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EFFECT OF FABRICATION TECHNIQUE ON THE STRUCTURE AND THERMOELECTRIC PROPERTIES OF Bi_2Te_3 FILMS

Considerable increase in thermoelectric (TE) figure of merit of Bi_2Te_3 thin films under the effect of annealing has been emphasized in several papers. However, there are practically no works on the effect of annealing on TE properties and structure of Bi_2Te_3, films prepared by one-source thermal evaporation in vacuum. This investigation is concerned with unannealed and annealed at 500 K for 1 hour Bi_2Te_3 thin films of thickness d ~ 200 nm, prepared by one-source thermal evaporation in vacuum using different initial charge compositions (60 and 62.8 at.% Te) and different substrate temperatures (T_{sub} = 320 – 500 K). It is shown that regardless of the initial charge composition and substrate temperature, annealing contributes to structural perfection of Bi_2Te_3 films and formation of a well-expressed texture, however, unlike the films grown from a charge with 60 at.% Te, TE power P of films prepared from a charge with Te excess is reduced. Optimal parameters of Bi_2Te_3 films growth have been determined, yielding maximum P values comparable to TE power of films prepared by more costly and labour-consuming methods.

Key words: bismuth telluride, film, annealing, structure, thermoelectric properties.

Introduction

Semiconductor compound Bi_2Te_3 and solid solutions on its basis are among the best low-temperature thermoelectric (TE) materials possessing TE figure of merit Z within $1.0 – 2.9 \cdot 10^{-3}$ K^{-1} [1-3]. These materials have found a wide application when creating coolers, temperature and infrared sensors and other TE devices.

New vistas for practical application of low-dimensional structures draw attention to investigation of bismuth telluride in the thin-film state. Bi_2Te_3 films are prepared by various methods: molecular-beam epitaxy, magnetron sputtering, hot wall, liquid-phase epitaxy, laser evaporation, two-source thermal evaporation, etc. [4-10].

It is known that annealing produces a considerable effect on TE properties of Bi_2Te_3 [4-9]. Owing to recrystallization and homogenization during annealing, the material approaches the equilibrium state, the degree of perfection of crystalline structure is improved, the size of grains is increased, the width of their boundaries is reduced and well-expressed texture is formed. These processes are particularly important in the fabrication of bismuth telluride films tending to formation of concentration inhomogeneities during crystallization, resulting in the emergence of additional antisite defects and concentration growth of major charge carrier [4-10]. On the other hand, high-temperature annealing can lead to activation of tellurium re-evaporation processes, violating film stoichiometry and causing formation of additional number of defects.

It should be also noted that positive impact of annealing on TE and galvanomagnetic properties of Bi_2Te_3 films differs essentially with the use of different sputtering methods. Thus, for films prepared by one-source magnetron sputtering just a slight growth of TE power P (by ~ 20 %) is recorded [4],

whereas for films prepared with the use of molecular beam epitaxy (MBE), P is increased by a factor of almost 4. In so doing, all the works mention the emergence of a well-expressed texture and grain size increase in the structure of annealed films. In the majority of papers [4-6], films with the best TE properties were obtained after annealing for 1 hour at T_a = 570 K, though with the use of two-source magnetron sputtering [7] optimal film parameters were observed after 8 hours of annealing at T_a = 470 K. This indicates the necessity of special research of the effect of annealing for each method of growing the Bi_2Te_3 films.

One of the simple, accessible and cheap methods for preparation of bismuth telluride films is one-source thermal evaporation in vacuum. As compared to other, technologically more complicated methods, such as molecular beam epitaxy, it requires considerably less time for the fabrication of one film, which is important for large production volumes. However, the main disadvantage of this method is a restricted control of evaporation process resulting in formation of microstresses, concentration inhomogeneities and defects in synthesized films. This disadvantage can be at least partially removed by annealing.

The subject of research are bismuth telluride thin films of thickness $d \sim 200$ nm, prepared by one-source thermal evaporation in vacuum with the use of different initial charge compositions (60 and 62.8 at.% *Te*) and different substrate temperatures (T_{sub} = 320 – 500 K), and unannealed and annealed at a temperature of T_a = 500 K for 1 hour.

The purpose of the work is to study the effect of annealing on TE properties of Bi_2Te_3 films.

Experimental procedure

Polycrystalline samples of both stoichiometric composition (60.0 at. % *Te*) and with tellurium excess (62.8 at. %), used as a charge for preparation of films, were made by direct alloying of *Bi* and *Te* components of high purity (99.999 %). The initial components were placed into quartz ampoules, evacuated (to $\sim 10^{-5}$ Pa), then synthesized at a temperature of 800 K with subsequent annealing at 670 K within 300 hours.

Films were grown by thermal evaporation of charge in oil-free vacuum ($10^{-5} – 10^{-6}$ Pa) and subsequent condensation on glass substrates heated to temperatures in the range of T_{sub} = 320 – 500 K. Annealing was performed directly in the installation, immediately after evaporation of the film. The accuracy of measuring substrate temperature T_{sub} was 5 %. Prior to evaporation, the substrates were consecutively cleaned with acid, distilled water and alcohol. Film thickness d and condensation rate were controlled by means of a calibrated quartz resonator located beside the substrates. The resonator calibration for films up to 100 nm thick was made with the use of *X*-ray diffraction patterns of small-angle scattering for single-layer films by comparing the experimental and calculated *X*-ray patterns. Diffraction curves were obtained on DRON-2.0 diffractometer with a primary-beam graphite monochromator. For fitting the calculated curve to the experimental one, two parameters were varied independently: film thickness and roughness. The accuracy of d determination by *X*-ray diffraction method was not lower than ~ 0.5 nm. Resonator calibration for large thicknesses ($d > 100$ nm) was performed using MII-4 interferometer to an accuracy of ± 10 %. Fig. 1 exemplifies the experimental and calculated diffraction curves for a film of 26 nm in thickness and 2 nm in roughness. *X*-ray diffraction analysis of the bulk crystals and Bi_2Te_3 thin films was performed on DRON-2 setup in CuK_α-radiation in the mode $\Theta – 2\Theta$.

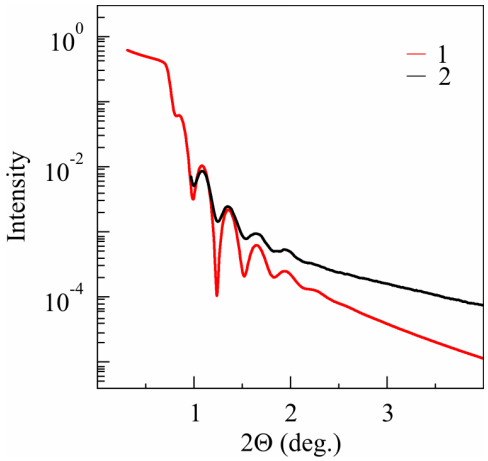

Fig. 1. Fitting of calculated curve (1) to experimental curve (2) for a film 26 nm in thickness and 2 nm in roughness.

The Hall coefficient R_H and electric conductivity σ were measured by direct current and constant magnetic field method on polycrystalline samples shaped as a parallelepiped of size 3 × 2 × 10 mm and film samples shaped as a double Hall cross of size 3 × 1 mm. The Seebeck coefficient S was determined by compensation method with respect to copper electrodes. The error in measuring σ, R_H and S did not exceed ± 5 %. The Hall concentration $n_H(p_H)$ and mobility μ_H were determined by the formulae for one type of charge carriers: $n_H(p_H) = 1/e{\cdot}R_H$ (where e is electron charge) and νδ $\mu_H = \sigma{\cdot}R_H$. All investigations were performed at room temperature.

Discussion of results

Based on the results of other works [4-9], annealing was first performed at a temperature of $T_a \sim 570$ K, however, under conditions of oil-free vacuum this caused partial film evaporation, as testified by the absence of electrical conductivity, reduction of film thicknessи, structural imperfection, as well as considerable inhomogeneity, noticeable even during visual inspection of the film. Therefore, as the annealing temperature we selected maximum temperature ($T_a = 500$ K) causing no visible imperfections of film structure.

X-ray structural analysis of the resulting films showed an improved degree of structural perfection and grain enlargement under the influence of annealing (Fig. 2).

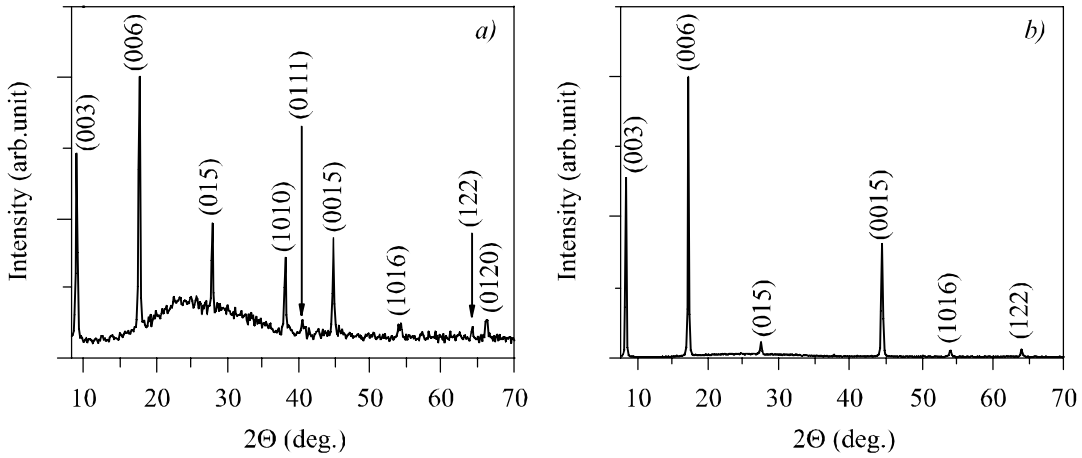

Fig. 2. X-ray diffraction patterns of Bi_2Te_3 (60 at.% Te) films prepared at T_{sub} = 500 K: without annealing (a) and with annealing at temperature T_a = 500 K within 1 hour (b).

For comparison, peak (006) was selected as the most intensive peak present on *X*-diffraction patterns of films subjected to annealing and prepared without the use of annealing. The half-width of the peak was determined by means of NewProfile 3.4 program. It was established that for films obtained from a charge of stoichiometric composition the half-width of the peak (006) on *X*-ray diffraction patterns of annealed films is ~ 40 % smaller than the half-width of a similar peak in the case of unannealed films. Moreover, on *X*-ray diffraction patterns of annealed films obtained from a charge of stoichiometric composition, considerable increase is recorded in the intensity of peaks (003), (006), (0015) corresponding to crystallographic direction (001), which can testify to formation of texture in this direction.

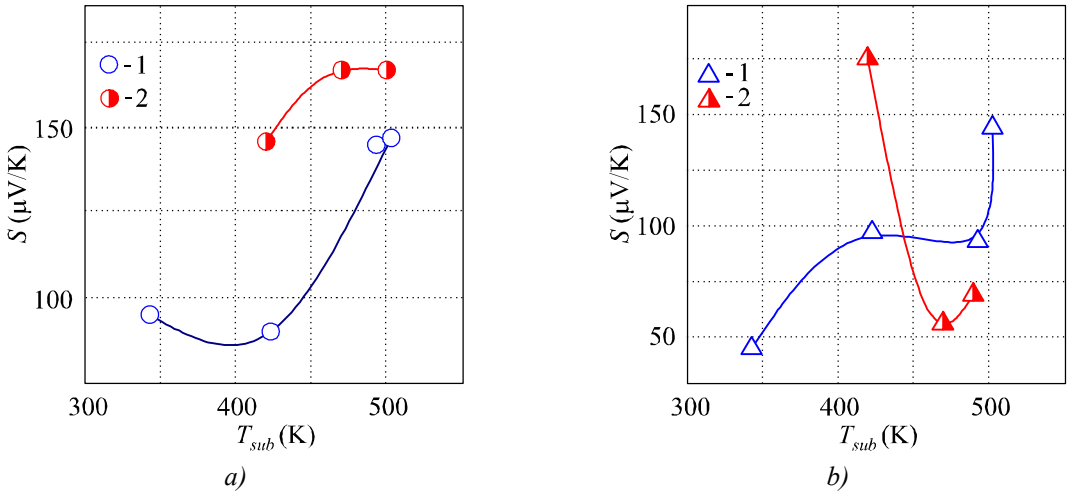

Fig. 3. The Seebeck coefficient S as a function of substrate temperature T_{sub} for films prepared from Bi_2Te_3 (60.0 at. % Te) charge (a) and films prepared from a charge with tellurium excess (62.8 at. % Te) (b): 1 – films manufactured without annealing, 2 – films manufactured with the use of annealing (T_a = 500 K within 1 hour).

To establish the effect of annealing on the basic TE properties (S, σ, μ_H and n_H (p_H)), the dependences of respective properties on substrate temperature (Figs. 3 – 7) were obtained for unannealed and annealed films. Conduction type in the unannealed and annealed films coincided with the conduction type of the initial crystals of which films were prepared: *p*-type conduction in stoichiometric crystals and *n*-type conduction in bismuth telluride crystals with tellurium excess.

Table 1

Thermoelectric parameters of unannealed and annealed films

Initial charge composition, at. % *Te*		60		62.8	
T_{sub}, K		420	500	420	490
S, μV/K	prior to annealing	90	147	–97	–93
	after annealing	146	167	–175	–69
σ, Ω^{-1} cm^{-1}	prior to annealing	456	357	272	387
	after annealing	640	603	21	363
μ_H, cm^2/V·s	prior to annealing	53	71	22	49
	after annealing	131	436	84	25
$n_H(p_H)$, 10^{19} cm^{-3}	prior to annealing	5	3	79	4
	after annealing	3	1	2	9
P, 10^{-4} W/K^2·m	prior to annealing	4	8	26	34
	after annealing	14	18	6	17

As is clear from Fig. 3 *a*, in the case of films obtained from a charge of stoichiometric composition, regardless of substrate temperature, annealing contributes to *S* increase apparently caused by p_H reduction (Fig. 6 *a*). It can be explained by improved perfection of crystal structure and increased size of grains leading to reduced concentration of antisite defects, i.e., the main reason for high charge carrier concentrations in Bi_2Te_3 films [1]. This hypothesis is confirmed by the results of *X*-ray structural analysis and is in good agreement with the observed growth of μ_H (Fig. 5 *a*).

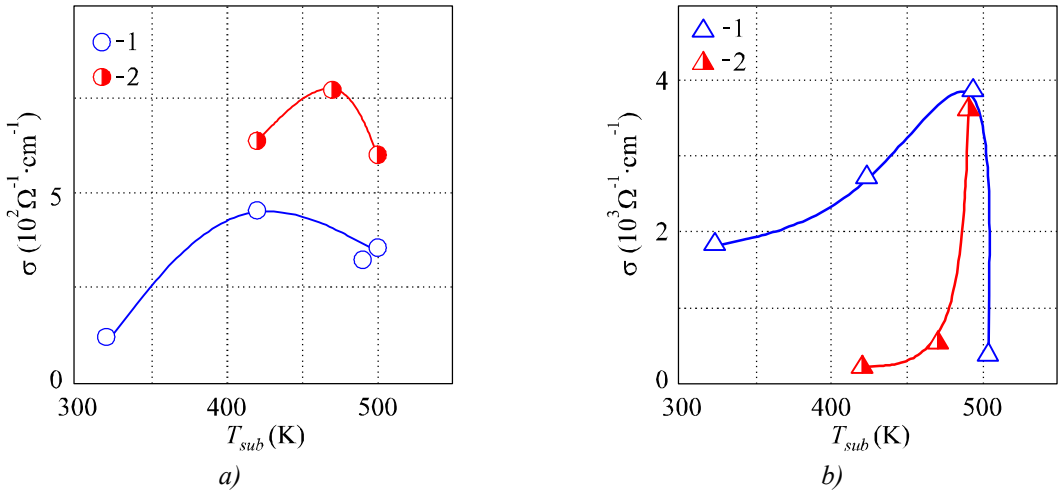

Fig. 4. Electric conductivity σ as a function of substrate temperature T_{sub} for films prepared from Bi_2Te_3 (60.0 at. % Te) charge (a) and films prepared from a charge with tellurium excess (62.8 at. % Te) (b): 1 – films manufactured without annealing, 2 – films manufactured with the use of annealing (T_a = 500K within 1 hour).

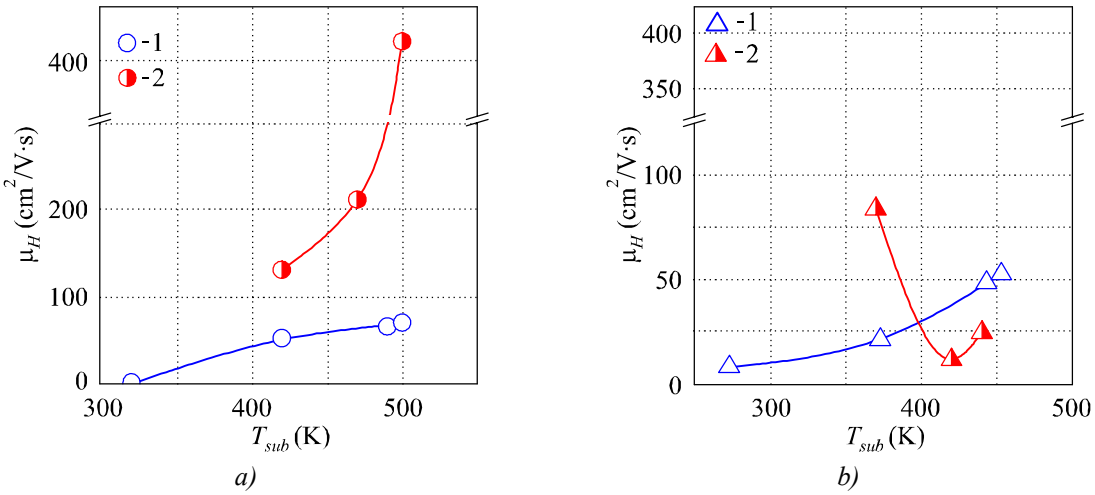

Fig. 5. Charge carrier mobility μ_H as a function of substrate temperature T_{sub} for films prepared from Bi_2Te_3 (60.0 at. % Te) charge (a) and films prepared from a charge with tellurium excess (62.8 at. % Te) (b): 1 – films manufactured without annealing, 2 – films manufactured with the use of annealing (T_a = 500 K within 1 hour).

It should be noted that positive effect of annealing on TE properties of films prepared from a charge of stoichiometric composition is observed over the entire range of substrate temperatures, but annealing produces different effect at different T_{sub}. The effect of annealing is increased with a rise in substrate temperature for all TE and galvanomagnetic properties, except for the value of *S* which at $T_{sub} > 470$ K achieves its maximum and essentially does not increase with further growth of T_{sub}. At the

same time, increase in T_{sub} above 470 K leads to further reduction of hole concentration and, despite mobility growth, leads to electric conductivity reduction. Thus, the optimal substrate temperature for films prepared from a charge of stoichiometric composition and subjected to annealing is $T_{sub} = 470$ K (Fig. 7 *a*), rather than 500 K, as in the case of films grown without annealing [10]. In so doing, TE power of annealed films is about 2.5 times higher than that of unannealed ones and is comparable to the highest values of TE power obtained in the films grown by other methods. Thus, the value of TE power obtained in this paper ($P \sim 20 \cdot 10^{-4}$ W/K^2·m) practically coincides with the P value of films obtained by magnetron sputtering method or two-source thermal evaporation method [7, 8], but is lower than for films prepared by ion-beam sputtering method ($P \sim 65 \cdot 10^{-4}$ W/K^2·m) [9].

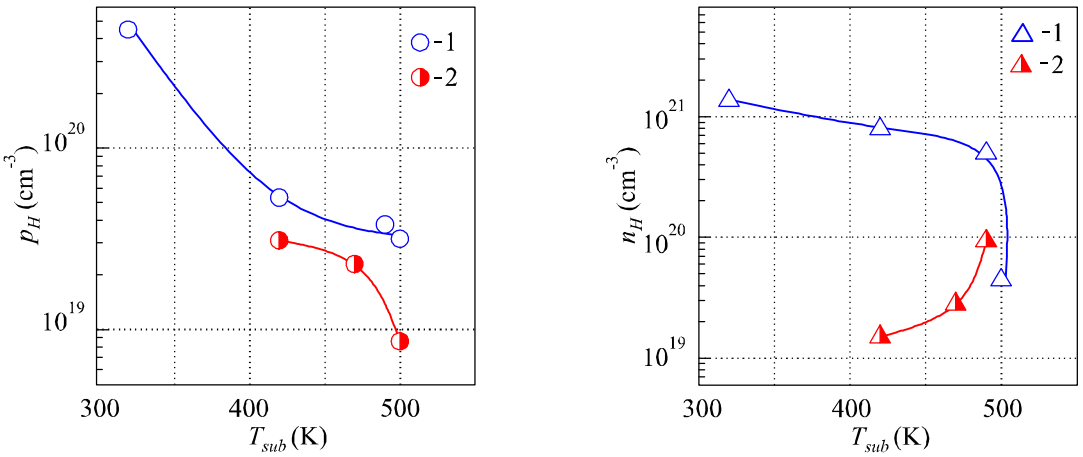

Fig. 6. Concentration of charge majority carriers $n_H(p_H)$ as a function of substrate temperature T_{sub} for films prepared from Bi_2Te_3 (60.0 at. % Te) charge (a) and films prepared from a charge with tellurium excess (62.8 at. % Te) (b): 1 – films manufactured without annealing, 2 – films manufactured with the use of annealing (T_a = 500 K within 1 hour).

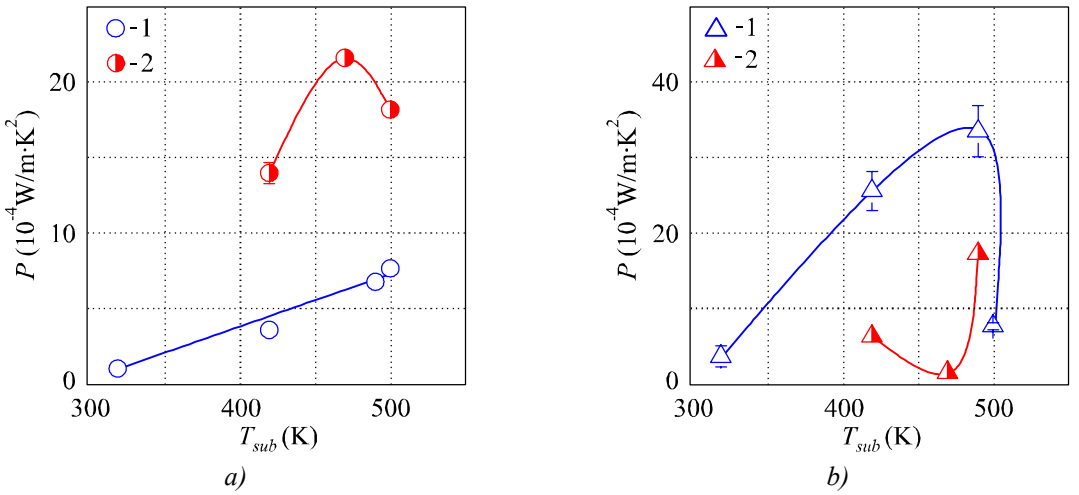

Fig. 7. Thermoelectric power P as a function of substrate temperature T_{sub} for films prepared from Bi_2Te_3 (60.0 at. % Te) charge (a) and films prepared from a charge with tellurium excess (62.8 at. % Te) (b): 1 – films manufactured without annealing, 2 – films manufactured with the use of annealing (T_a = 500 K within 1 hour).

The situation is quite different with the use of annealing the films prepared from a charge with *Te* excess. As in the case of films prepared from a charge of stoichiometric composition, annealing

leads to crystal structure perfection and reduction of crystal lattice defects concentration. This is supported by the fact of increase in electron mobility μ_H after the use of annealing (Fig. 5 *b*), testifying to reduced scattering on crystal lattice defects, as well as a decrease in n_H (Fig. 6 *b*), which, as mentioned before, is related to a reduced concentration of intrinsic defects [1]. Nevertheless, in the annealed films, *S* does not increase more than ~ 2 times, whereas σ is reduced by a factor of almost 20 (Fig. 4 *b*), which yields a considerable reduction of TE power (Fig. 7 *b*). It can be supposed that at optimal substrate temperature $T_{sub} = 490$ K the unannealed films are in the nonequilibrium state characterized by concentration inhomogeneity, high content of antisite defects and high charge carrier concentration ($n_H \sim 10^{20} - 10^{21}$ cm^{-3}) [11], and that in this state there is mainly low-energy electron scattering, which creates energy filtration of current carriers and, accordingly, preserves high values of *S*. Annealing results in relaxation processes leading not only to reduction of n_H and increase of μ_H, but also disturbing the energy filtration with a consequent reduction of *S*. Thus, it can be concluded that although annealing contributes to structural perfection of Bi_2Te_3 films prepared from a charge with *Te* excess, on the whole, TE parameters of unannealed films are higher due the nonequilibrium state. Therefore, annealing of films prepared from a charge with tellurium excess is unreasonable.

Conclusions

1. The method of one-source thermal evaporation in vacuum at different substrate temperatures ($T_{sub} = 300 - 500$ K) has been used to prepare bismuth telluride films from a charge of stoichiometric composition (60 at. % *Te*) and from a charge comprising 62.8 at. % *Te* without annealing and with the use of annealing at $T_{sub} = 500$ K within 1 hour.
2. It has been established that regardless of the initial charge composition, annealing contributes to structural perfection, increase of grain size and formation of a well-expressed texture.
3. It has been shown that for films prepared from a charge of stoichiometric composition annealing leads to increase in thermoelectric power *P*, the maximum value of which ($P = 20 \cdot 10^{-4}$ W/K^2·m) is observed at substrate temperature $T_{sub} = 470$ K and is 2.5 times larger than the maximum value of *P* in a film prepared under optimal conditions, but without the use of annealing.
4. It has been established that although annealing contributes to structural perfection of Bi_2Te_3 films prepared from a charge with *Te* excess, annealed films have lower values of TE power than unannealed ones, which is due to the nonequilibrium state in the latter.
5. The results of this work are of practical interest, since they can be used for improvement of TE parameters of Bi_2Te_3 films grown by the method of one-source thermal evaporation in vacuum.

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