# ATOMIC-FORCE MICROSCOPY OF THE SURFACE OF CRYSTALS AND BISMUTH FILMS

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- *Development of scanning probe microscopy methods is considerably expand possibilities of structure investigation of crystal, films, mesostructure and nanostructure surfaces, modification of surface structures. In this work the scanning probe microscope of Russian company NT-MDT has been developed for structure investigation of single crystals and bismuth and bismuth antimony alloys surfaces. New methods for surface structure investigations combining preliminary chemical and electrochemical treatment with subsequent atomic-force microscopy have been developed. Method of defect and grains boundary decoration by natural oxidation during surface exposure in air for a specified time is recognized as the most simple and effective method. Obtaining of detailed information on films structure with the use of the developed methods provides the possibility for correction of film preparation condition by thermal evaporation in vacuum and obtaining of films with structure near to metallic one. It is also developed a new method for electrochemical modification of surface during the prob scanning of crystals and films that is of interest for nanostructure modification.*

## 1. Introduction

The development of scanning probe microscopy methods significantly extended the possibilities of investigating the surface structure of crystals, films, mesostructures and nanostructures, modification of surface structure [1, 2]. Different investigation methods of structure, defects, surface modification of bismuth-based films and single crystals using Solver scanning probe microscope by Russian company NT-MDT are developed and approved. The obtained results provide optimization of films production modes by the method of thermal sputtering in vacuum with the structure close to single-crystal one.

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## 2. Experimental

The preparation of bismuth-based single crystals was performed by zone recrystallization method [3]. 99.999% purity bismuth was used for films and single crystals. Bismuth films were obtained by the method of continuous thermal evaporation in vacuum about $3\times10^{-3}$ Pa. Deposition rate was about 5 nm/s. The annealing of films was performed at 240°C for 30 min. Mica was used as a film substrate. The resulting films were maintained under room atmosphere conditions for up to 80 days. Investigation of film structure was conducted in air using atomic- force microscope Solver by NT-MDT in semi-contact mode. Cantilevers with resonance frequency of about 150 kHz, point curvature radius of ≤ 10 nm and the angle with its apex of ≤ 22° were used.

## 3. Experimental results and discussion

### 3.1. Study of the defects emerging on the surface of bismuth-based single crystals

The image of crystalline structure of cleavage plane (111) of bismuth single crystal is obtained in the work by the method of tunneling microscopy (Fig. 1*a*). The images of twin layer (Fig. 1*b*) and screw dislocation (Fig.1*c*) are obtained in the work by the method of atomic-force microscopy (AM).

The obtained results indicate the possibility of using probe microscopy for determining defect density of bismuth single crystals.

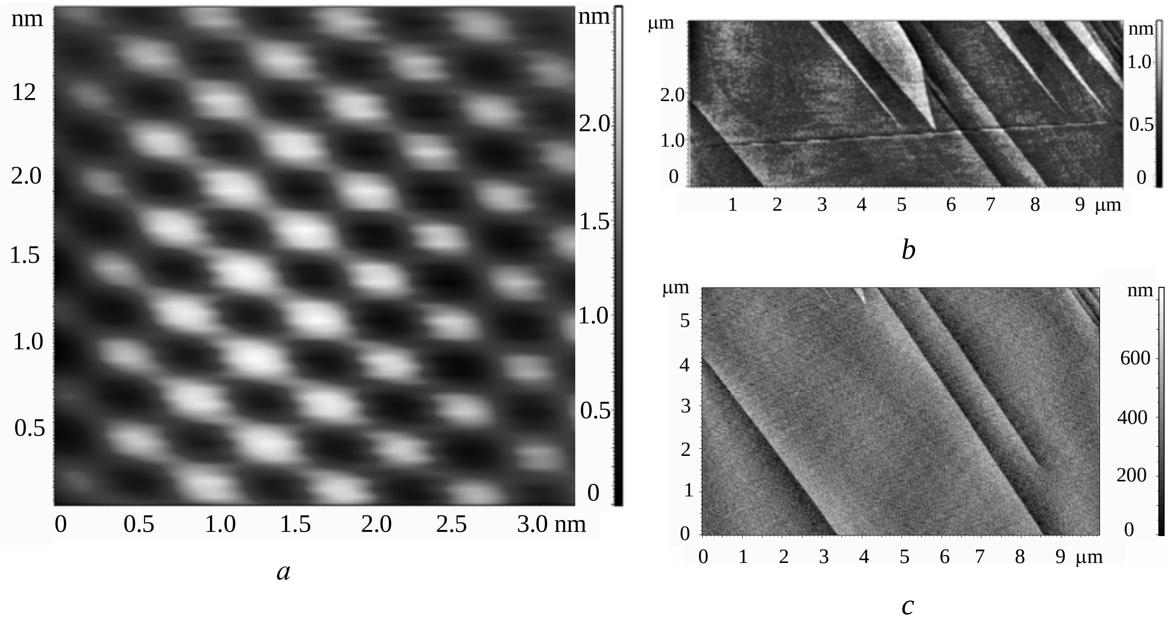


*Fig. 1. Structure of  bismuth crystal surface obtained by probe microscopy methods.*

**3.2. Study of structure and defects of bismuth-based films**

Crystallographic orientation and structure defects have an essential effect on the properties of bismuth films. Crystallographic orientation and dimensions of crystals are important parameters of film structure. During bismuth film preparation by thermal sputtering method in vacuum on mica substrates the films usually have the following structure: the film consists of crystallites with $C_3$ axis perpendicular to the substrate. To determine the orientation of $C_2$ axes of bismuth film crystallites in substrate surface and to determine the dimensions of crystallites, the methods are developed with the results of their application given below.

**3.2.1. Determination of crystallite orientation of bismuth films**

The pattern of bismuth film surface obtained by AM method of as-prepared film on mica at substrate temperature higher than 50°C, is a totality of triangular-shaped growth figures covering the entire film surface and hillocks located separately [4]. The growth figures reflect the crystallographic orientation of film region where they are located [4]. Thus, it is possible to use them for determining crystallite orientation, similarly to the way the dislocation etch pits are used [5].

To determine the arrangement of axes relative to the growth figure, a study of bismuth film in which a chip of *Bi* single crystal served as a substrate was carried out. It is known that during this film sputtering epitaxial growth occurs [6].

From Fig. 2 it is evident that crystallographic orientation of the film is similar across the entire area. Furthermore, the protrusion step of one of the planes {111} is visible on the surface. The orientation of $C_2$ axes in single crystal by the steps of planes {111} protrusion to  plane (111), perpendicular to the axis $C_3$ of bismuth single crystal is determined, following which the orientation of growth figures in the film and etch pits in the single crystal was determined by AM method. As a result of these experimental data comparison, mutual orientation of growth figures and etch pits was established: $C_3$ axis is oriented perpendicularly to the plane of the triangular growth figure, $C_2$ axes are directed parallel to the sides of growth figures and etch pits, $C_1$ axes are directed perpendicularly to $C_3$ and $C_2$ (Fig. 2).

For clear separation of crystallite boundaries, two methods of surface treatment are proposed that make it possible to separate precisely the boundary of crystallite and to determine its size by means of AM.

### 3.2.2. Crystallite boundaries separation. Etching

Preliminary chemical treatment of film surface by etching agent, which is 5÷10% aqueous solution of acid mixture: nitric – 7 parts, and acetic – 6 parts, is the first method of separation of intercrystallite boundaries by the AM method. The time of etching lasted from 2 to 20 seconds. Etching reveals the pattern caused by different structural defects, including those caused by boundaries of blocks, which becomes clearly visible on AM images. During optimal selection of solution concentration and the time of etching on the film it is possible to obtain etch pit dislocations, which make it possible to determine mutual orientation of crystallites. In [7] it is established that with one and the same crystallographic orientation of a film, the etch pits and growth figures are arranged with triangle apexes to the opposite sides. The selection of concentration of etching agent and time of etching is the most complicated stage of this method. These parameters depend, in particular, on the film storage time under the atmospheric conditions, during which film surface is covered with a thin layer of bismuth oxide.

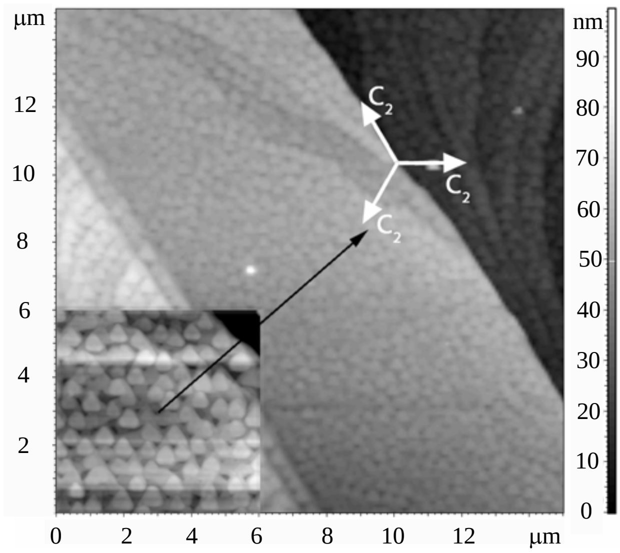


*Fig. 2. Bi film, film thickness is 500 nm. Substrate material: chip of bismuth single crystal across the plane [111]. Substrate temperature is 150 °C. Insert - film scan portion increased by a factor of 1.5. Scan size: 15×15 μm.*

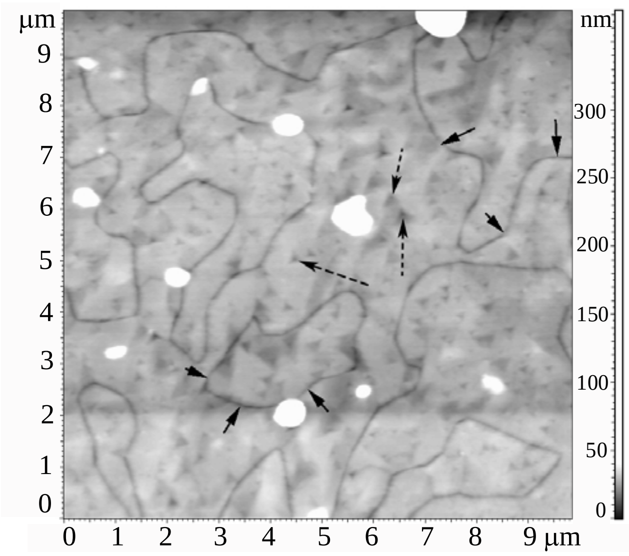


*Fig. 3. Bi film, film thickness is 300 nm. Substrate material: mica. Substrate temperature is 150 °C. Size of a scan is 10×10 μm. Film underwent etching. Firm arrows show etched boundaries of crystallites, broken arrows show etch pits.*

### 3.2.3. Separation of crystallite boundaries. Decoration

Another way for separation of intercrystalline boundaries by AM method is a preliminary decoration [5] of crystallite boundaries by means of natural oxidation [8]. Oxidation was carried out under room atmosphere conditions. In Fig. 4 the images of bismuth films prepared by AM method: (*a*) several hours after preparation and (*b*) stored under the conditions of room atmosphere for 45 days, are represented. In the image of a film (Fig. 4) stored for a long period of time the chains of bismuth oxide formed along the boundaries of blocks were examined.

Investigation of the process of formation of bismuth oxide on film surface of different thickness shows that minimal time necessary for the formation of oxide which decorates crystallite boundaries on film surface depends on its thickness. In the range of thicknesses from 100 nm to 1 μm it makes up approximately 24 hrs per 8 nm of thickness. With a longer duration of *Bi* film presence in the air, the surface is covered with oxide more evenly, which hampers separation and observation of crystallite boundaries. This method is easier to realize in comparison with etching, but it requires long time of film exposure to air for films of larger thickness.

The dependence of time of oxide decoration of block boundaries on the thickness of bismuth film indicates that this process occurs by the mechanism of electrochemical corrosion under the conditions of differential aeration [9] that lies in dependence of oxygen concentration on the defect depth and dependence of the time of oxide formation on the surface on the diffusion of ions to film surface.

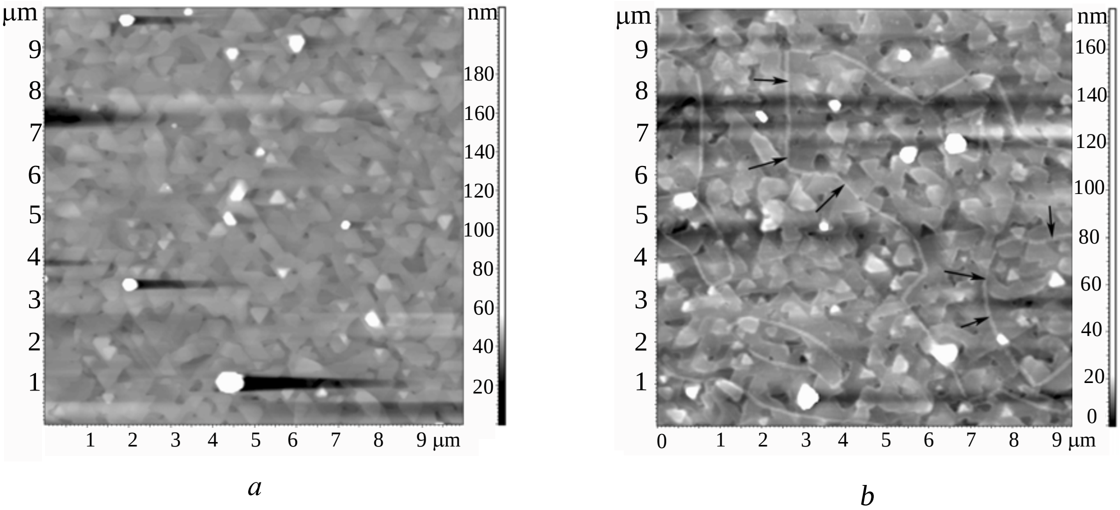


*Fig. 4. Bi film, film thickness is 300 nm. Substrate material: mica.*
*Substrate temperature is 110 °C. Size of a scan: ×10 μm.*
*a – scan is obtained several hours after film formation; b – scan is obtained 45 days after film formation, arrows show crystallite boundaries separated by decoration.*

### 3.2.4. Obtaining of films with the most perfect structure

Decoration by means of natural oxidation and detection of crystallite boundaries of bismuth films using APSM method, determination of dimensions of crystallites ensured the possibility of correcting production modes of bismuth films by thermal sputtering method in vacuum and obtaining films with the structure, close to single-crystal one (the sizes of crystallites exceed by an order or more the film thickness, and the film consists of two types of crystallites which are characterized by opposite crystallographic orientation). Substrate temperature of 140°C and the need for film annealing are optimal. High perfection of film structure is confirmed by the comparison of temperature dependence of specific resistance of films obtained at optimal conditions and single-crystal film of similar thickness (Fig. 5). Single-crystal film was produced by zone recrystallization method under coating [10].

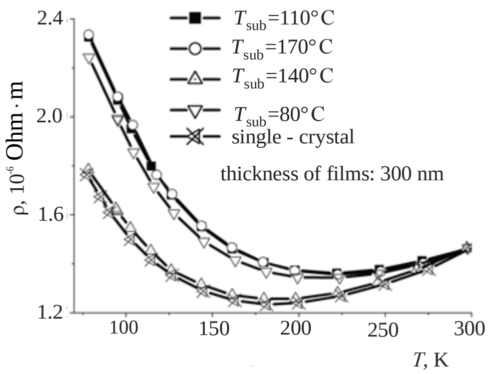


*Fig. 5. Temperature dependence of specific resistance of bismuth films.*

### 3.3. Surface modification of crystals and films of bismuth by the method of the atomic- power microscopy

Atomic- power microscopy provides extended possibilities for solids surface modification, which is of current importance for developing methods and techniques for producing nanostructures and changes in their properties [2].

In current work contact atomic-power microscopy using cantilevers of considerably harder material than bismuth is used for modification of surface pattern of bismuth films and shaping on the basis the films of quasi-one-dimensional and quasi-zero-dimensional structures. The essence of the method consists in performing contact force microscopy with sufficiently large pressing force (engraving), so that cavities (scratches) of different depth up to film thickness are formed in the sample at contact point. In Fig. 6 the image of such cavity in the form of a circle with the depth of a 20 nm groove is presented.

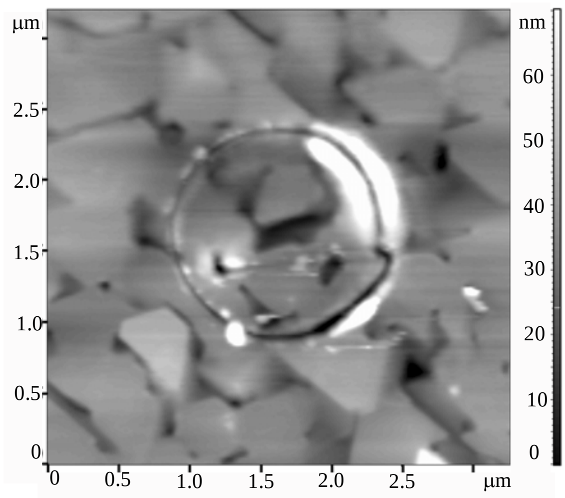


*Fig. 6. AM lithography – engraving on Bi film.*

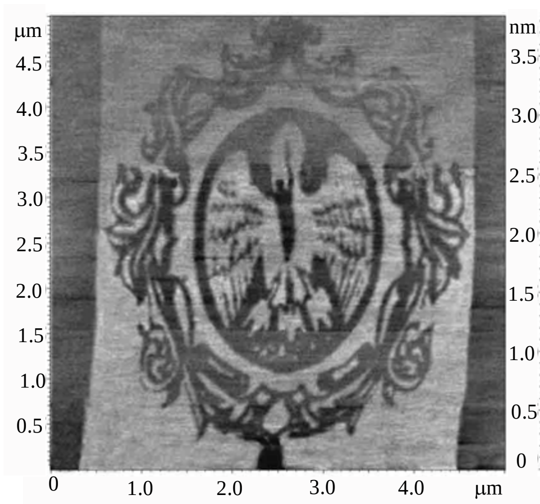


*Fig. 7. AM – anode-oxidizing lithography on Bi single crystal.*

Local electrochemical surface modification, the partial case of which is AM - anode-oxidizing lithography, which consists in formation of oxide on the surface of sample in humid medium during the application of potential difference between probe and sample can be used as a second approach. As an example, in Fig. 7 the image of coat of arms of A.Herzen Russian State Pedagogical University formed by bismuth oxide on the surface of bismuth single crystal by AM - anode-oxidizing lithography method is presented. Lithography was conducted in air at humidity of more than 80% and positive potential supply of approximately 10 V to the sample. Control of oxidation process was conducted by varying electric voltage versus the level of depicted surface blackness.

## 4. Conclusion

The images of surface and structural defects of bismuth single crystals are obtained by scanning probe microscopy methods, and the methods of controlled modification of crystal surface and bismuth films are developed.

Nondestructive method of detection of crystallite boundaries, determination of block dimensions and their mutual crystallographic orientation in bismuth films on mica substrates, based on decoration of structural defects by oxidation in combination with scanning of film surface by atomic-power microscopy method, is developed.

The obtained results can be used for investigation of the structure of crystals and films of other materials.

The parameters of the production of bismuth films by vacuum precipitation method on mica substrates whereby the films with the most perfect structure are obtained are determined.

The obtained results provide the possibility of optimization of production modes of bismuth films and single crystals with the purpose of enhancing perfection of their structure, quantitative calculation of structure defectiveness of films and single crystals for studying the influence of structural defects on transport phenomena and other physical properties.

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