Nanoscale films of bismuth and antimony: production technologies and properties

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Abstract. We studied the line of bismuth and antimony thin films obtained by thermal evaporation with or without additional annealing or zone recrystallization under a coating. The dependence of film structure on the production technology and substrate type has been shown. The dependence of galvanomagnetic properties of thin films on the structure has been investigated.

1. Introduction

Currently, one of the most important areas in physics is the study of physical phenomena of nanoscale objects, one of which is a film. The variety of physical properties of thin films is most often explained by the manifestation of size effects associated with film thickness and crystallite size. The structure of the films strongly depends on the method of production and the type of substrate. The articles [1-3] describe the variety of galvanomagnetic properties associated with the diversity of the structure and substrates on which thin films are obtained.

The films based on bismuth and antimony are of great interest for research. In these films, with the thickness of several tens of nanometers, one can observe quantum size effects. This is due to the fact that at a temperature of 4.2 K the de Broglie wavelength of charge carriers in bismuth is close to 40 nm. In films with a thickness of more than 100 nm a classic size effect is observed [1].

2. Technologies and methods for producing thin films of bismuth

Using various methods, it is possible to change the structure of thin films from monocrystalline to fine-grained. The most optimal technology for producing thin films of bismuth and antimony is thermal evaporation in vacuum.

For our study, films were obtained continuously and discretely by the method of thermal evaporation in a working vacuum of 10⁻⁵ Torr, the modes for producing block films are shown in Table 1. For bismuth films with an antimony sublayer, an antimony sublayer was first formed on the substrate with the temperature of 150 °C, and then cooled in accordance with the regimes shown in Table 1.
For zone recrystallization under a coating, it is necessary to apply a KBr protective coating on the resulting film in vacuum. Then, the resulting billet is placed in the unit for zone recrystallization, where the film is grown as a single crystal.

Mica and polyimide were used as the substrates. Mica has a crystalline structure and has an orienting effect on the film structure during the growth. Polyimide does not have such an effect. Polyimide and mica have different temperature coefficients of linear expansion \( \alpha (\alpha_{\text{mica}} < \alpha_{\text{Bi}} < \alpha_{\text{polyimide}}) \). Such a difference in \( \alpha \) of the substrate and film materials can lead to various deformations (stretching and compression).

### Table 1. Modes of obtaining thin films of bismuth.

| Film        | Substrate temperature, °C | Annealing temperature, °C | Zone melting | Annealing time |
|-------------|----------------------------|----------------------------|--------------|----------------|
| Fine-Grained| 20                         | -                          | -            | -              |
| Annealed    | 120                        | 250                        | -            | 30 or 60 min   |
| Monocrystalline | 20                         | -                          | +            | -              |

3. Experimental results

3.1. The structure of bismuth films

Using X-ray analysis, it was shown that for films subjected to annealing [4] or zone recrystallization, the crystallites are oriented in the \( C_3 \) axis perpendicular to the substrate plane.

The surface of thin bismuth films was subjected to chemical etching in order to reveal the boundaries of crystallites and other structural defects. The atomic force microscopy (AFM) was used to scan the surface of bismuth thin films. It was found that:

- for fine-grained structure - the size of the crystallites does not exceed 0.5 microns, and there is no difference in structure depending on the substrate type. All crystallites are hexahedral or octahedral ‘figure 1’.

![Figure 1](image1.png)

**Figure 1.** AFM - image of the film surface after chemical etching.

- for annealed films - the size of the crystallites depends on the deposition by the discrete or continuous method, the annealing time and the type of the substrate.

In mica-based films the crystallite size exceeds several tens of micrometers. Crystallites have intertwined shapes without specific geometrical form, and the borders of the crystallite occurs approximately every 3-6 microns in any selected direction ‘figure 2’. There are more boundaries in the films sputtered by the discrete method and annealed for 30 minutes, and less in the films obtained by continuous spraying method and annealed for 60 minutes.
In polyimide-based films the crystallite size does not exceed five micrometers. The etch dislocation pits has triangular shape, indicating that the C₃ crystallographic axis is perpendicular to the film plane 'figure 3'. There is one film having crystallite sizes with a length of more than 10 microns 'figure 4'. This bismuth film was obtained by continuous evaporation on a polyimide with further annealing for 60 minutes.

After chemical etching of recrystallized films the boundaries of the crystallites do not appear on the entire surface of the film. The etch dislocation pits have triangular shape, and all the etch pits have the same orientation on the surface within entire film. This study confirms that the obtained film is monocrystalline, the crystallographic axis C₃ is directed perpendicular to the substrate plane.
3.2. Galvanomagnetic properties

The study of galvanomagnetic properties showed that the properties of nanoscale films strongly depend on the size and orientation of the crystallites and on the type of substrate. The energy spectra of massive crystals based on bismuth and antimony are very sensitive to the deformations [5]. With the temperature change due to different α values of the film and the substrate, a similar deformation occurs uniaxial along C₃ [6]. This leads to a change in the band structure of the films and the concentration of charge carriers. The change in the concentration of charge carriers affects the nature of resistivity, magnetoresistance, and the Hall coefficient temperature dependences ‘figures 5-8’.

![Figure 5](image5.png)

**Figure 5.** Temperature dependence of resistivity: a) films on mica, b) films on polyimide.

![Figure 6](image6.png)

**Figure 6.** Temperature dependence of relative magnetoresistance a) the films on mica substrate, b) the films on polyimide substrate.

With the decrease of temperature, mica substrate stretches the film and the overlap of the energy bands decreases. Therefore, the concentration of free charge carriers in the film at low temperatures decreases, and the increase in the specific resistance is observed ‘figure 5, a’. The increase of charge mobility carriers leads to the increase in the magnetoresistance ‘figure 6, a’.

The reverse picture is observed in the samples with polyimide substrate: polyimide compresses the film, that leads to the increase in the overlap of the energy bands and to the charge carrier concentration. That leads to the lower values of resistivity compared to the films on mica ‘figure 5, b’. In addition, the mobility of charge carriers in the films on the polyimide is lower than in the films on mica, which shows lower values of relative magnetoresistance on polyimide ‘figure 6, b’.
Figure 7. Temperature dependence of the Hall coefficient: a) the films on mica substrate, b) the films on polyimide substrate.

Figure 8. Temperature dependences of a) resistivity, b) relative magnetoresistance and c) the Hall coefficient. Thin films of bismuth on mica.
The graphs show that the magnetoresistance at the lower temperatures in fused films substantially higher than in the deposited bismuth films of the same thickness ‘figure 8, b’. This result indicates a greater value of carrier mobility in fused bismuth films in comparison with the films that have not been undergone zone recrystallization, which is a consequence of higher structure perfection of fused films.

Monocrystalline films have positive Hall coefficient at all measured temperatures, and at the lowered temperature the values of Hall coefficient increases ‘figure 8, c’. This indicates a higher hole mobility than electron mobility. In bismuth block films, the Hall coefficient at low temperatures may in some cases take the negative values, while the Hall coefficient tends to positive values with the increasing crystallite size ‘figure 7 and 8, c’. This indicates that the negative value of the Hall coefficient in films obtained by thermal evaporation is due to their block structure.

4. Conclusions
The structure of bismuth films produced on mica substrate strongly depends on the deposition method (discrete or continuous). Also, the annealing time strongly affects the crystallite size. For films on a polyimide substrate, such a strong dependence of the crystal structure on the annealing time is not observed. Films without annealing have a fine-grained structure. The effect of the antimony sublayer on the structure and galvanomagnetic properties is insignificant both for annealed and not annealed films. The structure of the film and the substrate on which the film is located, strongly influence the properties of thin films of bismuth and antimony.

Monocrystalline films have the highest magnetoresistance. Positive Hall coefficient is observed over the entire temperature range examined in the study. The usage of ultrathin layer of antimony with a thickness of 10 nm allows to obtain monocrystalline bismuth films with the thickness of 200 nm.

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