

Effect of aging on thermoelectric properties of the Bi_2Te_3 polycrystals and thin films

*E.I.Rogacheva, K.V.Novak, A.N.Doroshenko,
A.Yu.Sipatov, T.I.Khramova, S.A.Saenko*

National Technical University "Kharkiv Polytechnic Institute",
2 Kyrpychova Str., 61002 Kharkiv, Ukraine

Received September 22, 2020

The temperature dependences (77–300 K) of the thermoelectric (TE) properties (the Seebeck coefficient S , electrical conductivity σ , Hall coefficient R_H , Hall charge mobility μ_H , and TE power factor P) were studied for freshly prepared and for exposed to air at room temperature during 5 years p - Bi_2Te_3 (60.0 at.% Te) and n - Bi_2Te_3 (62.8 at.% Te) polycrystals and thin films grown from them by thermal evaporation in vacuum. It was found that after aging, in the p - and n - Bi_2Te_3 bulk crystals and in the n -type film obtained from the n - Bi_2Te_3 crystal, type of conductivity is reserved but the p -type film obtained from the p - Bi_2Te_3 crystal, change the type of conductivity from hole to electronic. The activation energies of possible defect states were determined using the $R_H(T)$ dependences. After aging, at the temperatures close to room temperature, the P values of n - Bi_2Te_3 and p - Bi_2Te_3 polycrystals decreases by ~ 20 %, but P values of the n -type film grown from n - Bi_2Te_3 crystal increases by 20–30 %. In the p -type film obtained from p - Bi_2Te_3 polycrystal, and having changed the type of conductivity after aging, the P values exceed the P values of a film obtained from n - Bi_2Te_3 polycrystal by ~ 35 % at 250 K and by 25 % at 300 K, remaining at these temperatures below the P values for n - Bi_2Te_3 polycrystal after aging by ~ 15 %.

Keywords: bismuth telluride, polycrystal, film, aging, Seebeck coefficient, electrical conductivity, Hall coefficient, Hall mobility, thermoelectric power factor, temperature dependences, activation energy.

Вплив старіння на термоелектричні властивості кристалів і тонких плівок Bi_2Te_3 .
О.І.Рогачова, К.В.Новак, А.М.Дорошенко, О.Ю.Сипатов, Т.І.Храмова

Досліджено температурні залежності (77–300 К) термоелектричних (ТЕ) властивостей (коефіцієнта Зеебека S , електропровідності σ , коефіцієнта Холла R_H , холлівської рухливості μ_H носіїв заряду та ТЕ потужності P) полікристалів p - Bi_2Te_3 (60.0 at.% Te) та n - Bi_2Te_3 (62.8 at.% Te) і тонких плівок, що вирощені з цих кристалів методом термічного випаровування у вакуумі. Вимірювання проводили на зразках відразу після приготування та після старіння на повітрі протягом 5 років за кімнатної температури. Встановлено, що після старіння у полікристалах p - та n - Bi_2Te_3 і у плівках n -типу, одержаних із кристалів n - Bi_2Te_3 , тип провідності зберігався, але у плівках p -типу, вирощених із кристалів p - Bi_2Te_3 , тип провідності змінився з діркового на електронний. На основі залежностей $R_H(T)$ визначено енергії активації дефектних станів. Значення P за температур, близьких до кімнатної, у полікристалах n - Bi_2Te_3 та p - Bi_2Te_3 після старіння зменшувалися на ~ 20 %. Значення P для плівки n -типу, яку вирощено із кристала n - Bi_2Te_3 , після старіння збільшилося на 20–30 %, у плівці p -типу, яка одержано із полікристала p - Bi_2Te_3 , і змінила після старіння тип провідності, значення P перевищують значення P плівки, вирощеної з полікристала n - Bi_2Te_3 , на ~ 35 % при 250 К і на 25 % при 300 К, маючи при цих температурах нижчі значення P , ніж полікристал n - Bi_2Te_3 після старіння на ~ 15 %.

Исследованы температурные зависимости (77–300 К) термоэлектрических (ТЭ) свойств (коэффициента Зеебека S , электропроводности σ , коэффициента Холла R_H , холловской подвижности носителей заряда μ_H и ТЭ мощности P) поликристаллов p - Bi_2Te_3 (60.0 at.% Te) и n - Bi_2Te_3 (62.8 at.% Te) и выращенных из них методом термического испарения в вакууме тонких пленок. Измерения проводились на свежеприготовленных образцах и образцах, пребывавших на воздухе при комнатной температуре в течение 5 лет. Установлено, что после старения в поликристаллах p - и n - Bi_2Te_3 и в пленках n -типа, полученных из кристаллов n - Bi_2Te_3 , тип проводимости сохранился, но в пленках p -типа, полученных из кристаллов p - Bi_2Te_3 , тип проводимости изменился с дырочного на электронный. На основе зависимостей $R_H(T)$ определены энергии активации дефектных состояний. Значения P при температурах, близких к комнатной, в поликристаллах n - Bi_2Te_3 и p - Bi_2Te_3 после старения уменьшились на ~ 20 %, значения P пленки n -типа, выращенной из кристалла n - Bi_2Te_3 , после старения увеличиваются на 20–30 %, в пленке p -типа, полученной из поликристалла p - Bi_2Te_3 , и изменившейся после старения тип проводимости, значения P превышают значения P пленки, полученной из n - Bi_2Te_3 поликристалла на ~ 35 % при 250 К и на 25 % при 300 К, оставаясь при этих температурах ниже значений P для n - Bi_2Te_3 поликристалла после старения на ~ 15 %.

1. Introduction

Solid solutions based on the V_2VI_3 semiconductor compounds (Bi_2Te_3 , Bi_2Se_3 , Sb_2Te_3) are currently among the best materials for thermoelectric (TE) cooling devices of various types [1–4]. Every day the area of application of low-dimensional structures (thin films, quantum wires, quantum dots, etc) based on these materials is expanding [5,6]. Interest in the theoretical and experimental study of V_2VI_3 has sharply increased in recent years after the establishment of the fact that they belong to a new class of objects of solid state physics — topological insulators, which have unique properties that make it possible to predict the possibility of their successful use in spintronics, quantum computers and other fields of science and technology, including thermoelectricity [7–10].

Bi_2Te_3 melts congruently and has a layered rhombohedral crystal lattice of a tetradymite type [1–4]. Possessing a narrow two-sided homogeneity region in the Bi–Te system, bismuth telluride can exhibit both electronic and hole conductivity depending on character and degree of deviation from stoichiometry [1–4, 11]. Near 61.0 at.% Te, the $p \rightarrow n$ transition takes place. When deviating from this composition towards the excess of Bi, the p -type of conductivity is manifested, and towards the excess of Te, — the n -type; the main types of non-stoichiometric structural defects in the crystal lattice are antisite defects — Bi_{Te} and Te_{Bi} , respectively. The p -type conductivity in a crystal of stoichiometric composition (60 at. % Te) is associated with the deviation of the maximum on the liquidus

and solidus curves in the Bi–Te system towards an excess of Bi.

In [12–16], we showed that using the method of thermal evaporation in vacuum from a single source, taking stoichiometric Bi_2Te_3 (60.0 at.% Te) and a crystal containing 62.8 at.% Te as initial crystals, it is possible to obtain p - and n -type Bi_2Te_3 thin films, respectively.

In the research and practical use of semiconductors, it is important to know how sensitive their properties are to the environment, in particular to oxidation in air. This is especially important to know for thin films, for which the role of the surface layer in determining properties increases.

In [17], the time-dependent process of oxidation of the freshly cleaved surfaces of Bi_2Te_3 single crystals was investigated experimentally using X-ray photoelectron spectroscopy (XPS) method and theoretically on the basis of the developed by the authors [17] model for the layered structure. According to [17], after the thickness of the oxidized layer d_o reaches in the course of time the value of 1.1 nm (when the first quintuple layer of Bi_2Te_3 surface is oxidized completely), the rate of the oxidized layer thickness growth with time decreases sharply because the O_2 molecule has to jump over the van der Waals gap. In [17], very good agreement was found between the experimental data and the results of the theoretical calculations.

It was of interest to compare the results obtained for the Bi_2Te_3 single crystals [17] with those for thin films which are more sensitive to oxidation. In [18], we have studied the oxidation processes in the Bi_2Te_3 polycrystalline thin films at room

temperature by XPS method. It was established that the surface layer of the Bi_2Te_3 films undergoes oxidation. Using the model developed by the authors of [17] for single crystals, we estimated the thickness d_o of the oxidized layer in the Bi_2Te_3 films. The obtained value ($d_o \sim 1\text{--}2$ nm) is in good agreement with the value of d_o in the single crystals, as well as with the value of the Debye shielding distance λ_D , estimated in [18]. It was shown that like in single crystals, oxidation velocity sharply slows down after oxidation processes spread to a single quintuple layer.

The goal of this work was to find out how the TE characteristics of n - and p - Bi_2Te_3 crystals and thin films obtained from these crystals, without a protective coating, change after a long stay in air (prolonged exposure to air) at the room temperature.

Conducted research have shown that after aging in air at room temperature for 5 years, p -type thin films changed the conductivity type ($p \rightarrow n$), but in the p - and n - Bi_2Te_3 bulk crystals and in the n -type films obtained from the n - Bi_2Te_3 crystal, type of conductivity was reserved. After aging, TE power factor values at the temperatures close to room temperature (working temperature range for materials based on Bi_2Te_3) in n - Bi_2Te_3 and p - Bi_2Te_3 polycrystals, decreased compared to values obtained for freshly prepared samples, but in the thin films, P values increased.

2. Experimental

Polycrystalline stoichiometric Bi_2Te_3 (60.0 at.% Te) exhibiting p -type conductivity and $\text{Bi}_{37.2}\text{Te}_{62.8}$ (62.8 at.% Te) with n -type conductivity were used as the starting materials for the thin films preparation. The polycrystals were synthesized by direct melting of Bi and Te of high purity (99.999 at. %) at the temperature (1020 ± 10) K in evacuated quartz ampoules and subsequent annealing at 670 K for 300 h. The films with thicknesses $d = 620$ nm and $d = 335$ nm were grown from p - Bi_2Te_3 and n - Bi_2Te_3 polycrystals, respectively, by thermal evaporation of the starting materials in oil-free vacuum ($\sim 10^{-5}$ Pa) and subsequent deposition onto a glass substrates heated to the temperature $T_S = 500$ K. The grown films were subjected to annealing at $T = 500$ K during 1 h. The condensation rate was 0.1–0.3 nm/s. The film thickness was controlled using a calibrated quartz resonator.

The Hall coefficient R_H and electrical conductivity σ were measured in the range 77–300 K using a conventional dc method and a magnetic field of 0.8 T using double Hallcross-shaped bulk and thinfilm samples. Six ohmic contacts were made by soldering indium to the crystal and film surface. The error in the R_H and σ measurements did not exceed ± 5 %. Based on the measured R_H and σ values, the Hall charge carrier mobility μ_H values were calculated as $\mu_H = R_H\sigma$. The Seebeck coefficient S was measured by compensation probe method relative to Cu electrodes with an accuracy of $\pm 2\text{--}3$ %. Based on the measured S and σ values, TE power factor $P = S^2\sigma$ values were calculated. The measurements were carried out on the polycrystals and thin films without a protective coating, which had been kept at room temperature for 5 years. The results of measurements carried out on the same freshly prepared samples are described in our works [15, 16].

3. Results and discussions

Measurements of R_H and S showed that after prolonged aging, the conductivity type in p - Bi_2Te_3 and n - Bi_2Te_3 polycrystals and in the thin film with a thickness of $d = 335$ nm obtained from n - Bi_2Te_3 crystal did not change: freshly prepared and aged crystal with 60.0 % Te had p -type conductivity, the crystal containing 62.8 at. % Te and thin film retained the electronic type of conductivity. But the p -type film with $d = 620$ nm obtained from the p - Bi_2Te_3 polycrystal, after aging changed the type of conductivity from hole to electronic.

In Fig. 1, a–c, the temperature dependences of the σ , R_H , and μ_H for the p - and n - Bi_2Te_3 polycrystals and for thin film with $d = 335$ nm, are shown for samples aged in air at room temperature for 5 years. For comparison, the temperature dependences of σ , R_H , and μ_H measured on the crystals and thin film immediately after their production [15, 16] are presented. It is seen that in all cases, the values of σ and μ_H decrease with increasing temperature which indicates the degeneracy of the electron and hole gases and is confirmed by the high concentration of charge carriers ($\sim 10^{19}$ cm $^{-3}$). Besides, in all cases, the aging leads to a decrease in σ and μ_H values compared to freshly prepared samples. However, with an increase in temperature, this difference in σ and μ_H values

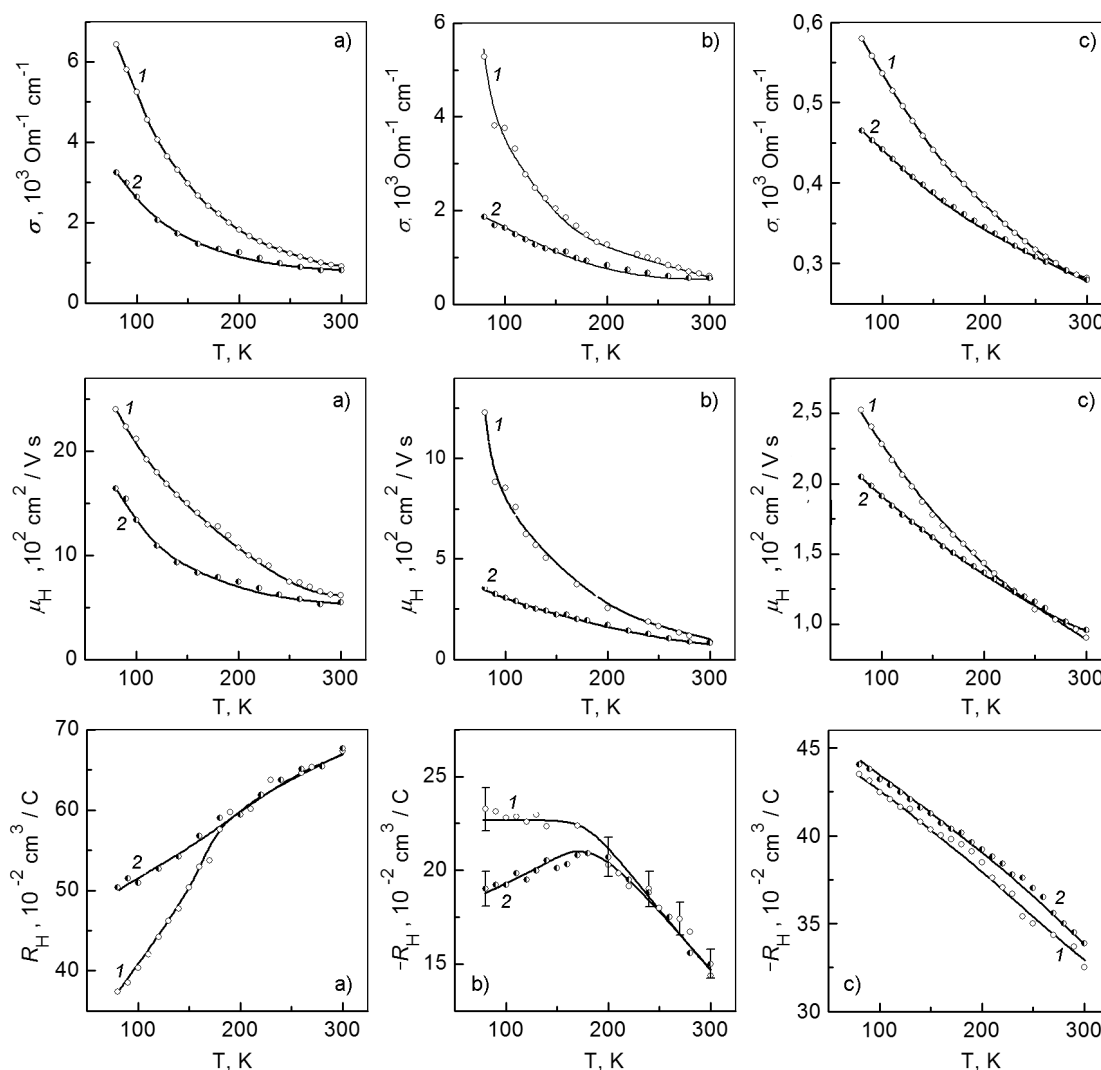


Fig. 1. Temperature dependences of electrical conductivity σ , charge carrier Hall mobility μ_H , the Hall coefficient R_H for bulk *p*-type (a) and *n*-type (b) polycrystals (60.0 and 62.8 at.% Te, respectively) and for *n*-type thin films with thickness $d = 335$ nm, obtained from *n*-type polycrystal (c). 1 — freshly prepared films [15, 16], 2 — films after aging.

before and after aging decreases and at 300 K is practically completely absent.

The $R_H(T)$ curve for a freshly prepared Bi_2Te_3 polycrystal has an unusual form (Fig. 1,a): R_H increases with the temperature growth having an inflection point near 170 K. From the point of view of the one-band valence band model, this fact could indicate a decrease in the carrier concentration with increasing temperature. Meanwhile, for a strongly degenerate semiconductor, this is unlikely, since one would expect the practical independence of R_H on temperature, and a sharp decrease in R_H when passing to the region of intrinsic conductivity. Various assumptions can be made regarding the possible causes of this phe-

nomenon (complex structure of the valence band, change in the degree of degeneracy of the hole gas with temperature, change in the mechanism of charge carriers scattering, kinetic factors) [3]. To date, the band structure of Bi_2Te_3 has not been finally established, although assumptions have been made about a two-band model of not only the valence band, but also the conduction band [3, 19–21]. According [21], the distance between the ceiling of the upper "light" valence subband and the ceiling of the "heavy" subband is 19 meV, and there are two extrema in the conduction band with a distance of 25 meV between them.

The authors of [19, 20] reported on an increase in the hole and electron effective

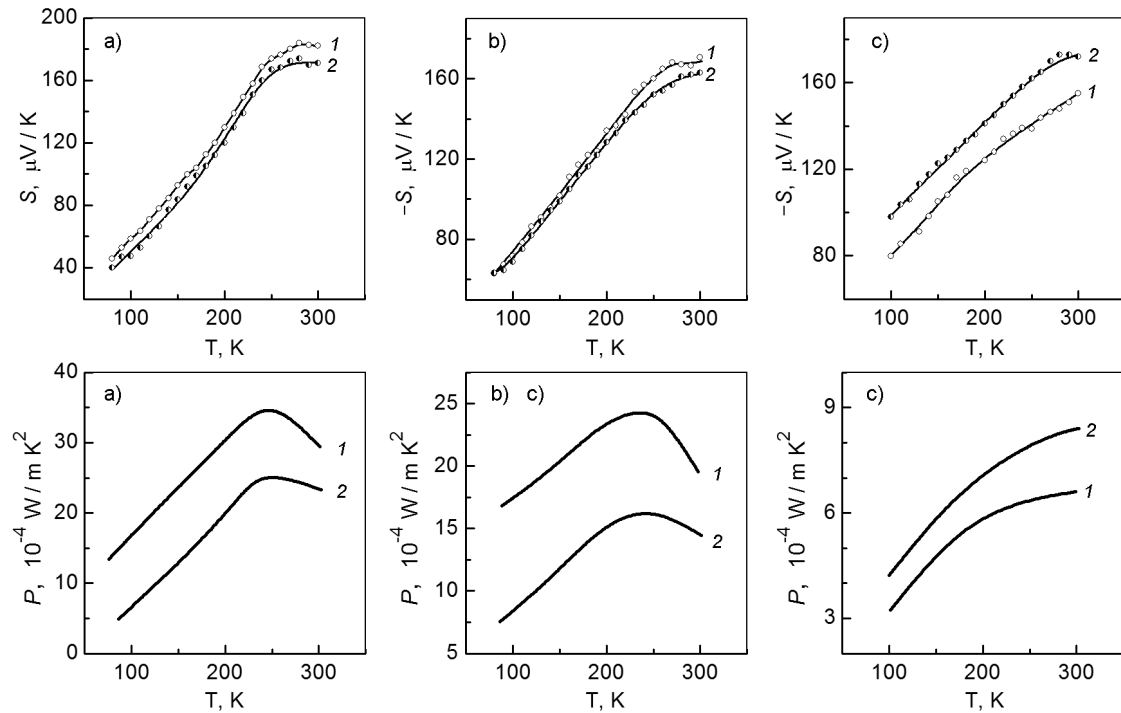


Fig. 2. Temperature dependences of the Seebeck coefficient S and thermoelectric power factor $P = S^2\sigma$ for p -type (a) and n -type (b) polycrystals (60.0 and 62.8 at.% Te, respectively) and for n -type thin films with thickness $d = 335$ nm, obtained from n -type polycrystal (c). 1 — freshly prepared films [15, 16], 2 — films after aging.

mass with charge carrier concentration and temperature, which becomes noticeable near 160 K. They established that electron effective mass was to be less than that of the holes, at least below room temperature, and these facts may be due to a stronger warping of the valence band at higher energies than the conduction band. That is why, the most probable reason of the R_H growth with temperature for p - Bi_2Te_3 is the existence of a second "heavy" subband in the valence band whose contribution to the kinetic coefficients changes with changing temperature. The presence of an inflection in the $R_H(T)$ dependence near 170 K (Fig. 1a) is consistent with the fact that according to [19, 20], the effective mass starts to grow noticeably with a temperature of about 160 K.

After a long interaction of the p - Bi_2Te_3 polycrystal with the air, the general character of the $R_H(T)$ dependence in the temperature range 170–300 K did not change, the inflection at ~ 170 K was no longer observed, and R_H increased almost linearly with temperature. A possible reason for this may be the appearance of new electroactive defects as a result of oxidation processes going on the crystal surface, although very slowly [17, 18], a change in the position of

the Fermi level and, in accordance with this — change in the contributions of "light" and "heavy" holes to the conductivity of the crystal. It is possible that the dependence of the effective mass on temperature becomes another and the effective mass increases over the entire temperature range.

For a freshly prepared n - Bi_2Te_3 polycrystal, the curve $R_H(T)$ consists of two sections: from 77 to ~ 170 K, R_H practically did not change with temperature increasing, and then decreases indicating the transition from the region of depletion of impurities (defects) to the temperature region where there are the generation of electrically active defects. After aging the nature of the dependence $R_H(T)$ in the temperature range 170–300 K practically did not change, and in the range 77–170 K, the R_H values decreased by $\sim 10\%$ and instead of R_H being constant, a slight increase with temperature growth was observed. A slight decrease in the R_H after aging, apparently, indicates the appearance of additional defects. In p - Bi_2Te_3 polycrystal in the temperature range 77–170 K, the opposite phenomenon is observed: R_H increases after aging.

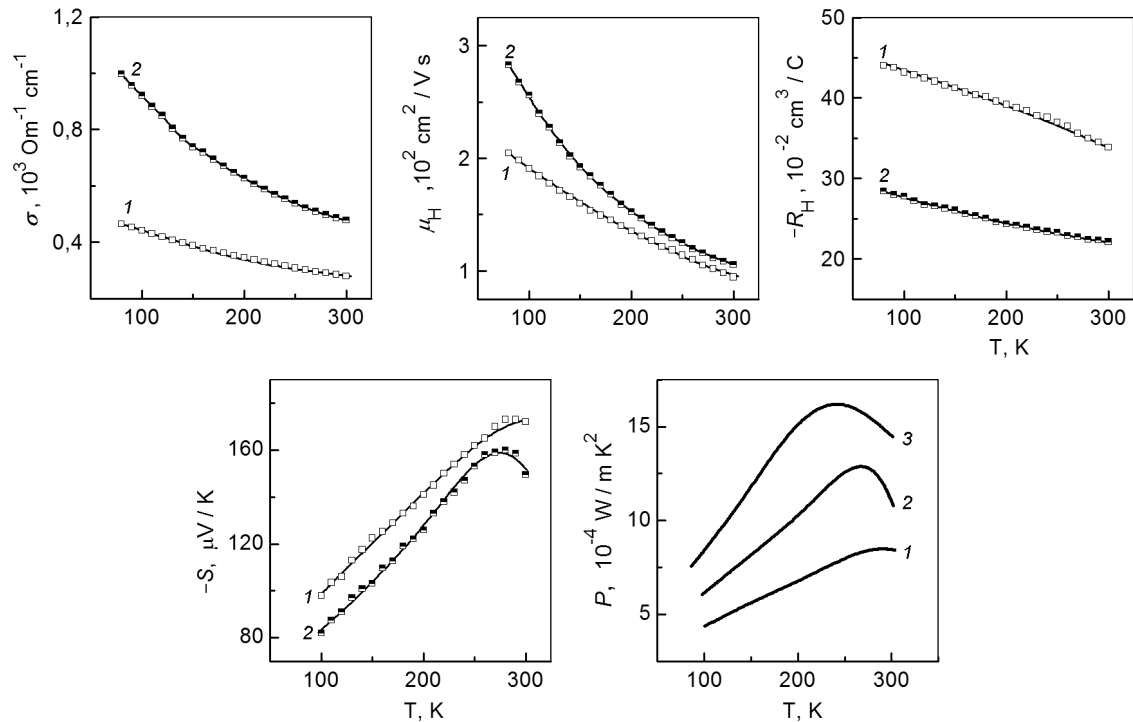


Fig. 3. Temperature dependences of electrical conductivity σ , charge carrier Hall mobility μ_H , the Hall coefficient R_H , Seebeck coefficient S and thermoelectric power factor $P = S^2\sigma$ for n -type Bi_2Te_3 film with thickness $d = 335$ nm obtained from n - Bi_2Te_3 polycrystal (1) and n -type Bi_2Te_3 film with thickness $d = 620$ nm grown from p - Bi_2Te_3 polycrystal after aging (2). 3 — the dependence $P(T)$ for n - Bi_2Te_3 polycrystal after aging.

Thus, it can be seen that, although the $R_H(T)$ dependences for polycrystals of p - and n -types has a different character, in the temperature range 170–300 K, for crystals of both types, the $R_H(T)$ dependences before and after aging practically coincide. The different character of the $R_H(T)$ dependences in the temperature ranges of 77–170 K and 170–300 K, observed for crystals of both p - and n -types, and the subsequent complete coincidence of the $R_H(T)$ dependences in the ranges 170–300 K before and after aging, also observed in crystals both p - and n -types, and the fact that aging acts in different ways on R_H values (increasing R_H in a p -type crystal and decreasing R_H in an n -type crystal) may indicate the appearance of electroactive p -type defects that do not actually contribute to conductivity after ~ 170 K. The observed phenomenon can be associated with surface oxidation and the formation, in this connection, of acceptor-type defects, the effect of which is noticeable at sufficiently low temperatures, when the contribution of intrinsic conductivity decreases.

The fact that kinks in the $R_H(T)$ dependences were observed before aging and both

for p - and n -samples indicates that there is a reason that does not depend either on the presence of aging or on the type of conductivity: something changes in the temperature region of 77–170 K. This may be due to 1) kinetic effects; it can be assumed that after lowering the crystals into liquid nitrogen, nonequilibrium quenching defects are formed, which disappear after the crystal is warmed up with an increase in temperature; 2) the beginning of a noticeable contribution of intrinsic conductivity; 3) the effective mass starts to grow noticeably with a temperature of about 160 K. which was reported in the works [19, 20] and testified from the point of view of the authors about the two-band structure of both valence and conductivity bands.

The Hall coefficient for both studied freshly prepared [16] and aged thin films, regardless of the composition of the initial material, conductivity type, film thickness, decreases with increasing temperature in the range 77–300 K (Fig. 1,3). 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

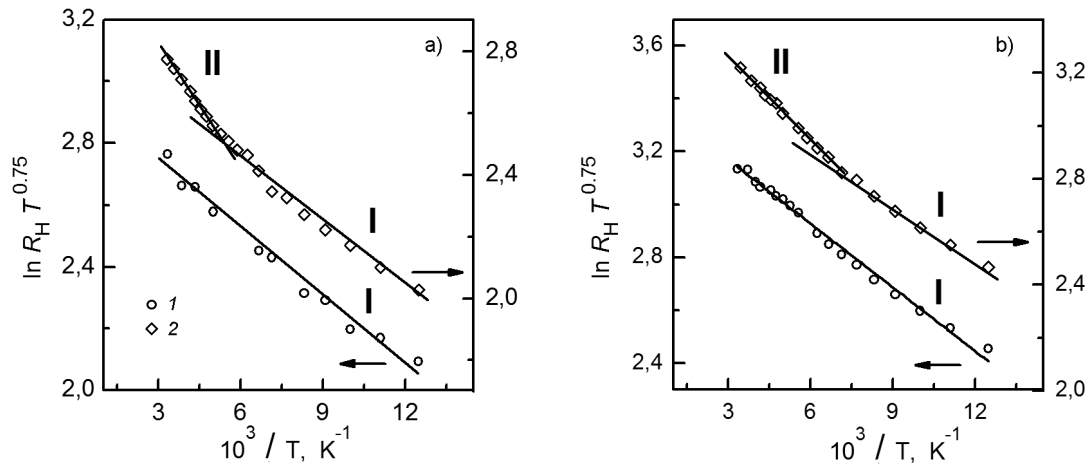


Fig. 4. Dependences of $\ln(R_H T^{0.75})$ on inverse temperature ($1/T$) for thin Bi_2Te_3 films with thicknesses $d = 620$ nm (a) and $d = 335$ nm (b). The Hall coefficient R_H values are given in units of cm^3/C . 1 — freshly prepared films [15, 16], 2 — films after aging.

of defect states whose sources may be grain boundaries and surface defects. The change in the type of conductivity in the p -type film as a result of aging could be explained by several reasons:

1) upon prolonged exposure to air, even at room temperature, the system slowly approaches the equilibrium corresponding to a lower temperature. In this case, the defect structure changes with a high probability, for example, the predominant defects are not antisite defects, but Te vacancies. In films, this occurs faster than in a bulk crystal, and therefore, even in a thick film ($d = 620$ nm) after 5 years, this happened, but in a bulk crystal the conductivity sign did not change;

2) since the film was not coated in air, oxygen could penetrate into the film from all sides, and not only through the surface layer. Since this process took place for a very long time, a very high concentration of n -type charge carriers could be created in the volume of the film, as a result of which an inversion $p \rightarrow n$ of the conductivity type could occur;

3) the fact that the character of the $R_H(T)$ dependences qualitatively changes in the freshly prepared p -type thin film compared with p -type polycrystal, indicates, as noted above, about changes in the band structure, which, in turn, can lead to a shift in the position of the inversion point; the p -type film, obtained from the Bi_2Te_3 crystal of stoichiometric composition, is very sensitive to the effect of various factors on the conductivity sign, since the composition of this film is very close to the point of the inversion of the conductivity sign in the Bi-Te system.

In Fig. 2(a-c), the temperature dependences of the S and P for the p - and n - Bi_2Te_3 polycrystals and for thin film with $d = 335$ nm, which was grown from n - Bi_2Te_3 are presented. You can see that the Seebeck coefficient increases with increasing temperature for crystals and the film both before and after aging.

Since materials based on the V_2VI_3 compounds operate most efficiently at temperatures close to room temperature, the main interest was the behavior of the kinetic coefficients after aging precisely at these temperatures. At 300 K, in a polycrystal, the values of σ , μ_H , R_H for freshly prepared and aging samples practically coincide, the values of S decrease for a polycrystal, as a result of which P decreases. It was found that after aging the P of p - and n - Bi_2Te_3 polycrystals at 300 K decreases by ~ 10 – 15 %.

A different picture is observed for thin films. For n -type thin film ($d = 335$ nm) obtained from n - Bi_2Te_3 polycrystal, P after aging increases by ~ 20 %. Even higher values of P are obtained after aging of n -type films obtained from a p - Bi_2Te_3 crystal. In Fig. 3, the temperature dependences of σ , R_H , μ_H , S and P of an n -type film obtained from n - Bi_2Te_3 polycrystal and an n -type film grown from a p - Bi_2Te_3 polycrystal after aging are shown. The dependences $P(T)$ for the n - Bi_2Te_3 crystal after aging are also shown. From the $P(T)$ dependences, it can be seen that at room temperature, after aging, the TE power factor values of the film obtained from the p - Bi_2Te_3 polycrystal are ~ 20 % higher than the P values of the film obtained from the n - Bi_2Te_3 polycrystal. The P value for n - Bi_2Te_3 polycrys-

Table. Activation energy values for freshly prepared and aged p - and n - Bi_2Te_3 films

	ΔE_1 , meV	ΔE_2 , meV	Reference
Freshly prepared films			[16]
p - Bi_2Te_3 film $d = 620$ nm	12.0 ± 0.5		
n - Bi_2Te_3 film $d = 335$ nm	13.05 ± 0.5		
Films after aging in air at room temperature for 5 years			Present work
n - Bi_2Te_3 film $d = 620$ nm	12.0 ± 0.5	22.0 ± 1.0	
n - Bi_2Te_3 film $d = 335$ nm	12.5 ± 0.5	20.0 ± 1.0	

tal at room temperature is about 15 % higher than the P value for n -type thin film obtained from p - Bi_2Te_3 .

From Figs. 1,3, it can be seen that for films both of n - and p -types, the R_H value decreases with increasing temperature, as before aging. This nature of the $R_H(T)$ dependence before the intrinsic conductivity begins to make a significant contribution, 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 and aging.

For more detailed information on the effect of such centers on the kinetic properties, the dependences $\ln(R_H T^{0.75}) - (1/T)$ were constructed, from which the activation energies of the possible defects were determined. 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. In Fig. 4, the $\ln(R_H T^{0.75}) - (1/T)$ dependences plotted on the basis of the $R_H(T)$ curves (Fig. 1) are presented for freshly prepared and aged films. For freshly prepared from n - Bi_2Te_3 polycrystal film of n -type with $d = 335$ nm, the level with activation energy $\Delta E_1 = 13.5 \pm 0.5$ meV was detected [16] but in the aged film, two levels with activation energies $\Delta E_1 = 12.5 \pm 0.5$ meV and $\Delta E_2 = 20.0 \pm 1.0$ meV are found. In freshly prepared from p - Bi_2Te_3 polycrystal p -type film with $d = 620$ nm, the level with activation energy $\Delta E_1 = 12.0 \pm 0.5$ meV was detected [16] but in aged film, which changed the type of conductivity ($p \rightarrow n$), two levels with activation energies $\Delta E_1 = 12.0 \pm 0.5$ meV and $\Delta E_2 = 22.0 \pm 1.0$ meV are found. Calculated from the data in Fig. 4 activation energies together with data for freshly prepared films are presented in Table. It can be seen that the activation energies ΔE_1 are very close for p - and n -type films, for freshly prepared and aged films, and practi-

cally independent of thickness. It can be seen also that the activation energies ΔE_2 are very close for aged n -type films, obtained from n - Bi_2Te_3 and p - Bi_2Te_3 polycrystals and practically independent of thickness. This fact indicates the similarity of origin of the defects in all these cases. It can be assumed, for example, that the source of defects with the activation energy ΔE_1 are grain boundaries in the polycrystal, and the source of defects with the activation energy ΔE_2 are defects that appear as a result of the interaction of the films with the surrounding air. However, to clarify the genesis of these defects, more detailed studies are required.

It is clear that an important parameter determining the degree of film oxidation is the film thickness, because with decreasing d , the role of the oxidized layer in the formation of the properties of a thin film structure increases. It should be noted that it is of interest to study the effect of aging on the properties of thinner Bi_2Te_3 films of both p - and n -types. Such studies are of growing interest both from an applied point of view, taking into account the increasing use of low-dimensional structures in thermoelectricity and other fields of science and technology, and from a fundamental point of view. Today there is a severe shortage of research shedding light on the properties of a metal surface layer with a Dirac dispersion law in the newest objects of solid state physics — topological insulators, which include and Bi_2Te_3 . To carry out such studies, very thin films are required, in which the surface topological layer makes a significant contribution to the film conductivity. The study of aging processes in thinner films is the subject of our current research.

4. Conclusions

Electrical conductivity and Hall charge carrier mobility both for the p - and n - Bi_2Te_3 polycrystals and films decrease with increasing temperature. This fact and the

magnitude of the charge carrier concentration ($n(p) \sim 10^{19} \text{ cm}^{-3}$) indicate the degeneracy of electron and hole gases.

After aging, in the p - and n - Bi_2Te_3 bulk crystals and in the n -type film obtained from the n - Bi_2Te_3 crystal, type of conductivity is reserved, but the p -type film obtained from the p - Bi_2Te_3 polycrystal, changes the type of conductivity from hole to electronic.

In the p - Bi_2Te_3 crystal (60.0 at.% Te), before and after aging, an increase in R_H with temperature is observed, which we associate with the two-band structure of the valence band of p - Bi_2Te_3 . In freshly prepared crystal, R_H growth is characterized by the presence of an inflection point near 170 K, the existence of which we associate with the beginning of the growth of the effective mass of holes. After aging, the $R_H(T)$ dependence does not change in the range 170–300 K, but the inflection disappears, and the $R_H(T)$ dependence becomes almost linear over the entire temperature range (77–300 K).

In the n - Bi_2Te_3 crystal (62.8 at.% Te), before aging, R_H value practically does not change in the range 77–170 K, after which it decreases. After aging, the $R_H(T)$ dependence does not change in the range 170–300 K, and in the range 77–170 K, the value of R_H decreases and a slight increase in R_H with temperature takes place. The observed features are attributed to the presence of two subbands in the conduction band of n - Bi_2Te_3 , the temperature dependence of the effective mass, and a change in the defect structure.

5. After aging, all films obtained both from the p - and n - Bi_2Te_3 polycrystals, have n -type conductivity and R_H decreases with increasing temperature in the range 77–300 K. This fact is attributed to the existence of defect states.

After aging, at the temperatures close to room temperature, the P values of n - Bi_2Te_3 and p - Bi_2Te_3 polycrystals decrease by ~ 20 –25 %, but P values of the n -type film grown from n - Bi_2Te_3 crystal increase by 20–30 %. In the p -type film obtained from p - Bi_2Te_3 polycrystal, and having changed the n -type of conductivity after aging, the P values exceed the P values of a film obtained from n - Bi_2Te_3 polycrystal by ~ 35 % at 250 K and by 25 % at 300 K, remaining at these temperatures below the P values for n - Bi_2Te_3 polycrystal after aging by ~ 15 %.

The activation energies of possible defect states are determined by plotting the $\ln(R_H T^{0.75}) - (1/T)$ dependences. It turned out that in the n - and p -type Bi_2Te_3 freshly prepared and aged films there are defect

states with an activation energies $\Delta E_1 = 12$ –13) meV. After aging, in thin films, new defect states with activation energy of $\Delta E_2 = 21$ –22) meV appear additionally.

Acknowledgements. This work was supported by the Ministry of Education and Science of Ukraine (Project # M 0625).

References

1. Thermoelectrics Handbook: Macro to Nano, ed. by D.M.Rowe, CRC Press, Taylor & Francis Group, Boca Raton (2005). <https://doi.org/10.1201/-9781420038903>
2. Materials Aspect of Thermoelectricity, ed. by C.Uher, CRC Press, Boca Raton (2016). <https://doi.org/10.1201/9781315197029>.
3. B.M.Goltsman, V.A.Kudinov, I.A.Smirnov, Semiconducting Thermoelectric Materials Based on Bi_2Te_3 , Nauka, Moscow (1972) [in Russian].
4. H.J.Goldsmid, Introduction to Thermoelectricity, Springer Berlin Heidelberg, Berlin (2016).
5. M.S.Dresselhaus, G.Chen, M.Y.Tang et al., *Adv. Mater.*, **19**, 1043 (2007). DOI: 10.1002/adma.200600527
6. R.Venkatasubramanian, E.Siivola, T.Colpitts, B.O.Quinn, *Nature*, **413**, 597 (2001).
7. L.Fu, C.L.Kane, *Phys. Rev. B*, **76**, 045302 (2007).
8. M.Z.Hasan, C.L.Kane, *Rev. Mod. Phys.*, **82**, 3045 (2010).
9. L.Muchler, F.Casper, B.Yan et al., *Phys. Status Solidi RRL*, **7**, 91 (2013). DOI: <http://dx.doi.org/10.1002/pssr.201206411>
10. D.Culcer, *Physica E*, **44**, 860 (2012). DOI: <http://dx.doi.org/10.1016/j.physe.2011.11.003>
11. E.I. Rogacheva, A.V.Budnik, O.S.Vodorez et al., *J. Thermoelectricity*, **6**, 42 (2014).
12. A.V.Budnik, E.I.Rogacheva, V.I.Pinegin et al., *J. Electron. Mater.*, **42**, 1324 (2013). <https://doi.org/10.1007/s11664-012-2439-1>
13. E.I.Rogacheva, A.V.Budnik, A.Yu.Sipatov et al., *Appl. Phys. Lett.*, **106**, 053103 (2015). DOI: <https://doi.org/10.1063/1.4907319>.
14. E.I.Rogacheva, A.V.Budnik, A.Yu.Sipatov et al., *Thin Solid Films*, **594**, 109 (2015). DOI: <https://doi.org/10.1016/j.tsf.2015.10.023>.
15. E.I.Rogacheva, K.V.Novak, A.N.Doroshenko et al., *J. Nano-Electron. Phys.*, **5**, 04001 (2019).
16. E.I.Rogacheva, K.V.Novak, A.N.Doroshenko et al., *Functional Materials*, **27**, 67 (2020).
17. H.Bando, K.Koizumi, Y.Oikawa et al., *J. Phys.:Condens. Matter.*, **12**, 5607 (2000).
18. E.I.Rogacheva, O.N.Nashchekina, A.V.Budnik et al., *Thin Solid Films*, **612**, 128 (2016).
19. C.H.Champness, A.L.Kipling, *Can. J. Phys.*, **44**, 769 (1966).
20. C.H.Champness, A.L.Kipling, *J. Phys. Chem. Solids*, **27**, 1409 (1966).
21. V.A.Kulbachinski, X.Osaku, I.Miahara, K.Funagay, *Zh. Eksper. Teor. Fiziki*, **124**, 1358 (2003).