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Optimization of the Conditions for Vacuum Thermal Deposition of Bismuth Films with Control of Their Imperfection by Atomic Force Microscopy

V. M. Grabov*, E. V. Demidov, and V. A. Komarov

Herzen Russian State Pedagogical University, nab. Reki Moĭki 48, St. Petersburg, 191186 Russia

** e-mail: vmgrabov@yandex.ru*

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Abstract—The structure and defects of bismuth films prepared through vacuum thermal deposition on mica substrates under different conditions (deposition rates, substrate temperatures, temperatures and times of annealing) have been investigated using atomic force microscopy. The conditions are determined under which recrystallization occurs with increasing crystallite size during annealing, which provides a decrease in the degree of imperfection of the films and an increase in the mobility of charge carriers.

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1. INTRODUCTION

Physical phenomena in crystalline films are largely determined by the degree of perfection of the structure, namely, the sizes of the blocks, their crystallographic orientation, and the type and concentration of defects. For bismuth films, the methods of chemical etching and decoration using natural oxidation with the subsequent investigation on an atomic force microscope (AFM) have been developed [1–3]. These methods allow one to reveal the boundaries of crystallites and to determine the sizes and mutual orientation of the blocks, as well as the concentration of other outcropping defects.

In the present work, to improve the structure of the bismuth films fabricated by thermal deposition under vacuum on mica substrates, which provides the orienting effect on the crystallizing film [4, 5], we optimized the deposition rate, substrate temperature, and temperature and duration of annealing with controlling the structure by AFM methods.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Bismuth films were prepared by continuous thermal evaporation at a residual pressure of about 3×10^{-3} Pa. As the starting material, we used a single crystal grown from bismuth Bi-000 by zone recrystallization [6]. The range of varying the substrate temperature T_{sub} was 50–230°C, that of the deposition rate V was 0.5–20.0 nm/s, and that of the annealing temperature T_{ann} was 110–270°C. If another is not stipulated in the text, the films were obtained at a deposition rate of approximately 5 nm/s and annealed at 240°C for 30 min. As the substrate, mica (muscovite) was used. The structure of the films was studied in air on a Solver atomic force microscope (NT-MDT) operating in a semicontact mode. We used cantilevers with a resonant frequency of about 150 kHz, a tip radius of ≤10 nm, and a tip cone angle of ≤22°.

The mutual orientation of crystallites was determined by the orientation of the growth patterns revealed by the AFM method [1, 3]. Intercrystallite boundaries were revealed by decoration using natural oxidation with the subsequent investigation on the atomic force microscope [2, 3]. The crystallite sizes D were determined as follows. On a scan no less than 30×30 μm in size, the number of boundaries N_i intersecting the segment of length L_i equal to the scan length was determined. After this, the quantity $D_i = \dfrac{L_i}{N_i}$ was determined. The value of D_i was determined for 20 segments in the X direction and 20 segments in the Y direction; the segments were selected through equal distance. The crystallite size D was determined as the arithmetic mean of D_i. The relative error in determining D for all scans was about 20%.

The magnetoresistance was determined in the temperature range 77–300 K in a weak magnetic field ($B = 0.1$ T) with the vector of magnetic induction oriented perpendicular to the substrate plane.

3. EXPERIMENTAL RESULTS AND DISCUSSION

All investigated bismuth films on the mica substrates are characterized by the texture, in which the threefold axis C_3 is directed perpendicular to the substrate, while crystallites differ by orientation of the axes C_1 and C_2 in the plane parallel to the substrate.

Crystallite sizes are mainly determined by technological parameters of their obtaining, namely, substrate temperature, evaporation rate, and annealing temperature [3, 4]. Therefore, in this investigation, we studied the effect of the substrate temperature, deposition rate, and annealing parameters on the size and mutual crystallographic orientation of crystallites in the bismuth film.

As evident from Fig. 1, at low deposition rates, the crystallite size remains almost invariable. An increase in the deposition rate approximately to 20 nm/s leads to an insignificant decrease in the crystallite size. No effect of the deposition rate in the studied rate range on the mutual orientation of crystallites is revealed.

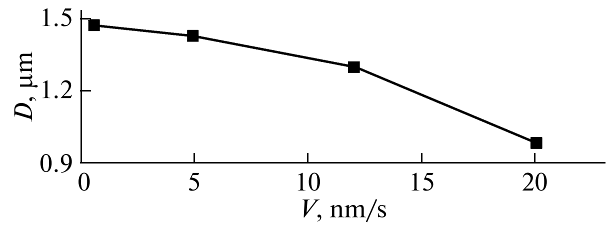

Fig. 1. Influence of the deposition rate on the average size of the crystallites. The film thickness is 300 nm. $T_{sub} = 110°C$. The films are unannealed.

Figure 2 represents the results of investigation of the effect of the substrate temperature and annealing process on the crystallite size. For unannealed films, the average crystallite size increases monotonically as the substrate temperature increases. It is evident from Fig. 2 that annealing leads to an increase in the crystallite size for the films obtained at the substrate temperature up to 140°C by several factors, while for the films obtained at the substrate temperature higher than 150°C, annealing almost does not lead to an increase in the crystallite size. Annealing duration longer than 30 min exerts no substantial effect on the crystallite size. The largest crystallite size achieved as a result of annealing is observed for the films obtained at the substrate temperature in the range of 80–140°C.

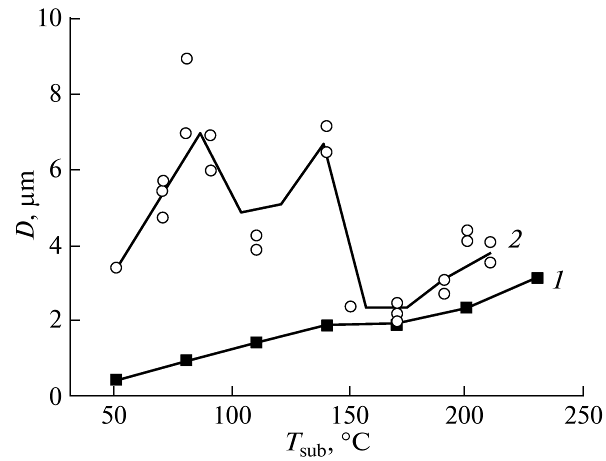

Fig. 2. Influence of the temperature of the substrate and annealing on the average size of the crystallites (*1*) before and (*2*) after annealing. The film thickness is 300 nm.

Figure 3 represents the temperature dependence of the magnetoresistance in a weak magnetic field for the bismuth films deposited on the mica substrates at 140 and 170°C and subjected to annealing. Higher values of magnetoresistance for the films obtained at the substrate temperature of 140°C confirm the conclusions on the larger crystallite sizes in these films.

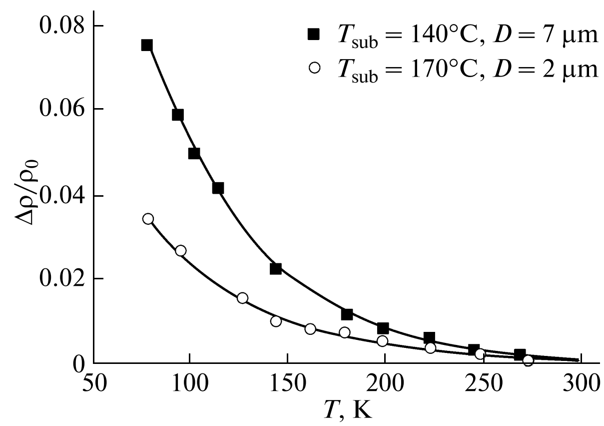

Fig. 3. Influence of the crystallite size in films 300 nm thick on the magnetoresistance.

Investigations by the AFM methods [2, 3] showed that in the films obtained at the substrate temperature from 50 to 140°C, crystallites have only two crystallographic orientations, in which the C_3 axis is perpendicular to the substrate plane, while the directions of axes C_1 and C_2 of neighboring crystallites are opposite (antiparallel) as shown in Fig. 4. As the substrate temperature increases above 140°C, orientation of the C_3 axis perpendicular to the substrate is retained; however, orientation of axes C_1 and C_2 of crystallites in the substrate plane becomes arbitrary. Because of this, as evident from Fig. 2, annealing of the films differently affects their structure.

The existence of structural defects outcropping in the form of hillocks on the bismuth films was previously established [1]. It follows from Fig. 3 that in the

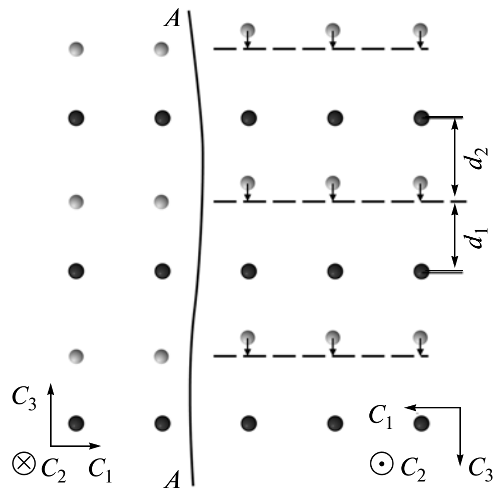

Fig. 4. Double layers of the bismuth crystal in blocks of two orientations with the opposite direction of the crystallographic axes. The *A–A* line is the boundary between the blocks. Short arrows indicate the atomic displacement during annealing of the film, $d_1 = 0.160$ nm is the distance between the atomic planes inside the double layer, and $d_2 = 0.236$ nm is the distance between the nearest atomic planes of the neighboring double layers.

bismuth films on the mica substrates, the concentration of hillocks and the surface area of the film occupied by them substantially decrease as the substrate temperature increases.

Therefore, to obtain the bismuth films on the mica substrate having large-block structure with a low content of hillocks, the optimal substrate temperature is 140°C with the subsequent annealing.

4. MODEL OF ANNEALING OF BISMUTH FILMS ON MICA SUBSTRATES THAT LEADS TO AN INCREASE IN THE CRYSTALLITE SIZE

It follows from the presented experimental results that annealing at 240°C for 30 min leads to substantial increase in the size of blocks of the bismuth films obtained at the substrate temperatures in the range of 80–140°C, at which correlation in the mutual orientation of crystallographic axes of neighboring crystallites, which consists in that the crystallographic axes C_1, C_2, and C_3 are antiparallel, takes place (Fig. 4). In the case of the absence of such correlation with an arbitrary mutual orientation of the C_1 and C_2 axes of the crystallites, which is observed in the films at a substrate temperature above 140°C, the annealing under the conditions used does not lead to a noticeable variation in the crystallite size. Based on the aforesaid, we can conclude that in the presence of correlation in the orientation of crystallographic axes of neighboring crystallites, the recrystallization during annealing proceeds at lower values of the energy and time characteristics.

The lattice of the bismuth-type crystal can be represented as two face-centered sublattices elongated along one of body diagonals and shifted with respect to each other in the direction of this diagonal for a distance smaller than a quarter of the body diagonal of one of sublattices [6]. Because of this, the crystal has the structure in a form of double layers perpendicular to the C_3 axis (Fig. 4) with stronger bonds inside the layer compared with the bonds between the atoms in the neighboring layers. Each atom of the lattice has three nearest and three more remote neighboring atoms, while the angles of valence bonds differ from 90° [6]. Because of this, in the unit cell of Bi in the form of rhombohedron with two atoms per cell, the atom inside the cell is localized at a distance smaller than a half of the rhombohedron diagonal [6]. During the deposition of the bismuth film on mica at a substrate temperature lower than 140°C, the film consists of two types of crystallites differing by the opposite orientations of axes C_1, C_2, and C_3. The position of the atom inside the rhombohedron differs by that at one orientation, it is at the distance of 0.038 nm below the rhombohedron center, while at the opposite orientation, it is at the distance of 0.038 nm above the rhombohedron center. Upon the passage through the boundary of such crystallites, atomic planes with interlayer distances transform into the double layers and, vice versa, double layers transform into the planes with interlayer distances, as shown in Fig. 4. This corresponds to the shift of atomic rows even in Fig. 4 with respect to their positions in the single-crystal structure by approximately 0.076 nm. During annealing, recrystallization takes place; during it, both crystallites depicted in Fig. 4 acquire the same structure, which leads to the disappearance of the boundaries and to an increase in the crystallite size.

With this annealing mechanism, the atomic shift proceeds over small parts of the interatomic distance. Because of this, it is characterized by low activation energy and proceeds for a relatively short time interval since no diffusion process is required for its performance.

An abrupt decrease in the annealing efficiency for the films with the starting structure containing randomly oriented crystallites is caused by impossibility of recrystallization by the mechanism described above. For a more detailed investigation of the recrystallization mechanism during annealing of the bismuth films, we investigated the effect of the annealing temperature in the range of 110–270°C on the average crystallite size. To increase the reliability of the results, we used the films obtained at the substrate temperature close to the middle of the range of 70–140°C as the starting films. In this range, annealing exerts the strongest effect on the crystallite size (Fig. 2).

If an increase in the size of a crystallite proceeds due to the motion of its boundary, the process can be described by the equation [7, 8]

$$\frac{dD}{dt} = \frac{k}{D}, \tag{1}$$

where k is the coefficient that depends on the temperature T_{ann} as follows [8]:

$$k = k_0 \exp\left(\frac{-Q}{RT_{ann}}\right). \tag{2}$$

Here, k_0 is independent of T_{ann}, Q is the activation energy of the process, R is the universal gas constant, and T_{ann} is the absolute annealing temperature.

The solution of Eq. (1) allowing for expression (2) for a specified time interval of annealing Δt gives the dependence of the crystallite size on the annealing temperature T_{ann}:

$$D(T) = \sqrt{D_0^2 + A\exp\left(\frac{-Q}{RT_{ann}}\right)}, \tag{3}$$

where D_0 is the average size of the film crystallite before annealing, and A is the coefficient depending on the time interval of annealing Δt, which is constant in the case of fixed Δt.

The obtained equation can be used for the experimental determination of the activation energy Q of the annealing process. Figure 5 represents the dependence of the crystallite size on the annealing temperature. The annealing time in all experiments was 30 min. It is evident from Fig. 5 that as the annealing temperature increases, the crystallite size exponentially increases until the melting point of the film is reached. With the use of expression (3), the activation energy of annealing $Q = 109 \pm 27$ kJ/mol is determined. The films obtained by annealing have the structure close to the single-crystal one, although we failed to fabricate the monoblock single-crystal films apparently because of the presence of dislocations and other defects preventing the described recrystallization mechanism.

In the case of annealing of the bismuth films with a random orientation of the axes C_1 and C_2 of neighboring crystallites, an increase in the crystallite size requires recrystallization with the change in direction of axes C_1 and C_2 and reconstruction of strongest bonds in the bismuth crystal, the energy of which can be evaluated starting from the data on the heat of vaporization. The heat of vaporization of bismuth is 180 kJ/mol [9]. A noticeably smaller value of the activation energy of annealing determined in this work confirms the above-presented conclusions on its mechanism.

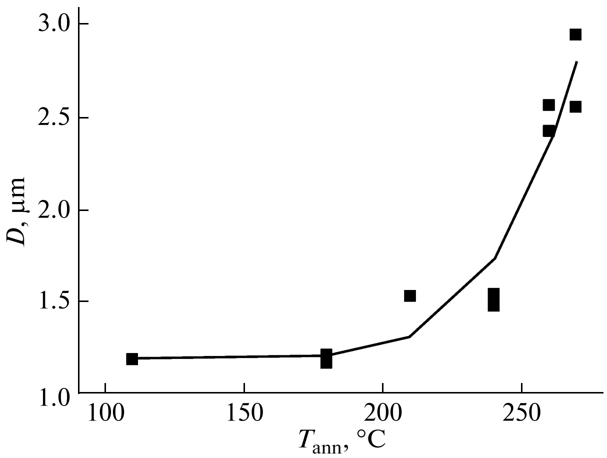

Fig. 5. Dependence of the average crystallite size on the annealing temperature. The initial films 100 nm thick were prepared at a substrate temperature of 110°C. The annealing time for all films was 30 min.

5. CONCLUSIONS

To obtain the bismuth films by vacuum deposition on the mica substrate with a large-block structure and orientation of the C_3 axis perpendicular to the substrate, antiparallel orientation of crystallographic axes of neighboring blocks, and a small content of hillocks, the substrate temperature of 140°C is optimal.

During annealing of thus obtained bismuth films in vacuum at a temperature no lower that 220°C, recrystallization with an increase in the size of crystallites of one of opposite orientations takes place due to a decrease in the number and size of crystallites of the opposite orientation. This provides a decrease in the imperfection of the structure and an increase in the mobility of charge carriers.

The studied process of recrystallization of bismuth films during their annealing is characterized by a small shift of atoms and, because of this, by low activation energy and short duration.

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