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Abstract

The thermoelectric and galvanomagnetic properties of nanometer structured epitaxial films and foliated layers based on bismuth and antimony chalcogenides were investigated, and an increase in the figure of merit $Z$ up to $3.85 \times 10^{-3} \text{ K}^{-1}$ was observed in the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ films over the temperature range of 180–200 K. It is shown that an increase in the Seebeck coefficient and the change in the slope on temperature, associated with changes in the effective scattering parameter of charge carriers and strong anisotropy of scattering in the films, lead to enhance power factor due to the growth of the effective mass of the density of states. These features are consistent with the results of research of oscillation effects in strong magnetic fields at low temperatures and research of Raman scattering at normal and high pressures in the foliated layers of solid solutions $(\text{Bi, Sb})_2(\text{Te, Se})_3$, in which the topological Dirac surface states were observed. The unique properties of topological surface states in the investigated films and layers make topological insulators promising material for innovation nanostructured thermoelectrics.

Keywords: thermoelectric films, topological surface states, power factor, scattering on interphase, block boundaries

1. Introduction

Thermoelectrics based on bismuth and antimony chalcogenides are well known and have been extensively studied for their excellent thermoelectric properties [1–3]. Recently, the nanostruc-
tured (Bi,Sb)$_2$(Te,Se)$_3$ epitaxial films were shown to possess an enhanced thermoelectric figure of merit $Z$ compared to corresponding bulk crystals due to mechanical stresses and intensive phonon scattering at the grain boundaries. Lattice thermal conductivity of heteroepitaxial nanostructured films may be substantially diminished, as compared to corresponding bulk crystals, due to acoustic phonon scattering by grain and interface boundaries. Boundaries and strain may be easily induced in thin Bi$_2$Te$_3$-based films grown on mismatched substrates. In contrast to point defects, which suppress heat transfer by short wave phonons, grain and interface boundaries are efficient in scattering of long wave ones. That is why, investigation of thin films with different structure and level of mechanical stresses looks quite important for development of thermoelectric materials with enhanced performance.

At the current stage, a new property of these materials, known as topological insulator, became one of the important subjects of the investigations [4–6]. These novel quantum states are the result of the electronic band inversion due to strong spin-orbit interaction, so the bulk becomes insulating and the surface displays an unusual metallic electronic surface state of Dirac fermions with linear dispersion and spin texture that ensures high mobility of charge carriers due to the lack of backscattering on defects. The nanostructured films of topological materials [7, 8] theoretically proved the possibility of formation of topological excitons that can condense in a wide temperature range with the appearance of superfluidity and thus a significant increase in the mobility of the charge carriers. Currently, there is only a preliminary report on the pilot study of the heterostructure Sb$_2$Te$_3$/Bi$_2$Te$_3$, which assumes the realization of exciton condensation [9]. The theoretical model [10] for topological thermoelectrics based on the Landauer transport theory shows that the value of the Seebeck coefficient and thermoelectric efficiency is determined by the ratio of the mean free path of Dirac fermions to the mean free path of bulk electrons. According to the proposed model, an increase in the contribution of the surface states and the energy dependence of the lifetime of the electronic states provide the maximum amount of the Seebeck coefficient and the increase in the thermoelectric efficiency. Experimental research of transport of thin films (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ [11] carried out in a wide range of compositions, and temperatures have confirmed validity of this model. It follows that the study of surface states of Dirac fermions is promising for thermoelectricity to improve the energy conversion efficiency of nanostructured thermoelectrics. This chapter includes the thermoelectric properties under normal conditions and under high pressure, galvanomagnetic and optical properties of nanostructured films based on Bi$_2$Te$_3$, obtained by different methods, in order to determine the possible effect of the topological surface states of Dirac fermions depending on the composition, the Seebeck coefficient and temperature.

2. Features of formation and structure of the grown (Bi,Sb)$_2$Te$_3$ films

Because of incongruent evaporation/sublimation of (Bi,Sb)$_2$Te$_3$ solid solutions and pronounced volatility of tellurium at temperatures higher than 400°C, formation of stoichiometric epitaxial films of bismuth and antimony chalcogenides is a nontrivial task. Hot wall technique [12, 13] was used to grow stoichiometric Bi$_{0.5}$Sb$_{1.5}$Te$_3$ layers with a thickness of 30–500 nm.
Structure of the grown thermoelectric films was investigated by X-ray (Philips X'pert MRD, CuKα1, ω/2Θ- and φ-scans). Surface morphology of the grown (Bi,Sb)₂Te₃ films was studied by atomic force microscopy (Nanoscope IIIa, tipping mode). Nanostructured epitaxial thermoelectric films of (Bi,Sb)₂Te₃ were grown by hot wall technique on mica (muscovite) substrates. Usage of a mica substrate promotes small in-plane misorientation of the blocks in the BST film, but relatively high deposition temperature is in favor of low density of defects in their volume. Thickness of the grown thermoelectric layers was in the range of 30–500 nm. Substrate temperature during thermoelectric film formation was roughly 70°C less than temperature of sublimating stoichiometric Bi₀.₅Sb₁.₅Te₃ burden. X-ray ω/2Θ scans were traced for the grown Bi₀.₅Sb₁.₅Te₃ films when plane including incident and reflected Roentgen beams was in plane normal to (000.1) of mica or (101.₅) of the thermoelectric layer (see Figures 1 and 2). From obtained scans follow that c-axis in the (Bi,Sb)₂Te₃ films grown on mica by hot wall technique was normal to substrate plane. Driving force for preferential orientation of c-axis in the grown films along normal to a substrate plane was substantial anisotropy of a surface free energy of the bismuth and antimony chalcogenides. From X-ray, φ-scan traced for a (101.₅) Bi₀.₅Sb₁.₅Te₃ reflex, see insert in Figure 1, follows that thermoelectric films grown on mica were well in-plane preferentially oriented as well. In-plane disorientation of blocks in the films was ~0.3°. (The estimation obtained from full width at half of a maximum of a peak on the φ-scan. Roughly, equidistant system of growth steps was clearly detectable at the film surface (see Figure 2), at AFM image of free surface of the (Bi,Sb)₂Te₃ film grown on mica. Height of the growth steps was about 1 nm.

Figure 1. X-ray ω/2Θ scan traced for the grown Bi₀.₅Sb₁.₅Te₃ film when plane including incident and reflected Roentgen beams was in plane normal to (000.1) plane of substrate. Insert plots φ-scan of a (101.₅) reflex from the same film.
3. Thermoelectric properties

Efficiency of thermoelectric energy conversion is dependent on figure of merit ($Z$) of the used materials ($Z = S^2 \sigma/\kappa$, where $S$—Seebeck coefficient, $\sigma$—electrical conductivity, and $\kappa$—thermal conductivity) with electron and hole conductance. Thermoelectric properties of bismuth telluride and related solid solution $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ heteroepitaxial nanostructured films were investigated below room temperature. The temperature dependences of the Seebeck coefficient $S$ and the electroconductivity $\sigma$ of the $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ films are shown in Figure 3. The electrical conductivity of bulk samples grows more sharply with temperature decrease for both $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ solid solution than for films (Figure 3, curves 6, 8 and 5, 7). The observed decrease in electrical conductivity in the films is related to the influence of scattering on interphase and intercrystallite grain boundaries.

The temperature dependences of the Seebeck coefficient (Figure 3), unlike such electrical conductivity dependences, are located higher for films than for bulk $\text{Bi}_2\text{Te}_3$ (curves 1, 2) and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (curves 3, 4). The highest power factor values were obtained in submicrometer $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ film at $S = 242 \mu\text{V K}^{-1}$ over the temperature range of 80–300 K and in the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ film at $S = 234 \mu\text{V K}^{-1}$ over the range of 130–260 K (Figure 4, curves 5, 3). An

Figure 2. X-ray $\omega/2\Theta$ scan traced for the grown $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ film when plane including incident and reflected Roentgen beams was normal to (101.5) plane of the thermoelectric layer. AFM image of free surface of the grown thermoelectric layer is shown on insert.
enhancement of the Seebeck coefficient and change in its temperature dependence slope both indicate the changes of charge carrier scattering mechanisms in grown films [14, 15] compared those to the bulk thermoelectric materials (Figure 4, curves 1–5 and curves 6–9).

Figure 3. Temperature dependences of the Seebeck coefficient $S$ (1–9), electroconductivity $\sigma$ (10–18) in heteroepitaxial films (1–5, 10–14), and bulk samples (6–9 and 15–18) of $Bi_{0.5}Sb_{1.5}Te_3$ (1–3, 6–9, 10–12, 16–18) and $Bi_2Te_3$ (4, 5, 13, 14).

Figure 4. Temperature dependences of power factor $S^2\sigma$ for heteroepitaxial films (1–5) and bulk samples (6–9) of $Bi_{0.5}Sb_{1.5}Te_3$ (1–3, 6–9) and $Bi_2Te_3$ (4, 5) for $S$ ($\mu$V K$^{-1}$) at room temperatures: 1—214, 2—224, 3—242, 4—203, 5—234, 6—214, 7—207, 8—233, 9—221.
The results of the study of galvanomagnetic and thermoelectric properties in epitaxial films have been used to determine the average effective mass of the density of states $m/m_0$ and mobility $\mu_0$ of charge carriers taking into account the effective scattering parameter in the model with an isotropic relaxation time similar to the bulk thermoelectrics [14, 16, 17]. Calculations of the effective mass $m/m_0$ and mobility $\mu_0$ have showed that the effective mass of the films is higher than in the bulk samples (Figure 5, curves 1–5 and 6, 7) with slight reduction of the mobility in the films (Figure 5, curves 13, 14). From the study of the galvanomagnetic properties, the behavior of the effective mass and mobility in the films was found to depend on the scattering mechanism of charge carriers and the parameters of the ellipsoidal constant energy surfaces [13, 18].

Figure 5. Temperature dependences of the density-of-states effective mass $m/m_0$ (1–7) and charge carrier mobility $\mu_0$ (8–14) for films (1–5, 8–12) and bulk samples (6, 7, 13, 14) of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ (1–3, 6–7, 8–10, 13–14) and Bi$_2$Te$_3$ (4, 5, 11, 12).

The product $(m/m_0)^{3/2}\mu_0$, proportional to the figure of merit $Z$, is higher for films than bulk thermoelectrics due to growth of the effective mass of the density states, which determines an increase in power factor of the films (Figure 6). At temperatures below 200 K, an increase in the $(m/m_0)^{3/2}\mu_0$ was observed in the solid solution Bi$_{0.5}$Sb$_{1.5}$Te$_3$ at a value of the Seebeck coefficient $S = 242$ $\mu$V K$^{-1}$ at room temperature (Figure 6, curve 3).

An estimated value of the figure of merit $Z$ in heteroepitaxial Bi$_{0.5}$Sb$_{1.5}$Te$_3$ film increases to $3.85 \times 10^{-3}$ K$^{-1}$ over the temperature range of 180–200 K. Such increase in $Z$ is approximately by 60% compared to conventional bulk materials and by 20% compared with multicomponent bulk thermoelectrics optimized for temperatures below 200 K [19, 20]. Reduction in thermal conductivity in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ films can reach 20–30% due to additional scattering of charge carriers in the intercrystallite and interphase boundaries [3, 21] that give an additional rise in the figure of merit.
4. Mechanisms of charge carriers scattering

The charge carrier scattering mechanisms of Bi$_2$Te$_3$ and solid solution Bi$_{0.5}$Sb$_{1.5}$Te$_3$ films were investigated from analysis of the galvanomagnetic coefficients including transverse and longitudinal components of magnetoresistivity tensor $r_{ijkl}$, electroresistivity $r_{ij}$, and Hall coefficient $r_{ijk}$ within many-valley model of energy spectrum for isotropic scattering mechanism [14, 18, 22]. A relaxation time for isotropic carrier scattering depends on energy $E$ by power law: $\tau = \tau_0 E^r$, where $\tau_0$ is an energy independent factor and $r$ is the scattering parameter. The least square analysis of experimental galvanomagnetic coefficients for isotropic scattering mechanism permits to determine the degeneracy parameter $\beta_d$ [13, 15]. The dependence of $\beta_d$ on temperature obtained in magnetic field at $B = 10$ T is in agreement with that at $B = 14$ T (Figure 7, curves 1, 2).

The parameter $\beta_d$ depends on temperature more sharply in the film than in the bulk Bi$_{2-x}$Sb$_x$Te$_3$ solid solutions (Figure 7, points 3, 4). The temperature dependence of the $\beta_d$ of the films is supposed to be explained by an additional charge carrier scattering on interphase and intercrystallite boundaries of monocrystalline grains of the films. As shown in Figure 8, the dependence of the degeneracy parameter $\beta_d$ on the reduced Fermi level $\eta$ shows that the $\beta_d$ values in films are less than in bulk materials. Therefore, the degeneracy of films is smaller than bulk thermoelectrics [13].

The effective scattering parameter $r_{\text{eff}}$ and the reduced Fermi level $\eta$ were calculated by Nelder-Mead least square method from the temperature dependences of the degeneracy parameter $\beta_d$ and the Seebeck coefficient $S$ [14, 24]. As compared to bulk materials, the values of the parameter $r_{\text{eff}}$ are considerably different from the value $r = -0.5$, specific for an acoustic phonon scattering mechanism due to sharper energy dependence of electron relaxation time in the films, that is, explained by an additional charge carriers scattering on interphase and intercrystallite boundaries of epitaxial films (Figure 8).
Figure 7. Temperature dependence of the degeneracy parameter $\beta_d$ (1–2) in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ film. $\beta_d$ is (1) 10 T and (2) 14 T. Points for bulk solid solutions: 3 [23], 4 [14].

Figure 8. The degeneracy parameter $\beta_d$ (1–6) and the effective scattering parameter $r_{\text{eff}}$ (7–12) on reduced Fermi level $\eta$ in Bi$_2$Te$_3$ (1, 7), Bi$_{0.5}$Sb$_{1.5}$Te$_3$ (2, 8) films, and Bi$_{2-x}$Sb$_x$Te$_3$$_{-y}$Se$_y$, ($x = 1.2$, $y = 0.09$), (3, 4, 9, 10); Bi$_{2-x}$Sb$_x$Te$_3$$_{-y}$Se$_y$, ($x = 1.3$, $y = 0.07$), (5, 11); Bi$_{2-x}$Sb$_x$Te$_3$ ($x = 1.6$), (6, 12) bulk solid solutions.

The materials under study exhibit both anisotropy of the transport properties and anisotropy of charge carrier scattering. In a six-valley model of the energy spectrum with anisotropic scattering of charge carriers, the components of the relaxation time tensor $\tau(\epsilon)$ can be presented as $\tau_{ij} = \phi(\epsilon)\tau_{ij}$ where $\phi(\epsilon)$ is an isotropic function depending on $\mu$ and $\tau_{ij}$ is an anisotropic multiplier that is independent on energy. The ratios of the $\tau(\epsilon)$ tensor components
were determined in the temperature interval from 10 to 300 K [15, 17, 25, 26]. The relation between the τ(ε) components was found as follows: τ_{22} > τ_{11} > τ_{33}, and charge carrier scattering along bisector directions was dominant in the film as in the bulk thermoelectrics at low temperatures [17, 25, 27]. The ratio τ_{22}/τ_{11} in the Bi_{2-x}Sb_{x}Te_{3} film is increased along bisector axes, but the ratio τ_{33}/τ_{11} is diminished along the trigonal direction in contrast to corresponding bulk thermoelectrics at low [17, 25] and room [27] temperatures. The value τ_{23} is near the same as τ_{11} for the films, while for bulk materials τ_{23} is less than τ_{11}. These specific features of charge carriers scattering lead to increase in the slope of the Seebeck coefficient dependence on temperature (Figure 3) and to enhance the thermoelectric power factor for films. Optimization of structure and charge state of the grains and/or interface boundaries might be in favor of a large thermoelectric power factor and figure of merit.

5. Thermoelectric properties under high pressure

The thermoelectric properties of n-Bi_{2}Te_{3-x-y}Se_{x}S_{y} solid solutions with atomic substitutions in the tellurium sublattice at (x = 0.27, 0.3, y = 0, and x = y = 0.09) and p-Bi_{2}Te_{3} were studied under pressure of 8 GPa on submicron layer samples at room temperature using the technique described in Ref. [28–30]. It was found that the Seebeck coefficient decreases and the electroconductivity increases with increase in pressure, but the power factor S^2/σ increases for all compositions, and becomes maximum at pressures of 3–4 GPa (Figure 9). The effective mass m/m_0 and mobility μ_0 in the n-Bi_{2}Te_{3-x-y}Se_{x}S_{y} and p-Bi_{2}Te_{3} films were obtained taking into account of the change in the scattering mechanism depending on the solid solution composition and carrier density [14, 31]. With increasing pressure P, the effective mass m/m_0 [29] in the n- and p-type compositions decreases (Figure 10). For p-Bi_{2}Te_{3} and for composition at x = y = 0.09, the dependence of m/m_0 and μ_0 on P has an inflection at pressures about 3–4 GPa [29, 30]. These inflections in the dependences of m/m_0 and μ_0 on P, observed at nearly the same pressure as for the maximum value of power factor S^2/σ, were explained by the influence of topological phase transition at room temperature (Figure 10, curves 3, 7).

The existence of the topological transition in Bi_{2}Te_{3} is confirmed by precise diffraction studies of the pressure dependence of lattice parameters [32], abrupt change in the elasticity modulus and its derivative [33], and the change in the Fermi surface section from study of de Haas-van Alphen [32, 34]. This topological transition in Bi_{2}Te_{3} was also confirmed by study of Raman spectroscopy under high pressure [35]. The maximum of the product (m/m_0)^{3/2}μ_0 proportional to the figure of merit, was observed at about the same pressure range as for the topological transition (Figure 11). The estimations of the thermal conductivity κ in the n- and p-type materials show that increase in κ in the pressure range ~3–4 GPa is not higher than 50% [36]. But the power factor of n-Bi_{2}Te_{3-x-y}Se_{x}S_{y} solid solutions and the p-type compositions Bi_{2-x}Sb_{x}Te_{3} [29] increases under pressure more significantly, and thus, enhancement of the figure of merit values can reach 50–70% taking into account the influence of topological transition at room temperature.
Figure 9. Pressure dependences of power factor of the $n$-Bi$_2$Te$_{3-x-y}$Se$_x$S$_y$ solid solution layers; $x, y$ are (1) 0.27, 0; (2) 0.3, 0; (3) 0.09, 0.09 and p-Bi$_2$Te$_3$ (4).

Figure 10. Pressure dependences of the effective mass $m/m_0$ and the mobility $\mu_0$ of the $n$-Bi$_2$Te$_{3-x-y}$Se$_x$S$_y$ solid solutions; $x, y$ are (1, 5) 0.27, 0; (2, 6) 0.3, 0; (3, 7) 0.09, 0.09 and p-Bi$_2$Te$_3$ (4, 8).

Figure 11. Pressure dependences of the product $(m/m_0)^{3/2}\mu_0$ of the $n$-Bi$_2$Te$_{3-x-y}$Se$_x$S$_y$ solid solutions; $x, y$ are (1) 0.27, 0; (2) 0.3, 0; (3) 0.09, 0.09 and p-Bi$_2$Te$_3$ (4).
6. Quantum oscillations of magnetoresistance

Quantum oscillations of the magnetoresistance associated with surface electronic states in three-dimensional topological insulators have been studied in $p$-type Bi$_2$Te$_3$ films [37] in strong magnetic fields from 6 to 14 T at low temperatures (Figure 12). The main parameters of surface charge carriers in the films (Tables 1 and 2) were determined by analyzing the temperature dependences of normalized amplitude of magnetoresistance oscillations [38]. The phase shift of oscillation period, evaluated by extrapolation of dependence of the Landau level indexes ($n = 2, 3, 4, 5$) (Figure 12) on inverse magnetic field in the limit of $1/B = 0$, was found to be consistent with the value of $\pi$ Berry phase, which is characteristic of surface states of Dirac fermions with linear dispersion [37]. The obtained parameters of the surface states of charge carriers in the nanostructured materials under consideration are important for the development of new high-performance thermoelectrics. The parameters of the surface states of Dirac fermions, such as the mean free path and the energy dependence of lifetime of the charge carriers at the surface, the Fermi energy and respective position of the Fermi level, have a specific influence on the Seebeck coefficient and power factor.

![Figure 12. Magnetoresistance dependence $\rho_{xx}$ (1–3) on magnetic field B and quantum oscillations $\Delta \rho_{xx}$ (4–6) dependence on inverse magnetic field 1/B; $\rho_{xx}$ at the temperatures: 1, 4–1.6 K, 2, 5–4.2 K, 3, 6–10 K and the Landau level index ($n = 2, 3, 4, 5$) corresponding to the minimum amplitudes of the oscillations.](image-url)

| $v_f$, THz | $v_F$, $10^4$, m/s | $E_F$, meV | $\mu$, m$^2$/Vs | $l_F$, nm | $\tau$,$10^{-13}$, s | $T_D$, K |
|---|---|---|---|---|---|---|
| 2.0 | 1.06 | 19.3 | 0.33 | 59 | 5.5 | 2.2 |

Table 1. Cyclotron resonance frequency $v$, Fermi velocity $v_F$, Fermi energy $E_F$, charge carrier mobility $\mu$, mean free path of charge carriers $l_F$, the relaxation time $\tau$, and Dingle temperature $T_D$ of the Bi$_2$Te$_3$ films.
Table 2. Frequency of quantum oscillations of the magnetoresistance $F$, cross section of the Fermi surface $S(k_F)$, Fermi wave vector $k_F$, and surface concentration of charge carriers $n_F$ in the Bi$_2$Te$_3$ films.

| $F$, T  | $S(k_F)$, nm$^{-2}$ | $k_F$, nm | $n_F \times 10^{12}$, cm$^{-2}$ |
|---------|---------------------|-----------|-------------------------------|
| 24      | 0.23                | 0.27      | 0.58                          |
| 30 [39] | 0.29                | 0.30      | 0.72                          |
| 41.7 [40]| 0.40               | 0.36      | 1.0                           |
| 50 [39] | 0.48                | 0.39      | 1.21                          |

7. Raman spectra

The resonance Raman scattering and morphology of an interlayer van der Waals surface (0001) in thin layer films of chalcogenides based on bismuth and antimony were studied in dependence on the composition, the Seebeck coefficient, and the thickness of the samples. Raman spectra of optical phonons $E_g^2$, $A_{1u}^2$, and $A_{1g}^2$ in thin layers of binary compound $n$-Bi$_2$Te$_3$ and alloys Bi$_{2-x}$Sb$_x$Te$_3$ and Bi$_2$Te$_3$-ySe$_y$ in heteroepitaxial films of $p$-Bi$_2$Te$_3$ and chemically foliated solid solutions Bi$_{2-x}$Sb$_x$Te$_3$-ySe$_y$ are shown in Figures 13 and 14. The morphology of the interlayer surfaces (0001) of these samples was studied by atomic force microscopy.

Figure 13. Raman spectra of mechanically split thin layers of $n$-Bi$_2$Te$_3$ (1-1, 1-2), $n$-Bi$_2$Te$_{2.88}$Se$_{0.12}$ (2-1, 2-2) and $n$-Bi$_{2-x}$Sb$_x$Te$_3$ (3-1, 3-2, 4-1, 4-2). (1-1, 1-2): $S = -270 \mu$V K$^{-1}$, $R_q = 0.45$ nm, $H_a = 1.75$ nm. (2-1, 2-2): $S = -285 \mu$V K$^{-1}$, $R_q = 3.8$ nm, $H_a = 8$ nm. (3-1, 3-2): $S = -305 \mu$V K$^{-1}$, $R_q = 4.6$ nm, $H_a = 15$ nm. (4-1, 4-2): $S = -315 \mu$V K$^{-1}$, $R_q = 2.9$ nm, $H_a = 2.3$ nm.
Figure 14. Raman spectra of the thin films of n-Bi$_{1.6}$Sb$_{0.4}$Te$_{2.91}$Se$_{0.09}$ (5-1, 5-2), p-Bi$_2$Te$_3$ (6-1, 6-2) and foliated Bi$_{0.9}$Sb$_{1.1}$Te$_{2.94}$Se$_{0.06}$ (7-1, 7-2) solid solution. (5-1, 5-2): $S = -280 \, \mu V \, K^{-1}$, $R_q = 0.36 \, nm$, $H_a = 1.55 \, nm$. (6-1, 6-2): $R_q = 0.56 \, nm$, $H_a = 1.8 \, nm$. (7-1, 7-2): $S = -280 \, \mu V \, K^{-1}$. (7-1) dissolution time $t = 150 \, h$, $R_q = 36 \, nm$, $H_a = 180 \, nm$. (7-2) $t = 200 \, h$, $R_q = 26 \, nm$, $H_a = 80 \, nm$.

The roughness $R_q$ and $H_a$ corresponding to the maximum of the distribution function of nanofragment heights on the surface of samples [41] are indicated in the captions of Figures 13 and 14.

The appearance of the inactive phonons $A_{1u}^2$ in the Raman spectra, caused by a violation of the inversion symmetry of the crystal, was revealed at decreasing sample thickness and also at high pressure for which topological phase transition in Bi$_2$Te$_3$ [35] was observed. Therefore, the occurrence of the $A_{1u}^2$ was explained by the behavior of surface electronic states of Dirac fermions [42, 43]. The relative intensities $I(A_{1u}^2)/I(E_g^2)$ have maximal values in the most thin layers of solid solutions of n-Bi$_2$Te$_{2.7}$Se$_{0.3}$, n-Bi$_{1.6}$Sb$_{0.4}$Te$_{2.91}$Se$_{0.09}$ and epitaxial film of the p-B$_2$Te$_3$ with high Seebeck coefficients (Figure 15) with high quality of the interlayer (0001) surface with small roughness $R_q$ and $H_a$ values (Figures 13 and 14). In the samples n-Bi$_{2.88}$Te$_{2.88}$Se$_{0.12}$ prepared by the Czochralski technique and by the chemical foliated p-Bi$_{0.9}$Sb$_{1.1}$Te$_{2.94}$Se$_{0.06}$, the ratio $I(A_{1u}^2)/I(E_g^2)$, is quite lower (Figure 15, curves 2, 7). So the ratio $I(A_{1u}^2)/I(E_g^2)$ is strongly affected by the used technology, composition and thickness of the samples. The analysis of the Raman spectra of bismuth telluride and its solid solutions allows to optimize the Seebeck coefficients, composition, sample thickness, and morphology of the surface, which provide the significant role of surface states of Dirac fermions at room temperature.
8. Conclusion

The thermoelectric and galvanomagnetic properties of heteroepitaxial films based on bismuth telluride, grown by the hot wall epitaxy method, were investigated. The highest power factor was obtained in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ films. An enhancement of the Seebeck coefficient and change in its temperature dependence slope both indicate the variation in the charge carrier scattering mechanisms compared to the bulk thermoelectric materials. The increase in the power factor and $(m/m_0)^{3/2} \mu_0$, associated with the increase in the effective mass of density of states $m/m_0$ and the reduction in thermal conductivity lead to an increase in the figure of merit $Z$ in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ films up to $3.85 \times 10^{-3}$ K$^{-1}$ over the temperature range of 180–200 K. Such increase in $Z$ is approximately more by 60% compared to similar bulk materials. The charge carrier scattering mechanisms of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ films were investigated from the data on galvanomagnetic properties for isotropic and anisotropic scattering within many-valley model of energy spectrum. For isotropic scattering, the degeneracy parameter $\beta_d$, the effective scattering parameter $r_{\text{eff}}$, and the reduced Fermi level $\eta$ were calculated. As compared to bulk materials, the values of the parameter $r_{\text{eff}}$ are considerably different from $r = -0.5$, specific for an acoustic phonon scattering in the epitaxial films. The difference of the $r_{\text{eff}}$ values is related to an additional charge carriers scattering on interphase and intercrystallite boundaries in the films.

The account of anisotropy of the carrier scattering mechanism has shown that scattering along bisector crystallographic axes is main as compared with corresponding bulk thermoelectrics. Revealed charge carrier scattering peculiarities affect transport properties of the films and might be in favor of a large thermoelectric power factor and the figure of merit.
The studies of the thermoelectric properties of the $n$-Bi$_{2}$Te$_{3-x-y}$Se$_{x}$S$_{y}$ solid solutions under pressure have shown the increase in power factor and product $(m/m_{0})^{3/2}μ_{0}$ which is determined by the growth of the effective mass $m/m_{0}$. In the composition $n$-Bi$_{2}$Te$_{3-x-y}$Se$_{x}$S$_{y}$ ($x = y = 0.09$) and $p$-Bi$_{2}$Te$_{y}$, the change in the slopes of the pressure dependence of the effective mass and the mobility in the range of 3–4 GPa are coincident with maximum of power factor and explained by an influence of the topological transition. An increase in the thermoelectric figure of merit, as compared to normal conditions, was estimated as 50–70% under pressure due to effect of the topological transitions.

Quantum oscillations of the magnetoresistance were revealed at low temperatures $T$ below 10 K in the range of magnetic field from 6 to 14 T in nanostructured submicron Bi$_{2}$Te$_{3}$ films grown by hot wall technique. From the analysis of the magnetoresistance oscillations, the cyclotron resonance frequency, cross-sectional Fermi surface, Landau level indexes and π Berry phase, effective cyclotron mass, Fermi wave vector, velocity and Fermi energy, surface charge carrier concentration, lifetime, and mobility of charge carriers were evaluated. The estimated parameters of topological electronic surface states of nanostructured chalcogenides of bismuth and antimony are of special interest for development of new high-performance thermoelectrics, because the Seebeck coefficient and hence power factor are significantly determined by the basic parameters such as charge carriers lifetime, the mean free path of charge carriers, and Fermi energy level position.

The resonance Raman scattering and morphology of the interlayer surface (0001) of bismuth and antimony chalcogenides were studied at room temperature depending on the composition, the Seebeck coefficient, and the thickness of the layers. Raman shifts and the relative intensities of phonon modes were studied in mechanical and chemical foliated thin layers and epitaxial films of bismuth telluride and its solid solutions. The increase in relative intensity ratio of Raman inactive phonons $I(A_{1u}^{2})/I(E_{g}^{2})$, sensitive to the topological surface states, was observed for thin layers of $n$-Bi$_{2}$Te$_{3}$Se$_{0.3}$ and $n$-Bi$_{1.6}$Sb$_{0.4}$Te$_{2.9}$Se$_{0.09}$ solid solutions at low carrier density with Seebeck coefficient values more than -280 $\mu$V K$^{-1}$ and in epitaxial $p$-Bi$_{2}$Te$_{3}$ film grown by the hot wall method on mica with perfect interlayer surface. Thus, the resonance Raman spectra analysis allows to optimize the composition, thickness, Seebeck coefficient values, and morphology of the layers and films with enhanced contribution of the topological surface states at room temperature, which increases the prospects of application of these thermoelectrics.

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