# Thermoelectric Properties of PbTe/Bi Heterostructures

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**Abstract**

PbTe/Bi two-layer structures with fixed PbTe layer thickness ($d_{PbTe}$=50 nm) and various Bi layer thicknesses ($d_{Bi}$=1-80 nm) grown by thermal evaporation in vacuum on mica substrates and covered with an $Al_2O_3$ layer were studied. The dependences of the Seebeck coefficient, electrical conductivity, Hall coefficient, thermoelectric power factor on $d_{Bi}$ and temperature (80-300 K) were obtained. It was established that thickness dependences exhibit an oscillatory behavior (the oscillation period is $\Delta d$=15 ±2 nm) caused by size quantization of the energy spectra when electron movement is confined in Bi quantum well. The experimental data were analyzed within the framework both of the model assuming infinite barriers and of the model assuming non-identity and finite barrier heights. It is established that in PbTe/Bi heterostructures one can attain higher values of the power factor than in thin Bi films.

**Introduction**

The theoretical prediction of a possible substantial increase in ZT in Bi-based quantum wells (QWs) and superlattices (SLs) with decreasing Bi layer thickness down to nanosizes [1] draws attention to the detailed study of the quantum size effects (QSEs) in these structures.

One of the manifestations of the quantization of the quasi-momentum and energy spectra of charge carriers is oscillations in the thickness dependences of the kinetic, in particular thermoelectric, properties [2]. There are a number of works (for example, [3-8]) in which quantum oscillations with period $\Delta d$=25-40 nm in the dependences of the transport properties on thickness of thin Bi films grown on mica and other substrates were observed. Using the model of rectangular quantum well with infinite barriers for such films proved to be successful and yielded good agreement between theoretically calculated and experimentally determined $\Delta d$ values. However, when Bi is applied in real QWs and SLs the possibility of applying such model is not obvious. This determines the necessity of establishing the effect of boundary conditions on the character of the manifestation of QSEs in Bi layers, in particular on the oscillation period. To carry out such studies, it is necessary to prepare high quality ultrathin Bi layers, which, in turn, requires appropriate barrier material. Suitable candidate for the barrier material is PbTe semiconductor compound, because it has sufficiently high resistivity and low thermal conductivity as compared with Bi, and its crystal structure is favorable for realization of the layer-by-layer growth mechanism: lattice mismatch between PbTe (111) and Bi (111) planes is as small as ~ 0,3% and can be accommodated elastically.

According to [9], Bi grows on PbTe in a layer-by-layer fashion. In [10] at T=1.8 K the galvanomagnetic properties of the compositionally modulated PbTe-Bi films for a series of samples with a fixed thickness of the PbTe layer (4.5 nm) and varying thicknesses of the Bi layer (0.8-9.5 nm) were studied as a function of $d_{Bi}$. In the dependences of the electrical resistivity, magnetoresistence and Hall coefficient on Bi layer thickness, the oscillations with $\Delta d$ ~3.2 nm were observed and attributed to the manifestation of size quantization of the energy spectrum. The smaller value of $\Delta d$ as compared with thin Bi films was explained by the contribution of the hole part of the Fermi surface to the QSE.

In [11], it was found that in the PbTe/Bi structures with a fixed thickness of the PbTe layer (40 nm) and varying thicknesses of the Bi layer (0-60 nm) as well as in the thin Bi films on mica [3-8], the thickness dependences of the thermoelectric properties at room temperature exhibit an oscillatory behavior with period $\Delta d$ = 25±2 nm. However, the studies [11] were carried out on the PbTe/Bi structures without a cover layer. Yet, earlier we had shown [12] that the exposure of sufficiently thin (< 200-300 nm) IV-VI films to air even at room temperature leads to a significant change in the thermoelectric properties, in particular, a change in the dependences of the thermoelectric properties on thin film thickness. That is why, although properties of Bi films on mica practically do not change even after a long exposure to air at room temperature, at a small thickness of the Bi layer oxygen from atmosphere can penetrate through this layer into PbTe and cause changes in the properties of the heterostructure.

The goal of the present work is the investigation of the dependences of the thermoelectric properties on Bi layer thickness for the mica/PbTe/Bi heterostructures covered with $Al_2O_3$ layer to prevent penetration of oxygen into PbTe layers.

**Experimental details**

Two-layer PbTe/Bi structures were prepared by the thermal evaporation in vacuum ($10^{-5}$-$10^{-6}$ Pa) of *n*-PbTe crystals with the electron concentration $n$=1.0·$10^{17}$ cm$^{-3}$ on mica substrates at $T_S$ = (520±5) K, cooling of PbTe layer down to 380 K and subsequent deposition of Bi at this temperature. The upper Bi layer was covered with an $Al_2O_3$ layer with thickness $d$≈20 nm by electron-beam evaporation.

The thickness of PbTe layer was fixed ($d_{PbTe}$=50 nm) whereas the Bi layer thickness was varied in the range $d_{Bi}$ = 0-80 nm. The condensation rate was 1-3 Å/s. The layer thickness was controlled using a calibrated quartz resonator. The crystal structure of the films was studied by electron microscopy and electron diffraction. The electrical conductivity σ and Hall coefficient $R_H$ were measured in the temperature range 80-300 K by a conventional dc method, with an error not exceeding ± 5 %. The Hall mobility was

calculated as $\mu_H = R_H \cdot \sigma$. The Seebeck coefficient S was determined relative to Cu with an accuracy ~ 3 %.

**Results**

Electron microscopy studies showed that the PbTe films grow on mica substrate epitaxially in an island like fashion predominantly in the (111) orientation, which is in good agreement with the results of the previous studies [13]. On the surface of (111) oriented PbTe crystallites, Bi grows epitaxially in a layer-by-layer fashion in the (111) orientation. In this case the mismatch of Bi and PbTe crystal lattices is only ~ 0.3 %.

In Figs 1, a-d, the temperature dependences of σ, S, $R_H$ and thermoelectric power factor $P=S^2\cdot\sigma$ for mica/PbTe/Bi/$Al_2O_3$ heterostructures are shown. It is seen that with increasing Bi layer thickness the behavior of the dependences σ(T) changes in a regular way. For $d_{Bi}$=1 and 2 nm electrical conductivity increases in the entire investigated temperature range. For $d_{Bi}$=8 nm, first σ increases with increasing temperature (up to ~100 K), and after that σ practically remains constant. In the heterostructures with $d_{Bi}$=16 nm, σ does not change in the entire temperature range of measurements. Under further increasing $d_{Bi}$ ($d_{Bi}$=25 nm, 32.5 nm), first σ decreases with increasing temperature like in bulk Bi crystals, then at still larger thicknesses ($d_{Bi}$=44.5 nm, 52.5nm) the σ(T) dependences represent curves with a minimum at ~200 K, and at $d_{Bi}$=59 nm σ increases in the whole temperature range under investigation, like in Bi films grown on mica substrates [3-8].

The Hall coefficient decreases as temperature increases (Fig. 1,b). At thicknesses $d_{Bi}$ smaller than ~ 30 nm, the sign of $R_H$ remains negative in the entire temperature range, which corresponds to the sign of $R_H$ in PbTe thin films with a protective layer. However, under further increase in $d_{Bi}$, with increasing temperature, the sign of $R_H$ for a number of films changed to positive at ~ 125 - 200 K. At the same time because of the oscillatory character of the thickness dependences of the properties, in particular $R_H$, for some thicknesses, even when the condition $d_{Bi} > 30$ nm was fulfilled (for example, at $d_{Bi}$ =40.5 nm; 52.5 nm), the sign of $R_H$ remained negative in the entire investigated temperature range, but the character of the dependence became more complex. The behavior of the temperature dependences of the Hall mobility $\mu_H$ was practically similar to the behavior of the $R_H$(T) dependences. The difference consisted in the fact that in those heterostructures, where the change in the $R_H$ sign occurred, the inversion point corresponded to the minimum in the $\mu_H$(T) dependences.

The Seebeck coefficient had negative sign for all heterostructures and increased with temperature in the whole temperature range (Fig. 1,c). At the smallest Bi layer thicknesses ($d_{Bi}$=1-2 nm) the behavior of the S(T) dependences and the value of S were very similar to those observed in PbTe thin films with $d$ ~50 nm. However, under increasing $d_{Bi}$ both values of S and the character of change in S with changing temperature resembled the behavior of the Seebeck coefficient in thin Bi films with the same thickness.

It is seen from Fig.1,d that with increasing temperature thermoelectric power factor ($P=S^2\cdot\sigma$) increases, reaching its maximum value at 300 K.

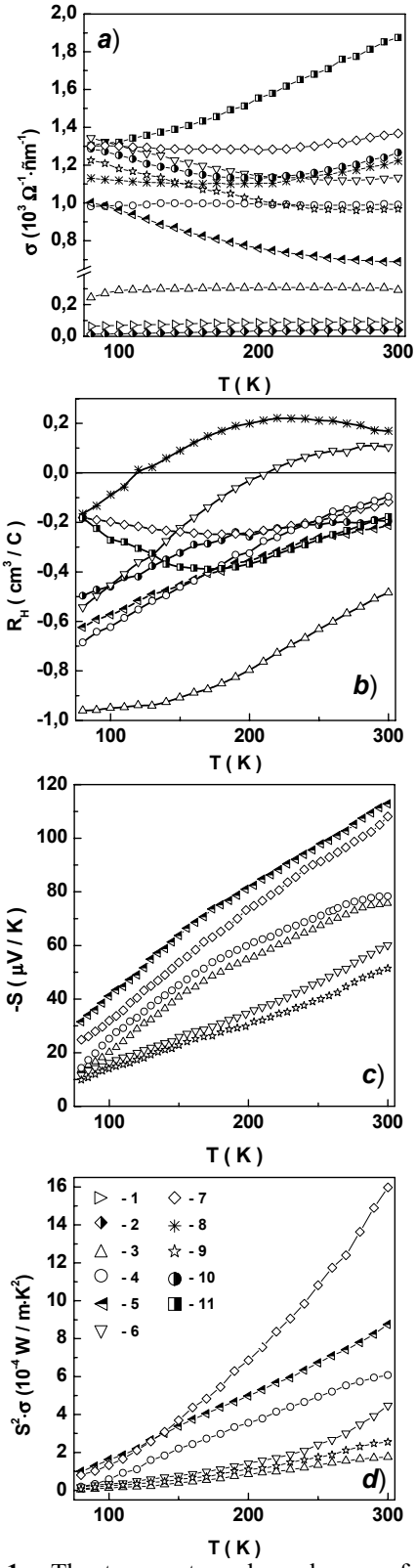


**Figure 1**. The temperature dependences of the electrical conductivity σ (a), the Hall coefficient (b), the Seebeck coefficient S (c), and thermoelectric power factor $S^2\sigma$ (d) of the mica/PbTe/Bi/ $Al_2O_3$ structures ($d_{PbTe}$.= 50 nm).

$d_{Bi}$ : 1 - 1 nm ; 2 - 2 nm; 3 - 8 nm ; 4 - 16 nm; 5 - 25 nm; 6 - 32.5 nm;7 - 40 nm ;8 - 44.5 nm ; 9 - 50.5 nm; 10- 52.5 nm ; 11-59 nm

In Fig. 2, the dependences of σ, $R_H$, and $S^2\sigma$ on the Bi layer thickness in mica/PbTe/Bi/$Al_2O_3$ structures at room temperature and S(*d*) dependences at 80 and 300 K are presented. It is seen that the dependences exhibit an oscillatory behavior with oscillation period $\Delta d \approx 15\pm2$ nm. As was mentioned above, in the absence of a protective cover layer the oscillation period was $\Delta d$=25±2 nm [11]. $R_H$ oscillations are accompanied by the sign change: increase in $d_{Bi}$ at a fixed temperature leads to a drop in the absolute value of $R_H$, subsequent change in the sign (from negative to positive) and further oscillating behavior near certain constant value with possible change of the sign in the process of oscillating.

It is seen from Fig. 2, a that the oscillatory character of the *d*-dependences of the thermoelectric properties with the same $\Delta d$ is preserved in these heterostructures at low temperatures.

At room temperature the maximum value of $S^2\sigma$ (~$16\cdot10^{-4}$ W/m·K$^2$) corresponds to $d_{Bi} \approx 40$ nm. In a mica/PbTe/Bi/$Al_2O_3$ structure the value of $S^2\sigma$ is approximately twice as large as that in a thin Bi film on a mica substrate [8].

**Discussion**

Thus, it was found that in mica/PbTe/Bi/$Al_2O_3$ structures with a fixed thickness of the PbTe layer and varied Bi layer thickness, as well as in thin Bi films, the $d_{Bi}$ - dependences of the galvanomagnetic and thermoelectric properties exhibit oscillatory behavior. However, the character of the dependences and the oscillation periods for the PbTe/Bi structures differ from those for thin Bi films.

It is natural to assume that the oscillatory behavior of the observed *d*-dependences is due to the size quantization of the charge carrier spectra in the trigonal direction when Bi layer thickness becomes comparable to the Fermi wavelength $\lambda_F$.

The Bi layer sandwiched between mica, on the one hand, and air (or $Al_2O_3$), on the other hand, provides a QW, within which carriers are effectively confined in the trigonal direction perpendicular to the plane of the thin film. The simplest model which takes into consideration the confinement of the transverse electron motion, consists in approximating a film by a rectangular potential well with infinitely high walls. In the model the energy levels are given as

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

where $m_z^*$ is the effective mass for motion perpendicular to the QW, and $k_x$, $k_y$ and $m_x^*$, $m_y^*$ are the components of the wave vector and effective mass for motion parallel to the QW, N is the quantum number. One can then make an approximate estimate of the oscillation period $\Delta d$ [2]:

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

This model can be successfully used when the Bi layer is placed between two insulators. Knowing $m_z^*$ and $\varepsilon_F$, one can estimate $\Delta d$ using Eq. (2). Substituting the values of $m_z^* = 0.02\ m_0$ and $\varepsilon_F = 0.02$ eV in Eq. (2) [11], we obtain $\Delta d$=30±5 nm, which is in good agreement with the value of $\Delta d$ obtained experimentally in our work [8] as well as the values reported by other authors.

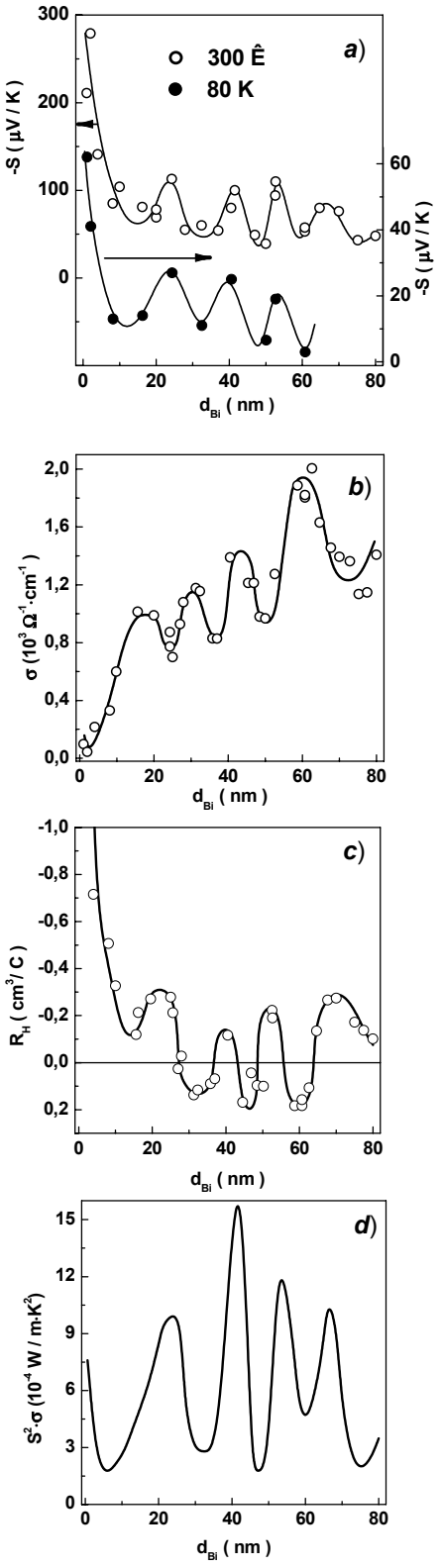


**Figure 2**. The dependences of the Seebeck coefficient S (a), Hall coefficient $R_H$ (b), electrical conductivity σ (c), and thermoelectric power factor $S^2\sigma$ (d) on Bi layer thickness $d_{Bi}$ in mica/PbTe/Bi/$Al_2O_3$ structures ($d_{PbTe}$=50 nm). b,c,d:-300K

The oscillation period observed in this work for mica/PbTe/Bi/ $Al_2O_3$ heterostructures ($\Delta d$=15±2 nm) is smaller than that for Bi films on mica substrates ($\Delta d$=30±5 nm). The observed effect can be explained as follows.

Taking into account the ratio of the PbTe and Bi work functions $\chi$ ($\chi_{Bi} < \chi_{PbTe}$), one can conclude that the PbTe layer is a barrier only for holes, and electrons must move from Bi into PbTe until the space charge region is formed at the interface. As a rule, for a degenerate semiconductor – metal heterojunction the width of the region of the energy band bending does not exceed several unit cell parameters, and such heterojunction is tunnel transparent. Assuming that the contact is ideal, one can neglect electron scattering on the interface and assume that the well represents a single well with a flat bottom and consists of two regions with different effective masses of electrons divided just by the transitional region between Bi and PbTe crystal lattices. Using Eq. (2), one can estimate $\Delta d$ in such a composite well, substituting the values of average $m_z^*$ and corresponding $\varepsilon_F$ in this equation. The value of effective mass of electrons in PbTe ($m_z^*=0.024 \cdot m_o$ [14]) is somewhat higher than that in Bi ($m_z^*=0.01\text{-}0.02 \cdot m_o$). The same is true for the Fermi energy. Both these factors can lead to a decrease in $\Delta d$ in the PbTe/Bi heterostructure in comparison with thin Bi film.

In Bi, apart from electrons, there are holes *(n=p)*, which are also located in the potential well. For the holes, the Bi layer is an ordinary asymmetrical potential well with considerably differing heights of the walls, and the Bi layer thickness is equal to the QW width. The effective mass of Bi holes significantly exceeds the mass of electrons, that is why $\Delta d$ must be smaller.

The smaller $\Delta d$ in the heterostructures covered with an $Al_2O_3$ layer as compared with $\Delta d$ in heterostructures without a cover layer ($\Delta d$=15±2 nm and $\Delta d$=25±2 nm, respectively) can be attributed to the fact that due to the protective layer oxygen does not penetrate into the PbTe layer through the thin Bi layer, does not create additional acceptor states and thus, does not change charge carrier concentration. A decrease in the electron concentration leads to a decrease in the Fermi energy and, consequently, to an increase in $\Delta d$.

**Conclusions**

Thermoelectric properties of the mica/PbTe/Bi/$Al_2O_3$ heterostructures as functions of Bi layer thickness ($d_{Bi}$=1-80 nm) at the fixed PbTe layer thickness ($d_{PbTe}$=50 nm) in the temperature range 80-300 K were investigated.

It was found that in the mica/PbTe/Bi/$Al_2O_3$ heterostructures as well as in thin Bi films on mica, the *d*-dependences of the thermoelectric properties exhibit oscillatory behavior with the oscillation period $\Delta d$=15±2 nm.

The experimental data were analyzed within the framework both of the model assuming infinite barrier and complete confinement of the wave function within the quantum well and of the model assuming non-identity and finite barrier heights and widths.

The smaller $\Delta d$ in comparison with the oscillation period in Bi/mica thin films ($\Delta d$=30±5 nm) is explained by the presence of the PbTe layer between thin Bi film and mica, which leads to an increase in the average values of the effective mass and Fermi energy.

It is shown that in the PbTe/Bi structures one can attain higher values of the thermoelectric power factor compare to those in Bi films.

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