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Size effects in the galvanomagnetic and thermoelectric properties of ultrathin bismuth-antimony films

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Abstract. The paper presents the results of a study of the electrical, galvanomagnetic, and thermoelectric properties of Bi and $Bi_{1-x}Sb_x$ (x = 0.03, 0.05, and 0.12) thin films (10–50 nm) on a mica substrate. All samples are characterized by an increase in conductivity with a decrease in film thickness, which can be associated with the presence of topologically protected surface states. It has been found that the band structure of the alloys significantly affects the appearance of the metallic type of conductivity in films with $a \leq 18$ nm thickness. It was found that the resistivity of $Bi_{0.97}Sb_{0.03}$ films ≤ 17 nm thick is almost independent of temperature. Despite the increase in the conductivity of the samples, with a decrease in the thickness, the thermoelectric power factor decreases, which casts doubt on the fact that surface states have a positive effect on the thermoelectric figure of merit of thin $Bi_{1-x}Sb_x$ films. However, the detection of a positive thermoelectric power in $Bi_{0.88}Sb_{0.12}$ samples may be of interest in the development of the p branch of thermoelectric converters.

Keywords: bismuth, bismuth-antimony alloys, galvanomagnetic properties, thermoelectric properties, thin films, thermoelectric power factor

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Размерные эффекты в гальваномагнитных и термоэлектрических свойствах сверхтонких пленок растворов висмут-сурьмы

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Аннотация. В работе представлены результаты исследования электрических, гальваномагнитных и термоэлектрических свойств тонких пленок (10–50 нм) Bi и $Bi_{1-x}Sb_x$ (x = 0,03, 0,05 и 0,12) на слюдяной подложке. Для всех образцов характерно увеличение проводимости при уменьшении толщины пленки, что может быть связано с наличием топологически защищенных поверхностных состояний. Установлено, что зонная структура сплавов существенно влияет на появление металлического типа проводимости в пленках толщиной ≤ 18 нм. Установлено, что удельное сопротивление пленок $Bi_{0,97}Sb_{0,03}$ толщиной ≤ 17 нм практически не зависит от температуры. Несмотря на увеличение проводимости образцов, с уменьшением толщины коэффициент термоэдс уменьшается, что ставит под сомнение положительное влияние поверхностных состояний на термоэлектрическую эффективность тонких пленок $Bi_{1-x}Sb_x$. Однако обнаружение положительной термоэдс в образцах $Bi_{0,88}Sb_{0,12}$ может представлять интерес для разработки p-ветви термоэлектрических преобразователей.

Ключевые слова: висмут, висмут-сурьмяные сплавы, гальваномагнитные свойства, термоэлектрические свойства, тонкие пленки, термоэлектрический фактор мощности

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Introduction

Theoretical and practical interest in the study of bismuth and bismuth-antimony alloys is due to the peculiarities of their physical properties: strong anisotropy of Fermi surfaces, small effective masses, large values of the mean free path and de Broglie wavelength of charge carriers, strong spin-orbit interaction, etc. In this regard, many works are devoted to the study of the transport properties of bismuth and bismuth-antimony crystals and thin films, in particular, their thermoelectric properties [1, 2]. In addition, it is of interest to study classical and quantum size effects on this class of materials [3, 4]. Theoretical works predict that the quantum size effect leads to the transition of bismuth thin films from a semimetallic state to a semiconductor one [5]. However, in ultrathin films of pure bismuth, a transition of the temperature dependence of resistivity to a metallic form is experimentally observed [6, 7], which is associated with the presence of metallic surface states [8]. According to various sources, the thickness of the films at which the transition is observed is different [9, 10]. In [7] we also observed the transition of the temperature dependence of the resistance of the ultrathin films of the $Bi_{0.88}Sb_{0.12}$ to a metallic form. Thus, a comprehensive investigation of the electrical, galvanomagnetic, and thermoelectric properties of bismuth and bismuth-antimony thin films is topical.

Bismuth-antimony alloys are of interest because the properties of a topological insulator in bulk crystals were experimentally confirmed for the first time on this material [11]. It is assumed that $Bi_{1-x}Sb_x$ have a nontrivial topological structure starting from $x > 0.04$, which corresponds to band inversion. In addition, recent ARPES and scanning electron microscopy studies of thin bismuth films have shown manifestations of the Rashba effect in the surface states of pure bismuth [12—14]. The nontrivial nature of the pure bismuth band structure is associated with an increase in the gap at the L point, which can be caused by the quantum size effect or in-plane deformation of the crystal lattice [15].

In this regard, of particular practical interest is the study of the thermoelectric power of thin films of bismuth and bismuth-antimony alloys. The high mobility of charge carriers of surface states can make it possible to increase the electrical conductivity without affecting the thermal conductivity of the material. This would make it possible to achieve an increase in thermoelectric figure of merit, which requires a combination of high electrical conductivity and low thermal conductivity.

Materials and Methods

The samples were produced by thermal evaporation in a vacuum ~ 10^{-5} Torr on a mica substrate. The thickness of the samples was 10–50 nm. The material for producing samples was 99.999% purity bismuth and bismuth-antimony solid solutions with 3, 5, and 12 at.% Sb. Sample preparation parameters: deposition temperature is 393 K; annealing temperature is 473 K, and annealing time is 1 hour. Manganin contact pads were deposited on the samples by thermal evaporation in a vacuum. In addition, to measure the thermoelectric properties, a film thermistor and heater structure was formed on the reverse side of the substrate by a similar method.

The samples surface structure was studied by atomic-force microscopy (AFM). The samples thickness and the crystallites size were measured using the AFM method in combination with the method of selective chemical etching, described in [16]. The etching time was chosen depending on the sample thickness, calculated from the mass of the evaporated substance, and was 5–30 s. The thickness measurement accuracy with this method is about 10%.

As shown in our previous work [17], the transport properties of thin films of bismuth and alloys based on it are significantly affected by mechanical deformations. Therefore, the classical techniques for measuring thermoelectric power, in which the temperature gradient in the sample is created using a rigid mechanical contact of the sample with a copper plate, are not suitable. A significant difference in the coefficients of thermal expansion (CTE) of the gradient plate, heat transfer paste and substrate leads to a distortion of the deformed state of the film-substrate system so the measurement result, especially in the low temperature region, may be ambiguous.

In this regard, to measure the temperature dependences of the Seebeck coefficient, a method was used that excludes the appearance of additional mechanical stresses in the film substrate system, which is described in detail in [18]. To do this, a copper film resistance temperature sensor and a film heater were formed on the reverse side of the substrate relative to the film. Since the mica substrate is fairly thin (5–40 μm), the temperature of the resistance thermometer and the film in the contact zone can be considered the same. Measurements on the setup are carried out at a constant current in a constant magnetic field up to 0.7 T in the temperature range of 77–300 K.

Results and Discussion

AFM images of the samples surface structure indicate that the crystals trigonal axis is perpendicular to the substrate plane. The films are polycrystalline; the average crystallite size is 0.3–1 μm. Both the addition of antimony and a decrease in thickness on average reduces the size of crystallites, however, it always significantly exceeds the thickness of the samples. This is essential for the appearance of a metallic type of conductivity [19].

It should be noted that the conductivity of all investigated ultrathin films is greater in absolute value than the conductivity of thicker films studied earlier [20].

The type of temperature dependences on the resistivity of the samples strongly depends on their thickness. Pure bismuth films are characterized by a sharp change in the form of resistivity dependence at a thickness of ≤ 18 nm (Fig. 1). The resistivity of films with a thickness of ≥ 20 nm increases with decreasing temperature, while the resistivity of the investigated films of smaller thickness decreases with decreasing temperature, i. e, it has the form of the metals. A similar sharp change in the form of the resistivity temperature dependence is observed for $Bi_{0.88}Sb_{0.12}$ samples. In absolute value, the resistivity of $Bi_{0.88}Sb_{0.12}$ samples ≤ 18 nm thick turns out to be lower than the resistivity of pure bismuth films of this thickness, even though bulk crystals of this alloy are semiconductors and don't have band overlap, as in pure bismuth.

Bulk solid solutions with a 3 and 5 at.% Sb characterize the transition from a semimetallic to a semiconductor state, so they are of interest in the context of this study. The resistivity temperature dependences of these two compositions increase with decreasing temperature over the entire thickness range. However, the resistivity of $Bi_{0.97}Sb_{0.03}$ ≤ 17 nm films changes insignificantly, i. e, it practically doesn't depend on temperature. The absolute value of the resistivity of the $Bi_{0.97}Sb_{0.03}$ and $Bi_{0.95}Sb_{0.05}$ samples is higher than that of pure bismuth samples of the corresponding thickness, which is associated with smaller crystallite sizes, and a decrease and disappearance of band overlap at the *L*- and *T*-points.

In Bi and $Bi_{0.97}Sb_{0.03}$ films with a thickness of > 20 nm, the magnetoresistance depends on temperature non-monotonically, while in films with a thickness of 10–18 nm, the magnetoresistance

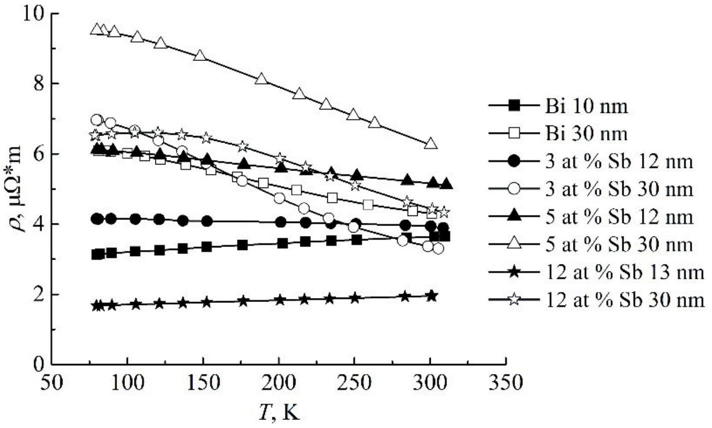

Fig. 1. Temperature dependence of the resistivity of films ~10 and 30 nm thick

is small and weakly depends on temperature. The relative magnetoresistance of the $Bi_{0.95}Sb_{0.05}$ and $Bi_{0.88}Sb_{0.12}$ films is close to zero, and doesn't depend on temperature over the entire investigated thickness range. A small or not observed magnetoresistance indicates a decrease in the mobility of charge carriers with a decrease in the film thickness. The combination of a decrease in resistivity and magnetoresistance qualitatively indicates an increase in the concentration of charge carriers with a decrease in the film thickness.

The Hall coefficient of Bi films is positive, which is also observed in polycrystalline films on a mica substrate ~1 μm thick, the crystallite sizes of which exceed the thickness of the film itself. In such films the limitation of the electron mobility by the thickness manifests itself more significantly than the limitation of the hole mobility by the size of the crystallites [17]. The Hall coefficient of $Bi_{0.97}Sb_{0.03}$ and $Bi_{0.95}Sb_{0.05}$ bulk crystals and thicker films has a negative value (Fig. 2). However, for all studied samples < 40 nm thick, it is positive. Crystals and thicker $Bi_{0.88}Sb_{0.12}$ films are also characterized by a negative value of the Hall coefficient, which is observed in the studied films > 20 nm thick. However, as the thickness decreases below 18 nm, the sign of the Hall coefficient changes from negative to positive. The temperature dependences of the Hall coefficient of Bi, $Bi_{0.97}Sb_{0.03}$, and $Bi_{0.95}Sb_{0.05}$ films exhibit a maximum, which shifts to higher temperatures with decreasing film thickness.

The value of the Hall coefficient strongly depends on the ratio of the electron and hole mobilities. The component of the Hall coefficient tensor in the trigonal plane of Bi and $Bi_{1-x}Sb_x$ crystals is negative and rather small, so it is sensitive to various factors. In bismuth, due to anisotropy, the lowest hole mobility is observed along the trigonal axis, and electrons in the trigonal plane; therefore, when interpreting the measurement results, it is necessary to take into account the different limitations of charge carrier mobilitiy on the film surface and crystallite boundaries [17]. In addition, the change in the ratio of the contributions of electrons and holes

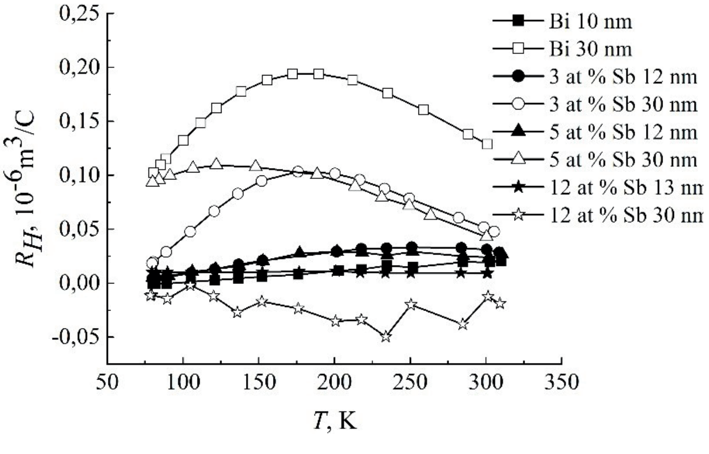

Fig. 2. Temperature dependence of the Hall coefficient of films ~10 and 30 nm thick

to the Hall coefficient can also be due to other factors, including the influence of surface states and deformations.

The Seebeck coefficient of the studied films decreases in absolute value with decreasing temperature. Thicker $Bi_{1-x}Sb_x$ films are characterized by an increase in thermoelectric power with decreasing temperature. In absolute value, the Seebeck coefficient is, on average, less than for samples with a thickness of 0.1–1 μm, i. e., with a decrease in the thickness of the samples, the thermoelectric power also decreases (Fig. 3).

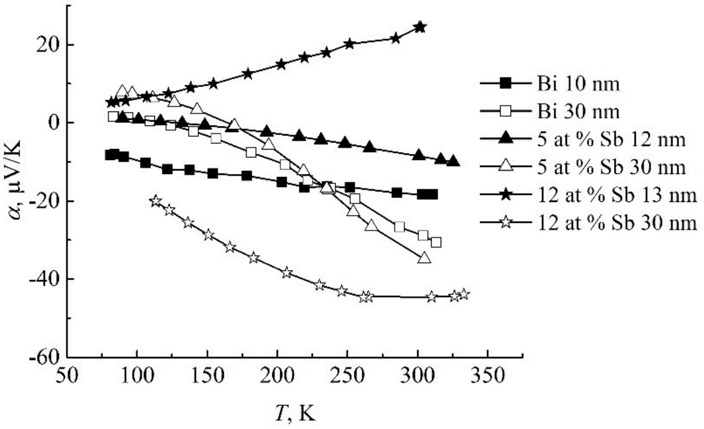

Fig. 3. Temperature dependence of the Seebeck coefficient of films ~ 10 and 30 nm thick

The temperature dependences of the Seebeck coefficient of the $Bi_{0.88}Sb_{0.12}$ films exhibit a sign reversal at thicknesses corresponding to the sign reversal of the Hall coefficient (18 nm). With an increase in the antimony concentration in the bismuth-antimony solid solution, the extremum of heavy holes at the *H*-point becomes actual. Therefore, the change in the sign of the thermopower in $Bi_{0.88}Sb_{0.12}$, in the case of ultrathin films, can be due not only to a significant limitation of the electron mobility but also to the manifestation of the contribution of holes at the *H*-point of the Brillouin zone.

Based on the results of measuring the thermopower and resistivity, the dependences of the power factor ($P = \alpha^2/\rho$) on temperature were calculated. It has been established that the power factor decreases with decreasing film thickness. I. e, an increase in the conductivity of ultrathin films with a decrease in thickness is insufficient to increase the thermoelectric power factor.

Conclusion

It has been found that all samples are characterized by a decrease in resistivity with decreasing thickness, which may be due to the contribution of the conductivity of surface states. A sharp change in the shape of the temperature dependence of the resistivity from a semiconductor type to a metallic one was found for films of pure bismuth and $Bi_{0.88}Sb_{0.12}$ films ≤ 18 nm thick. For $Bi_{0.97}Sb_{0.03}$ and $Bi_{0.95}Sb_{0.05}$ films no such transition was found. Interestingly, the resistivity of $Bi_{0.97}Sb_{0.03} \leq 17$ nm films is practically independent of temperature.

The Seebeck coefficient of all studied samples is lower in absolute value than that of films of 0.1–1 μm thickness. In this case, an increase in conductivity with decreasing sample thickness does not lead to an increase in the power factor. This casts doubt on the assumption that the contribution of surface states leads to an increase in the thermoelectric figure of merit of materials based on ultrathin films of bismuth-antimony. However, the detected positive thermoelectric power in $Bi_{0.88}Sb_{0.12}$ thin films may be of interest for creating a thermoelectric converter, the *p*- and *n*-branches of which will be films of the same composition but different thicknesses.

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