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Transport properties of the bismuth telluride thin films with different stoichiometry in the temperature range 77–300 K

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The objects of the present study are thin films with thicknesses d = 45–620 nm prepared by thermal evaporation in vacuum from a single source, using undoped p- and n-type Bi_2Te_3 polycrystals with different stoichiometry (60.0 and 62.8 at. % Te, respectively) as a charge, and subsequent condensation on glass substrates at 500 K. The temperature dependences of the Hall coefficient R_H, electrical conductivity σ, and Hall charge carrier mobility μ_H of thin films were obtained in the range 77–300 K. It was found that the films had the same type of conductivity as the initial polycrystals in the entire temperature range studied and, like in the initial crystals, σ and μ_H decreased with increasing temperature. The exponents ν in the $\mu_H(T)$ dependences for the bulk polycrystals were larger than those for the films and increased with increasing d. In contrast to the p-type bulk polycrystals, R_H of the p-type films decreased under increasing temperature. In the n-type Bi_2Te_3, R_H decreased with temperature for both thin films and bulk crystals, however, the character of the $R_H(T)$ dependences for the crystals and films differed. The decrease in R_H with temperature before the range of intrinsic conductivity in all thin films is attributed to the existence of donor and acceptor defect states.
Keywords: bismuth telluride, thin film, stoichiometry, electrical conductivity, Hall coefficient, charge carrier mobility.

Объекты исследования — тонкие пленки толщиной d = 45–620 нм, приготовленные путем термического испарения в вакууме из одного источника нелегированных поликристаллов Bi_2Te_3 p- и n-типа с различной стехиометрией (60.0 и 62.8 ат. % Te соответственно) и последующей конденсацией на стеклянные подложки при 500 K. Получены температурные зависимости коэффициента Холла R_H, электропроводности σ и холловской подвижности носителей заряда μ_H тонких пленок в интервале 77–300 K. Установлено, что пленки имели такой же тип проводимости, как и исходные кристаллы, во всем исследуемом интервале температур, σ и μ_H уменьшались как и в исходных кристаллах с ростом температуры. Степенные коэффициенты ν в зависимостях $\mu_H(T)$ в объемных кристаллах больше, чем в пленках, и увеличивались с ростом d. В отличие от кристаллов p-типа, R_H пленок p-типа уменьшался с ростом температуры. В n-Bi_2Te_3, R_H уменьшался с температурой и для пленок, и для кристаллов, но характер зависимостей $R_H(T)$ различен. Уменьшение R_H с температурой до наступления собственной проводимости, наблюдаемое для всех тонких пленок, связывалось с существованием донорных и акцепторных дефектных состояний.

Транспортні властивості тонких плівок телуриду вісмуту з різною стехіометрією у температурному інтервалі 77–300 К. *О.І.Рогачова, К.В.Новак, Г.М.Дорошенко, О.М.Нащекіна, О.В.Будник*

Об'єкти дослідження — тонкі плівки товщиною d = 45–620 нм, виготовлені шляхом термічного випаровування у вакуумі з одного джерела нелегованих полікристалів Bi_2Te_3 p- та n-типу з різною стехіометрією (60.0 і 62.8 ат. % Te відповідно) і наступної конденсації на скляні підкладки при 500 К. Одержано температурні залежності ко-

ефіцієнта Холла R_H, електропровідності σ та холлівської рухливості носіїв заряду μ_H тонких плівок в інтервалі 77–300 K. Встановлено, що плівки мали той же тип провідності, що і вихідні кристали у всьому інтервалі температур, та, як і у вихідних кристалах, σ та μ_H зменшувалися із зростанням температури. Ступеневі коефіцієнти ν у залежностях $\mu_H(T)$ у кристалах більші, ніж у плівках, і зростають із збільшенням d. На відміну від кристалів p-типу, R_H плівок p-типу зменшувався із зростанням температури. У n-Bi_2Te_3 R_H зменшувався із температурою і для тонких плівок, і для кристалів, проте характер залежностей $R_H(T)$ різний. Зменшення R_H із температурою до настання власної провідності, яке спостерігалося для усіх тонких плівок, пов'язувалося із існуванням донорних та акцепторних дефектних станів.

1. Introduction

The development of the electronic industry stimulates demand for low-power and small-sized thermoelectric (TE) power supplies.

Materials based on Bi_2Te_3 semiconductor compound are promising TE materials widely used in the production of various kinds of cooling devices, IR sensors, microcaloremeters, etc., operating most efficiently near room temperature [1–5]. This accounts for the increased interest in studying TE materials in a low-dimensional state, in particular, in the thin film state [6, 7]. Recently, interest in investigating the surface states of Bi_2Te_3 crystals and thin films has grown due to the theoretical prediction and subsequent experimental confirmation of their exhibiting special properties characteristic of 3D-topological insulators [8, 9]. It is easier to carry out studies of the properties of a topological surface layer on thin films, in which the contribution of the surface to the conductivity is larger than in bulk crystals. All this stimulates a detailed investigation of the transport properties of thin Bi_2Te_3 films.

Bi_2Te_3 crystallizes in a layered rhombohedral structure with five-layer packets perpendicular to the third-order symmetry axis, has a narrow homogeneity region in the Bi–Te system and, depending on the character of the deviation from stoichiometry, can exhibit either p- or n-type conductivity [1–5]. Theoretical and experimental studies have shown that predominant defects in p- and n-type Bi_2Te_3-based materials are antisite defects (Bi_{Te} and Te_{Bi}, respectively), which is caused by the small difference in the electronegativities of Bi and Te. The stoichiometric Bi_2Te_3 (60.0 at.% Te) exhibits p-type conductivity due to the shift of the maximum in the liquidus and solidus curves towards the excess of Bi and the presence of antisite Bi_{Te} defects [1–3]. The authors of [10] conducted a detail study of the behavior of the Hall coefficient R_H, electrical conductivity σ, Hall charge carrier mobility μ_H, the Seebeck coefficient S, TE power factor $P = S^2 \cdot \sigma$, and microhardness H within and near the Bi_2Te_3 homogeneity region at room temperature on polycrystalline samples subjected to a long-term homogenizing annealing at 670 K. They established that after such heat treatment, at ~ 60.8 at.% Te the inversion of the conductivity type occurs, that the boundaries of the homogeneity region correspond to ~ 59.5–61.0 at.% Te, and that in the dependences of the properties on Te content extremes are observed at 60.0 and 62.8 at.% Te (the compositions corresponding to p- and n-regions, respectively). In [11], the temperature dependences of the transport properties of Bi_2Te_3 polycrystals with different stoichiometry were obtained and the isotherms of transport properties were plotted. The behavior of the isotherms turned out to be similar to that of the room-temperature isotherms obtained in [10].

The authors [12–17] have shown that using a quite simple method of thermal evaporation in vacuum of Bi_2Te_3 polycrystals, it is possible to obtain thin Bi_2Te_3 films of a sufficiently high quality with chemical composition being close to that of the charge and that the type of conductivity of thin films grown from polycrystals with 60.0 or 62.8 at.% Te corresponded to that of the initial materials [12, 13]. The high structural quality of the films was confirmed by the observation of quantum oscillations both in p- and n-Bi_2Te_3 thin films [14–17]. However, all these results were obtained at room temperature. Since Bi_2Te_3 belongs to the low-temperature TE materials, it is necessary to know how TE parameters change and what is the effect of deviation from stoichiometry on transport properties below room temperature.

In a number of works, the temperature dependences of the transport properties of the Bi_2Te_3 bulk crystals and thin films were investigated [1–5, 18–29]. In most works the authors reported their observing a degeneracy of the electron or hole gas and the metallic character of the temperature dependences of transport properties. However,

the results obtained for thin films by different authors are quite contradictory, since the films were grown by different methods, on different substrates, had different thicknesses d, and measurements were carried out in different temperature ranges. Besides, it was thin films obtained from the stoichiometric Bi_2Te_3 that were usually studied, and the effect of deviation from stoichiometry in the composition of the charge from which the films were grown on their transport properties was not investigated. Besides, practically in none of the works, films were obtained by thermal evaporation in vacuum from single source. In most studies, Bi_2Te_3 films prepared by different methods exhibited n-type conductivity, which was explained either by the presence of excess Te or by the presence of a second phase. The films obtained in a number of works were p-type due to a slight excess of Bi in the composition of the films and their kinetic properties were close to the properties of single crystals. The highest values of S, σ, R_H, μ_H, P were observed for textured films with a composition close to the stoichiometric one.

The purpose of this work was to establish the effect of the deviation from stoichiometry and the conductivity type in the initial Bi_2Te_3 polycrystals that were used as the charge on the behavior of the temperature dependences (77–300 K) of the transport properties of thin films grown by thermal evaporation in vacuum from a single source on glass substrates.

2. Experimental

The objects of the study were thin films with thicknesses $d = 620$ and 45 nm grown using a Bi_2Te_3 polycrystal with 60 at.% Te as a charge and the films with $d = 325$ and 110 nm grown from a polycrystal with 62.8 at.% Te.

The bulk crystals were synthesized by fusing high purity (99.999 at.% of the main component) Bi and Te in evacuated quartz ampoules at (1020±10) K, subsequent annealing at (670±5) K for 300 h and cooling to room temperature with the cooling rate of a switched off furnace. Using polycrystals with 60.0 and 62.8 at.% Te as initial materials, the films with different d were prepared by thermal evaporation in vacuum onto glass substrates at 500 K. For each sample, transport coefficients were measured in the temperature range 77–300 K. R_H and σ were determined using a conventional *dc* method and a magnetic field of 0.8 T. Six ohmic contacts were soldered with indium to the sample surface. The error in the R_H and σ measurements did not exceed ±5 %. The Hall charge carrier mobility μ_H was calculated as $\mu_H = \sigma \cdot R_H$. All measurements were performed on freshly prepared films.

3. Results and discussions

3.1 Thin films with p-type of conductivity

In Fig. 1,a,b, the temperature dependences of σ, R_H, and μ_H for thin films with thicknesses $d = 620$ and 45 nm prepared from a stoichiometric p-Bi_2Te_3 polycrystal are presented. For comparison, in Fig. 1,c, similar dependences obtained in [11] for a polycrystal with 60.0 at.% Te that was used as a charge for growing p-type thin films are shown. It can be seen that for the polycrystal and thin films, σ and μ_H decreases with increasing temperature which indicates the metallic nature of the conductivity characteristic of strongly degenerate semiconductors, for which R_H usually does not depend on temperature. However, R_H for both the bulk crystal and films changes with temperature but in different ways: in the bulk crystal, R_H increases with temperature, and in thin films it decreases.

Possible reasons for the increase in R_H with temperature for bulk p-Bi_2Te_3 can be a change in the degree of degeneracy of the hole gas, a change in the mechanism of scattering of charge carriers or a change in the band structure [3]. From our point of view [11], the most probable explanation of this fact is based on a two-band model of the valence band of p-Bi_2Te_3 (with "light" and "heavy" subbands) proposed in some works [3]. According to this model, the increase in R_H with temperature can be explained as a result of the increasing contribution of the "heavy" subband to conductivity due to the sinking of the Fermi level into the valence band with increasing temperature. This can occur both as a result of a change in the distance between the subband tops and/or an increase in the hole concentration with temperature growth. When the Fermi level enters the "heavy" subband, "heavy" holes with a larger effective mass start contributing to the conductivity, which leads to an increase in R_H. Indeed, in this case, R_H should be calculated according to the formula, which takes into account the presence of "light" and "heavy" holes:

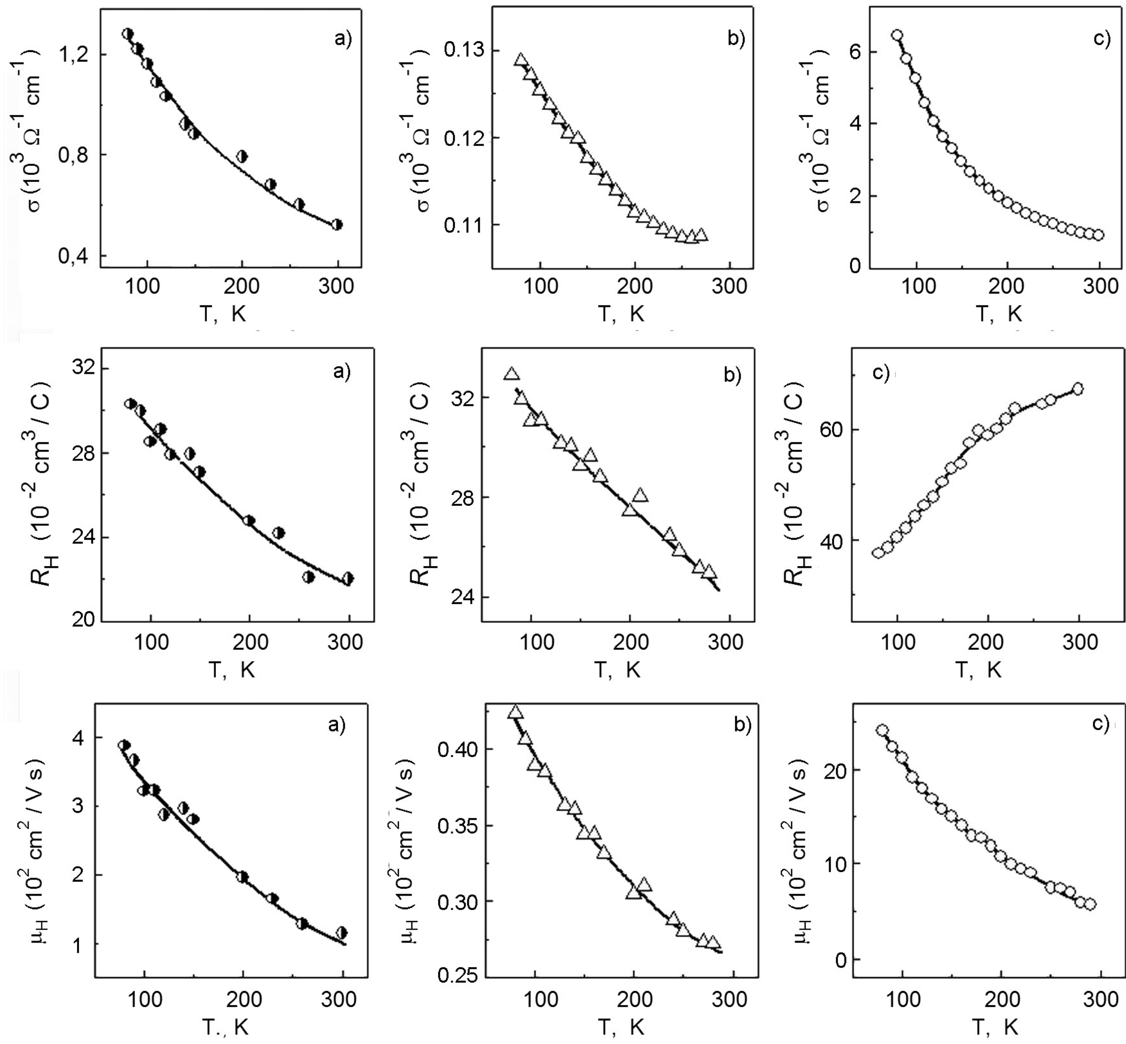

Fig. 1. Temperature dependences of electrical conductivity σ, the Hall coefficient R_H, and Hall hole mobility μ_H for *p*-type thin films with different thicknesses *d* and for bulk *p*-Bi_2Te_3 polycrystal with 60.0 at.% Te from which thin films were obtained: a — thin film with $d = 620$ nm, b — thin film with $d = 45$ nm, c — bulk crystal.

$$R_H = \frac{p_l\mu_l^2 + p_h\mu_h^2}{e\left(p_l\mu_l + p_h\mu_h\right)^2},$$

where p_l and p_h are the concentrations and μ_l and μ_h are the effective masses of "light" and "heavy" holes, respectively.

It can also be seen in Fig. 1,a,b, that, regardless of the film thickness, in the range 77–300 K, R_H does not change sign and decreases with increasing temperature. So, it does not remain constant despite the strong degeneracy, nor does it increase like in the case of a bulk crystal. The qualitative difference in the behavior of the $R_H(T)$ dependences for the bulk *p*-Bi_2Te_3 polycrystal and for the thin films shows that in the films, the second valence subband does not manifest itself with increasing temperature. In this case, a single-band model can be used to calculate the carrier concentration. According to this model, a decrease in R_H means an increase in the charge carrier concentration ($R_H = 1/(p \cdot e)$ where *p* is the hole concentration and *e* is the electron charge). Such situation can be associated with the appearance of new *p*-type charge carriers in thin films as a result of the greater number of structural defects in thin films as compared with bulk crystals and / or with the transition to intrinsic conductivity. However, the intrinsic conductivity in Bi_2Te_3 (whose appearance is manifested through a

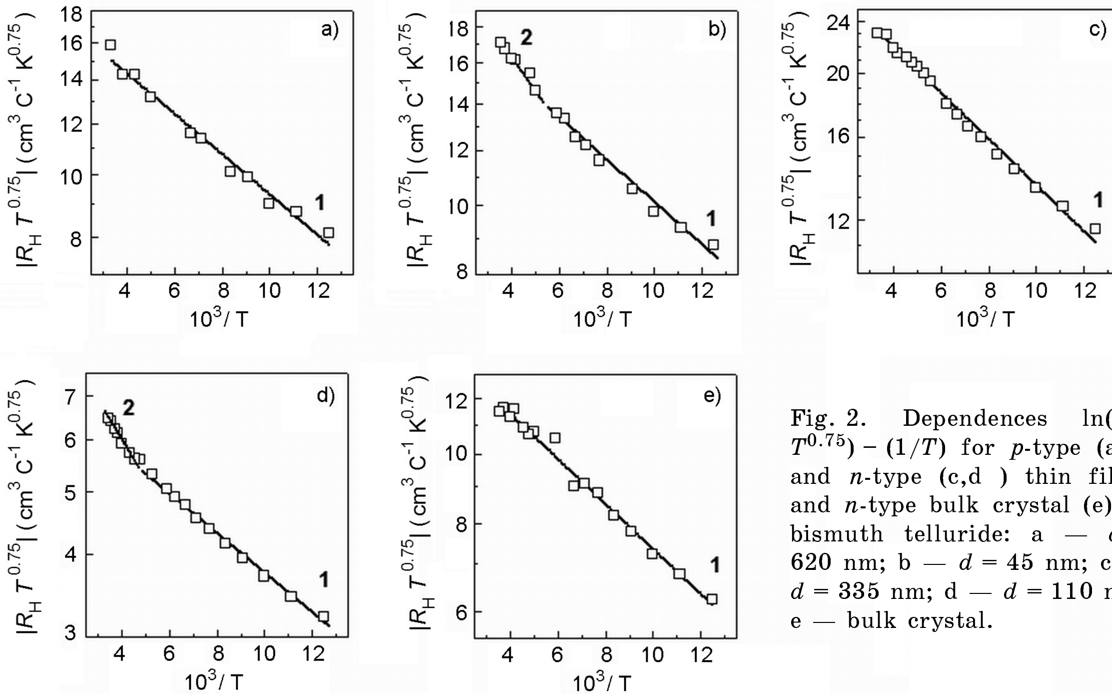

Fig. 2. Dependences $\ln(R_H T^{0.75}) - (1/T)$ for p-type (a,b) and n-type (c,d) thin films and n-type bulk crystal (e) of bismuth telluride: a — d = 620 nm; b — d = 45 nm; c — d = 335 nm; d — d = 110 nm; e — bulk crystal.

sharp decrease in R_H with temperature) begins at higher temperatures [1–5]. That is why a decrease in R_H with increasing temperature in thin films before the appearance of intrinsic conductivity indicates that there are charged centers, which become activated with increasing temperature. It is natural to assume that these centers are associated with defects formed during the thin film growth. An increase in the concentration of defects in a thin film leads to the increased scattering by defects and an expansion in the temperature range in which scattering manifests.

For a more detailed study of the temperature dependences of kinetic coefficients in thin films, the $\ln(R_H T^{0.75}) - (1/T)$ dependences were plotted (Fig. 2). Using these dependences we determined the activation energies of the possible defects. The change in the type of predominant defects with increasing temperature is manifested through a change in the slope of linear sections of the $\ln(R_H T^{0.75}) - (1/T)$ dependences. It turned out that in the p-type films with thicknesses d = 620 nm and d = 45 nm, there are levels with activation energy ΔE_1 = 12±0.5 meV. Another level with a higher activation energy of ΔE_2 = 17±0.5 meV is detected in the p-type film with thickness d = 45 nm.

To identify the types of defects, clarify their genesis and stability, additional more detailed studies are required. The situation is complicated by the possible influence of the thin-film state on the type and concentration of intrinsic defects, as well as on the concentration interval of the Bi_2Te_3 homogeneity region. It can be assumed that defects with an activation energy ΔE_1 correspond to the grain boundaries that are present in both the films and in the initial polycrystals. The presence of defects with a higher activation energy ΔE_2 in thinner films can be associated with surface states that are more pronounced in thin films.

The calculation of the exponents ν in the temperature dependences of charge carrier mobility ($\mu_H \sim T^{\nu}$) in the range 200–300 K for the thin films with d = 620 and 45 nm gave the values ν = 1.3 and ν = 0.3 respectively, which are lower than ν for the Bi_2Te_3 crystal ($\nu \sim 1.5$ [11]) and approach this value as d increases. It is natural to associate the decrease in ν in thin films with a change in the defect structure: there are more defects in thin films in comparison with bulk crystals, and the smaller the film thickness, the smaller the grain size [16].

It was established earlier [16], and confirmed for the films studied in this work, that the preferred direction of crystallite growth in p-type Bi_2Te_3 films is the [001] direction, which corresponds to the C3 axis of the crystal (in the hexagonal representation). In p-type films, as the film

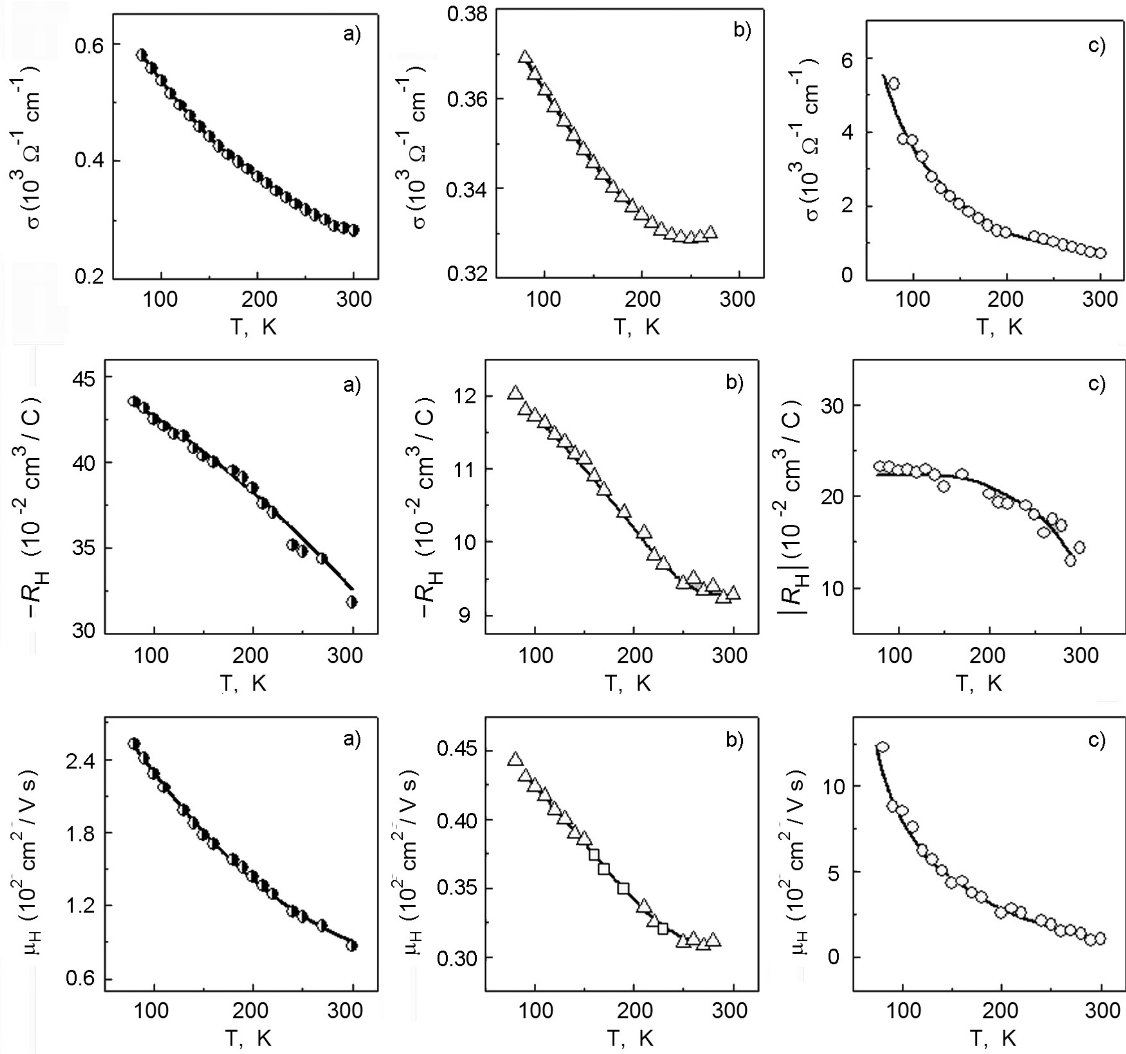

Fig. 3. Temperature dependences of electrical conductivity σ, the Hall coefficient R_H, and Hall electron mobility μ_H for n-type thin films with different thicknesses d and for bulk n-Bi_2Te_3 polycrystal with 62.8 at.% Te from which thin films were obtained: a — thin film with d = 335 nm, b — thin film with d = 110 nm, c — bulk crystal.

thickness increases above d ~ 200–250 nm, crystallite misorientation appears. However, despite this, at d = 620 nm, the exponent ν is greater than at d = 45 nm (1.3 and 0.3, respectively). Therefore, apparently, the main reason of this is scattering by additional boundaries that appear as a result of a decrease in grain size (the grain size for the film with thickness 620 nm is almost 8 times as large as that for the film with d = 45 nm [16]).

Thus, the most likely reason for the observed increase in R_H with increasing temperature for the polycrystal with 60.0 at.% Te may be the two-band structure of the valence band of the stoichiometric p-Bi_2Te_3, the presence of which does not appear in a thin films due to the defect structure changing under transition in thin-film state.

3.2 Thin films with n-type of conductivity

In Fig. 3,a,b, the temperature dependences of σ, R_H and μ_H of thin films, grown from polycrystal with 62.8 at.% Te, are presented. For comparison, in Fig. 3,c, similar dependences obtained in [11] for a polycrystal with 62.8 at.% Te, which was used as a charge for n-type thin film preparation, are shown. It can be seen that for both the polycrystal and thin films, σ and μ_H decrease with increasing temperature like in the case of thin films obtained from a stoichiometric Bi_2Te_3 polycrystal, which in-

dicates strong degeneracy of electron gas, for which R_H usually practically does not change with temperature.

However, for films, the Hall coefficient decreases as temperature increases. Like in the case of the *p*-type films, a decrease in R_H with increasing temperature before the appearance of intrinsic conductivity indicates that there are charged centers and as temperature increases, these centers get activated. It is natural to assume that these centers are associated with defects formed in the process of the thin film growth.

In Fig. 2,c,d, the $\ln(R_H\ T^{0.75}) - (1/T)$ dependences plotted on the basis of the $R_H(T)$ dependences are presented. In *n*-type films with thicknesses $d = 335$ nm and $d =$ 110 nm, levels with activation energy $\Delta E_1 =$ 13±0.5 meV are detected. Another level with a higher activation energy of $\Delta E_2 =$ 23±1.0 meV is detected in an *n*-type film with a smaller thickness $d = 110$ nm. It can be seen that the activation energies ΔE_1 are very close for *p*- and *n*-type films and practically independent of thickness. This fact indicates the similarity of origin of the defects in *p*- and *n*-films.

Plotting the $\ln(R_H\ T^{0.75}) - (1/T)$ dependence for the bulk crystal that was used to prepare *n*-type thin films, we estimated the activation energy ΔE_1 as (12.5±0.5) meV. The composition of the sample (62.8 at.% Te) is rather far from the conductivity type inversion point (~ 60.8 at.% Te [10]) and from the boundary of the homogeneity region of Bi_2Te_3 (~ 61.0 at. % Te [10]) in the Bi–Te system, and corresponds either to the two-phase region (Bi_2Te_3 + Te) or to the region of short-range or long-range ordering [10]. Therefore, a decrease in R_H can be caused both by the presence of a new phase and by the appearance of structural defects associated, for example, with the existence of interphase boundaries. It cannot be ruled out that under increasing temperature the transition to the region of mixed conductivity occurs.

The calculation of the exponents ν in the $\mu_H(T)$ dependences in the range of 200–300 K for films with $d = 325$ and $d = 110$ nm yielded 1.1 and 0.3, respectively, which are lower than the ν value for the polycrystal containing 62.8 at. % Te (μ ~ 2.3) [11].

In [17], it was shown that in the case of *n*-type Bi_2Te_3 films, starting from d ~ 100 nm, a gradual transition occurs from the preferred orientation in the [0 0 1] direction to the orientation in the [0 1 5] direction. Therefore, the very small value of the exponent for the film with thickness $d = 110$ nm can be associated not only with a decrease in the grain size for smaller film thicknesses, but also, at least partially, with the fact that the changes in the structure start to occur near the thickness d ~ 100 nm caused by a change in the preferred orientation and leading to an increase in the degree of disorder of the structure.

4. Conclusions

It was found that the Bi_2Te_3 films prepared by thermal evaporation in vacuum from a single source (*p*-Bi_2Te_3 and *n*-Bi_2Te_3 polycrystals) onto glass substrates had the same type of conductivity as the initial material (the charge) in the entire temperature range studied (77–300 K). Thus, the type of conductivity exhibited in the initial material is reproduced in thin films.

Electrical conductivity and Hall charge carrier mobility both for the *p*- and *n*-Bi_2Te_3 films decrease with increasing temperature. This fact and the magnitude of the concentration of charge carriers ($n(p)$ ~ 10^{19} cm^{-3}) indicate the degeneracy of electron and hole gases.

The Hall coefficient for all studied thin films, regardless of the composition of the initial material, conductivity type, film thickness, and for the polycrystal with *n*-type conductivity decreases with increasing temperature in the range 77–300 K. It does not remain constant despite the strong degeneracy. The decrease in R_H under increasing temperature before the range of intrinsic conductivity is attributed to the existence of donor and/or acceptor defect states whose sources may be grain boundaries and surface defects.

The activation energies of possible defect states were determined by plotting the $\ln(R_H\ T^{0.75}) - (1/T)$ dependences. It turned out that in the *n*-type crystal and in all *p*- and *n*-type films there are defect states with activation energies $\Delta E_1 = (12$–$13)$ meV. In *p*- and *n*-films ($d = 45$ nm and $d = 110$ nm, respectively) with smaller thicknesses, additional defect states with high activation energies $\Delta E_2 = (17$–$24)$ meV were detected.

The exponents ν in the $\mu_H(T)$ dependences for crystals are larger than those for films, and with increasing d, the exponents ν increase.

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