X-RAY INVESTIGATION OF Bi_2Te_3-Bi_2Se_3 <Tb> AND Bi_2Te_3-Bi_2Se_3 <Cl> FILMS

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The formation of new phase doesn't take place at annealing of Bi_2Te_3-Bi_2Se_3<Tb> и Bi_2Te_3-Bi_2Se_3<Cl> up to ~500K real increase of microparticle dimensions, any structural reconstructions, the polycrystalline structure is observed at film annealing. The calculations of interplanar spacings show that structure becomes strength at film annealing.

INTRODUCTION

The alternative power enginnering nowadays takes the big interest in film thermoelectric generators and also the infrared detector demand increases. The thermoelements and thermobatteries coated on substrates by the vacuum condensation method with the use of masks ans photolitographic processing [1] are used in such receivers.

It is known that monocrystalline films with complex technology of their production loose their properties in due course in exploitation process. The change of dispersion parameter in comparison with dispersion which is character for these compositions in volume crystals *r*=0 (the distance on acoustic photons) clearly reveals in $Bi_2Te_{2,1}Se_{0,9,}$ small-grained films evaporated on amorphous substrate [1]. The amorphous films have some lowered characteristics than polycrystalline ones. The Bi_2Te_3 lattice parameters have the some change in both at inclination from stoichiometric content and at impurity introduction. Bi_2Te_3 transits into another phase having the hexagonal lattice but belonging to space group R_{3m} [2] at hydrostatic pressure 40 kbar and temperatures higher than 700K.

The substrate temperature should be in optimal interval for obtaining of qualitative film. X-ray investigation of thin films is carried by Frankombe and Semiletov. At film investigation the temperature of (glass) substrate at which the film forms corresponding to Bi_2Te_3 content has been defined. The strong inclination from Bi_2Te_3 content begins at increase of t_{sub} higher than 500K [2]. The extremely low temperature of substrate opposes to equilibrium distribution of adsorbed atoms; they group in "islands" of different thickness. Vice versa, the extremely high temperature of substrate leads to separation of just lead-down atoms their revaporation [3].

The task of X-ray investigation of system Bi_2Te_3-Bi_2Se_3 polycrystalline film with terbium and chlorine impurities obtained by the method of hot wall before and after annealing has been established by us with the aim of improvement of thermoelement physical properties because of decrease of their geometric sizes of polycrystalline materials evaporated on amorphous substrate.

INVESTIGATION TECHNIQUE

The investigated films Bi_2Te_3 Bi_2Te_3-Bi_2Se_3<Tb> and Bi_2Te_3-Bi_2Se_3 <Cl> with optimal thickness 50-150nm prepared by evaporation of synthesized substances in ВУП-4 device in vacuum ~10^{-4}*Pa* on previously heated crystals NaCl and glass are grown up by the hot wall method [1,4]. The comfortable conditions for steam condensation are formed on substrate, the additionally heated wall leads to minimum the partial steam condensation on cap walls, where wall temperature at evaporation is 600K, substrate temperature is 500K at cooling velocity of thin layers ~2nm/s [5].

The obtained polycrystalline films Bi_2Te_3-Bi_2Se_3 <Tb> and Bi_2Te_3-Bi_2Se_3 <Cl> are investigated by roentgenography method. The film samples useable for X-ray investigation by thickness by thickness 50-150nm are produced by sublimation of synthesized compound of Bi_2Te_3 and Bi_2Te_3-Bi_2Se_3 <Tb> contents, i.e. $(Bi_2Te_3\text{-}Bi_2Se_3)_{1-x}Tb_x$ (*x*=0,15), and Bi_2Te_3-Bi_2Se_3<Cl> on new-cleaved faces of haloid crystal NaCl and glass substrates.

The obtained samples are treated by X-ray analysis on ДРОН-2,0 (CuK_α is radiation, Ni is filter) at 35kV, 10mA. The roentgenograms obtained by scanning of radiation angle of incidence in $5° \leq 2\theta \leq 70°$ limits on surface of (001) film layer are given on fig.1 and 2. From Wolf-Bragg relations it is obvious that rays reflected from planes parallel to (001) are registered at such incidence of roentgen rays. The Bi_2Te_3-Bi_2Se_3<Tb> and Bi_2Te_3-Bi_2Se_3<Cl> films are fixed in layered crystals correspondingly: 10; 13; 15; 16 clear diffraction reflections. The obtained diffraction patterns are almost identical ones with small difference of reflex intensity and reflection angles. The film roentgenogram of Bi_2Te_3-Bi_2Se_3 <Tb> and Bi_2Te_3-Bi_2Se_3 <Cl> polycrystals before and after annealing are well induced on the basis of hexagonal lattice Bi_2Te_3 [6].

RESULTS

The thermoannealing influence at ~500K on structure and film properties deposited on glass has been investigated. The films deposited on glass are treated by annealing in vacuum for taking out of elastic stress fields. The annealing is carried out in vacuum ~10^{-4}*Pa* during 24 hours with temperature decrease up to 25 degree/min.

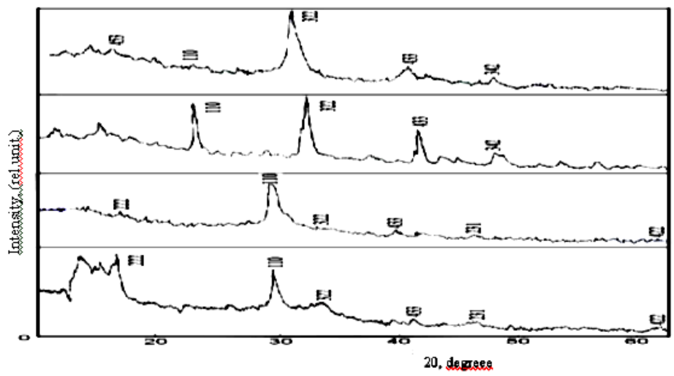

Fig.1. (up) The roentgen of annealed and non-annealed films Bi_2Te_3-Bi_2Se_3 <Cl> and Bi_2Te_3-Bi_2Se_3 <Tb>.

The roentgenogram obtained by the radiation of polycrystalline films Bi_2Te_3-Bi_2Se_3 <Tb> and Bi_2Te_3-Bi_2Se_3

<Cl> is well induced on the basis of hexagonal lattice of Bi_2Te_3 (a=0,43835, c=3,0487nm; sp.gr.D^5_{3d} , R_{3m}, Z=3) polycrystal and corresponds to data [7]. The absolutely all reflexes having the strong and average intensities which are character for the given structure are observed on roentgenogram.

The results of calculated hkl, I/I_0 and experimental interplanar distances d_{exp} in films of p-type Bi_2Te_3-Bi_2Se_3<Tb> and n- type Bi_2Te_3-Bi_2Se_3 <Cl> for comparison of reference data d_{ref} are given in table 1[7-8].

Table

№	$d_{ref,}$ p-type	d_{exp}, p-type	I/I_0	hkl	$d_{exp,}$ n-type	I/I_0
1	5,050	5,415	2	222	5,523	1
2	3,770	3,849	10	110	3,889	5
3	3,210	3,292	1	221	3,366	1
4	-	2,716	10	332	3,029	10
5	-	2,593	10	444	2,869	7
6	2,370	2,450	20	433	2,629	10
7	2,230	2,344	2	443	2,469	7
8	2,190	2,215	6	011	2,230	5
9	2,030	2,110	9	555; 231; 544	-	-
10	1,996	2,007	5	554; 11 $\bar{1}$;200	-	-
11	1,809	1,868	2	220; 342; 311	1,926	10
12	-	1,802	17	331	1,819	10
13	1,696	1,755	15	665; 442	-	-
14	1,608	1,611	20	453	1,637	10
15	1,486	1,526	20	665 442	1,551	10
16	1,450	1,458	10	533	1,492	5

The analysis of obtained data and calculations ones show that contents of annealed films Bi_2Te_3-Bi_2Se_3 <Tb> and Bi_2Te_3-Bi_2Se_3 <Cl> form the isostructure on the basis of hexagonal structure of chalcogenide of bismuth telluride.

CONCLUSION

On the basis of roentenographic investigation of thin film structure obtained by thermal spraying on glass, it is cleared up, that polycrystalline films of Bi_2Te_3-Bi_2Se_3 <Tb> and Bi_2Te_3-Bi_2Se_3 <Cl> with thickness 50-150nm form at substrate temperature ~500K.

Therefore at film annealing Bi_2Te_3-Bi_2Se_3 <Tb> and Bi_2Te_3-Bi_2Se_3 <Cl> up to ~500K doesn't take place the real increase of microparticle sizes, any structural reconstructions, formation of new phases, the polycrystalline structure is observed on roentgenogram. The calculations of interplanar distances d_{exp} in crystals of p- and n-types show that structure becomes more strength one at film annealing at temperature ~500K.

[1] *N.S. Lidorenko*. Plenochniye termoelementi: fizika i primeneniye. M., Nauka, 1985, 3, 7, 179, 199. (in Russian).

[2] *B.M. Golcman, V.A. Kudinov, I.A. Smirnov*. Polupro-vodnikoviye termoelektricheskiye materiali na osnove Bi_2Te_3. M., Nauka, 1972, 18, 302. (in Russian).

[3] *S.I.Mehdiyeva, N.Z.Jalilov, N.M.Abdullayev, N.R.Mem-medov, M.I.Veliyev, V.Z.Zeynalov*. TPE-06, 3-rd Intern.Conf. on Techn.&Phys.Probl. in Pow.Engin., Ankara, Turkey, May 29-31, 2006, 695.

[4] *S.I. Mekhdiyeva, N.Z. Dzhalilov, N.M. Abdullayev, N.P. Memmedov, V.Z. Zeynalov*. AMEA, Khabarlar, C. XXVII, № 2, Baki, 2007, 148. (in Russian).

[5] *A.A. Abdullayev, E.I. Veliyulin, S.Sh. Kakhramanov*. Vliyaniye legirovanya i interkalirovanoya na svoystva khalkogenidov vismuta. Баку, 1991. (in Russian).

[6] *D.I. Ismailov, G.M. Akhmedov, R.Sh. Shafizade*. Dokl.AN Azerb.SSR, 45, №4, 1998, s. 6-8. (in Russian).

[7] Spravochnik. Minerali, tom I, Izd. AN SSSR M. 1960, 573. (in Russian).

[8] *S.S. Tolkachev*. Tablici mejploskostnikh rastoyaniy. Izd.. «Khimiya» Leningradskoye otdeleniye. 1968, 78. (in Russian).

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Bi_2Te_3-Bi_2Se_3 <Tb> VƏ Bi_2Te_3-Bi_2Se_3 <Cl> TƏBƏQƏLƏRİNİN RENTGENOGRAFİK TƏDQİQİ

Bi_2Te_3-Bi_2Se_3<Tb> və Bi_2Te_3-Bi_2Se_3<Cl> təbəqələri ~500K temperaturadək qızdırıldıqda yeni fazaların əmələ gəlməsi və hər hansı bir struktur dəyişikliyi, mikrohissəciklərin ölçülərində real böyüməsi baş vermir. Rentgenoqrammada polikristalik struktur müşahidə olunur. Laylararası məsafələrin hesablanması göstərir ki, qızdırıldıqda təbəqələrin strukturu möhkəmlənir.

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РЕНГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ ПЛЁНОК Bi_2Te_3-Bi_2Se_3 <Tb> И Bi_2Te_3-Bi_2Se_3 <Cl>

При отжиге пленок Bi_2Te_3-Bi_2Se_3<Tb> и Bi_2Te_3-Bi_2Se_3<Cl> до ~500K реального увеличения размера микрочастиц, каких либо структурных перестроек, образование новых фаз не происходит, на рентгенограмме наблюдается поликристаллическая структура. Расчёты межплоскостных расстояний показывают, что при отжиге пленок структура упрочняется.

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