Dependence of the Galvanomagnetic Properties of Bismuth-Antimony Thin Films on Their Composition and Crystal Structure

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***Abstract* — The influence of composition and structure on galvanomagnetic and thermoelectric properties of Bi-Sb thin films is studied. The comparison of properties of block textured and monocrystalline films, made by the method of floating-zone refining under covet, is carried out. The influence of grain-boarder scattering of charge carriers on galvanomagntic properties is pointed out. Mechanical deformation, which occurs in film-substrate system, essentially effects galvanomagntic properties. According to the experimental data, charge carrier mobilities were counted for BiSb films.**

***Index Terms* — bismuth-antimony, thin films, single-crystal films, transport phenomena, galvanomagnetic phenomenon, size effect, mechanical deformation of films.**

I. INTRODUCTION

Bismuth antimony alloys are attractive both for theoretical investigations and for prospects in thermoelectric applications [1-3]. Recently special attention is paid to low dimensional structures, in particular nanowires and films based on bismuth and bismuth antimony [4, 5].

There are two types of size effects observable in low dimensional structure. The classical size effect, which is seen when the charge-carrier mean free path is comparable with or greater than the sample thickness, results in a resistivity which is higher than the bulk value, due to the additional scattering of the charge carriers at the sample surface. The quantum size effect, which manifests itself when the carrier wavelength is comparable with or greater than the sample thickness.

The effect of the surface on the transport properties of films has been long studied in the classical-size-effect regime [6, 7]. Classical size effects arise when the thickness of the film approaches the hulk mean free path, and have largely been interpreted according to the theories [8, 9]. These theories are based on the Boltzmann equation in which the surface in incorporated via boundary conditions on the electron distribution function. In particular, the surface is characterized by a specularity parameter ρ according to the degree of scattering from the surface, with ρ lying between 0 (for completely diffuse) and 1 (for completely specular). Extensions of these theories to include angle-dependent specularity parameters [10].

Theoretically, quantum size effects in a film with perfect surfaces were first studied by Sandomirskii [11].

The properties of bismuth-antimony thin films are affected by solid solutions, defects in the crystal structure, the sample size, and deformation at the film – substrate interface.

Grain-boundary scattering can also contribute to the scrambling of the phase of the electron wave function, in which case l_i is of the order of the size of a grain.

The goal of the present work was to obtain a monocrystalline $Bi_{1-x}Sb_x$ films and to study the effect of various factors on the mobility of charge carriers.

II. SAMPLES

Block bismuth-antimony films were obtained by discrete thermal spraying in a vacuum (10^{-5} mm Hg.) on the a substrate at a temperature of 410 K. Muscovite mica and a polyimide film were used as substrates. After deposition, the films were annealed at 540 K. The single-crystal films were obtained by zone recrystallization under cover films by discrete thermal spraying [12, 13]. The choice of material for substrates was primarily due to two reasons. Mica has a crystalline structure that exerts an orienting effect on a bismuth film and bismuth-antimony solid solutions, so that, the orientation of crystallites of the films is usually characterized by the C_3 axis perpendicular to the substrate plane. A polyimide substrate is amorphous and a pronounced orienting effect on the film.

In addition, the coefficient of linear thermal expansion of mica, bismuth, and polyimide is $(7{,}5\text{-}8{,}5)\cdot 10^{-6}$ K^{-1} < $11\cdot 10^{-6}$ K^{-1} < $(30\text{-}50)\cdot 10^{-6}$ K^{-1} respectively. Therefore, at a temperature below the temperature of formation of the film, in-plane tensile tested on mica and plane compression on a polyimide substrate.

Investigation of the structure of films using metallography and atomic force microscopy showed that the films are single crystal with an orientation of the trigonal axis normal to the plane of the substrate. Thermally evaporated films block have the same orientation with respect to the trigonal axis of the plane of the substrate (Figs. 1 and 2).

The growth from the vapor phase is clearly expressed in the figures.

The results of X-ray diffraction studies of single-crystal bismuth-antimony films, with 3.5at%Sb, are shown in Fig. 3. The small width of the diffraction peaks of the film, as well as a good resolution of X-ray peak of the doublet in the fifth order (a), confirm the perfection of the crystal structure of the films and indicate a uniform distribution of antimony over the film (Fig. 3).

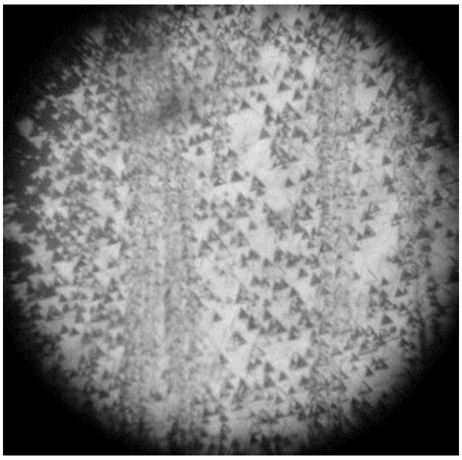

Fig. 1. Image of the etched surface of single-crystal bismuth antimony films on mica in a metallographic microscope. The diameter of the field of view is 100 µm.

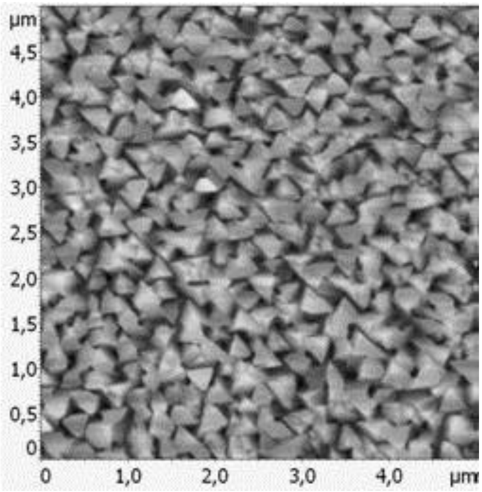

Fig. 2. AFM image of the surface of the original thermally deposited bismuth-antimony film.

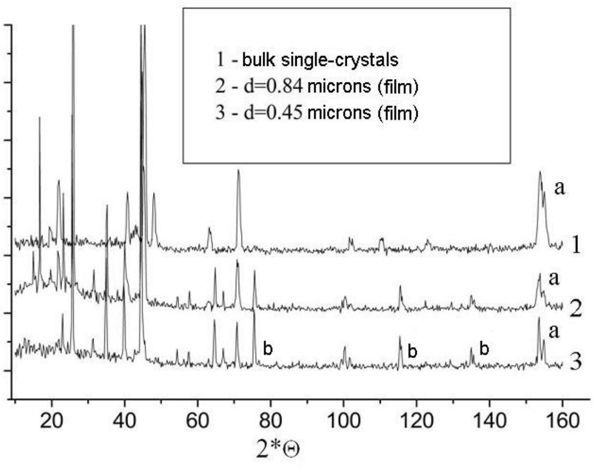

Fig. 3 X-ray diffraction from the trigonal plane of the single-crystal bismuth-antimony films with 3.5at %Sb and the plane of single-crystal bismuth-antimony films with 3.5at%Sb on mica.

III. RESULTS AND DISCUSSION

Effect of crystal structure on the transport phenomena.

An important factor that affects the properties of the films is their crystal structure; this is clearly evident from the comparison of the properties of samples of bismuth-antimony films with the same thickness and composition.

Figures 4 and 5 show the reduced temperature dependence of the resistivity and magnetoresistance of two pairs of films, the solid solution of bismuth-antimony alloys with 5at%Sb on mica and polyimide. The films have the same thickness of 0.5 µm, and the pairs differ in the degree of perfection of the crystal structure; one of them is a block; the other a single crystal (no intercrystalline boundaries).

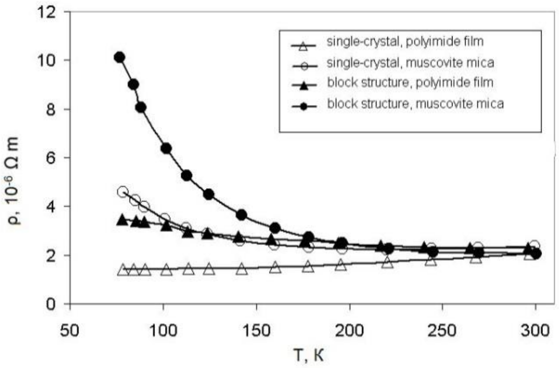

Fig.4. Temperature dependence of the resistivity of the block and single-crystal films of $Bi_{95}Sb_5$.

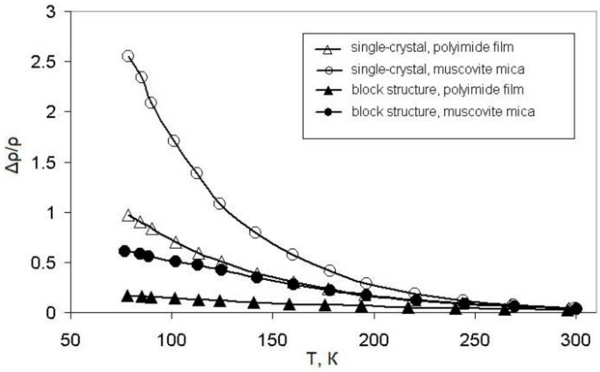

Fig.5. Temperature dependence of the magnetoresistance of the block and single-crystal films of $Bi_{95}Sb_5$.

The resistivity of the block of films both on mica and on polyimide is higher and magnetoresistance is less than that of the single-crystal films on similar substrates. This difference in the temperature dependence of the resistivity and magnetoresistance of single-crystal films and blocks indicates a significant effect of block boundaries on transport phenomena.

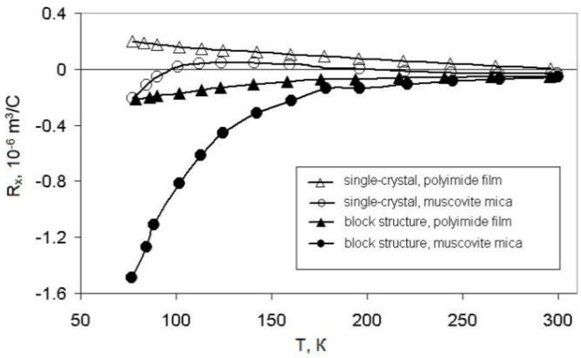

Fig. 6. Temperature dependence of the Hall coefficients of the block and single-crystal films of $Bi_{95}Sb_5$.

Figure 6 shows the temperature dependence of the Hall coefficient of the single-crystal films and block with the same composition on mica and polyimide. In block films, the Hall coefficient is negative and increases in absolute value with decreasing temperature; the effect is most significant on polyimide substrates.

In the single-crystal films with decreasing temperature, the Hall coefficient shifts to positive values and increases in magnitude. For the films on mica, with a further decrease in temperature, the Hall coefficient shifts to negative values.

Dependence of the transport phenomena in the bismuth-antimony films on the ratio of the solid solution components

Figure 7 shows the temperature dependence of resistivity of crystal-crystal films of bismuth-antimony alloys with different composition and a thickness of 0.6 μm on mica. In these films, the resistivity increases with decreasing temperature.

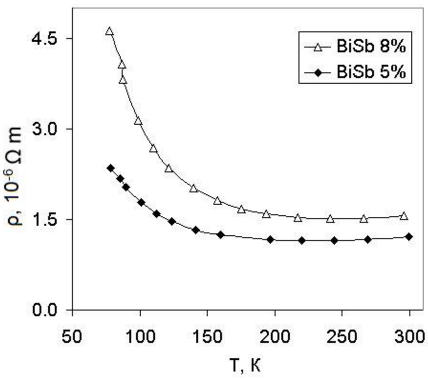

Fig.7. Temperature dependence of the resistivity of single-crystal films.

The resistivity of single-crystal films with 8at% antimony is higher than that of the films containing 5at% antimony, similar to the resistivity of bulk single crystals of antimony content.

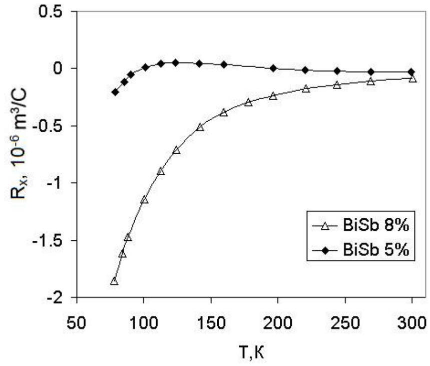

Fig.8. Temperature dependence of the Hall coefficient of single-crystal films.

Figure 8 shows the temperature dependence of the Hall coefficient of single-crystal films. For bismuth-antimony films containing 8at% antimony, the Hall coefficient is negative and increases in absolute value with decreasing temperature. For films with 5at% antimony, the Hall coefficient has a low positive value to the transition to negative values at temperatures below 100 K. The difference in the sign, magnitude and temperature dependence of the Hall coefficient in single-crystal bismuth-antimony films containing 5at% antimony, and 8at% is caused by due to the different structure of the bands in the vicinity of the Fermi energy.

Charge carrier mobility in bismuth-antimony films

On the basis of experimental data on transport phenomena with the known expression of the theory of transport phenomena in crystals such as bismuth, the mobility of charge carriers in the bismuth-antimony films was calculated.

During the simulation process, it was necessary to separate the effect of deformation of films on the concentration and mobility of charge carriers [14, 15]. Given the small difference in the coefficients of thermal expansion of bismuth and mica, the carrier concentration for films on mica was assumed to be the same as in bulk single crystals.

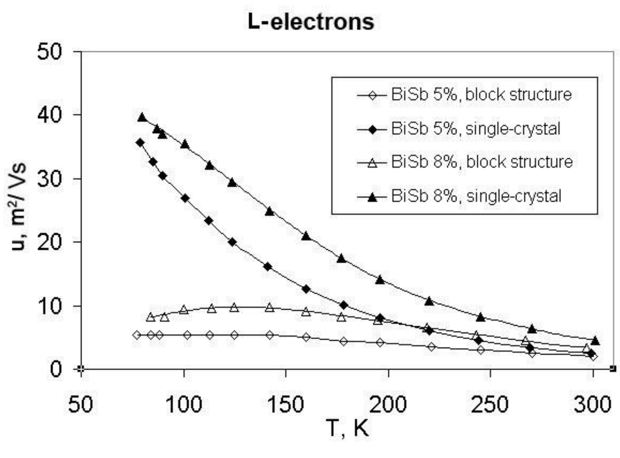

Fig. 9. Temperature dependence of the charge carrier mobility L- electrons in the block and single-crystal films on mica.

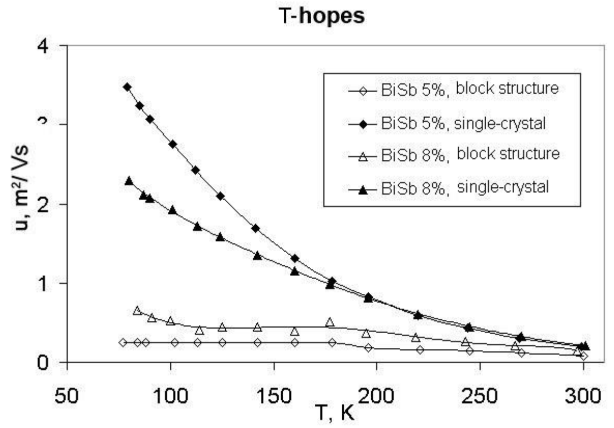

Fig. 10. Temperature dependence of the charge carrier mobility T-holes in the block and single-crystal films on mica.

Figures 9, 10 shows that the mobility of electrons and holes is higher in single-crystal films. The mobility of charge carriers in the films increases with the antimony content in the solid solution, as well as in bulk crystals.

For the calculation of the mobility in the films on polyimide, it is necessary to determine the effect of deformation on the concentration and mobility of charge carriers. A model, that will take into account the effect of deformation on energy spectrum and the parameters of the charge carriers in the films of bismuth-antimony solid solutions is currently being developed.

IV. CONCLUSION

Monocrystalline $Bi_{1-x}Sb_x$ films with homogeneous Sb distribution were made by method of floating-zone refining under covet. The study of their galvanomagnetic properties and the comparison with block textured films allowed to reveal the features of influence of charge carrier grain-boarder scattering.

The comparison results for thin films of BiSb on substrates with different thermal expansion reveal the essential influence of mechanical deformations, which occur in film-substrate system, on galvanomagntic properties of BiSb films.

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REFERENCES

[1] *CRC Handbook of Thermoelectrics, Ed. D.M. Row-CRC Press*, Bocaraton, London, New York, Washington DC, pp. 1703, (1995).

[2] W.U. Yin, and Amith. *Solid State Electron*, vol. 15, 1141 (1972).

[3] L.I. Anatychuk. *J. Thermoelectricity*, vol. 2, pp. 348, (2005).

[4] O. Rabin, Yu. Ming Lin, and M.S. Dresselhaus. J. *Phys. Rev. B*, vol. 79, 1, pp. 81, (2001).

[5] Mei Lu, R.J. Zieve, A. van Hulst, H.M. Jaeger, T.F. Rosenbaum, S. Radelaar. *Phys. Rev. B*, vol. 53, 3, pp. 1609, (1996-I).

[6] K.L. Chopra. *Thin Film Phenomena (McGraw-Hill, New York*, 1969).

[7] P. Wissmann and K. Muller, *in Surface Physics, vol. 77 of Springer Tracts in Modern Physics, edited by G. Hohler* (Springer, New York, 1975).

[8] K. Fuchs. *Proc. Cambridge Philos. Soc*. vol. 34, pp. 100, (1938).

[9] E.H. Sondheimer. *Adv. Phys*., vol. 1, pp. 1, (1952).

[10] S. Soffer. *J. Appl. Phys*., vol. 38, pp. 1710, (1967).

[11] V.B. Sandomirskii. *Zh. Eksp. Teor. Fiz.* vol. 52, pp. 158, (1967) [*Sov. Phys. – JETP* vol. 25, pp. 101, (1967)].

[12] V. Grabov, V. Komarov, E. Demidov, M. Klimantov. “Transport phenomena in monocrystalline bismuth films.” *Izvestia: Herzen university journal of humanities & sciences. - St. Petersburg, Russia,* vol. 122, 2010.

[13] V. Grabov, G. Ivanov, V. Naletov, V. Ponaryadov, T. Yakovleva. *Solid state physics, St. Petersburg, Russia*, 1969.

[14] N.B.Brant, R. Herman, V.A. Kulbachinskii. *Solid state physics, St. Petersburg, Russia*, vol. 7, 1982.

[15] V. Kulbachinskii. “The change of the energy spectrum of bismuth and bismuth-antimony alloys with strong deformations such uniaxial compression and tension.” // *Thesis PhD physicist and mathematical: 01.04.09 - Moscow,* 1978.