Academic Press (San Diego, 2001), pp. 1–121.
3. Lifshits, I. M., Kosevich, A. M., “About oscillations of thermodynamics value for degenerated fermi-gas at low temperatures,” *Izv. AN USSR: Ser. Fiz.*, Vol. 19, No 4 (1955), pp. 395-403.
4. Ogrin, V. N., Lutskii, M. I., Elinson, O., “On Observation of Quantum Size Effects in Thin Bi Films,” *Pis'ma ZhETF*, Vol. 3, No. 1 (1966), pp. 114-118.
5. Tavger, B. A., Demihovskii, V. Ya., “Quantum Size Effects in Semiconductor and Semimetal Films,” *Usp. Fiz. Nauk*, Vol. 96, No. 1 (1968), pp. 61-86.
6. Filatov, O. N., Karpovich, I. A., “Quantum size effects in thin InSb films,” *Pis'ma ZhETF*, Vol. 10, No 1 (1969), pp. 142-143.
7. Zdanowicz, L. *et al*, “Quantum size effect in thin Cd_3As_2 films,” *Thin Solid Films*, Vol. 28 (1975), pp. 345-349.
8. CRC Handbook of Thermoelectrics, Ed. Rowe D. M., CRC Press, (Boca Raton, London, New York, Washington, D.C., 1995)
9. Tsui, D. S., Kaminsky, G., Schmidt, P. H., “Tunneling Study of Surface Quantization in n -PbTe,” *Phys. Rev. B*, Vol. 9, No. 8 (1974), pp. 3524-3531.
10. Schaber, H., Doezema, R. E., “Magnetorelectivity of the Inversion Layer on p -PbTe in the Far Infrared,” *Phys. Rev. B*, Vol. 20, No. 12 (1979), pp. 5257-5266.
11. Hicks, L. D. *et al*, “Experimental Study of the Effect of PbTe Quantum-Well Structures on the Thermoelectric Figure of Merit,” *Phys. Rev. B*, Vol. 53, No. 164 (1996), pp. R10493-R10496.
12. Harman, T. C. *et al*, “PbTe/Te Superlattice Structures with Enhanced Thermoelectric Figures of Merit,” *J. Electronic Materials*, Vol. 28, No. 1 (1999), pp. L1-L4.
13. Ravich, Yu. I., Efimova, B. A., Smirnov, I. A., Semiconducting Lead Chalcogenides, Plenum Press (New York, 1970), pp. 156-227.
14. Rogacheva, E. I. *et al*, “Effect of oxidation on the thermoelectric properties of PbTe and PbS epitaxial films,” *Appl. Phys. Lett.*, Vol. 78, No. 12 (2001), pp. 1661-1663.
15. Rogacheva, E. I. *et al*, “Effect of oxidation on the thermoelectric properties of PbSe thin films,” *J. Electron. Materials*, Vol. 31, No. 4 (2002), pp. 298-303.
16. Rogacheva, E. I. *et al*, “Effect of oxidation on thickness dependences of thermoelectric properties in PbTe/mica thin films,” *Thin Solid Films*, Vol. 476, No. 2 (2005), pp. 391-395.
17. Rogacheva, E. I. *et al*, “Investigation of the Growth Mechanism, Structure and Thermoelectric Properties of Thin PbTe Films Grown on Mica,” *Funct. Mater.*, Vol. 12, No. 1 (2005), pp. 21-27.
18. Rogacheva, E. I. *et al*, “Growth mechanism and thermoelectric properties of PbTe/SnTe/PbTe heterostructures,” *Thin Solid Films*, Vol. 493 (2005), pp. 41-48.
19. Rogacheva, E. I. *et al*, “Quantum Size Effects in PbSe Quantum Wells,” *Appl. Phys. Lett.*, Vol. 80, No. 15 (2002), pp. 2690-2692.
20. Rogacheva, E. I. *et al*, “Quantum Size Effects in IV-VI Quantum Wells,” *Physica E*, Vol. 17 (2003), pp. 313-315.
21. Rogacheva, E. I. *et al*, “Effect of Thickness on the Thermoelectric Properties of PbS Thin Films,” *Thin Solid Films*, Vol. 423, No. 1 (2003), pp. 115-118.
22. Rogacheva, E. I. *et al*, “Oscillatory Behavior of the Transport Properties in PbTe Quantum Wells,” *Nanotechnology*, Vol. 14, No. 1 (2003), pp.53-59.
23. Rogacheva, E. I. *et al*, “Quantum Size Effects in PbTe/mica Films,” *Proc. 4th European. Conference on Thermoelectrics*, Cardiff, UK, April, 2006, pp. 1-4.
24. Seeger, K., Semiconductor Physics. An Introduction, Springer (Berlin, 1997).
25. Rogacheva, E. I. *et al*, “Oscillations in the Thickness Dependences of the Room-Temperature Seebeck Coefficient in SnTe Thin Films,” *Thin Solid Films*, Vol. 484, No. 1-2 (2005), pp. 433-437.
26. Abrikosov, N. Kh., Shelimova, L. E., Semiconducting Materials based on A^{IV}B^{VI} Compounds, Nauka (Moscow, 1975), pp. 59-85.
27. Bis, R. F., Dixon, T. R., “Electric-Susceptibility Mass of free Holes in SnTe,” *Phys. Rev.*, Vol. 2, No 4 (1970), pp.1004-1012.
28. Tsu, R., Howard, W. E., Esaki. L., “Optical and Electrical properties and band structure of GeTe and SnTe,” *Phys. Rev.*, Vol. 172, No 3, (1968), pp. 779-788.
29. Rogacheva, E. I. *et al*, “Quantum Size Effects in n -PbTe/ p -SnTe/ n -PbTe Heterostructures,” *Appl. Phys. Lett.*, Vol. 86 (2005), pp. 063103.
30. Herman, M. A., Semiconductor Superlattices, Akademie-Verlag (Berlin, 1986), pp.19-21 (in Russian).