Block and single-crystal films of bismuth-antimony alloy 3−12 at.% with an underlayer of antimony

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Received September 19, 2021
Revised September 24, 2021
Accepted September 24, 2021

The influence of an antimony sublayer (10 nm) on the structure and galvanomagnetic properties of thin films of a bismuth-antimony solid solution (3−12 at.% Sb) up to 1 μm thick has been studied. The films were produced on mica substrates by discrete vacuum evaporation and zone recrystallization. We found that the misorientation of the crystallite plane (111) increases relative to the film plane as well as the crystallite sizes decrease. The antimony underlayer does not change the crystallographic orientation during recrystallization and increases the film adhesion. The change in the galvanomagnetic coefficients when using a sublayer is due to the classical dimensional effect and increasing plane deformation.

Keywords: bismuth, antimony, thin film, antimony underlayer, single-crystal film, atomic force microscopy

DOI: 10.21883/SC.2022.02.53034.20a

1. Introduction

The diversity and variability of the properties of semimetals thin films constantly expands the possibilities of their application. Most of the information about these properties was obtained by studying the effect of external influences — pressure, temperature, magnetic field. The study of the properties of thin films of bismuth−antimony is difficult due to the strong sensitivity of the film properties to many factors. First of all, these are the factors associated with the deposition method, the vacuum level, the substrate (the material and the perfection of its crystal structure, the difference in mating lattices, the substrate temperature, etc.), the composition of the residual gases, and the deposition rate.

A small overlap of energy bands in thin semimetal films causes a strong sensitivity of their properties to mechanical effects and deformations in the film−substrate system [1]. In bismuth−antimony films on mica substrates due to the difference in the thermal expansion of the film and the substrate materials the tensile deformation is observed, which has a significant effect on the galvanomagnetic properties of the film. Weak adhesion of bismuth and bismuth−antimony films on mica sometimes leads to a partial removal of the deformation, and, consequently, to change in the film properties [2].

Incomplete mica wetting by bismuth and its alloys makes it difficult to obtain single-crystal films by zone recrystallization under a coating. At thickness of $\sim$ 300 nm bismuth and bismuth−antimony films roll into drops during recrystallization under the coating, and no conductive film is formed.

The use of a thin transition layer of a substance close in its crystal composition to bismuth−antimony, which has good mutual wetting with the film material, as well as a thermal expansion coefficient closer to same of the substrate, can improve adhesion. Knowledge of the mechanisms of such a sublayer effect on the nature of deformation and galvanomagnetic properties of the film will allow its use as one of the tools for improving the stability of film properties under deformation conditions. For bismuth and bismuth−antimony films, antimony can be chosen as such a underlayer. The paper [3] shown that in the case of bismuth films the underlayer does not penetrate into the bulk of the film during recrystallization and improves the film adhesion to the substrate, slightly changing the galvanomagnetic properties.

The paper includes the studies of the effect of an ultrathin (10 nm) antimony underlayer on the structure and galvanomagnetic properties of thin films of bismuth−antimony with antimony content of 3 to 12 at% and thickness of up to 1 μm.

2. Experimental procedure

Thin films of bismuth−antimony with thickness of 0.3 to 1 μm were produced by discrete thermal deposition in vacuum 10^{-5} Torr on muscovite mica substrates. All films were produced at the substrate temperature of 140°C. Annealing at temperature of 260°C was carried out for 30

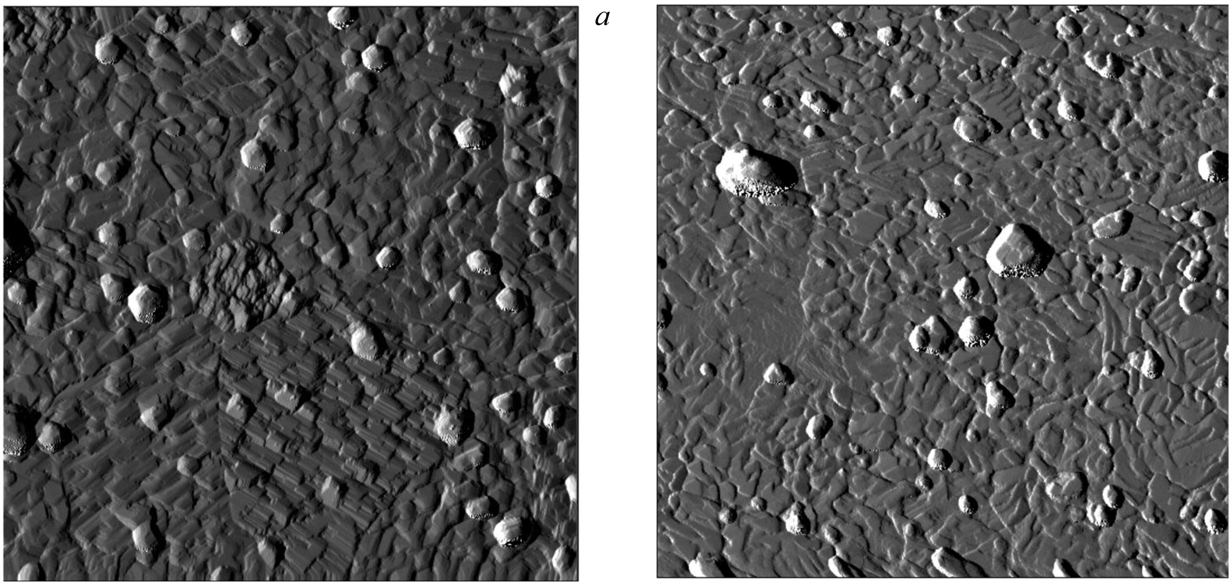

Figure 1. AFM-image of the surface of thin film (*a*) $Bi_{95}Sb_5$ $1\,\mu$m thick on a underlayer of antimony 10 nm, (*b*) $Bi_{92}Sb_8$ $0.5\,\mu$m thick on underlayer of antimony 10 nm. Image size is $10 \times 10\,\mu$m.

min. The antimony underlayer was created by continuous thermal deposition immediately before deposition of the bismuth–antimony film. The substrate temperature during the underlayer deposition was 160°C. Potential and current contacts with the film were produced by continuous thermal evaporation in the course of a separate technological process. Manganin was chosen as the contact material.

Single-crystal films of the same compositions and thicknesses were obtained by zone recrystallization under a coating of potassium bromide [2]. The films for recrystallization and the potassium bromide coating were obtained by thermal deposition at the substrate temperature of 20°C.

The thickness of the obtained films was measured by the optical method using a Linnik interference microscope. The structure of the obtained films was studied by X-ray diffraction analysis, atomic force and optical microscopy using chemical etching. A mixture of nitric and acetic acids was used as an etchant.

The galvanomagnetic properties (resistivity, relative magnetoresistance, Hall coefficient) were measured at direct current and constant magnetic field with the temperature step change from 77 to 300 K. The measurements were carried out in the magnetic field with induction of 0 to 0.65 T.

3. Results and their discussion

An atomic force microscopy (AFM) investigation of the structure of films obtained by thermal deposition showed that they have a block structure with block sizes that by more than an order of magnitude are greater than the thickness of the bismuth–antimony film.

The mica substrate has an orienting effect on the film, so that in films without the underlayer of all investigated thicknesses, crystallites are predominantly of two orientations: the trigonal axis is parallel to the normal to the film, and the binary axes of neighboring crystallites are directed oppositely. Since the unit cell of bismuth and its solid solutions is a rhombohedron, whose trigonal axis on mica is parallel to the normal to the film, the growth shapes reflecting the crystal structure form a triangular texture [4].

As the papers [3,5] show, an ultrathin antimony layer has a nanoblock structure and does not significantly affect the structure of pure bismuth thin films. In the case of bismuth–antimony films, on the antimony underlayer, as it can be seen on the AFM-images of the surface (Fig. 1, *a*), there are areas with growth shapes that are not triangular forms. This means that the antimony underlayer increases the disorientation of crystallites, so that the trigonal axis makes a significant angle with the normal to the film, and the crystallographic orientation of such regions differs from (111). As the thickness decreases, and the concentration of antimony in the solution increases, the relative area of such regions increases (Fig. 1, *b*). Films on the underlayer are also characterized by a greater number of bumps.

The study of the surface of block films after chemical etching using optical microscopy (Fig. 2, *a, b*) showed that the use of the antimony underlayer leads to the decreasing of the crystallites size.

The structure study of the films both without and with the antimony underlayer, and subjected to zone recrystallization showed that the etch pits on the film surface are oriented in the same way, and there are no block bounders. This

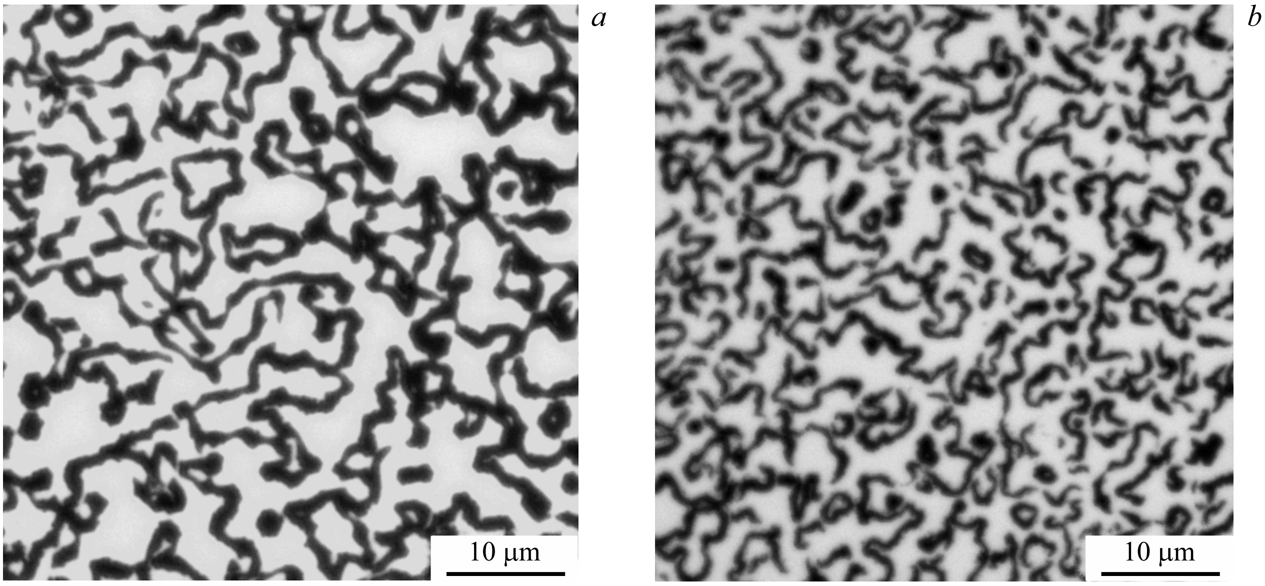

Figure 2. Micrograph of surface of thin film $Bi_{97}Sb_3$ with thickness of $0.5\,\mu$m after chemical etching (*a*) without antimony underlayer, (*b*) on antimony underlayer 10 nm. The image size is $50 \times 50\,\mu$m.

indicates that such films are single crystal. The diffraction patterns of the films obtained by zone recrystallization exhibit well-resolved and sufficiently intense maxima of 5th-order, which also indicates a more perfect structure of such films. Since the deformation is partially removed during recrystallization, the peaks of the single-crystal film without the underlayer are shifted towards small angles in comparison with the peaks of the block film without the underlayer. In this case, the peaks of the recrystallized film on the underlayer and of the block film without the underlayer coincide. The latter may indicate that the antimony underlayer prevents the deformation removal during recrystallization, and the films on the underlayer are in a more stressed state [6].

The antimony underlayer in most cases does not significantly affect the general nature of the temperature dependences of the galvanomagnetic properties of the films. The differences in the galvanomagnetic properties of films with and without the underlayer are due primarily to the the underlayer effect on the films structure and the nature of the mechanical stresses change during the study. Analysis of the results is hampered by the fact that both of these factors can occur simultaneously and differently for films with different antimony concentrations.

As an example, such a multifactorial effect of the underlayer is shown for films with thickness of $0.5\,\mu$m (Fig. 3). The block sizes decreasing, their misorientation increasing, and the number of bumps increasing in films on the underlayer lead to a stronger limitation of charge carrier mobility due to the classical size effect. Such films have higher resistivity and lower relative magnetoresistance. These are films with antimony content of 3 and 5 at%. In films with a higher content of antimony (8 and 12 at%)

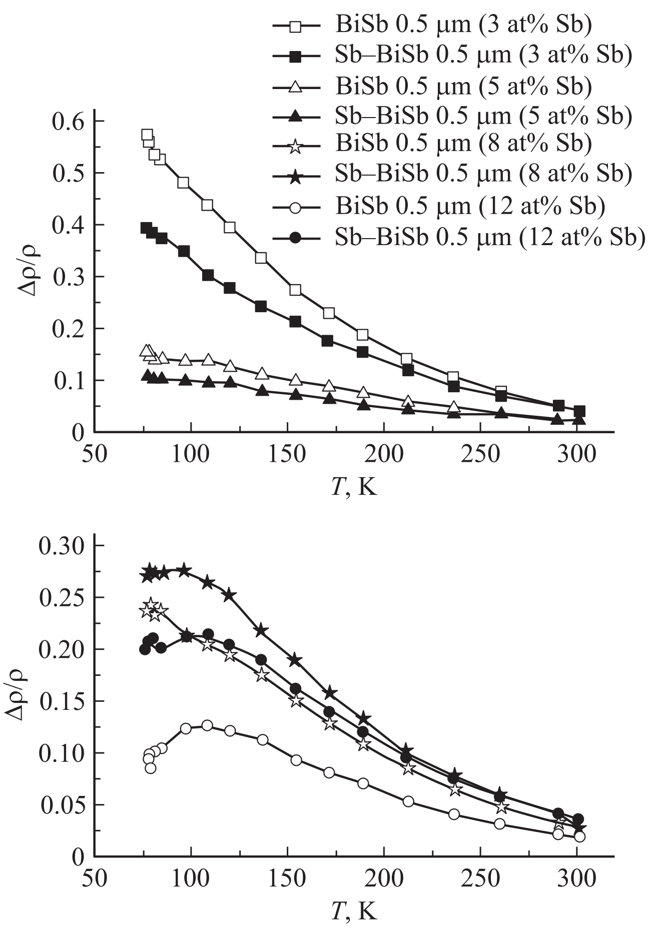

Figure 3. The relative magnetoresistance vs. temperature of bismuth–antimony block films with different antimony concentrations on the antimony underlayer and without it.

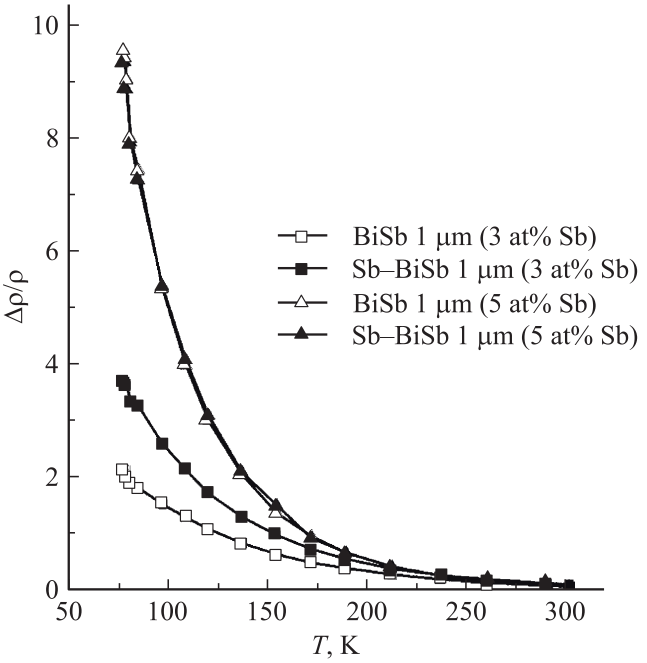

Figure 4. Relative magnetoresistance of vs. temperature of bismuth–antimony single-crystal films with different antimony concentrations on the antimony underlayer and without it.

the use of the underlayer, on the other hand, leads to the relative magnetoresistance increasing and the resistivity decreasing. This may indicate that in block films with high content of antimony on the underlayer during the study the deformation may not be removed as much as in films without the underlayer. The greater in-plane tensile strain in such films means that the overlap of the energy bands is smaller; therefore, the mobility of charge carriers and the relative magnetoresistance are greater than in analogous films without the underlayer.

For single-crystal films with low antimony concentration (3 at%), the use of the underlayer leads to a significant increasing of the relative magnetoresistance over the entire temperature range under consideration (Fig. 4), which may be associated with the increased carriers mobility, caused, in particular, by the deformations increasing in the film-substrate system when using the underlayer [1]. The magnetoresistance of the single-crystal films on the underlayer with higher antimony concentration (5 at%) differs little from the magnetoresistance of films without the underlayer. This may indicate that the underlayer use in films with high content of antimony will no longer lead to such significant increasing of in-plane deformation, and the probability of its removal with temperature decreasing becomes higher [6]. For films with the antimony content of 3 and 5 at%, the use of the underlayer led to the adhesion stabilization, and conductive single-crystal films $0.3\,\mu$m thick were obtained.

4. Conclusion

The use of the antimony underlayer in the preparation of bismuth–antimony single-crystal films by zone recrystallization under the coating showed that in some cases the films on the underlayer are in a more stressed state, which is associated with film adhesion increasing. The ultrathin underlayer of antimony has the nanoblock structure, and during recrystallization the antimony does not penetrate into the bulk of the film and does not significantly affect its crystal structure. The revealed changes in the process of zone recrystallization of films on the underlayer indicate the adhesion stabilization and the possibility of obtaining single-crystal films with thickness of < 300 nm.

Block films of bismuth–antimony obtained by thermal evaporation on the antimony underlayer, along with the predominant crystallographic orientation of (111) plane parallel to the substrate, also have regions with a strong misorientation of crystallites relative to the film plane. In such blocks the trigonal axis makes a significant angle with the normal to the film. The blocks in the films on the underlayer are smaller, there are more bumps on their surface. The change in the galvanomagnetic coefficients in the films on the underlayer is due to two main factors. Firstly, the classic size effect, which is manifested to a greater extent in films with the antimony concentration of 3 and 5 at%. Secondly, increasing of the in-plane tensile strain, which is more pronounced in films with high content of antimony (8 12 at%).

Funding

The study was performed under the national task with financial support of Ministry of Education of Russia (project FSZN-2020-0026). Part of the experimental studies was carried out on the equipment of the Shared-access Center of Scientific Equipment „Composition, structure and properties of structural and functional materials“ Research Center „Kurchatov Institute“— Central Research Institute of Structural Materials „Prometey“ with the financial support of the Ministry of Science and Higher Education — Agreement No. 13.TsKP.21.0014 (075-11-2021-068). Unique identification number — RF — 2296.61321Kh0014.

Conflict of interest

The authors declare that they have no conflict of interest.

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