## **OPTICAL PROPERTIES OF Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> FILMS**

## S.I. MEHDIYEVA, N.Z. JALILOV, N.M. ABDULLAYEV, N.R. MEMMEDOV, M.I. VELIYEV, V.Z. ZEYNALOV

Institute of Physics of NAS of Azerbaijan Baku, AZ-1143, H. Javid ave., 33

The spectrums of film samples  $Bi_2Te_3$ - $Bi_2Se_3$  of p-type with Tb impurity and n-type conductivity with Cl impurity have been investigated by methods of optical reflection (in region 1÷6,5eV) and transmission (in region 1-3,5 eV). The more intensive peaks, showing on the existence of interband transitions, are observed in the dependence of reflectivity factor (*R*) on energy (*E*) of incident radiation.

The  $Bi_2Te_3$ - $Bi_2Se_3$  is more effective electron thermoelectric material of refrigeratoring thermoelements and thermogenerators in temperature interval 200-550K. It gives way to the set of medium-temperature materials higher 550K. Firstly thermoelectric material on  $Bi_2Te_3$ - $Bi_2Se_3$  base was synthesized and investigated by S.Sinani [1]. The composition 80% (mol.)  $Bi_2Te_3$  – 20% (mol.)  $Bi_2Se_3$  with the width of prohibited band 0.27eV at room temperature has the best thermoelectric properties [2].

The Bi2Te3-Bi2Se3 system creates the constant set of solid solutions. This means, that Te atoms in any quantity (from 0 till 100%) can be changed by their analogue selenium in Te<sub>1</sub>-Bi-Te<sub>11</sub>-Bi-Te<sub>1</sub> chains, that is caused to the technology flexibility, moreover firstly Se atoms are changed by all  $Te_{11}$  atoms, and further  $Te_1$  atoms. The  $Bi_2Te_3$ - $Bi_2Se_3$ (structure of 20%Bi<sub>2</sub>Te<sub>3</sub>) crystallizes in hexanal structure with lattice parameters a = 4,296Å and c = 5,988Å [3]. The calculations of band structure of semiconductors of  $A_2^{IV} B_3^{VI}$ type, and also the set of the experiments on the investigation of optical properties show on the fact, that electron spectrum in Bi<sub>2</sub>Te<sub>3</sub> has the three-dimensional character [3]. Moreover, the meaning of effective electron mass of the given composition achieves of maximal meaning  $m_n^* = 1, 2m_0$ . The relatively big value of prohibited band is the important factor for the use of this material in thermoelements till the temperatures 600-650K.

At the synthesis of poly-crystal samples the initial components with doping additions are melted in quartz ampoules at temperature 1000K [4]. At the doping by Cu, as the long investigations have shown, the sample properties are changing during the time [5].

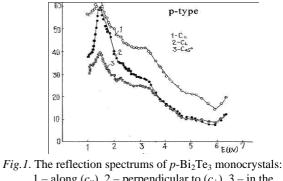
The investigation of reflection and transmission spectrums of  $Bi_2Te_3$ - $Bi_2Se_3$  films of *p*- and *n*-type conductivity, doped by Tb and Cl is the task of the given paper.

The obtaining method of films  $Bi_2Te_3-Bi_2Se_3$  was considered in the ref [6].

The doped binary films by the width of 300Å have been obtained by us by cathode scattering on usual glass, on the glass, covered by carbon film, on mica and NaCl. The films, created on carbon, on the limit (100) of rack salt in range 200-400°C, textured or crystallized in plane (001) parallel to the substrate.

Cl was the main doping addition. This impurity was introduced with the aim of the change of conductivity type of material and increase of its thermoelectric effectiveness. Maximal value  $\alpha^2 \sigma$  are achieved at the doping of the composition by the Cl till 0,3% (mol.) in CdCl<sub>2</sub> form. In the

given paper the investigation results on massive samples of p- and n-types Bi<sub>2</sub>Te<sub>3</sub> at the normal light falling, directed parallel and perpendicular to chip plane at 300K with the aim of the comparison of the results of the given paper with the results of ref [4], where different minimums of reflection coefficients at 1,11eV, possibly corresponding to three different effective masses are given.

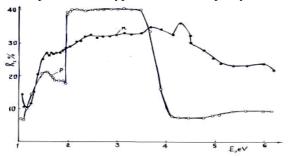


 $1 - \text{along } (c_{11}), 2 - \text{perpendicular to } (c_{\perp}), 3 - \text{ in the direction 45°C to C axes.}$ 

The reflection spectrums in [4] were investigating on massive samples Bi<sub>2</sub>Te<sub>3</sub> of *p*-type conductivity, containing the impurity of terbium and n-type conductivity ones containing the impurity of chlorine. In the dependence of reflectivity factor (R) on energy of falling radiation, as p-, so *n*-type conductivity along  $(c_{\parallel})$  perpendicular  $(c_{\perp})$  and in the direction 45° to the axes of C crystal at 1,1 and 1.45eV the more intensive peaks are observed. The reflection spectrums of film samples Bi2Te3-Bi2Se3 of p-type conductivity, consisting terbium impurity and *n*-type conductivity, consisting Cl impurity have been also investigated in the paper. The intensive peaks are observed in the dependence of reflectivity factor (R) of Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> films on radiation energy for *n*-type conductivity (fig.2), at 1,1eV and 1.45eV. The repeating splitting at 1,1eV and 1.45eV in  $Bi_2Te_3$ spectrum the authors interpret as spin-orbital scattering of valence band and conductivity band. The peaks are observed for the *n*-type films at 3,8 eV. This fact corresponds with the data of ref [4], showing on the existence in Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> films in 0,2-1,8eV interval of strong interband transitions.

The dependence of reflection spectrum of film  $Bi_2Te_3$ - $Bi_2Se_3$  *p*-type conductivity, doped by Tb, and *n*-type conductivity with Cl impurity on the wave length, are given on the fig.2.

The texture was changed on the disorder oriented polycrystal with increase of film width up to 3 mcm at temperature higher, than 500K at the evaporation. The doped polycrystal of film width 0,30; 0,35; 0,40mcm have been obtained by us. Thus, the weak and more intensive peaks, which are connected with transfers in critic points of Brillouin band were observed at the investigation of reflection spectrums of  $Bi_2Te_3$ - $Bi_2Se_3$  monocrystals as *p*-type with Tb impurities, so *n*-type with CdCl<sub>2</sub> impurity.



*Fig.2.* The reflection spectrums of film polycrystal *p*-Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> with Tb impurity; *n*-Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>3</sub>Se<sub>3</sub> with Cl impurity.

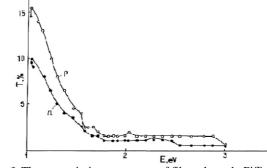
From the dependence of absorption coefficients (*T*) of  $Bi_2Te_3$ - $Bi_2Se_3$  films of *p*-and *n*-types of conductivity, given on the figure 3 it is seen, that in the region 1 eV the films  $Bi_2Te_3$ - $Bi_2Se_3$  of *p*-type absorb the light energy on 16%, and of *n*-type conductivity absorb on 10%. These films can be used for the production of thermobatteries.

It is known, that at the production of film thermobatteries the special coverings with big coefficients of transmission are needed.

For the decrease of oxygen influence on the films at the high temperatures in the process of its exploitation and also in exclusion of electric shorting of thermoelectric branches at the creation of manylayered compact batteries the following demands are needed for such coverings: high electric density, low heat conductivity, thermostability at the widths less, than 1mcm. The polymer coverings, widely used in microelectronics in the capacity of passivation and insulating

- [1] S.S. Sinani, G.N. Gordjakova. JTF 1956, 2398,10, 26.
- [2] *E.K. Iordanishvili*. Semiconductor thermoelectric materials, Leningrad, 1963, p.16.
- [3] B.M. Goltsman, V.A. Kudinov, I.A. Smirnov. Semiconductor thermoelectric materials on the basis Bi<sub>2</sub>Te<sub>3</sub>, "Nauka", Moscow 1972, p.320, 229,234.
- [4] S.I. Mehdiyeva, N.Z. Jalilov, N.M. Abdullayev, M.I Veliyev, V.Z Zeynalov., N.R. Memmedov. Spectra of reflection monocrystals Bi<sub>2</sub>Te<sub>3</sub>. Materials of international conference, devoted to the 85-anniversary from birthday of academician G.B. Abdullayev. Baku - 2003.

coverings, have high disruptive pressure (more than  $10^{6}$ V/sm), specific resistance (more than  $10^{10}$ Om·cm), low specific heat conductivity ( $\alpha$ =(3-4) $10^{-3}$ Vt/cm K)) [7], high density of elastic deformation, high chemical stability to the different inorganic dissolvents. The polymer coverings are profitable on the given properties, than inorganic dielectric materials (CuO<sub>2</sub>, MgF<sub>2</sub>, etc.).



*Fig. 3.* The transmission spectrums of film polycrystal *p*-Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>3</sub>Se<sub>3</sub> with Tb impurity; *n*-Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>3</sub>Se<sub>3</sub> with Cl impurity.

In the conclusion we can say, that the intensive peaks, showing on the existence of interband transitions in the films in the interval 0,2-1,8 eV are observed in dependence of reflectivity factor (R) of p-Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> films on radiation energy for p-type conductivity at 1,1 and 1.45 eV, for n-type conductivity at 3,8 eV. The repeating splitting 1,1eV and 1.45eV in the spectrum are interpreted as spin-orbital splitting of valence band and conductivity band. From the dependence of absorption coefficients (T) of Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> films of p- and n-type conductivity it is seen, that in region 1eV the Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> films of p-type conductivity ones absorb on 10%.

- [5] A.G. Abdullayev, E.I. Veliulin, S.S. Kahramanov. Influence doping and intercalation on properties chalcogenides bismuth. Pre-print, Baku, 1991, p.25.
- [6] D.I. Ismailov, G.M. Ahmedov, R.B. Shafizadeh. Electronografic research of the binary films Bi<sub>2</sub>Te<sub>3</sub>. Reports Of The Academy Of Sciences Azerbaijan SSR, XLV, #4, 1989, p.6-10
- [7] *L.V. Gregor.* Drawing dielectric of the films from a gas phase. Physics thin films. Under red. G. Hassa, R.E. Tuna. M, 1968. T.3.

## S.İ. Mehdiyeva, N.Z. Cəlilov, N.M. Abdullayev, N.R. Məmmədov, M.İ. Vəliyev, V.Z. Zeynalov Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> TƏBƏQƏLƏRİNİN OPTİK XASSƏLƏRİ

Optik əksolma (1-6 eV intervalında) və buraxılma (1-3,5 eV intervalında) metodu ilə Tb ilə aşqarlanmış p-tip və Cl ilə aşqarlanmış n-tip Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> əsasında alınmış nazik təbəqələr tədqiq olunmuşlar. Əksolma əmsallarının(R) düşən şüalanmanın enerjisindən (E) asılı olaraq, 1,1 və 1,45 eV-də zonalararası keçidlərin mövcudluğunu göstərən daha intensiv piklər müşahidə olunmuşdur.

## С.И. Мехтиева, Н.З. Джалилов, Н.М. Абдуллаев, Н.Р. Меммедов, М.И. Велиев, В.З. Зейналов ОПТИЧЕСКИЕ СВОЙСТВА ПЛЁНОК Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub>

Методами оптического отражения (в области  $1\div6,5\ni B$ ) и пропускания (в области  $1-3,5 \ni B$ ) исследованы спектры плёночных образцов Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub> *p*-типа с примесью Tb и *n*-типа проводимости с примесью Cl. Зависимость коэффициента отражения (*R*) от энергии подающего излучения (*E*) показывает, что при значениях *E* равных 1,1эB и 1,45эB наблюдаются более интенсивные пики, указывающие на наличие межзонных переходов.

Received: 22.12.05