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STRUCTURE OF *p*-Bi_2Te_3 THIN FILMS PREPARED BY SINGLE SOURCE THERMAL EVAPORATION IN VACUUM

The growth mechanism, microstructure, and crystal structure of thin Bi_2Te_3 films with thicknesses d = 28 – 620 nm prepared by thermal evaporation of stoichiometric Bi_2Te_3 crystals in vacuum onto glass substrates were studied using X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, and atomic force microscopy. The obtained thin films were polycrystalline, exhibited p-type conductivity and did not contain any other phases except for Bi_2Te_3. It was shown that with increasing film thickness, the crystallite size increased up to ~ 700-800 nm. It was established that the preferential orientation of crystallite growth was [00*l*] *direction corresponding to a trigonal axis C_3 in hexagonal lattice. When the film thickness exceeded ~ 200-250 nm, along with reflections from (00l) planes, reflections from other planes appeared, which indicated a certain disorientation of crystallites. The results obtained show that using a simple and inexpensive method of thermal evaporation from a single source and choosing optimal technological parameters, one can grow thin p-Bi_2Te_3 films of sufficiently high quality.*
Key words: bismuth telluride, thermal evaporation, thin film, thickness, structure, growth orientation.

Introduction

Bi_2Te_3 semiconductor compound and Bi_2Te_3-based solid solutions belong to the best low-temperature thermoelectric (TE) materials, which are widely used in the manufacture of different types of refrigerating devices [1-4]. A growing interest in low-dimensional nanostructures based on bismuth telluride [5-7] stimulates conducting detailed studies of properties of the indicated materials in the thin film state and establishing correlations among technological parameters, structure, and TE characteristics. In recent years, the interest in studying bulk crystals and thin films of Bi_2Te_3 has grown even more after the discovery of new unique physical objects – topological insulators. It was established that Bi_2Te_3 possesses properties of a 3D topological insulator, which attracted attention to studies of thin Bi_2Te_3 films, in which the contribution of the surface layer to electrical conductivity increases in comparison with bulk crystals, thus making it possible to reveal the specificity of topological objects [8-10]. Works have appeared which showed a connection between topological and TE properties and pointed out the possibility to use this fact in searching for principally new ways of increasing TE efficiency [11-19].

Bi_2Te_3 crystallizes in a rhombohedral structure (space group $R3m$-D_{3d}^5) [2, 4]. Often for describing Bi_2Te_3 structure, instead of rhombohedral a hexagonal unit cell is used whose parameters correspond to a = 0.4386 nm and c = 3.0497 nm [2, 4]. The structure is composed of five-layer packets

(quintets) − Te^1− Bi− Te^2− Bi− Te^1 (indices 1 and 2 denote different positions of *Te* atoms in the crystal lattice), perpendicular to a third-order symmetry axis (a trigonal axis C_3 in a hexagonal lattice). Within each layer, similar atoms constitute a hexagonal flat lattice forming a hexagonal close packing with atoms of lower layers. Chemical bonds within quintets are predominantly covalent-ionic, whereas between quintets there are weak van der Waals bonds. This determines a low mechanical strength, easy splitting of crystals along cleavage planes (perpendicular to a C_3 axis) and substantial anisotropy of all physical properties of Bi_2Te_3 single crystals.

Bi_2Te_3 has a narrow homogeneity region (59.75 – 60.2 at.% *Te* at 770 K [20]) in the *Bi – Te* system. The stoichiometric Bi_2Te_3 (60.0 at.% *Te*) exhibits *p*-type conductivity due to the presence of anti-site defects *BiTe*.

Bi_2Te_3 films can be grown by a variety of methods: thermal evaporation in vacuum from a single source [21-30], thermal co-evaporation from two sources [31-33], hot wall epitaxy [34-36], quasi-closed volume technique [37], ion-beam deposition [38], magnetron sputtering [26, 39], molecular-beam epitaxy [27-29, 40], liquid phase epitaxy [30], metal organic chemical vapor deposition [41], laser deposition [42-44], explosive evaporation [45] and so on. Both amorphous and crystalline materials can be used as substrates. It was established that on amorphous substrates (glass [21-26, 39], SiO_2 [34-36], kapton [35, 31]), films grow in an island-like fashion, while on crystalline substrates (BaF_2 [27], *Si* [34, 28, 36, 40], sapphire [29]) both island-like [27] and layer-by-layer [27-29] growth can be realized. The growth mechanism, film morphology, grain size, and grain crystallographic orientation depend on the film preparation technique and technological parameters.

For anisotropic materials like Bi_2Te_3, the transport properties depend significantly on the direction in the crystal. For example, it was reported in [39] that in Bi_2Te_3 films the preferential growth of (00*l*) planes leads to substantially higher values of electrical conductivity, charge carrier mobility and the Seebeck coefficient in comparison with the preferential growth of (015) planes. That is why, when growing films, it is important to know and to control the preferential growth direction.

The growth mechanism and structure of Bi_2Te_3 thin films prepared by thermal evaporation in vacuum from a single source onto glass substrates were investigated in few works [23-25]. In [23], where the authors did not indicate the substrate temperature, it was established using X-ray diffraction analysis that in films with thicknesses d = 36 – 330 nm deposited onto glass substrates the preferential orientation of crystallites corresponded to [015] direction, although under increasing film thickness additional peaks appeared in X-ray diffraction patterns, which indicated a partial grain disorientation. In [24], X-ray diffraction analysis was used to study the structure of Bi_2Te_3 films of the fixed thickness (d = 100 nm) but deposited onto glass substrates heated to different temperatures (T_S = 303 – 573 K). The authors found out that for all values of T_S the preferential growth takes place along the [015] direction, although there is some disorientation of grains relative to this direction. Note that in [23, 24] the films were not subjected to annealing which could improve the quality of their structure, and perhaps because of this the crystallite size D in the films was small (D = 15 – 45 nm). The authors of [25] investigated sufficiently thick Bi_2Te_3 films (d = 170 – 342 nm), which were annealed at T = 443 K for one hour. They reported that the film with thickness d = 342 nm had the preferential orientation of growth along the [015] direction, which manifests clearly only after annealing. With increasing film thickness from 170 nm to 342 nm, the grain size increased from 60 up to 160 nm. Thus, in the available works on Bi_2Te_3 films prepared by thermal evaporation of Bi_2Te_3 crystals in vacuum onto glass substrates and characterized by X-ray diffraction method, authors reported their observation of preferential orientation only along the [015] axis. There arises a question whether it is possible to

obtain another preferential orientation, specifically [00*l*], which as was mentioned above is more desirable because of the possibility to obtain higher values of TE figure of merit.

The goal of the present work is to carry out a detailed comprehensive investigation of the microstructure and crystal structure of thin Bi_2Te_3 films grown by thermal evaporation of stoichiometric bismuth telluride crystals in vacuum and subsequent condensation onto glass substrates.

Experimental procedure

As a charge for thin films preparation, *p*-type Bi_2Te_3 polycrystal of stoichiometric composition was used. Crystal synthesis was made by direct alloying of *Bi* and *Te* of high purity (99.999 at. %) in evacuated quartz ampoules at a temperature of (1020 ± 10) K for 5 – 6 hours with subsequent annealing at 670 K for 300 hours.

Films of thickness d = 28– 620 nm were grown by method of thermal evacuation in vacuum (~10^{-5} Pa) of Bi_2Te_3 polycrystal of stoichiometric composition and subsequent condensation onto glass substrates heated to temperature T_S = 500 K. Condensation rate was 0.1 – 0.3 nm/s. Prior to deposition, substrates were consecutively cleaned with hydrochloric acid, distilled water and 95% alcohol. Immediately after deposition, grown films in the same vacuum chamber were annealed at a temperature of T = 500 K for 1 hour. For a simultaneous preparation of several films of different thickness d in one technological process, three substrate holders were installed at different distances from the source. Earlier we showed [21, 22] that the properties of Bi_2Te_3 thin films are essentially dependent on the stoichiometry of source crystal, substrate temperature T_S, the presence or absence of annealing, annealing temperature, on which basis the above technological parameters were determined that corresponded to maximum values of TE power $P = S^2\sigma$ (S is the Seebeck coefficient, σ is electric conductivity).

The thickness and roughness of films, as well as condensation rate, were controlled by quartz resonator. Calibration of resonator for film thicknesses less than d ~ 100 nm was performed with the use of X-ray diffraction patterns of small-angle scattering by comparing the experimental and calculated diffraction patterns. At layer thicknesses d < 100 nm close to primary beam an interference X-ray diffraction is observed, namely the Kissing oscillations whose period can be used to determine film thickness to an accuracy of 0.5 nm. Numerical simulation was performed with the use of Frenkel's formulae. For fitting of calculated curve to the experimental one two parameters were varied independently, namely film thickness and roughness. For large thicknesses (d > 100 nm), quartz resonator was calibrated using MII-4 interferometer.

Chemical composition, homogeneity degree and films morphology were studied by electron probe analysis method with the use of scanning electron microscope (SEM) JSM-6390LV (Jeol Ltd., Japan), equipped with energy-dispersive X-ray spectrometer X-max N50. The surface morphology of films was also studied using atomic force microscope (AFM) Solver Pro NT-MDT. Crystal structure, phase composition and direction of preferential films growth were determined by X-ray structural analysis methods on DRON-2 diffractometer using *Cu* K_α – radiation.

Experimental results

Fig. 1, a shows X-ray diffraction pattern of Bi_2Te_3 polycrystal which was used as a charge for preparation of thin films. All the lines on X-ray diffraction pattern corresponded to values given in ASTM standards for Bi_2Te_3 (№ 15-863) [46], no additional phases were found.

Fig. 1, b-h show X-ray patterns of thin films of different thickness prepared with optimal technological parameters. The films have a marked crystalline structure, and all diffraction peaks correspond to Bi_2Te_3 compound, no peaks of other phases were found. To demonstrate the influence of films preparation technology on their phase composition and structure, Fig. 2 shows X-ray patterns of films (d = 250 nm) obtained at substrate temperature T_S = 320 K without annealing (Fig. 2, a) and at substrate temperature T_S = 500 K with annealing for one hour at 500 K (Fig. 2, b), i.e. prepared by the method used in the present paper. It can be seen that in the former case the film has a structure close to amorphous, with weakly expressed diffraction peaks, and the film has additional phases of *Te* and Bi_3Te_4. In this connection it can be assumed that due to higher partial pressure of *Te* vapour as compared to bismuth, during the initial stages of film deposition tellurium excess can be created on the substrate. As long as substrate temperature is sufficiently low (T_S = 320 K), no intensive reevaporation of *Te* atoms occurs, and part of *Te* atoms precipitates into second phase. With further formation of the film, deficit of *Te* atoms can result in formation of Bi_3Te_4 phase. High intensity of peak corresponding to (015) planes testifies to preferential formation in the film of hexagonal planes with respective structure.

As in seen in Fig. 1, b-e, in the films with thicknesses d lower than d ~ 140 nm, the intensity of peaks (003), (006), (0 0 15), (0 0 18) and (0 0 21) is increased more than twice as compared to the bulk crystal with practically complete disappearance of peaks corresponding to other crystallographic planes. Essential increase of the intensity of peaks corresponding to these planes as compared to similar peaks of X-ray diffraction pattern of the source powder indicate the presence of texture in [001] direction. To confirm the presence of preferential orientation of crystallites along [00*l*] direction, fim of thickness d = 85 nm (Fig. 1, h) was measured in a standard mode (in the initial position X-ray beam was oriented perpendicular to the film), and then the sample was rotated by 21.80°. As long as planes (0 0 21) and (0 1 20) are at an angle of 21.80° to each other, in the former case there is intensive peak only from (0 0 21) plane, and in the second case – only from (0 1 20) plane, confirming the presence of preferential orientation of all grains in one direction [0 0 *l*].

The authors [35, 36] attribute formation of texture in [0 0 1] direction to peculiarity of Bi_2Te_3 growth on amorphous substrates which assure higher surface mobility of deposited substance atoms as compared to crystalline substance. This allows reaching sufficiently fast the state close to equilibrium, when the atoms of deposited substance occupy thermodynamically most advantageous positions on the substrate, which contrtibutes to texture formation. Moreover, epitaxial growth peculiarities of layered structures with Van der Waals bonds [36, 37] and the absence of broken bonds on the substrate surface [34] cause the arrangement of layers with Van der Waals bonds along the film plane which in turn provides for orientation of crystallites in perpendicular direction [0 0 1] [37]. Strong anisotropy of growth rate assures a more intensive growth of crystallites along the directions perpendicular to texture direction, which contributes to fast intergrowth of crystallites in film plane, and growth rate of Bi_2Te_3 films parallel to substrate surface proves to be a factor of 5 to 8 higher than growth rate perpendicular to it.

On the X-ray diffraction patterns of films with thicknesses more than d ~ 140 nm (Fig. 1 f, g) along with reflexes (0 0 *l*) there appear peaks from crystallographic planes different from (0 0 1), the number increasing with increase in film thickness. This testifies to disorientation of crystallites and is likely to be a consequence of dislocation density growth and stress accumulation. Nevertheless, the intensity of peaks (0 0 *l*) for all films is almost not changed which testifies to the absence of essential disorientation in the direction of texture.

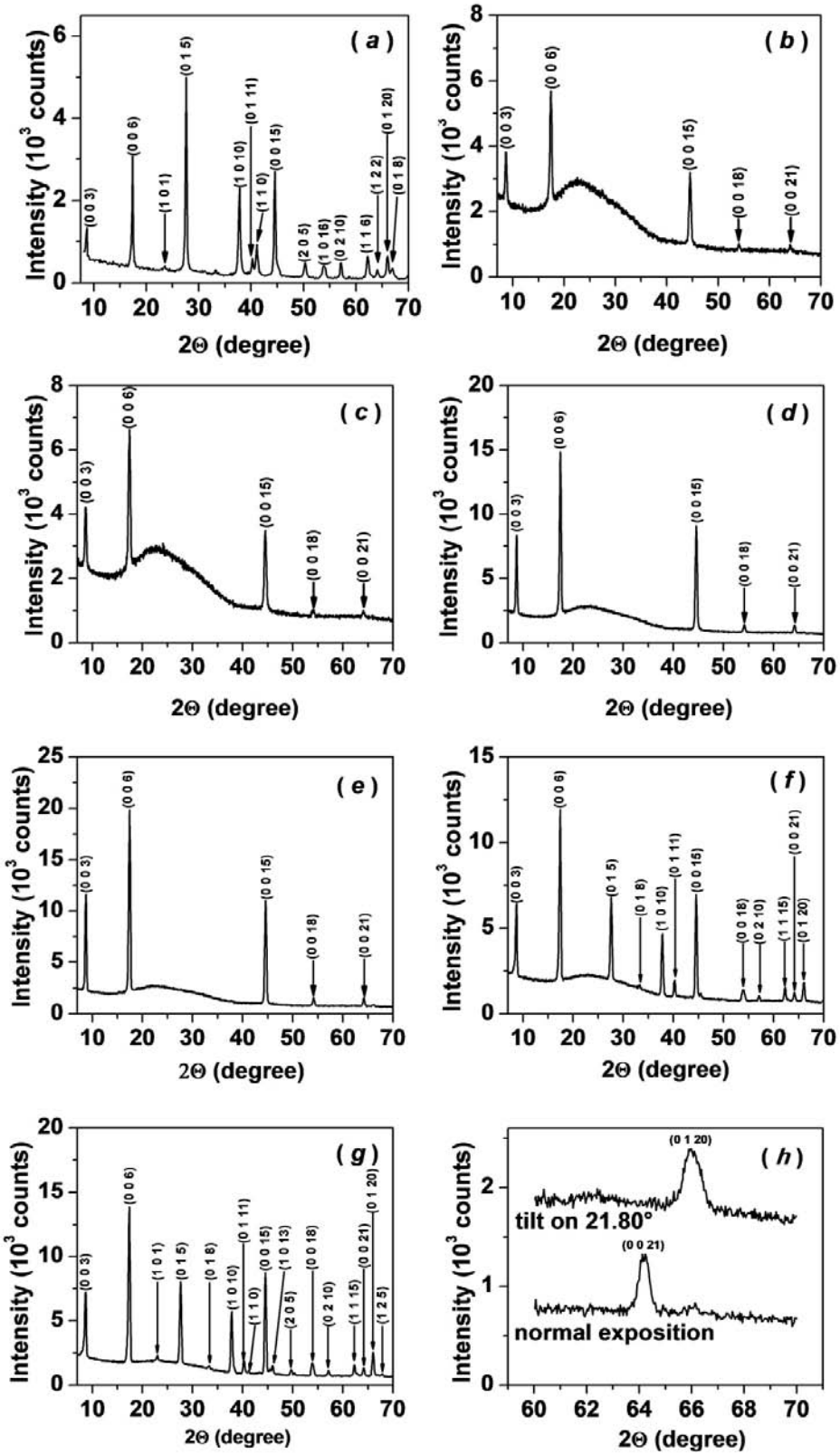

Fig. 1. X-ray diffraction patterns for polycrystalline Bi_2Te_3 powder (a) and for thin films with different thicknesses: d = 38 nm (b), 45 nm (c), 85 nm (d), 140 nm (e), 370 nm(f), 620 nm (g).
h: X-ray diffraction pattern for the thin film with d = 85 nm is measured in a standard mode (with a X-ray beam oriented perpendicular to the film surface) and after rotating the sample by 21.80° (see the text).

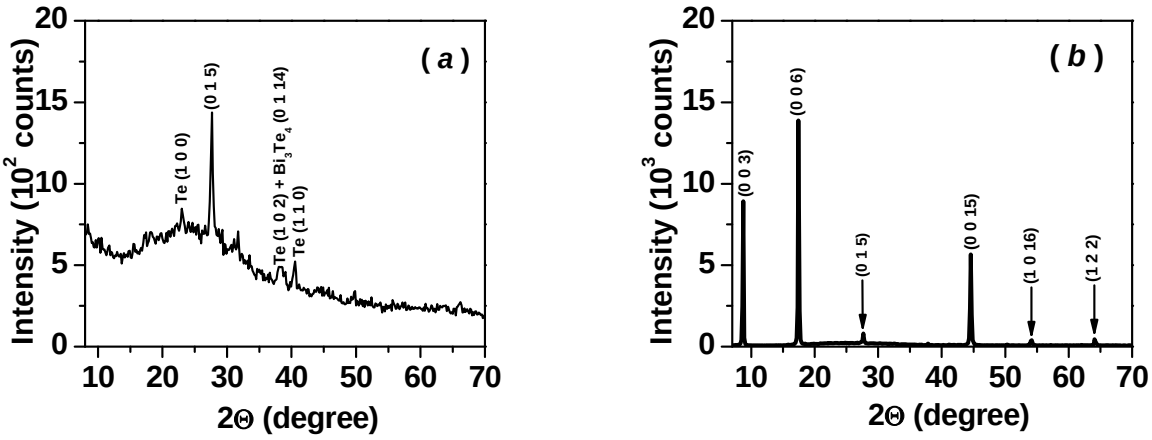

Fig. 2. X-ray diffraction patterns for Bi_2Te_3 films with thicknesses d = 250 nm prepared at the substrate temperature T_S = 320 K without annealing (a) and at T_S = 500 K with subsequent annealing at 500 K for one hour (b).

Studies of thin films by scanning electron microscopy method (Fig. 3) have confirmed that the films are polycrystalline and there are no second phase inclusions in them. The grains were of hexagonal shape (for illustrative purposes some grains are shown dashed) and their average size was increased with increase in film thickness (Fig. 4), which was in good agreement with the results of AFM. The results of energy-dispersive X-ray spectroscopy both at scanning along the sample surface and in the mode of probing from point to point have shown that all the films were characterized by high homogeneity degree and that within the error of this method one could speak of the conformity between the composition of the source polycrystal and that of grown films.

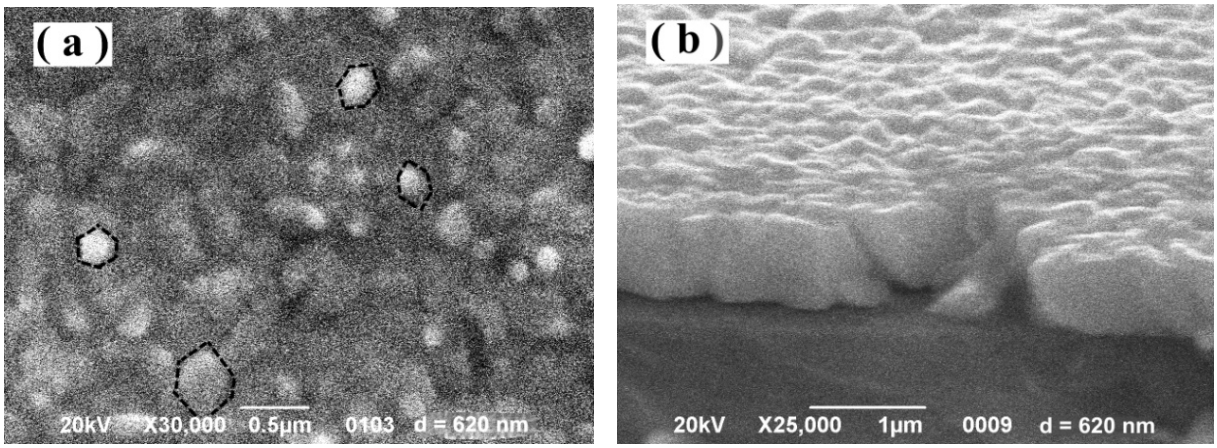

Fig. 3. Surface images obtained using a scanning electron microscope (SEM) for Bi_2Te_3 film with thickness d = 620 nm. a – no tilt, b - tilt angle 70^0.

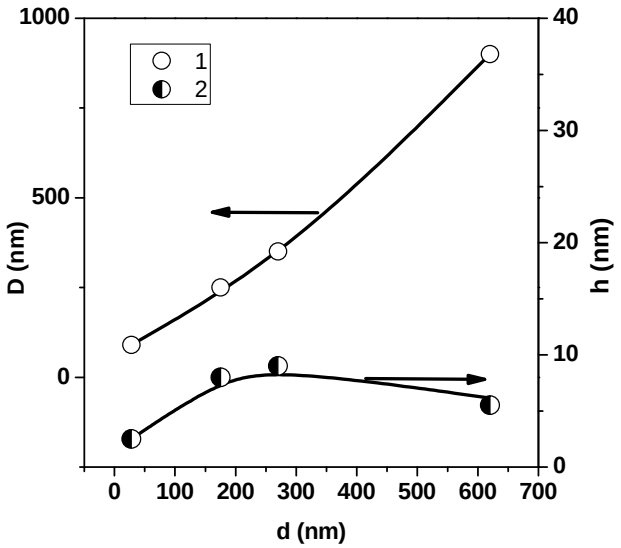

Fig. 4. Grain size D and roughness h as functions of p-Bi_2Te_3 thin film thickness d.
1 – grain size; 2 – roughness.

Fig. 5 represents the data of atomic force microscopy. On the obtained profilograms one can clearly see individual crystallites of mainly hexagonal shape, which points to their orientation in [0 0 1] direction perpendicular to film surface which is in good agreement with the results of X-ray structural analysis (Fig. 1), as well as with the data of scanning electron microscopy (Fig. 3). The sizes of crystallites *D* evaluated by two methods – SEM and AFM – practically coincide and show marked increase with increase in film thickness, reaching in the "thickest" of films under study (d = 620 nm) the value of D ~ 850 nm (Fig. 4). The roughness of films h with growth in their thickness d first increases (to d ~ 200 – 250 nm), following which there is a tendency to h reduction (Fig. 4).

Conclusions

A comprehensive study of growth mechanism, microstructure, and crystal structure of thin Bi_2Te_3 films with thicknesses d = 28 – 620 nm prepared by thermal evaporation of stoichiometric Bi_2Te_3 crystals in vacuum onto glass substrates heated to T_S = 500 K and subject to subsequent annealing at 500 K was performed using X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, and atomic force microscopy.

It was established that both the initial crystal and all obtained thin films exhibited *p*-type conductivity and did not contain any other phases except for Bi_2Te_3.

It was shown that the obtained thin films were polycrystalline; with increasing film thickness, the grain size D of the films increased to D ~ 850 nm, and roughness h increased with increasing film thickness to ~d ~ 200-250 nm, following which there was a tendency to reduction.

It was established that the preferential orientation of crystallite growth was [00l] direction corresponding to a trigonal axis C_3 in hexagonal lattice. When the film thickness exceeded ~ 200-250 nm, along with reflections from (00l) planes, reflections from other planes appeared, which indicated a certain disorientation of crystallites.

The results obtained show that using a simple and inexpensive method of thermal evaporation from a single source and choosing optimal technological parameters, one can grow thin *p*-Bi_2Te_3 films of sufficiently high quality.

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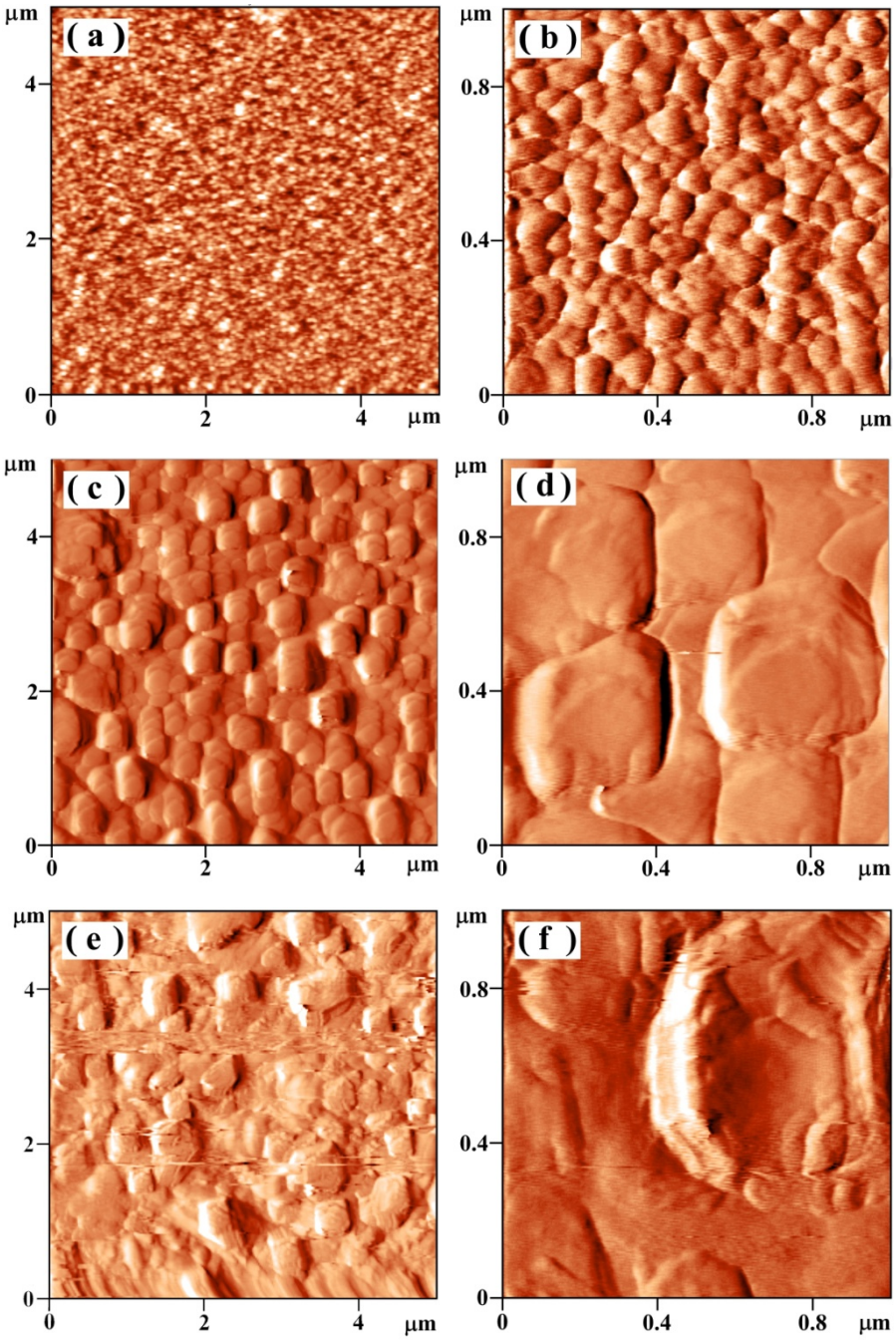

Fig.5. AFM surface profilograms for Bi_2Te_3 thin films with thickness d = 28 nm: 5x5 μm (a), 1x1 μm (b); d = 175 nm: 5x5 μm (c), 1x1 μm (d); d = 270 nm: 5x5 μm (e), b: 1x1 μm (f).

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