The Mechanism of Charge Transfer in Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$
Solid Solution Thin Films

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Abstract—The conductivity, Hall effect, and magnetoresistance of Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ solid solution thin films are studied in a wide temperature range from 2.5 to 300 K and in high magnetic fields of up to 8 T. It is found that the conductivity of Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ solid solution thin films is of the insulator type, whereas the conductivity of the corresponding bulk single crystals is of metallic type. It is inferred that, at high temperatures (100–300 K), the conductivity is controlled mainly by thermally activated charge-carrier transport over extended states in the conduction band, with an activation energy of about 15 meV. At lower temperatures (2.5–70 K), conductivity controlled by charge-carrier hopping between localized states in a narrow energy region close to the Fermi level is dominant. From the magnetoresistance and conductivity data, the localization radius, the density of localized states, and the average charge-carrier hopping length are estimated.

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1. INTRODUCTION

In the last decade, the development of solid state physics, and especially semiconductor physics, has depended to a large extent on the development of thin-film production techniques and studies of the properties of the films. In this respect, films of thermoelectric compounds based on Group-V chalcogenides (Bi$_2$Te$_3$, Bi$_2$Se$_x$, Sb$_2$Te$_3$, etc.) and their solid solutions produced by various techniques are no exception [1–3]. The practical significance of such studies gains strength in the context of the fact that, according to [4], devices based on Bi$_2$Te$_3$ and Bi$_2$Se$_3$ thin films make it possible to attain efficient cooling to 32 K and heat-flow circulation to 700 W cm$^{-2}$. Local cooling or heating proceeds about $2 \times 10^4$ times faster than it occurs in devices made of bulk materials.

It is clear that, in contrast to the properties of bulk crystals, the properties of thin films change with decreasing film thickness because of the noticeable contributions of surface charge-carrier conduction, the adsorption and diffusion of impurities, and surface energy states. A significant effect is produced also by the film–substrate transition layer, irregularities of the film thickness (caused by the preparation technique), and quantum size effects at very small film thicknesses. In addition, it is necessary to take into account the quality of the produced film, its polycrystalline structure, the presence of amorphous inclusions, numerous structural defects, etc.

Here we will produce and study Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ solid solution thin films. This composition was chosen in particular, since the data reported in publications [5, 6] suggest that, in the series of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ solid solutions, the Bi$_2$(Te$_{0.5}$Se$_{0.5}$)$_3$ compound exhibits the highest thermoelectric efficiency.

2. RESULTS AND DISCUSSION

The Bi$_2$(Te$_{0.5}$Se$_{0.5}$)$_3$ compound was synthesized by the alloying of the corresponding proportions of high-purity chemical elements in evacuated quartz cells at temperatures close to 800°C in a rotating furnace, with subsequent cooling in the turned-off furnace. The films were produced by the hot-wall technique, by thermal evaporation of the synthesized substance onto glassy substrates in vacuum at a residual pressure of 10$^{-5}$ mm Hg. The substrate temperature was kept at ~300°C. The film thickness was varied in the range 600–700 nm.

Previously [7], we presented a detailed description of the production procedure, structure, and Raman-active phonons in Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ films. In this paper, we report the data obtained in studying the conductivity, magnetoresistance, and Hall effect in the annealed Bi$_2$(Te$_{0.5}$Se$_{0.5}$)$_3$ film samples. The temperature dependences of the resistivity were studied in a wide temperature range from 2.5 to 300 K and in magnetic fields of up to 8 T. The measurements were conducted by the standard four-probe technique using the selective method at a frequency of 20.5 Hz. Point-shaped contacts were fabricated with silver paste; the ohmic character of the contacts was constantly monitored.

Figure 1a shows the typical temperature dependence of the resistivity of the Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ films in
the temperature range from 2.5 to 300 K. It can be clearly seen that the temperature dependence of the resistivity is of the insulator-type character, i.e., as the temperature is lowered, the resistivity of the film exponentially increases. For comparison, Figure 1b shows the temperature dependence of the resistivity in the layer plane \( \rho_{\text{par}}(T) \) for the bulk Bi\(_2\)(Te\(_{0.9}\)Se\(_{0.1}\))\(_3\) single-crystal samples [8]. It is known that the undoped single crystals, e.g., Bi\(_2\)Te\(_3\) crystals synthesized from stoichiometric melts, even initially contain a large number of intrinsic structural point defects formed by Bi atoms transferred to the sites of Te atoms and vice versa (so-called antisite defects). These defects behave as acceptors. Therefore, Bi\(_2\)Te\(_3\) single crystals always exhibit \( p \)-type conductivity, with a high hole concentration: \( p \approx 10^{18} - 10^{19} \text{ cm}^{-3} \). Such a high defect concentration is responsible for a large number of local states that form a wide impurity band in the band gap, so that this impurity band overlaps the intrinsic band of the pure crystals. Therefore, in studying the conductivity of the Bi\(_2\)Te\(_3\)-type bulk single crystals, one observes behavior of the temperature dependence of the resistivity that is typical of the metallic type: as the temperature is lowered, the resistivity decreases in the entire temperature range and plateaus at low temperatures [9].

As evident from Fig. 1, the resistivity of the films is three or four orders of magnitude higher than that of bulk crystals. To account for the thermally activated conductivity observed in the Bi\(_2\)(Te\(_{0.9}\)Se\(_{0.1}\))\(_3\) films, two variants of interpretation of the above-described data were suggested. One variant is based on the concept of so-called island conductivity observed in almost all, even pure-metal (copper, silver, tin, etc.) films at small film thicknesses (commonly tens of nanometers), at which island nuclei have not yet coalesced. In this case, two mechanisms of charge transport from one island to another, specifically, thermal electron emission and barrier tunneling can be responsible for the thermally activated conductivity.

In the case of thermal electron emission, the temperature dependence of the conductivity can be expressed as (Minn’s formula)

\[
\sigma = \frac{B e T}{k_B} a \exp\left(-\frac{\varphi - \gamma e^2/a}{k_B T}\right). \tag{1}
\]

Here, \( B \) is a constant characteristic of a particular film, \( T \) is temperature, \( e \) is the absolute elementary-charge magnitude, \( k_B \) is the Boltzmann constant, \( a \) is the spacing between islands, and \( \varphi \) is the electron work function for the bulk sample. The term \( \gamma e^2/a \) describes the contribution of the image forces to the conductivity. If the spacing \( a \) is rather small, the above-mentioned contribution is several eV, and the difference \( \varphi - \gamma e^2/a \) can be rather small. In this case, the conductivity can be rather high.

In the case of barrier tunneling, the temperature dependence of the conductivity is described as (Neugebauer–Webb’s relation)

\[
\sigma = A s \frac{2m\varphi}{\hbar^2} a \exp\left(-\frac{4\pi l}{h}\sqrt{2m\varphi}\right) B \exp\left(-\frac{e^2/\varepsilon r}{k_B T}\right). \tag{2}
\]

Here, \( A \) and \( B \) are constants, \( \varphi \) is the potential barrier between the islands (the barrier is approximately equal to the electron work function of the bulk samples with consideration for image forces); \( e \) is the elementary charge; \( m \) is the effective electron mass; \( \varepsilon \) is the permittivity, whose value lies in the range between the permittivity of the substrate and that of free space; and \( r \) is the average linear size of the islands.

Taking into account the large thicknesses of the Bi\(_2\)(Te\(_{0.9}\)Se\(_{0.1}\))\(_3\) films (600–700 nm), we think that, at low temperatures, another charge transport mechanism is more probable. Upon deposition, a highly disordered polycrystalline structure is formed, with various crystalite sizes (as suggested by the X-ray diffraction and atomic force microscopy data) [7]. Since the films are not single crystals, the concentration of antisite defects is not very high. Correspondingly, the wide impurity