

**E.I. Rogacheva**, *doc. phys.-math science, professor*

**A.N. Doroshenko**,

**A.Yu. Sipatov**, *doc. phys.-math science, professor*

National Technical University "Kharkiv Polytechnic Institute",  
2 Kyrpychova St., Kharkiv 61002, Ukraine; e-mail: rogachova.olena@gmail.com

## ELECTRONIC PHASE TRANSITIONS IN THIN $Bi_{1-x}Sb_x$ FILMS

---

*The purpose of the present work is to study the concentration dependences of thermoelectric (TE) and galvanomagnetic properties of thin  $Bi_{1-x}Sb_x$  films in the range  $x = 0 - 0.25$ . The thin films with thicknesses  $d = (250 \pm 10)$  nm were prepared by thermal evaporation in vacuum of  $Bi_{1-x}Sb_x$  polycrystals onto (111) mica substrates and the transport properties (the electrical conductivity, Seebeck coefficient, Hall coefficient, electronic and hole mobility, magnetoresistance) of the films were measured at room temperature. It was established that all anomalies in the concentration dependences of the properties, observed earlier in the  $Bi_{1-x}Sb_x$  bulk crystals and attributed to electronic phase transitions, were reproduced in thin films. The data obtained represent another evidence of the existence of the concentration peculiarities in the transport properties of  $Bi_{1-x}Sb_x$  solid solutions, indicate a good correspondence between the compositions of  $Bi_{1-x}Sb_x$  initial polycrystals and those of the thin films, and should be taken into account when interpreting the results of studies and predicting properties of  $Bi_{1-x}Sb_x$  crystals and thin films. Bibl. 21. Fig. 4.*

**Key words:**  $Bi_{1-x}Sb_x$ , solid solution, thin film, concentration, phase transition, thermoelectric properties, galvanomagnetic properties

### Introduction

$Bi_{1-x}Sb_x$  solid solutions have attracted much attention as promising n-type low-temperature thermoelectric (TE) materials for refrigeration devices at temperatures below  $\sim 200$  K [1-3]. Besides, these materials are among the physical objects whose unique properties continue to be revealed more and more every year, surprising us with the manifestation of new physical effects. Recently, interest in studying  $Bi_{1-x}Sb_x$  crystals and thin films has sharply increased after it was established that they exhibit properties of 3D-topological insulators [4,5] in which a strong spin-orbit interaction leads to the appearance of topologically protected metallic surface states with a Dirac dispersion law. However, by now, the simultaneous coexistence of the topological and good TE properties, which is also observed for other promising TE materials (e.g.  $V_2VI_3$  compounds), has not found an unambiguous explanation, but in recent years several works have appeared, related to possible effects of topological surface states on controlling TE properties of  $Bi_{1-x}Sb_x$  crystals and thin films [6, 7].

Due to the structural and electrochemical similarities of Bi and Sb semimetals, these elements form a continuous series of  $Bi_{1-x}Sb_x$  solid solutions [8], which makes it possible to study in detail the effect of the composition on the crystal structure, band structure and physical properties. It is known that although  $Bi_{1-x}Sb_x$  solid solutions have a rhombohedral crystal structure in the entire concentration range, the band structure changes in a non-monotonic way [9-12] (Fig. 1). In the valence band of pure Bi, there are subbands of "light" ( $L_\alpha$ ) and "heavy" ( $T$ ) holes and, as a result of the overlap of the hole  $T$  and electron  $L_s$  bands, Bi exhibits semimetallic properties. With an increase in the Sb concentration, the distance between the conduction band  $L_s$  and the subband  $L_\alpha$  decreases and at  $x = 0.023 - 0.04$  (different authors indicate different

values of this concentration) a gapless state is observed, the  $L_s$  and  $L_a$  bands invert. With a further increase in  $x$ , the gap between them increases again. Simultaneously with an increase in  $x$ , the overlap of  $T$  and  $L_s$  bands decreases, disappearing at  $x = 0.06 \div 0.07$ , and a semimetal – indirect semiconductor transition occurs. Then, at  $x = 0.08 \div 0.09$ , the ceilings of  $T$  and  $L_s$  of the valence bands converge, and in the concentration range  $x = 0.09 - 0.15$  the semiconductor becomes direct-gap. The maximum value of the energy gap in the semiconductor region ( $E_g \sim 0.025$  eV) is reached near  $x = 0.15 \div 0.17$ . With a subsequent increase in  $x$ , at  $x \sim 0.15$ , the semiconductor becomes indirect-gap again and at  $x > 0.22$ ,  $Bi_{1-x}Sb_x$  solid solutions acquire semimetal properties. Thus, the  $Bi_{1-x}Sb_x$  system is characterized by a number of electronic phase transitions, the presence of which should be reflected at the concentration dependences of properties.

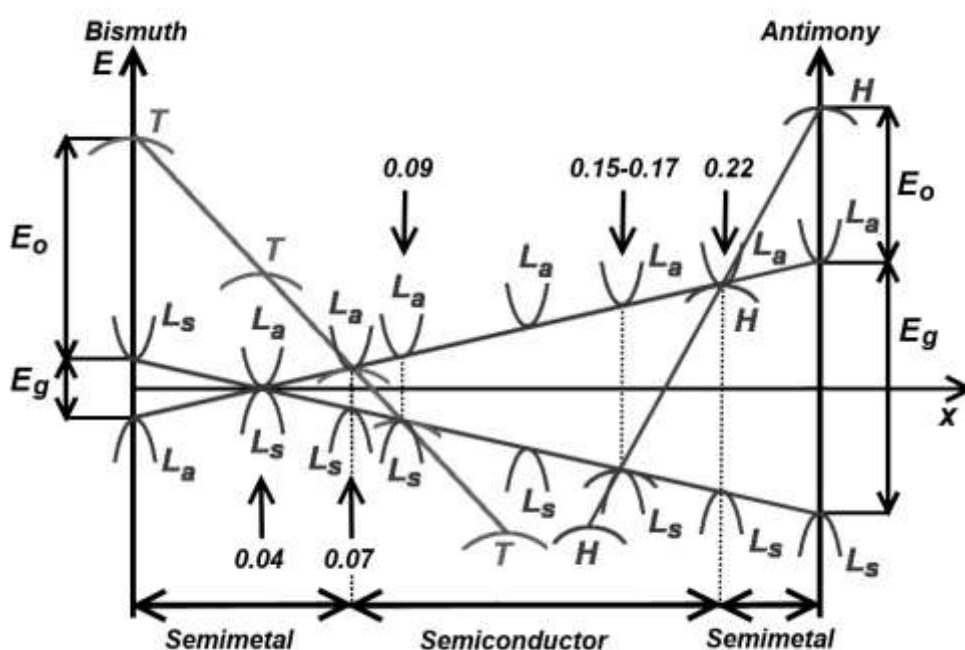


Fig. 1. Electronic band structure of the  $Bi_{1-x}Sb_x$  solid solutions

Although the majority of studies on the fundamental properties of  $Bi_{1-x}Sb_x$  solid solutions were carried out using single crystals, at present, an increasing number of works are devoted to the study of polycrystals [13-16]. This is due to both the great simplicity and cost-effectiveness of manufacturing polycrystalline materials and the convenience of manufacturing TE devices of various types from them. It was found that the nature of the concentration and temperature dependences of the TE properties of polycrystals and  $Bi_{1-x}Sb_x$  single crystals is basically the same, although the grain size has a significant effect on the properties of polycrystals.

Earlier, we revealed a nonmonotonic behavior of the concentration dependences of TE properties in polycrystalline  $Bi_{1-x}Sb_x$  solid solutions in the vicinity of  $x = 0.01, 0.03, 0.07, 0.08, 0.15, 0.22$  [17 – 25] and attributed the concentration anomalies of properties in the vicinity of  $x = 0.01$  to percolation effects in the impurity subsystem of crystal, and other anomalies to corresponding electronic phase transitions (to a gapless state, semimetal - semiconductor, indirect – direct-band-gap semiconductor).

Currently, in connection with the development of nanotechnology, low-dimensional structures (thin films, quantum wires, quantum dots) are widely used in various fields of science and technology, including

thermoelectricity. The possibility of enhancing the dimensionless TE figure of merit ( $ZT = (S^2 \div T) / \lambda$ , where  $S$  is the Seebeck coefficient,  $\lambda$  is electrical conductivity,  $\lambda$  is total thermal conductivity, and  $T$  is absolute temperature) in low-dimensional structures [26] have stimulated studies of  $Bi_{1-x}Sb_x$  thin-film structures. In particular, it was of interest to find out whether the revealed concentration anomalies would be observed in the thin films obtained from the bulk crystals. When studying thin  $Bi_{1-x}Sb_x$  films in the range  $x = 0 - 0.09$ , we have showed [27] that concentration anomalies of properties are also reproduced in the thin films. It was interesting to expand the range of compositions under study, taking into account that the highest  $Z$  values are observed in the concentration range  $x = 0.12-0.15$  [1 – 3]. In addition, it was of interest to find out whether technological factors or measurement conditions influence the fact of the presence of anomalies or the nature of their manifestation.

The objects of the present study were the  $Bi_{1-x}Sb_x$  thin films with thicknesses  $d = (250 \pm 10)$  nm prepared by thermal evaporation in vacuum onto mica substrates at  $T_s = 380$  K of  $Bi_{1-x}Sb_x$  polycrystals in the composition range  $x = 0 - 0.25$ .

As a result of the conducted studies, it was found that in the dependences of TE and galvanomagnetic properties on composition of thin  $Bi_{1-x}Sb_x$  films in the range  $x = 0 - 0.25$ , concentration anomalies were found as well as in  $Bi_{1-x}Sb_x$  polycrystals, and that changes in the polycrystal preparation technology and in the magnetic field value in which the galvanomagnetic properties are measured, do not change the general character of the dependences of the TE and galvanomagnetic properties on the composition.

## **Experimental details**

The  $Bi_{1-x}Sb_x$  thin films with the thicknesses  $d = (250 \pm 10)$  nm were obtained by the thermal evaporation of  $Bi_{1-x}Sb_x$  polycrystals ( $x = 0 - 0.25$ ) in a vacuum ( $\sim 10^{-6}$  Pa) from a single source and their deposition onto (111) mica substrates at a temperature  $T_s = 380$  K with a rate of  $0.1 - 0.3$  nm/s. Fabrication technique of the polycrystalline  $Bi_{1-x}Sb_x$  samples of various compositions ( $x = 0 - 0.25$ ) for the thin films obtaining is described in [27]. The only difference was that in the present work we used samples that were annealed for 720 hours after synthesis, and the samples used to obtain films in the work [27] were annealed for 1200 hours.

The film thicknesses and the condensation rate were controlled using a calibrated quartz resonator. The crystal structures and phase composition of the initial materials and thin films were characterized by the X-ray diffraction method. In the X-ray diffraction patterns for thin films similarly to the initial bulk crystals, only  $Bi_{1-x}Sb_x$  lines were seen. The obtained  $Bi_{1-x}Sb_x$  films had a mosaic structure with a trigonal axis perpendicular to the film surface. Using X-ray photoelectronic spectroscopy and microprobe analysis, it was shown that the film composition corresponded to the initial material composition with an accuracy ( $\Delta x$ ) not worse than  $\Delta x = \pm 0.002$ .

The measurements of the transport properties were carried out at room temperature on as-prepared films. The electrical conductivity  $\sigma$ , the Hall coefficient  $R_H$  and magnetoresistance  $\Delta\rho/\rho$  were measured by a conventional  $d_c$  method on bulk parallelepiped-shaped samples and double Hall-cross shaped thin films. Ohmic contacts were prepared by soldering indium to the bulk or film surfaces. The used value of the magnetic field ( $B = 0.05$  T) corresponded to a weak magnetic field in contrast to work [27], where a magnetic field equal to  $B = 0.9$  T was used, which corresponded to the region of a strong magnetic field. It is known that in the weak magnetic field,  $R_H$  value does not depend on  $B$  and  $\Delta\rho/\rho$  increases of quadratic function. The error in the  $R_H$ ,  $\sigma$  and  $\Delta\rho/\rho$  measurements did not exceed  $\pm 5$  %. The Seebeck coefficient  $S$  was measured relative to Cu with an accuracy of  $\pm 3$  %. The component of the TE power perpendicular to the trigonal axis was measured. The calculation of the Hall mobilities of electrons  $\mu_n$  and holes  $\mu_p$  was

carried out taking into account two types of charge carriers and assuming that  $n = p$  (which is observed with a high degree of accuracy in  $Bi_{1-x}Sb_x$  solid solutions) according to the equations:

$$\sigma = en(\mu_n + \mu_p); \quad R_H = \frac{1}{en} \frac{\mu_n - \mu_p}{\mu_n + \mu_p}; \quad \frac{\Delta\rho}{\rho B^2} = \mu_n \mu_p \quad (1)$$

Since the mobility of electrons  $\mu_n$  exceeds the mobility of holes  $\mu_p$ , the sign of  $R_H$  for  $Bi$  and  $Bi_{1-x}Sb_x$  solid solutions is determined by the mobility of electrons. This explains the resulting negative sign of  $R_H$  and  $S$  in bulk crystals. From the results of measuring  $\sigma$ ,  $R_H$ ,  $\Delta\rho/\rho$ , and  $S$  values and taking into account the value of  $B$ , the values of  $n = p$ ,  $\mu_n$ ,  $\mu_p$  and TE power factor  $P(x) = S^2 \sigma$  were calculated.

## Results

In Figs 2-4, the concentration dependences  $R_H(x)$ ,  $S(x)$ ,  $\Delta\rho/\rho(x)$ ,  $\mu_n(x)$ ,  $\mu_p(x)$ , and  $P(x)$  are presented for the  $Bi_{1-x}Sb_x$  bulk crystals and thin films. It can be seen that all dependences exhibit a distinctly non-monotonic oscillatory behavior.

According to the measurement of  $S$ , all obtained thin films, like the initial polycrystals, had an electronic type of conductivity. From the Fig. 2 (a) it can be seen that  $S(x)$  dependences for bulk polycrystals and thin films are very similar. The addition of Sb atoms to bismuth to  $x \sim 0.10$  leads to a significant increase in  $S$ , due to the reduction of the overlap of T and  $L_s$  bands and the formation of a semiconductor region (Fig. 1).

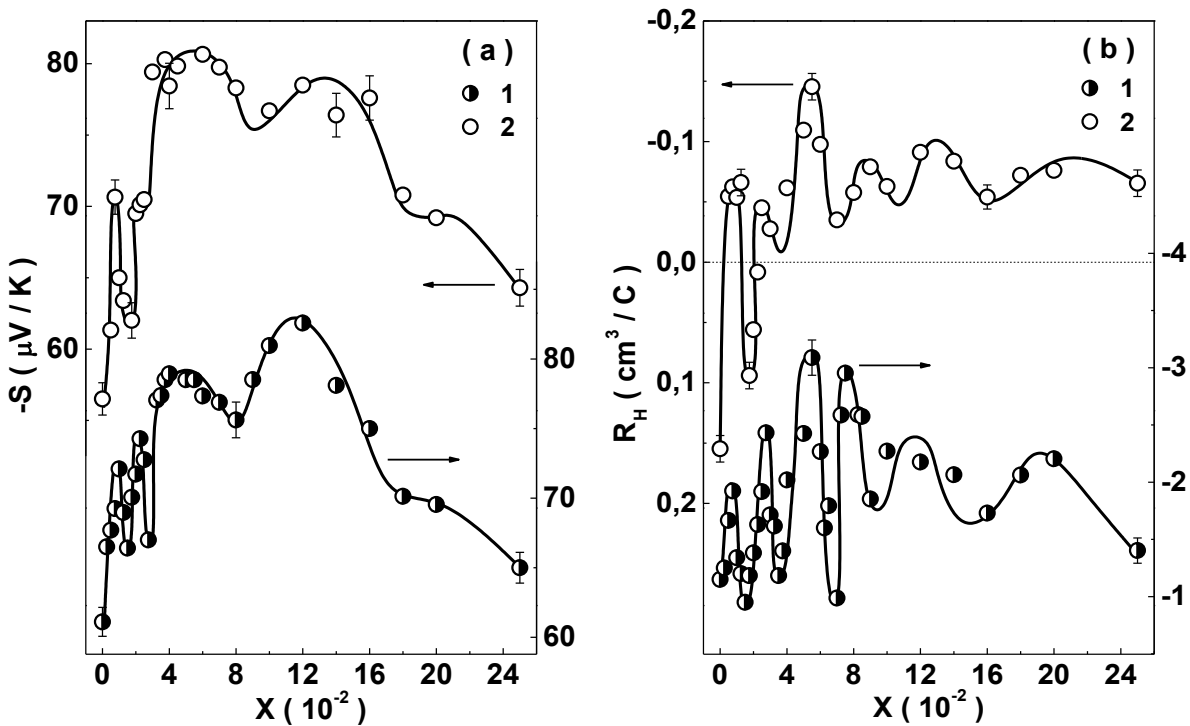


Fig. 2. Room-temperature dependences of the Seebeck coefficient  $S$  (a) and the Hall coefficient  $R_H$  (b) on the composition  $x$  of the  $Bi_{1-x}Sb_x$  polycrystals (1) and thin films (2). Solid lines are guides to the eye.

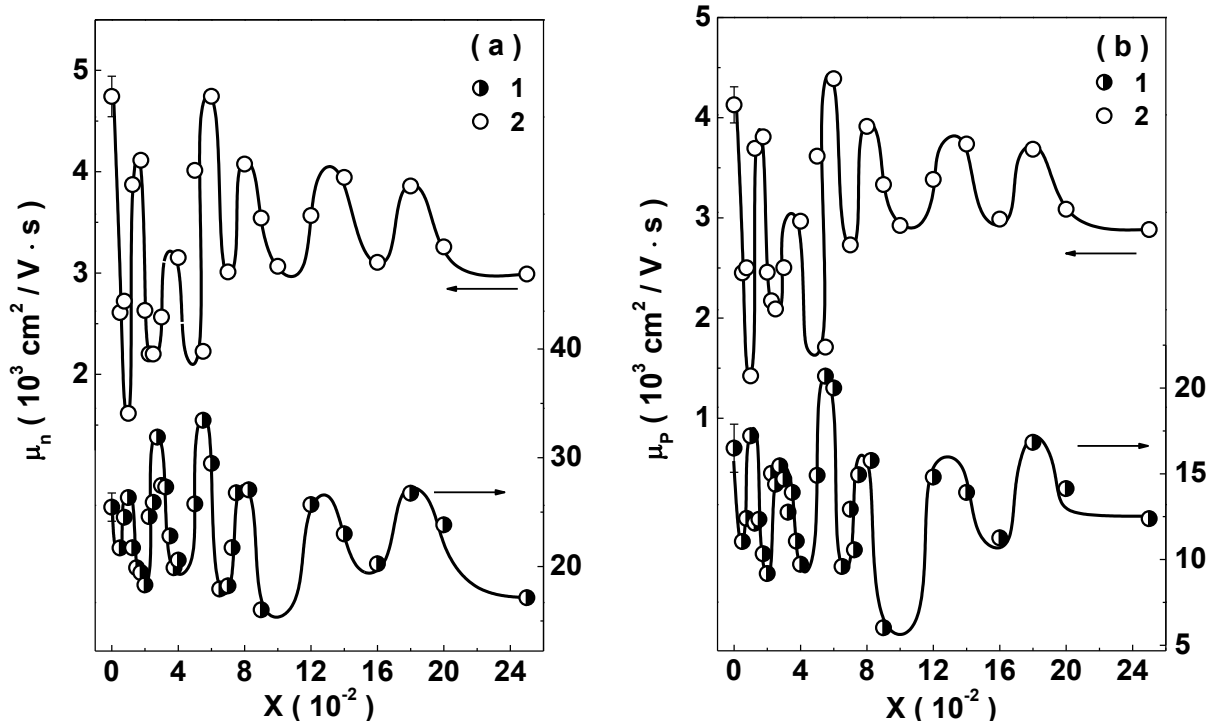


Fig. 3. Room-temperature dependences of the electron  $\mu_n$  (a) and hole  $\mu_p$  (b) mobilities on composition  $x$  of the  $\text{Bi}_{1-x}\text{Sb}_x$  polycrystals (1) and thin films (2). Solid lines are guides to the eye.

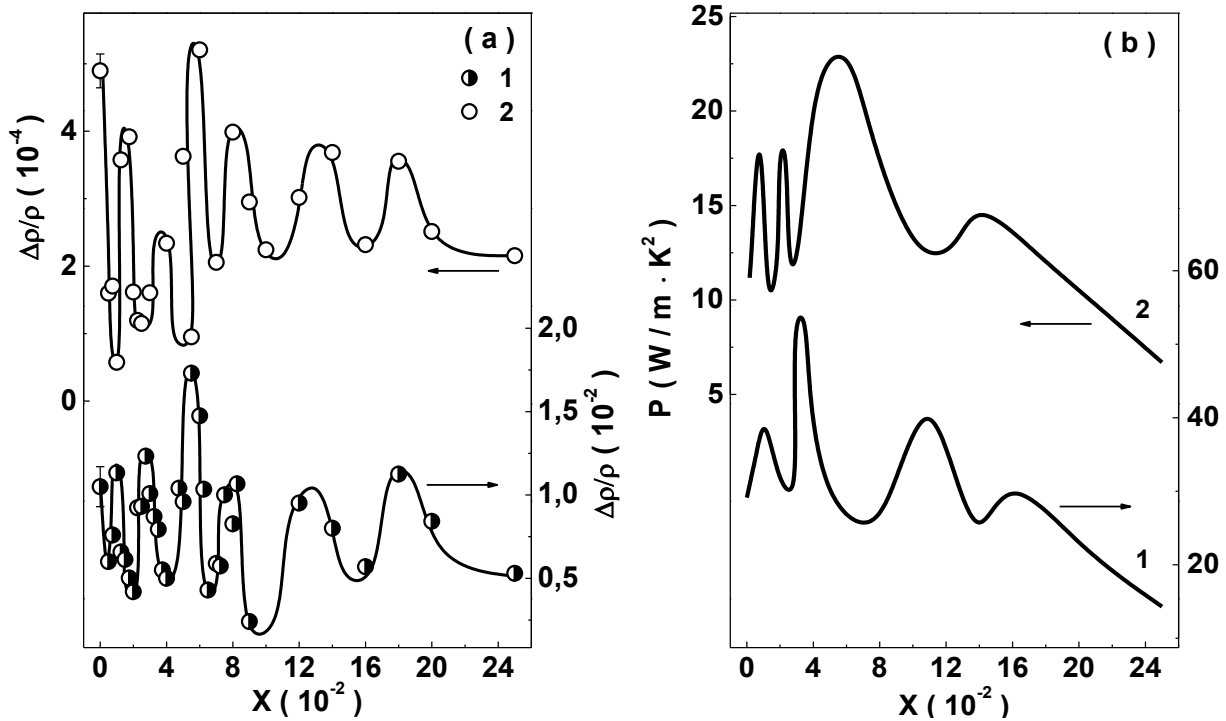


Fig. 4. Room-temperature dependences of magnetoresistance  $\Delta\rho/\rho$  and thermoelectric power factor  $P = S^2 \sigma$  on composition  $x$  of the  $\text{Bi}_{1-x}\text{Sb}_x$  polycrystals (1) and thin films (2). Solid lines are guides to the eye.

After that,  $S$  decreases. However, we are talking only about the general trend of  $S$  change in the range  $x = 0 - 0.25$ . Meanwhile, the  $S(x)$  dependence for both bulk crystals and thin films exhibit several

peaks or inflections near the compositions  $x = 0.01, 0.02, 0.05, 0.12$ , and  $0.18$  which we attributed [17 – 25] to a percolation and electronic phase transitions.

In accordance with the  $R_H$  measurements, all the initial polycrystals also had an electronic type of conductivity. In the  $R_H(x)$  dependence for polycrystals (Fig. 2,b), in addition to the indicated anomalies in  $S(x)$  dependence (Fig. 2,a), we were able at  $x \sim 0.08$  to reveal the peak associated with an indirect-gap - a direct-gap semiconductor transition, when the  $T$ -band top coincides with the  $L_s$ -band top [24, 25]. In  $S(x)$  dependence, in contrast to dependence  $R_H(x)$ , there is one diffuse anomalous section in the range  $x = 0.05 - 0.08$  (Fig. 2a).

The dependence  $R_H(x)$  for thin films (Fig. 2,b) turned out to be more complex:  $R_H(x)$  curve had a number of features connected with the change of conductivity type. Bi had p-type conductivity ( $R_H > 0$ ) but introduction of the first portions of Sb (to  $x \sim 0.007$ ) led to inversion sign of conductivity ( $p \rightarrow n$ ). Then, at  $x \sim 0.01$ , the conductivity type changed again ( $n \rightarrow p$ ) and followed by a new change in the sign of the conductivity at  $x \sim 0.02$  ( $p \rightarrow n$ ). After that, with a further increase in  $x$ , the  $R_H$  sign for all films was negative ( $R_H < 0$ ), as for bulk crystals. The reason for the difference between the  $R_H$  and  $S$  signs may be as follows. According to [28], in Bi monocrystals,  $R_H$  has a positive sign only along the direction of the trigonal axis, and in the perpendicular directions, the sign changes to a negative one. Unlike  $R_H$ , the coefficient  $S$  in any crystallographic directions remains negative.  $Bi_{1-x}Sb_x$  films were grown along the direction of the trigonal axis [001], which was perpendicular to the plane of the substrate. That is why a positive  $R_H$  sign and a negative  $S$  sign were observed for Bi films what we showed in our work [29]. The introduction of Sb leads to an elastic distortions of crystal lattice, and with increasing  $x$ , orientation along the trigonal axis [001] becomes less and less perfect, and at a certain concentration of Sb, orientation practically disappears. A convincing fact confirming this assumption is the negative  $R_H$  sign observed by the authors of [30] in polycrystalline Bi films in which there is no anisotropy of properties.

Let us point out the following circumstance. As noted above, it was previously assumed [17 – 25] that in the range  $x=0.005-0.01$ , there is a percolation transition from an impurity discontinuum to an impurity continuum, which is with a high degree of probability is accompanied by ordering processes [31]. These processes can stimulate the formation of a more perfect oriented structure and determine inversion of conductivity type ( $n \rightarrow p$ ). A subsequent increase in Sb concentration makes again the structure less perfect and leads to the inversion of the conductivity sign ( $p \rightarrow n$ ). Approach to transition to a gapless state leads to a decrease in  $R_H$  but it no longer causes an inversion of the conduction type ( $n \rightarrow p$ ) since a significant number of impurity atoms makes the oriented structure even more imperfect. Thus, the alternating change in the  $R_H$  sign reflects in some way the change in the degree of structure perfection (degree of orientation), which, in turn, is associated with the presence of phase transitions. In a sense, a conductivity type can be used to estimate the degree of anisotropy in the film structure. This, of course, only applies to the case if the type of conductivity depends on the direction in the crystal.

Let us note that in the work [27] in which the  $Bi_{1-x}Sb_x$  films were studied only in the concentration range  $x = 0 - 0.1$ , no change in the sign of  $R_H$  was observed at the percolation transition near  $x = 0.01$ . Perhaps this was due to the fact that the  $R_H$  measurements were carried out in a strong magnetic field ( $B = 0.9$  T), and not in a weak magnetic field ( $B = 0.05$  T), as in the present work.

A change in the  $R_H$  sign in films depending on  $x$  complicates the comparison of the  $R_H(x)$  dependences for bulk and film samples. However, it can be seen (Fig. 2b) that despite the alternating change of  $R_H$  sign in the range  $x = 0 - 0.02$ , the character of the  $R_H(x)$  dependence remains the same as for bulk crystals, having extrema corresponding to the phase transitions of the above types, if we take the  $R_H$  value of Bi as the reference point. In other words, a change in  $R_H$  sign does not prevent observation of the concentration anomalies.

The calculation of the  $\mu_n$  and  $\mu_p$  values using equation (1) showed that the dependences  $\mu_n(x)$  and  $\mu_p(x)$  have also a pronounced nonmonotonic character (Fig. 3). There are several clear maxima at  $x \sim 0.01$ ,  $\sim 0.03$ ,  $\sim 0.06$ ,  $\sim 0.08$ ,  $\sim 0.14$  and  $\sim 0.18$ . These concentrations correspond to the characteristic compositions (Fig. 1) at which there are qualitative changes in the  $Bi_{1-x}Sb_x$  band energy structure. It should be noted that, in these dependences, as well as in the  $R_H(x)$  dependence, two maxima can be distinguished, corresponding to the semimetal – indirect-gap semiconductor transition and indirect-gap semiconductor – direct-gap semiconductor ( $x \sim 0.06$  and  $x \sim 0.08$ , respectively). The dependence  $\Delta\rho/\rho(x)$  (Fig. 4a) actually repeats the character of the dependences  $\mu_n(x)$  and  $\mu_p(x)$ .

It was shown theoretically [32] that the  $Bi_{1-x}Sb_x$  band structure depends not only on the composition and thickness of the film, but also on the orientation of the film on the substrate. Therefore, it can be expected that at low Sb concentrations, when the degree of anisotropy in the film is sufficiently high, the extrema on the concentration dependences of the properties of the films can be shifted relative to these positions in the crystal. Some shift of the maxima on the dependences  $\Delta\rho/\rho(x)$ ,  $\mu_n(x)$  and  $\mu_p(x)$  for bulk crystals and films in the range of compositions  $x = 0 - 0.1$  is related, apparently, to this circumstance.

In Fig. 4,b, the concentration dependences of TE power factor  $P = S_2 \sigma$  for bulk crystals and thin films are presented. The lower values of  $P$  in thin films compared to bulk crystals can be explained by lower values of electrical conductivity in thin films, since the values of the Seebeck coefficient, are practically the same in crystals and films (Fig. 2a). Fig. 4 shows that the  $P(x)$  dependence, as well as the dependences on the composition for all other kinetic coefficients of crystals and films, has a distinctly nonmonotonic character. The compositions at which the maximum values of  $P$  are observed, are different for crystals and thin films (at  $x \sim 0.03$  and  $x \sim 0.06$ , respectively). however, these data correspond to 300 K, while the highest values of TE figure of merit correspond to temperatures below 200 K [1 – 3]. Therefore, our immediate task is to obtain the temperature dependences of the kinetic coefficients of thin  $Bi_{1-x}Sb_x$  films.

Thus, we can conclude that the concentration anomalies of TE and galvanomagnetic properties observed for  $Bi_{1-x}Sb_x$  polycrystals and attributed [17 – 25] to critical phenomena accompanying phase transitions, are reproduced in the thin films obtained from these crystals. A change in the technology for preparing initial bulk crystals (the reduction in the annealing time of bulk from 1200 to 720 hours) does not change the behavior of the concentration dependences of kinetic coefficient of bulk crystals and thin films qualitatively. The nature of the magnetic field (strong or weak) in which the galvanomagnetic properties are measured does not change the general character of the dependences of the properties on the composition and the presence of anomalies, but only affects the value of  $R_H$  and  $\Delta\rho/\rho$ .

However, it should be noted that this is observed in sufficiently "thick" films ( $d = 250 \pm 10$  nm), when quantum size effects (e.g, the oscillating nature of the  $d$  - dependences of properties) are practically not manifested. The transition to very thin films and manifestation of these effects can significantly change the physical picture. However, in a number of cases, thin-film TE energy converters are used with layer thicknesses when size quantum effects do not manifest themselves.

## Conclusions

1. It was established that the concentration anomalies of TE and galvanomagnetic properties associated with the manifestation of critical phenomena accompanying percolation and electronic phase transitions observed in  $Bi_{1-x}Sb_x$  polycrystals in the composition range  $x = 0 - 0.25$ , are largely reproducible in thin  $Bi_{1-x}Sb_x$  films with thicknesses  $d = (250 \pm 10)$  nm obtained from these crystals by thermal evaporation in vacuum on mica substrates.
2. A change in the magnetic field value used in the measurement of  $R_H$  and magnetoresistance, a change in

the technology of polycrystals of which the films were made (a decrease in the annealing time from 1200 to 720 hours) do not affect the fact of the presence of concentration anomalies of properties both in polycrystals and in thin films.

3. The alternation of the RH sign in the range  $x = 0 - 0.02$  with changing the composition under a constancy of sign of the Seebeck coefficient in  $Bi_{1-x}Sb_x$  thin films was found. The sign of the  $R_H$  in a film depends on the degree of film anisotropy, which, in turn, depends on the presence of a phase transition. A change in the  $R_H$  sign with a changing the composition is not an obstacle to the detection of anomalies in the concentration dependences of properties.
4. The results obtained is one more confirmation of the fact of the presence of percolation and electronic phase transitions in the  $Bi_{1-x}Sb_x$  solid solutions which manifest themselves in critical phenomena observed not only in crystals, but also in films.
5. Good agreement of the critical compositions in the concentration dependences of the properties of the  $Bi_{1-x}Sb_x$  crystals and thin films, indicates good reproducibility of the compositions of polycrystals in thin films obtained from these polycrystals.
6. The existence of the concentration anomalies of TE and galvanomagnetic properties in  $Bi_{1-x}Sb_x$  bulk and thin film states should be taken into account when interpreting the results of studies, predicting TE properties, and using the  $Bi_{1-x}Sb_x$  polycrystals and thin films in TE devices.

**Acknowledgements** This work was supported by the Ministry of Education and Science of Ukraine (Project # M 0625)

## References

1. Anatyshuk L.I. (1979). Termoelementy i termoelektricheskie ustroystva: spravochnik [Thermoelements and thermoelectric devices: reference book] Kyiv, Naukova dumka [in Russian].
2. Lenoir B., Scherrer H. and Caillat T. (2001). An overview of recent developments for BiSb alloys, Chapter 4, In: Tritt T.M. (ed.) Semiconductors and Semimetals: Recent Trends in Thermoelectric Materials Research I, Vol. 69. San Diego, Academic Press.
3. Uher C. (ed.) (2016). Materials aspect of thermoelectricity. CRC Press, Boca Raton: Taylor & Francis Group.
4. Fu L., Kane C.L. and Mele E.J. (2007). Topological insulators in three dimensions. Phys. Rev. Lett., 98(10), 106803.
5. Hsieh D., Qian D., Wray L., Xia Y., Hor Y.S., Cava R.J. and Hasan M.Z. (2008). A topological Dirac insulator in a quantum spin Hall phase. Nature, 452, 970-974.
6. Takahashi R. and Murakami S. (2012). Thermoelectric transport in topological insulators Semicond. Sci. Technol., 27(12), 124005-8.
7. Muehler L., Casper F., Yan B., Chadov S., and Felser C. (2013). Topological insulators and thermoelectric materials. Phys. Stat. Solidi RRL, 7(1-2), 91-100.
8. Ugay Ya.A., Goncharov Ye.G., Semenova G.V. and Lazarev V.B. (1989). Phase equilibria between phosphorus, arsenic and bismuth. Moscow, Nauka (in Russian).
9. Brandt N.B., Chudinov S.M., and Karavaev V.G. (1976). Investigation of the zero-gap state induced by a magnetic field in bismuth-antimony alloys. Sov. Phys. JETP, 43(6), 1198-1209; Zh. Eksp. Teor. Fiz. 70, 2296-2317 (in Russian)
10. Yasaki T. and Abe Y. (1968). Galvanomagnetic investigations of the  $Bi_{1-x}Sb_x$  ( $0 < x < 0.15$ ) system at 77 K. J. Phys. Soc. Jpn., 24(2), 290-295.



11. Mironova G.A., Sudakova M.B., Ponomarev Ya.G. (1980). Dispersion law of carriers in the  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *Sov. Phys. Solid State*, 22(12), 2124; *Fizika tverd. tela*, 22(12), 1980, pp. 3628-3634 (in Russian).
12. Mironova G.A., Sudakova M.B., Ponomarev Ya.G. (1980). Investigation of the band structure of semiconducting  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *Sov. Phys. JETP*, 51(5), 918-929.
13. Kitagawa H., Noguchi H., Kiyabu T., Itoh M. and Noda Y. (2004). Thermoelectric properties of Bi-Sb semiconducting alloys prepared by quenching and annealing. *J. Phys. Chem. Solids*, 65(7), 1223-1227.
14. Malik K., Das D., Mondal D., Chattopadhyay D., Deb A.K., Bandyopadhyay S. and Banerjee A. (2011). Sb concentration dependent structural and resistive properties of polycrystalline Bi-Sb alloys. *J. Appl. Phys.*, 112(12), 083706.
15. Dutta S., Shubha V. and Ramesh T.G. and D'Sa F. (2009). Thermal and electronic properties of  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *J. Alloy Compd.*, 467(1), 305-309.
16. Lenoir B., Dauscher A., Cassart M., Ravich Y.I. and Scherrer H. (1998). Effect of antimony content on the thermoelectric figure of merit of  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *J. Phys. Chem. Solids*, 59(1), 129-134.
17. Rogacheva E.I. and Drozdova A.A. (2006). Thermoelectric properties of polycrystalline bismuth-antimony solid solutions. *J. Thermoelectricity*, 2, 22-28.
18. Rogacheva E.I., Yakovleva A.A. (Drozdova A.A.), Pinegin V.I. and Dresselhaus M.S. (2008). Concentration anomalies of properties in Bi-Sb semimetallic solid solutions. *J. Phys. Chem. Solids*, 69(2-3), 580-584.
19. Rogacheva E.I., Drozdova A.A., Nashchekina O.N., Dresselhaus M.S. and Dresselhaus G. (2009). Transition into a gapless state and concentration anomalies in the properties of  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *Appl. Phys. Lett.*, 94(20), 202111.
20. Rogacheva E.I., Drozdova A.A. and Nashchekina O.N., Percolation effects in semimetallic Bi-Sb solid solutions, *Phys. Stat. sol. (a)*, 207(2), 2010, pp. 344-347.
21. Rogacheva E.I., Doroshenko A.N., Nashchekina O.N. and Yu.V. Men'shov. (2013). Thermal conductivity in  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *J. Electron. Mater.*, 42(7), 2098-2102.
22. Rogacheva E.I., Doroshenko A.N., Pinegin V.I. and Dresselhaus M.S. (2013). Electronic phase transitions and structural instability in  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *J. Thermoelectricity*, 6, 13-20.
23. Rogacheva E.I., Doroshenko A.N., Nashchekina O.N. and Dresselhaus M.S. (2016). Specific heat critical behavior in  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *Appl. Phys. Lett.*, 109(13), 131906.
24. Doroshenko A.N., Rogacheva E.I., Drozdova A.A., Martynova K.V., Men'shov Yu.V. (2016). Thermoelectric properties of polycrystalline  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions in the concentration range  $x = 0 - 0.25$ . *J. Thermoelectricity*, 4, 23-36.
25. Rogacheva E.I., Doroshenko A.N., Drozdova A.A., Nashchekina O.N., Men'shov Yu.V. (2020). Galvanomagnetic properties of polycrystalline  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions in the concentration range  $x = 0 - 0.25$ . *Functional Materials*, 27(3) 488-496. <https://doi.org/10.15407/fm27.03.488>
26. Dresselhaus M.S., Lin Y.-M., Cronin S.B., Rabin O, Black M.R., Dresselhaus G. (2001). Quantum wells and quantum wires for potential thermoelectric applications, In Tritt T.M. (ed.) *Semiconductors and Semimetals: Recent Trends in Thermoelectric Materials Research III*, Vol. 71. Academic Press, San Diego, CA.
27. Rogacheva E.I., Nashchekina O.N., Orlova D.S., Doroshenko A.N., Dresselhaus M.S. (2017). Influence of composition on the thermoelectric properties of  $\text{Bi}_{1-x}\text{Sb}_x$  thin films. *J. Electron. Mater.* 46(7), 3821-3825.
28. Jain A.L. (1959). Temperature dependence of the electrical properties of bismuth-antimony alloys. *Phys. Rev. B* 114(6), 1518 -1528.

29. Rogacheva E.I., Grigorov S.N., Nashchekina O.N., Lyubchenko S.G., Dresselhaus M.S. (2003). Quantum size effects in n-type Bi thin films. Appl. Phys. Lett. 82, 2628-2630.
30. Petrosyan V.I., Molin V.N., Dagman E.I., Tavger B.A., Skripkina P.A., Alexandrov L.N. (1971). Quantum size transition semimetal-semiconductor in super-thin Bi films. Phys. Metallov i Metallovedenie, 31, 725-730 (in Russian)
31. Rogacheva E.I. (2003). Self-organization processes in impurity subsystem of solid solution. J. Phys. Chem. Solids, 64(9-10), 1579-1583.
32. Tang Sh., Dresselhaus M.S. (2012). Phase diagrams of  $Bi_{1-x}Sb_x$  thin films with different growth orientations. Phys. Rev. B, 86(7), 075436(1-6). DOI: 10.1103/PhysRevB.86.075436

Submitted 07.04.2020

**Рогачова О.І.,** докт. фіз.-мат. наук, професор  
**Дорошенко Г.М.,**  
**Сіпатов О.Ю.** докт. фіз.-мат. наук, професор

Національний технічний університет "Харківський політехнічний інститут",  
вул. Кирпичова, 2, м. Харків 61002, Україна,  
e-mail: rogachova.olena@gmail.com

## **ЕЛЕКТРОННІ ФАЗОВІ ПЕРЕХОДИ У ТОНКИХ ПЛІВКАХ $Bi_{1-x}Sb_x$**

Метою даної роботи було вивчення концентраційних залежностей  $TE$  та гальваномагнітних властивостей тонких плівок  $Bi_{1-x}Sb_x$  в інтервалі  $x = 0 - 0.25$ . Тонкі плівки  $Bi_{1-x}Sb_x$  товщиною  $d = (250 \pm 10)$  нм були виготовлені термічним випаровуванням у вакуумі кристалів  $Bi_{1-x}Sb_x$  на (111) слюдяні підкладки, а транспортні властивості (електропровідність, коефіцієнт Зеєбека, коефіцієнт Холла, рухливість електронів і дірок, магнетоопір) плівок вимірювались за кімнатної температури. Було встановлено, що всі аномалії на концентраційних залежностях властивостей, що спостерігалися раніше в масивних кристалах  $Bi_{1-x}Sb_x$  і пов'язувалися із електронними фазовими переходами, відтворювались у тонких плівках. Отримані дані, з одного боку, – це ще один доказ існування концентраційних особливостей у транспортних властивостях твердих розчинів  $Bi_{1-x}Sb_x$ , а, з другого боку, ці дані вказують на добру відповідність складів вихідних кристалів складам тонких плівок. Одержані результати слід враховувати при інтерпретації результатів досліджень та прогнозуванні властивостей кристалів і тонких плівок  $Bi_{1-x}Sb_x$ . Бібл. 21, рис. 4.

**Ключові слова:**  $Bi_{1-x}Sb_x$ , твердий розчин, тонка плівка; концентрація, фазовий перехід, термоелектричні властивості, гальваномагнітні властивості.

**Рогачова Е.И.,** докт. фіз.-мат. наук, професор  
**Дорошенко Г.М.,**  
**Сипатов А.Ю.** докт. фіз.-мат. наук, професор

Национальный технический университет  
"Харьковский политехнический институт"  
ул. Кирпичева, 2, г. Харьков 61002, Украина,  
e-mail: rogachova.olena@gmail.com

## **ЭЛЕКТРОННЫЕ ФАЗОВЫХ ПЕРЕХОДОВ В ТОНКИХ ПЛЕНКАХ $Bi_{1-x}Sb_x$**

Целью данной работы было изучение концентрационных зависимостей  $TO$  и гальваномагнитных свойств тонких пленок  $Bi_{1-x}Sb_x$  в интервале  $x = 0 - 0.25$ . Тонкие пленки  $Bi_{1-x}Sb_x$  толщиной  $d = (250 \pm 10)$  нм были изготовлены термическим испарением в вакууме кристаллов  $Bi_{1-x}Sb_x$  на (111) слюдяные подложки, а транспортные свойства (электропроводность, коэффициент Зеебека, коэффициент Холла, подвижность электронов и дырок, магнитное) пленок измерялись при комнатной температуре. Было установлено, что все аномалии на концентрационных зависимостях свойств, которые наблюдались ранее в массивных кристаллах  $Bi_{1-x}Sb_x$  и связаны с электронными фазовыми переходами, воспроизводились в тонких пленках. Полученные данные, с одной стороны, - это еще одно доказательство существования концентрационных особенностей в транспортных свойствах твердых растворов  $Bi_{1-x}Sb_x$ , а с другой стороны, эти данные указывают на хорошую соответствие складов выходных кристаллов составам тонких пленок. Полученные результаты следует учитывать при интерпретации результатов исследований и прогнозировании свойств кристаллов и тонких пленок  $Bi_{1-x}Sb_x$ . Библ. 21, рис. 4.

**Ключевые слова:**  $Bi_{1-x}Sb_x$ , твердый раствор тонкая пленка; концентрация; фазовый переход; термоэлектрические свойства; гальваномагнитные свойства

## **References**

1. Anatyshuk L.I. (1979). Termoelementy i termoelektricheskie ustroystva: spravochnik [Thermoelements and thermoelectric devices: reference book] Kyiv, Naukova dumka [in Russian].
2. Lenoir B., Scherrer H. and Caillat T. (2001). An overview of recent developments for BiSb alloys, Chapter 4, In: Tritt T.M. (ed.) Semiconductors and Semimetals: Recent Trends in Thermoelectric Materials Research I, Vol. 69. San Diego, Academic Press.
3. Uher C. (ed.) (2016). Materials aspect of thermoelectricity. CRC Press, Boca Raton: Taylor & Francis Group.
4. Fu L., Kane C.L. and Mele E.J. (2007). Topological insulators in three dimensions. Phys. Rev. Lett., 98(10), 106803.
5. Hsieh D., Qian D., Wray L., Xia Y., Hor Y.S., Cava R.J. and Hasan M.Z. (2008). A topological Dirac insulator in a quantum spin Hall phase. Nature, 452, 970-974.
6. Takahashi R. and Murakami S. (2012). Thermoelectric transport in topological insulators Semicond. Sci. Technol., 27(12), 124005-8.
7. Muehler L., Casper F., Yan B., Chadov S., and Felser C. (2013). Topological insulators and thermoelectric materials. Phys. Stat. Solidi RRL, 7(1-2), 91-100.

8. Ugay Ya.A., Goncharov Ye.G., Semenova G.V. and Lazarev V.B. (1989). Phase equilibria between phosphorus, arsenic and bismuth. Moscow, Nauka (in Russian).
9. Brandt N.B., Chudinov S.M., and Karavaev V.G. (1976). Investigation of the zero-gap state induced by a magnetic field in bismuth-antimony alloys. *Sov. Phys. JETP*, 43(6), 1198-1209; *Zh. Eksp. Teor. Fiz.* 70, 2296-2317 (in Russian)
10. Yasaki T. and Abe Y. (1968). Galvanomagnetic investigations of the  $\text{Bi}_{1-x}\text{Sb}_x$  ( $0 < x < 0.15$ ) system at 77 K. *J. Phys. Soc. Jpn.*, 24(2), 290-295.
11. Mironova G.A., Sudakova M.B., Ponomarev Ya.G. (1980). Dispersion law of carriers in the  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *Sov. Phys. Solid State*, 22(12), 2124; *Fizika tverd. tela*, 22(12), 1980, pp. 3628-3634 (in Russian).
12. Mironova G.A., Sudakova M.B., Ponomarev Ya.G. (1980). Investigation of the band structure of semiconducting  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *Sov. Phys. JETP*, 51(5), 918-929.
13. Kitagawa H., Noguchi H., Kiyabu T., Itoh M. and Noda Y. (2004). Thermoelectric properties of Bi-Sb semiconducting alloys prepared by quenching and annealing. *J. Phys. Chem. Solids*, 65(7), 1223-1227.
14. Malik K., Das D., Mondal D., Chattopadhyay D., Deb A.K., Bandyopadhyay S. and Banerjee A. (2011). Sb concentration dependent structural and resistive properties of polycrystalline Bi-Sb alloys. *J. Appl. Phys.*, 112(12), 083706.
15. Dutta S., Shubha V. and Ramesh T.G. and D'Sa F. (2009). Thermal and electronic properties of  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *J. Alloy Compd.*, 467(1), 305–309.
16. Lenoir B., Dauscher A., Cassart M., Ravich Y.I. and Scherrer H. (1998). Effect of antimony content on the thermoelectric figure of merit of  $\text{Bi}_{1-x}\text{Sb}_x$  alloys. *J. Phys. Chem. Solids*, 59(1), 129-134.
17. Rogacheva E.I. and Drozdova A.A. (2006). Thermoelectric properties of polycrystalline bismuth-antimony solid solutions. *J. Thermoelectricity*, 2, 22-28.
18. Rogacheva E.I., Yakovleva A.A. (Drozdova A.A.), Pinegin V.I. and Dresselhaus M.S. (2008). Concentration anomalies of properties in Bi-Sb semimetallic solid solutions. *J. Phys. Chem. Solids*, 69(2-3), 580-584.
19. Rogacheva E.I., Drozdova A.A., Nashchekina O.N., Dresselhaus M.S. and Dresselhaus G. (2009). Transition into a gapless state and concentration anomalies in the properties of  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *Appl. Phys. Lett.*, 94(20), 202111.
20. Rogacheva E.I., Drozdova A.A. and Nashchekina O.N., Percolation effects in semimetallic Bi-Sb solid solutions, *Phys. Stat. sol. (a)*, 207(2), 2010, pp. 344–347.
21. Rogacheva E.I., Doroshenko A.N., Nashchekina O.N. and Yu.V. Men'shov. (2013). Thermal conductivity in  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *J. Electron. Mater.*, 42(7), 2098-2102.
22. Rogacheva E.I., Doroshenko A.N., Pinegin V.I. and Dresselhaus M.S. (2013). Electronic phase transitions and structural instability in  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *J. Thermoelectricity*, 6, 13-20.
23. Rogacheva E.I., Doroshenko A.N., Nashchekina O.N. and Dresselhaus M.S. (2016). Specific heat critical behavior in  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions. *Appl. Phys. Lett.*, 109(13), 131906.
24. Doroshenko A.N., Rogacheva E.I., Drozdova A.A., Martynova K.V., Men'shov Yu.V. (2016). Thermoelectric properties of polycrystalline  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions in the concentration range  $x = 0 - 0.25$ . *J. Thermoelectricity*, 4, 23-36.
25. Rogacheva E.I., Doroshenko A.N., Drozdova A.A., Nashchekina O.N., Men'shov Yu.V. (2020). Galvanomagnetic properties of polycrystalline  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions in the concentration range  $x = 0 - 0.25$ . *Functional Materials*, 27(3) 488-496. <https://doi.org/10.15407/fm27.03.488>
26. Dresselhaus M.S., Lin Y.-M., Cronin S.B., Rabin O, Black M.R., Dresselhaus G. (2001). Quantum wells and quantum wires for potential thermoelectric applications, In Tritt T.M. (ed.) *Semiconductors and*

- Semimetals: Recent Trends in Thermoelectric Materials Research III, Vol. 71. Academic Press, San Diego, CA.
27. Rogacheva E.I., Nashchekina O.N., Orlova D.S., Doroshenko A.N., Dresselhaus M.S. (2017). Influence of composition on the thermoelectric properties of  $\text{Bi}_{1-x}\text{Sb}_x$  thin films. *J. Electron. Mater.* 46(7), p. 3821-3825.
28. Jain A.L. (1959). Temperature dependence of the electrical properties of bismuth-antimony alloys. *Phys. Rev. B* 114(6), 1518 -1528.
29. Rogacheva E.I., Grigorov S.N., Nashchekina O.N., Lyubchenko S.G., Dresselhaus M.S. (2003). Quantum size effects in n-type Bi thin films. *Appl. Phys. Lett.* 82, 2628-2630.
30. Petrosyan V.I., Molin V.N. Dagman E.I., Tavger B.A., Skripkina P.A., Alexandrov L.N. (1971). Quantum size transition semimetal-semiconductor in super-thin Bi films. *Phys. Metallov i Metallovedenie*, 31, 725-730 (in Russian)
31. Rogacheva E.I. (2003). Self-organization processes in impurity subsystem of solid solution. *J. Phys. Chem. Solids*, 64(9-10), 1579-1583.
32. Tang Sh., Dresselhaus M.S. (2012). Phase diagrams of  $\text{Bi}_{1-x}\text{Sb}_x$  thin films with different growth orientations. *Phys. Rev. B*, 86(7), 075436(1-6). DOI: 10.1103/PhysRevB.86.075436

Submitted 07.04.2020