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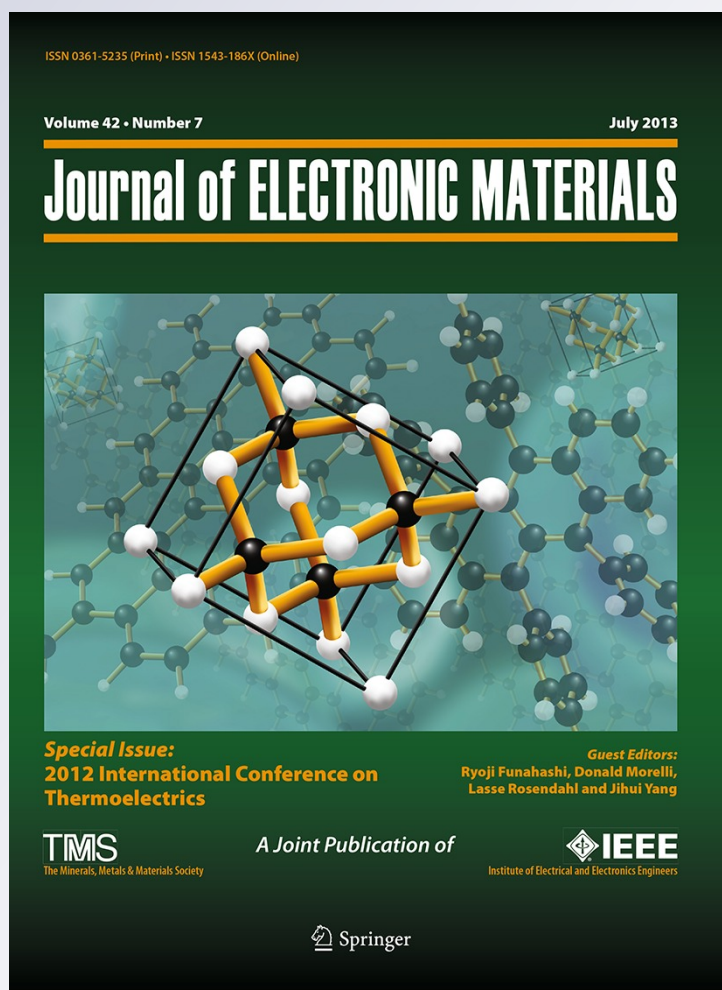
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Effect of Initial Bulk Material Composition on Thermoelectric Properties of Bi_2Te_3 Thin Films

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V_2VI_3 compounds and solid solutions based on them are known to be the best low-temperature thermoelectric (TE) materials. The predicted possibility of enhancement of the TE figure of merit in two-dimensional (2D) structures has stimulated studies of the properties of these materials in the thin-film state. The goal of the present work is to study the dependences of the Seebeck coefficient S , electrical conductivity σ , Hall coefficient R_H , charge carrier mobility μ_H , and TE power factor $P = S^2\sigma$ of Bi_2Te_3 thin films on the composition of the initial bulk material used for preparing them. Thin films with thickness $d = 200$ nm to 250 nm were grown by thermal evaporation in vacuum of stoichiometric Bi_2Te_3 crystals (60.0 at.% Te) and of crystals with 62.8 at.% Te onto glass substrates at temperatures T_S of 320 K to 500 K. It was established that the conductivity type of the initial material is reproduced in films fairly well. For both materials, an increase in T_S leads to an increase in the thin-film structural perfection, better correspondence between the film composition and that of the initial material, and increase in S , R_H , μ_H , σ , and P . The room-temperature maximum values of P for the films grown from crystals with 60.0 at.% and 62.8 at.% Te are $P = 7.5 \times 10^{-4}$ W/K² m and 35×10^{-4} W/K² m, respectively. Thus, by using Bi_2Te_3 crystals with different stoichiometry as initial materials, one can control the conductivity type and TE parameters of the films, applying a simple and low-cost method of thermal evaporation from a single source.

Key words: Bi_2Te_3 thin films, bulk material, stoichiometry, substrate temperature, thermoelectric properties

INTRODUCTION

Bi_2Te_3 semiconductor compound and Bi_2Te_3 -based solid solutions are among the best low-temperature thermoelectric (TE) materials, being widely applied in TE devices of different types.^{1,2} Broad prospects for practical applications of low-dimensional structures stimulate study of bismuth telluride in the thin-film state.

Bi_2Te_3 films can be obtained by different methods, such as molecular-beam epitaxy, magnetron sputtering,

hot-wall epitaxy, liquid-phase epitaxy, laser evaporation, thermal evaporation from a single or from two sources, electrochemical deposition, and others.³⁻⁹

Improvements in the technology of Bi_2Te_3 film preparation for TE applications are aimed at enhancing the dimensionless TE figure of merit $ZT = S^2\sigma T/\lambda$ (S is the Seebeck coefficient, σ is the electrical conductivity, λ is the thermal conductivity, and T is the absolute temperature) and TE power factor $P = S^2\sigma$, which determine the efficiency of TE materials.

One of the simplest low-cost methods for thin-film preparation is thermal evaporation in vacuum from a single source. However, the main deficiency of this method is limited control over the deposition process.

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The substrate temperature T_S is one of the most important factors determining the properties of Bi₂Te₃ thin films. On the one hand, increasing T_S leads to improvement of crystal structure, increase in grain size, and formation of more pronounced texture.^{5,7} On the other hand, an increase in T_S can cause deviation from stoichiometry in the film (for example, as a result of re-evaporation of tellurium) and, consequently, changes in the defect structure. The dominant defects in Bi₂Te₃ are antistructural defects.¹⁰ Excess (relative to the stoichiometric composition) bismuth atoms create antistructural defects with the formation of additional holes, whereas excess tellurium atoms create antistructural defects with the formation of additional electrons. This is why deviation from the stoichiometric composition to the side of Te excess leads to an increase in the electron concentration, while deviation to the side of Te deficit leads to an increase in the hole concentration.^{11,12}

Taking into consideration the above factors, it becomes clear that the optimum T_S must strongly depend on the method of thin-film preparation, technological parameters, and the composition of the bulk crystals of bismuth telluride used as the initial material for growing films.

Usually, stoichiometric Bi₂Te₃ (60 at.% Te) or high-purity (99.99 at.%) Bi and Te components are used as a charge for film preparation, and the optimum substrate temperature T_S is varied in the range of 500 K to 600 K.³⁻⁸

The goal of the present work is to establish the possibility of controlling the conductivity type and TE properties of thin films of bismuth telluride by changing the composition of the initial material when using the method of thermal evaporation in vacuum from a single source.

The objects of the study are bismuth telluride thin films with thickness $d = 200$ nm to 250 nm prepared by thermal evaporation in vacuum from initial materials with different compositions (60.0 at.% and 62.8 at.% Te) and at different substrate temperatures (320 K to 500 K).

EXPERIMENTAL PROCEDURES

Polycrystalline samples, which were used as the initial material for the thin-film preparation, were synthesized by direct melting of Bi and Te components of high purity (99.999 at.%) at temperature of 800 K in evacuated quartz ampoules with subsequent annealing at 670 K for 300 h. Polycrystals were obtained with both stoichiometric composition (60.0 at.% Te) and Te excess (62.8 at.% Te). The chemical compositions of the samples were determined by energy-dispersive x-ray spectroscopy (EDX) in a scanning electron microscope (SEM, EDS JXA-50A; JEOL) operated in point mode with accuracy of 0.5 at.%.

It is known that, at room temperature, stoichiometric bismuth telluride exhibits *p*-type conductivity,

whereas the composition 62.8 at.% Te, exhibiting *n*-type conductivity, lies near the boundary separating *p*- and *n*-regions in the Bi-Te system in the concentration range adjacent to Bi₂Te₃.^{11,12} In a number of works it was reported that, because of the large difference in partial pressure between Bi and Te vapors, a loss of tellurium occurs in the process of film preparation, so preservation of *n*-type conductivity in films obtained from bulk crystals with 62.8 at.% Te will provide evidence for good reproducibility of the initial material composition in the thin-film state.

The films were grown by thermal evaporation of the initial material in oil-free vacuum (10^{-5} Pa to 10^{-6} Pa) and subsequent condensation on glass substrates heated to temperatures in the range of $T_S = 320$ K to 500 K. The accuracy of the substrate temperature measurement was 5%. The evaporation took place at a rate of 0.1 nm/s to 0.3 nm/s from a tungsten boat in which 1 g to 3 g of initial material was placed. Before deposition, the substrates were thoroughly cleaned first by perchloric acid, then by distilled water and 95% ethanol during 15 min for each cleaning phase. For simultaneous deposition of several films with various thicknesses, two holders located at different distances from the source were used.

The film thickness and roughness, and the condensation rate were controlled using a calibrated quartz resonator placed near the substrates. Calibration of the resonator for film thicknesses less than $d \approx 100$ nm was performed using low-angle x-ray diffraction patterns for single-layer films by comparing experimental and computed diffraction patterns. To fit the calculated and experimental curves, the layer thickness was varied. The experimental diffraction curves were obtained using an x-ray diffractometer with a graphite monochromator placed before the detector on a primary beam. The film thickness and roughness were varied to fit the computed curve to the experimental one. Numerical modeling was carried out using the Frenkel equations. For larger thicknesses ($d > 100$ nm) the resonator was calibrated using a MII-4 interferometer. On the basis of the two indicated methods, a general calibration straight line was plotted. The error of determining d did not exceed $\pm 5\%$. The film roughness was within the range of 1 nm to 2 nm.

The crystal structures of the initial materials and the obtained thin films were characterized by the x-ray diffraction method. x-Ray diffraction studies were carried out with a DRON-2 diffractometer using Ni-filtered Cu K _{α} radiation. The half-width of the peaks was determined using special software, which allowed us to separate the background and to approximate experimental points using the Cauchy and Pearson distribution functions. Besides, instrumental broadening registered by the x-ray diffraction pattern for a Si single crystal was taken into account.

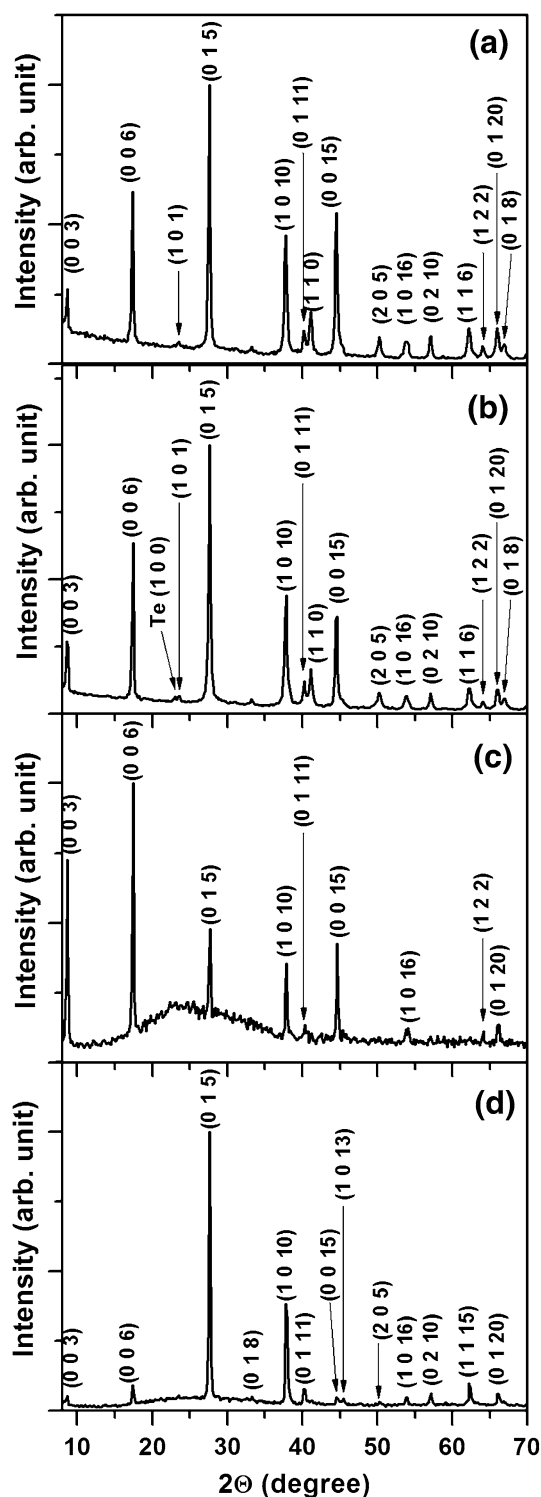


Fig. 1. Sections of diffractograms plotted as intensity in arbitrary units versus 2θ in degrees for bulk bismuth telluride polycrystals with 60.0 at.% Te (a), for bulk bismuth telluride polycrystals with 62.8 at.% Te (b), for thin films prepared from crystals with 60.0 at.% Te at substrate temperature $T_S = 500$ K (c), and for thin films prepared from crystals with 62.8 at.% Te at substrate temperature $T_S = 490$ K (d).

The in-plane electrical conductivity σ and the Hall coefficient R_H were measured at room temperature by a conventional direct-current (dc) method in a

constant magnetic field on bulk parallelepiped-shaped samples and double Hall cross-shaped thin films. The Seebeck coefficient S was measured using

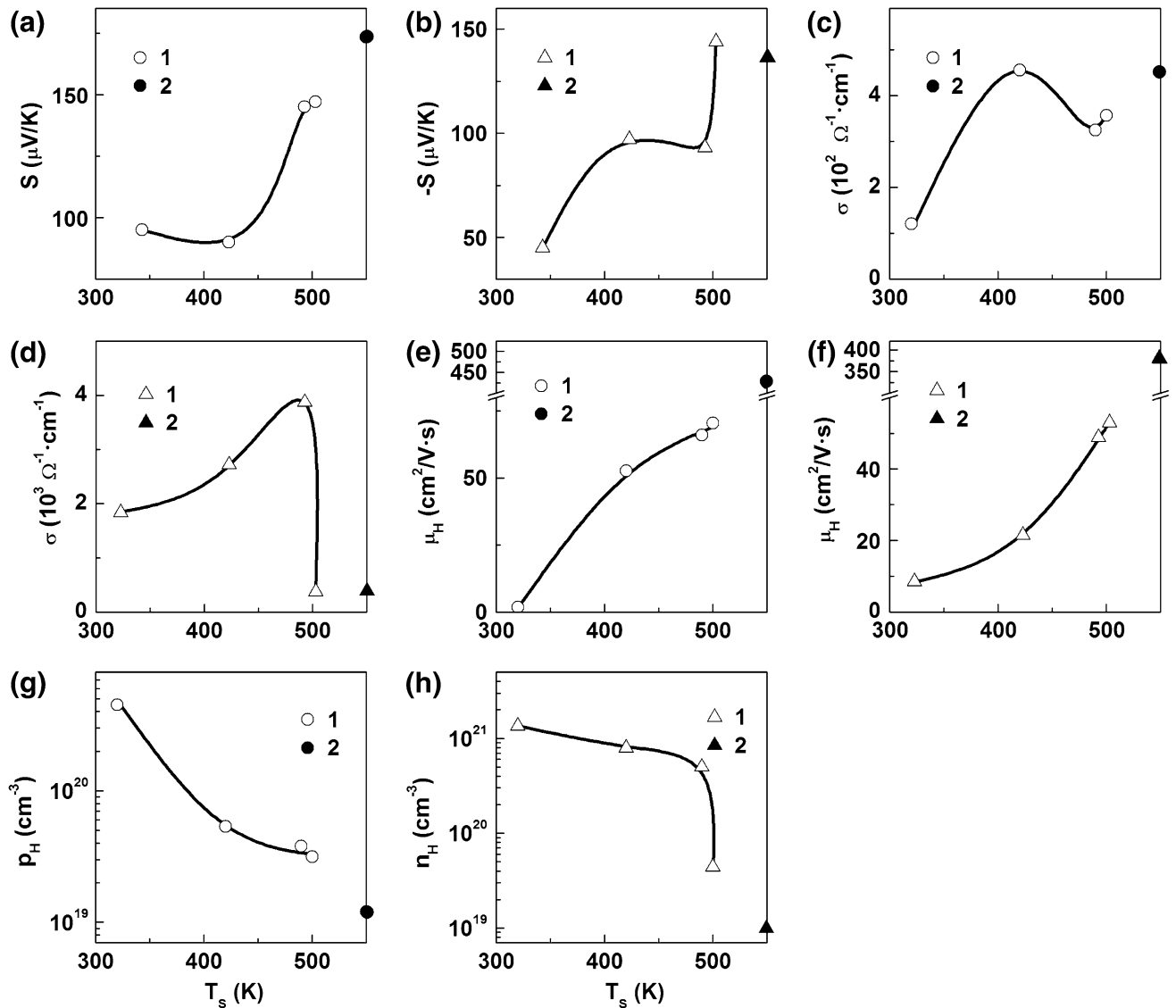


Fig. 2. Dependences of Seebeck coefficient S (a, b), electrical conductivity σ (c, d), Hall carrier mobility μ_H (e, f), and dominant charge carrier concentration $n_H(p_H)$ (g, h) of Bi_2Te_3 thin films on substrate temperature T_s . (a, c, e, g) Films prepared from stoichiometric Bi_2Te_3 (60.0 at.% Te). (b, d, f, h) Films prepared from crystals with Te excess (62.8 at.% Te); 1—thin films, 2—initial bulk crystals.

a compensation method relative to copper electrodes. The error in measuring σ and R_H did not exceed 5%, and for S was 2% to 3%. The Hall concentration $n_H(p_H)$ and charge carrier mobility μ_H were calculated using formulae for a single sort of charge carriers: $n_H(p_H) = 1/eR_H$ (where e is the electron charge) and $\mu_H = \sigma R_H$. The sign of the charge carriers was determined by the sign of the Seebeck coefficient and Hall coefficient. Control of the uniformity of the properties along the film surface performed by measuring the Seebeck coefficient at at least 10 to 15 points evenly distributed over the film surface showed that the dispersion of the S values did not exceed the error of measuring S , which indicates a rather high degree of film homogeneity. All measurements were carried out at room temperature on freshly prepared films.

RESULTS AND DISCUSSION

To find out whether the conductivity type and TE properties of bulk crystals used as initial material are reproduced in thin films, after the synthesis of the bulk crystals, the main TE characteristics [S , σ , μ_H , $p_H(n_H)$, and P] were measured for ingots of each composition. The measurements showed that the crystals with stoichiometric composition (60 at.% Te) exhibited p -type conductivity (in good agreement with literature data) and had the following TE parameters: $S = 170 \mu\text{V/K}$, $\sigma = 450 \Omega^{-1} \text{cm}^{-1}$, $\mu_H = 425 \text{cm}^2/\text{V s}$, $p_H = 1.2 \times 10^{19} \text{cm}^{-3}$, and $P = 14 \times 10^{-4} \text{W/K}^2 \text{m}$. The nonstoichiometric crystals containing 62.8 at.% Te exhibited n -type conductivity (also corresponding to available literature data) and the following TE properties:

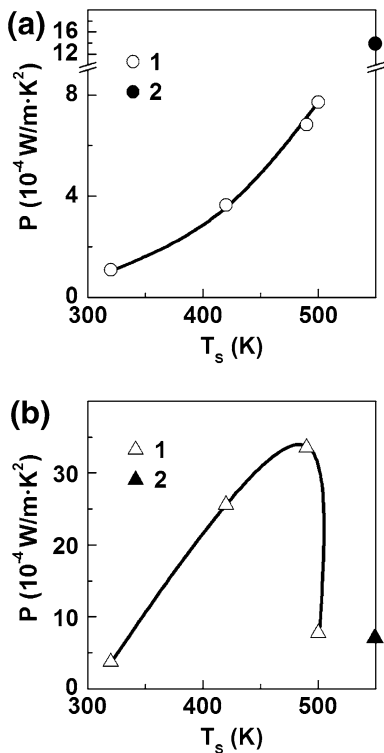


Fig. 3. Dependence of TE power factor P of the Bi_2Te_3 thin films on substrate temperature T_s : (a) films prepared from stoichiometric Bi_2Te_3 (60.0 at.% Te), (b) films prepared from crystals with Te excess (62.8 at.% Te); 1—thin films, 2—initial bulk crystals.

$S = -135 \mu\text{V/K}$, $\sigma = 380 \Omega^{-1} \text{cm}^{-1}$, $\mu_{\text{H}} = 380 \text{cm}^2/\text{Vs}$, $n_{\text{H}} = 1 \times 10^{19} \text{cm}^{-3}$, and $P = 7 \times 10^{-4} \text{W/K}^2 \text{m}$.

In Fig. 1, x-ray diffraction patterns for the initial bulk materials and obtained thin films are presented. The x-ray diffraction patterns for bulk crystals with both 60.0 at.% and 62.8 at.% Te (Fig. 1a, b) contain lines corresponding to Bi_2Te_3 . The plane indices obtained are in agreement with ASTM values of Bi_2Te_3 (card no. 15-863).¹³ In the x-ray diffraction pattern for the crystal with 62.8 at.% Te (Fig. 1b), additional very weak lines corresponding to tellurium are seen.

In the x-ray diffraction patterns for thin films prepared from stoichiometric Bi_2Te_3 crystals at substrate temperature $T_s = 500 \text{K}$ (the highest values of TE power factor correspond to this temperature), similarly to the initial bulk crystal, only Bi_2Te_3 lines are seen (Fig. 1c). However, one can clearly see that the films are textured, as the intensity of (001)-type peaks of Bi_2Te_3 is much higher in comparison with analogous peaks in the x-ray diffraction pattern of the initial material powder, indicating preferred growth along c -axis orientation.^{3,5} At lower substrate temperatures, in the x-ray diffraction patterns additional weak lines corresponding to tellurium are observed.

In the x-ray diffraction patterns for thin films prepared from nonstoichiometric crystals (62.8 at.% Te) at substrate temperature of 490 K (the maximum

values of P correspond to this substrate temperature), one can see only Bi_2Te_3 lines (Fig. 1d). The intensity of the (015) peak increases, which indicates that (015) orientation is preferred. When T_s is reduced, in x-ray diffraction patterns additional lines of tellurium are registered. The absence of Te lines in case of the films deposited from bulk crystals with 62.8 at.% Te is probably connected with loss of Te occurring in the process of film deposition.

With increasing substrate temperature, the x-ray diffraction intensity enhances, which indicates an enhancement in the degree of structural perfection of the thin films.

Estimation of the change in grain size from the change in half-width of the most intense peak (015), which was present in x-ray diffraction patterns for all samples, showed that with increasing substrate temperature the half-width of lines decreases and, consequently, the grain size increases.

In Fig. 2a, c, e, g the results of the TE properties measurement for the films grown from the charge with stoichiometric composition at different substrate temperatures are shown. One can see that, in these films, the p -type conductivity of the initial material is preserved. Increase in the substrate temperature to 500 K leads to increase in S , σ , μ_{H} , and P and decrease in the Hall charge carrier and, to all appearances, is connected with an enhancement in the degree of structural perfection and approach of the film composition to that of the initial bulk crystals. The values of S and σ at $T_s = 500 \text{K}$ are close to the corresponding values in the initial material; however, the charge carrier concentration in the films is ~ 3 times as high as p_{H} for the bulk Bi_2Te_3 polycrystals. The higher hole concentration in p -type Bi_2Te_3 films can be explained by the slight tellurium deficit appearing in the process of film preparation caused by the significant difference in partial pressure between Bi and Te vapors. The substrate temperature corresponding to the maximum TE power factor ($P_{\text{max}} \approx 7.5 \text{W/K}^2 \text{m}$) is $T_s = 500 \text{K}$ (Fig. 3a).

In Fig. 2b, d, f, h the results of the measurements of TE parameters in the films grown from nonstoichiometric initial material (62.8 at.% Te) are presented. As is seen, the films exhibit n -type conductivity, which corresponds to the conductivity type in the initial crystal. Like in case of the films prepared from stoichiometric Bi_2Te_3 , increase in the substrate temperature up to 490 K leads to growth in S , σ , μ_{H} , and P and decrease in the Hall charge carrier concentration. However, under further increase in T_s to 500 K, a sharp drop in σ and n_{H} as well as a drastic increase in S are observed, the values of S , σ , and P practically corresponding to those in the initial crystal containing 62.8 at.% Te, although the dominant charge carrier concentration remains ~ 3 times higher. That is why the optimum substrate temperature corresponding to the maximum TE power factor ($P_{\text{max}} \approx 35 \text{W/K}^2 \text{m}$) is $T_s = 490 \text{K}$ (Fig. 3b).

Regardless of the initial material composition, at substrate temperatures above 500 K, the prepared films had significant, even visual, defects and inhomogeneities caused, to all appearances, by tellurium re-evaporation.

Thus, it follows from the obtained results that, in case of the films grown from stoichiometric initial material, as the substrate temperature increases, the properties of the films approach those of the initial material. The higher charge carrier concentrations and consequently smaller values of the Seebeck coefficient indicate the presence of additional antistructural defects.

In case of films prepared from the nonstoichiometric charge, a somewhat different situation is observed. An increase in T_S up to 490 K leads, like in the former case, to growth in S , σ , μ_H , and P and decrease in charge carrier concentration, the values of σ and P at 490 K significantly exceeding those in the bulk crystal. At the substrate temperature of $T_S = 500$ K, a drop in σ , μ_H , and P and a sharp increase in S are observed, and, as mentioned above, these values practically coincide with those in the initial material. One can suggest that such a drastic change in the properties at $T_S = 500$ K is caused by a transition from a nonequilibrium state to a more equilibrium one.

It follows from the obtained data that, for films prepared from initial material with stoichiometric composition, the optimum substrate temperature corresponding to the maximum value of P is 500 K; for films grown from the nonstoichiometric charge containing 62.8 at.% Te, it is 490 K. The values of the TE power factor ($P \approx 35 \times 10^{-4}$ W/K² m) in the films attained in the present work when using initial material with 62.8 at.% Te exceed those obtained in most other works: 22×10^{-4} W/K² m for thermal hot-wall epitaxy,⁴ 18×10^{-4} W/K² m for thermal evaporation from two sources,⁵ 18×10^{-4} W/K² m for electrochemical deposition,⁹ and 21×10^{-4} W/K² m for close space vapor transport.³ At the same time, it should be noted that the described method of thin-film preparation is one of the simplest from a technological point of view and has low cost. The main task on the path to further enhancement of the TE power factor is reducing the defect concentration and increasing S under moderate reduction of electrical conductivity.

CONCLUSIONS

1. Bismuth telluride thin films were prepared by thermal evaporation in vacuum from a single source at different substrate temperatures (320 K to 500 K) using initial materials with stoichiometric composition (60 at.% Te) and with nonstoichiometric composition of 62.8 at.% Te.
2. It is established that the conductivity type of the initial material is preserved in the thin films,

although the charge carrier concentration is higher in comparison with the bulk crystals, whereas the charge carrier mobility is lower.

3. It is found that, regardless of the initial material composition, an increase in the substrate temperature in the range of 320 K to 490 K leads to growth in S , σ , μ_H , R_H , and the TE power factor P . Further increasing the substrate temperature up to 500 K results in a growth in P for films prepared from initial material with stoichiometric composition but a decrease in P for films obtained from the charge containing 62.8 at.% Te.
4. Under the optimum conditions for Bi₂Te₃ film preparation, the maximum values of the TE power factor for films grown from stoichiometric and nonstoichiometric Bi₂Te₃ amount to $P = 7.5 \times 10^{-4}$ W/K² m and $P = 35 \times 10^{-4}$ W/K² m, respectively. The maximum values of P attained for films grown from nonstoichiometric Bi₂Te₃ exceed not only the values of P in bulk crystals, used as initial materials in this work, but also the values of P in films prepared by other authors using different methods.
5. The results of this work are of practical interest because a technologically simple and low-cost method for preparation of films with rather high TE power factor is proposed.

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