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Extrema positions of charge carrier band spectrum in thin bismuth films

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Abstract. Many studies report an increase in charge carrier concentration in thin bismuth films as their thickness decreases at low temperatures. These results are obtained on the basis of data on resistivity, magnetoresistance, Hall coefficient, and thermal EMF measured in these films. The calculation is most often carried out within the framework of the two-band approximation assuming the quadraticity of the dispersion law of electrons and holes. Using these approximations, it is possible to estimate the change in the position of energy extremes relative to the chemical potential in these films based on concentration values of charge carriers. This article presents all these calculations and analyses the extrema movement of the charge carrier band spectrum in bismuth films with a change in their thickness.

Keywords: thin films, bismuth, transport phenomena, charge carriers' concentration, band structure

Introduction

For many decades, crystals and low-dimensional objects of bismuth and its alloys with antimony have been of theoretical and practical interest to researchers. This interest is associated with the crystal and energy structure of this class of materials, which determines their unique electronic and thermoelectric properties (Abdelbarey et al. 2020; Grabov et al. 2010; Hirahara et al. 2015; Hsieh et al. 2008; Lenoir et al. 1996; Lv et al. 2010; Singh et al. 2018).

Our several studies (Demidov 2022; Demidov et al. 2018; 2020; 2022; Grabov et al. 2017) calculated the mobility and charge carrier concentration in bismuth films (111) with the thickness up to 15 nm formed on the mica (muscovite) substrate. The calculations were based on the data of resistivity, magnetoresistance, Hall coefficient, and thermoelectric power measured at the temperature of 80 K within the two-band approximation, assuming the dispersion law squareness for electrons and holes, and a number of additional approximations. The increase of charge carrier concentration in the thin bismuth films with the decrease in their thickness was observed in all works. In one study (Demidov 2022), charge carrier concentration was calculated using all the four transfer coefficients. In another study (Demidov et al. 2022), the concentration was calculated for a larger number of films. It should be noted that differences in the obtained results are significant only in films with the thickness less than 50 nm. That is why the results for charge carrier concentration with the thicknesses less than 50 nm were taken from the former mentioned study (Demidov 2022), while those for thicker bismuth films—from the latter (Demidov et al. 2022).

Method of calculating the extrema positions of the charge carrier band spectrum in thin bismuth films

Based on the obtained values of electron (n) and hole (p) concentrations, it is possible to determine the energy extrema positions of the valence and the conduction bands relative to the chemical potential level.

In this case, the dispersion law for L-electrons and T-holes can be approximated by a simple quadratic model.

For electrons:

$$n = 3 * \frac{2\left(2m_{n1}^{*}m_{n2}^{*}m_{n3}^{*}\right)^{1/2}}{3\pi^{2}\hbar^{3}}\left(kT\right)^{3/2} \times F_{1/2}\left(\mu_{n}\right), \tag{1}$$

where $F_{1/2}(\mu)$—Fermi integral. For electrons, the Fermi integral is:

$$F_{1/2}\left(\mu_{n}\right) = \frac{1}{\sqrt{\pi}}\int_{0}^{\infty}\frac{\varepsilon^{1/2}}{e^{\varepsilon-\mu_{n}}+1}d\varepsilon, \tag{2}$$

where $\varepsilon = E/kT$, $\mu_n = E_{Fn}/kT$, E—energy, E_{Fn}—electron Fermi energy, m^{*}_{ni}—components of electron effective mass, in the coordinate system of the electron ellipsoid axes, where i = 1, 2, 3.

For holes:

$$p = \frac{2\left(2m_{p1}^{*}m_{p2}^{*}m_{p3}^{*}\right)^{1/2}}{3\pi^{2}\hbar^{3}}\left(kT\right)^{3/2} \times F_{1/2}\left(\mu_{p}\right), \tag{3}$$

where

$$F_{1/2}\left(\mu_{p}\right) = \frac{1}{\sqrt{\pi}}\int_{0}^{\infty}\frac{\varepsilon^{1/2}}{e^{\varepsilon-\mu_{p}}+1}d\varepsilon \tag{4}$$

Similar to electrons, in the case of holes $\mu_p = E_{Fp}/kT$, E_{Fp}—Fermi energy of holes, m^{*}_{pi}—components of electron effective mass, in the coordinate system of the electron ellipsoid axes, where i = 1, 2, 3.

Values of the effective mass components were taken equal to the corresponding values for massive monocrystals from V. M. Grabov's work (Grabov 1998).

By numerically solving equations (1), (2) and (3), (4), knowing the electron and hole concentrations for the thin bismuth film, it is possible to find the positions of energy extremes for the valence and the conduction bands.

Results and discussion

Figure 1 shows the dependence of electron and hole concentration on the thickness of bismuth films determined in previous studies (Demidov 2022; Demidov et al. 2022). In one of them (Demidov et al. 2022), electron and hole concentrations were assumed to be equal. However, in the other study (Demidov 2022), which took into account the thermoelectric coefficient in addition to the galvanomagnetic coefficients, it was possible not to use this approximation and to calculate the concentrations of electrons and holes separately. For thicknesses greater than 50 nm, the results obtained with the help of both approaches turned out to be quite close; however, for thinner films, different concentrations of electrons and holes were obtained (Demidov 2022), and this difference increased as the film thickness decreased.

Based on the values of electron and hole concentrations shown in Fig. 1, the energy extrema positions of the valence and the conduction bands relative to the chemical potential level were calculated. Fig. 2 shows the results of the calculations.

Figs. 1 and 2 show that, in a pure bismuth film, there is an overlap of energy extrema for all thicknesses, and its value increases with the decrease of film thickness. The strongest overlap growth begins in films with the thickness less than 30 nm. Notably, in the thinnest 15 nm film, the top of the valence band and

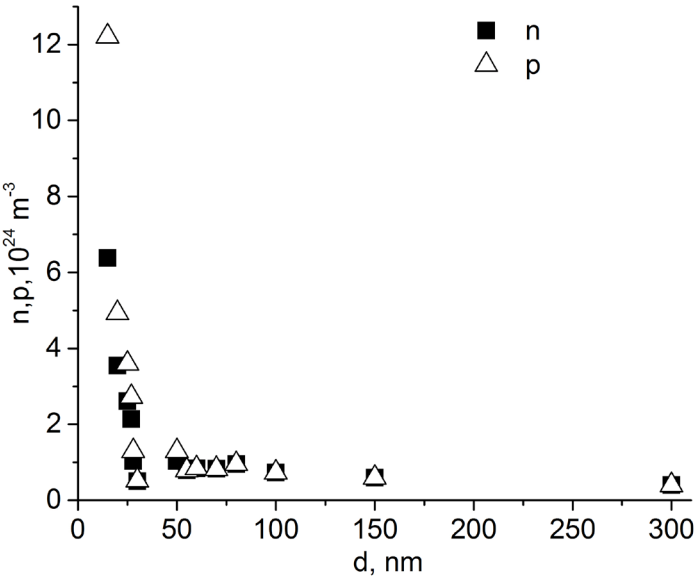

Fig. 1. Dependence of electron and hole concentration on bismuth film thickness at 80 K

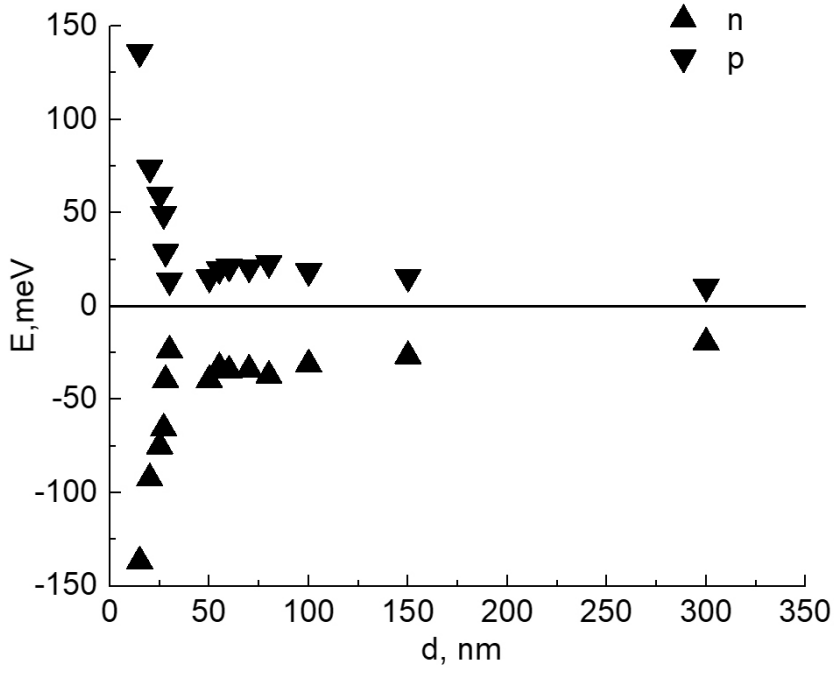

Fig. 2. The energy extrema positions of the valence and the conduction bands relative to the chemical potential level in the bismuth film at 80 K

the bottom of the conduction band are located symmetrically with respect to the chemical potential level.

In bismuth crystals in the massive state, the extrema of the valence and conduction bands with similar energy parameters of charge carriers are the extrema at the L point of the Brüllien zone. Thus, we can assume the actualisation of the hole extremum at point L in ultrathin bismuth films, in contrast to thicker films and bismuth monocrystals, where the valence band extremum at point T of the Brullien zone is actual. It is possible that the same takes place in solid solution films $Bi_{95}Sb_5$ at 77 K, created on various substrates with the temperature expansion coefficient from $1 \times 10^{-6}\,K^{-1}$ to $40 \times 10^{-6}\,K^{-1}$

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and, consequently, in a state of planar stretching or compression (temperature expansion coefficient of bismuth $10{,}5 \times 10^{-6}\,K^{-1}$) (Suslov et al. 2018). In the case of solid solution films $Bi_{95}Sb_5$, the thickness of the samples was 1 μm, while such an effect was not observed in the massive crystal of this material.

For a bismuth film with the thickness 15 nm, the overlap of the valence and conduction bands is almost 300 meV. This corresponds to the increase in the metallic properties of the bismuth surface (111) in relation to its volume. This result was obtained from the first principles calculation of the band structure of the bismuth surface (111) and its study by angular resolution photoelectron spectroscopy (ARPES) (Hofmann 2006). The review (Hofmann 2006) indicates that the surface states structure of the planes (111), (110) and (100) differs significantly from the massive band structure of bismuth. One of the manifestations of these differences can be the observed symmetry of the top of the valence band and the bottom of the conduction band in 15 nm films.

Conclusion

Based on the data on the increase of the charge carrier concentration with the increase of the bismuth film thickness (111) created on a mica substrate, the changes in the energy extrema position of the band structure of thin bismuth films with the thickness from 300 to 15 nm were calculated.

The increase in the overlap of the valence and conduction bands with decreasing film thickness was revealed. In addition, the symmetry of the top of the valence band and the bottom of the conduction band, which occurs in 15 nm films, was found.

Conflict of interest

The author declares that there is no conflict of interest, either existing or potential.

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