Chapter 111
Production of Nanoporous Alumina and Surface Studies by Atomic Force Microscopy

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Abstract Nanoporous alumina is formed by two-step anodization process on an aluminum foil (99.99 %). Process of anodization allows to generate stable patches of nanoporous alumina and can affect the size and depth of the nanopores. By varying the parameters of anodization process we can control the growth of pores and their size. The properties of alumina film were studied by atomic force microscopy (AFM) and scanning electron microscope (SEM). The diameters of pores were found to be dependent on the applied voltage. Nanoporous alumina can be used as different membranes, test samples, template for nanostructured materials. The AFM is an appropriate method to study the size and depth of nanopores and periodicity of surface features.

Keywords AFM image · SEM image · Alumina film · Anodization · Nanopores · Acidic solution

111.1 Introduction

Atomic force microscopy (AFM) is an integral part of the research in the field of nanotechnology. AFM allows us to study the surface of various samples: the roughness of the surface and its local properties, and can provide information

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about the size of the grains, pores or particles. Depending on the method of study one can get (receive) the different information about the sample surface. Using AFM and SEM we can assess relative size and depth of nanopores.

The AFM was first described by [1] Binnig et al. as a new technique for imaging the topography of surfaces with high resolution. AFM was created as a solution to the limitations of the scanning tunnel microscope (STM), which usually applied to study conductive samples. The AFM method plays important role in surface physics studies and applies to study the most non conductive materials. The AFM allows us to study a variety of materials, not only in vacuum but also in air and in liquid [2].

Anodizied nanoporous alumina is well known to be formed by the anodizing (electrochemical oxidation) of aluminum in an electrolytic cell in which the aluminum acts as the anode. Size and depth of the pores can be controlled by voltage, different types of acids and anodization time [3, 4]. The type and the concentration of the electrolyte for a given voltage is to be selected properly to obtain self-ordered pore growth. Nanoporous materials have promising properties for applications in such areas as biosensing [5], chemical sensing [6] or nanotemplates [7], etc. In particular, capillary condensation can be studied in nanoporous materials with pore sizes slightly larger than the molecular diameter of an adsorbate.

111.2 Experimental Part

Nanoporous alumina was obtained by a two-step anodization. The surface of high purity aluminum foil (99.99 %) was polished and cleaned in an ultrasonic bath after thermal annealing at 500 °C (3 h). Also process of electro-chemical polishing of the sample was performed in solution $H_3PO_4/CrO_3/H_2O$ (3.3:0.7:1 part) with the next parameters: T = 70–80 °C, t = 30 min, I = 100 mA, V = 3–4 V. It was done to remove impurities from the surface and to polish the surface. The anodization process was carried out in a special cell using oxalic acid $(COOH)_2$ (0.3 M). Then aluminum foil was anodized under constant voltage conditions (30 V) into contact with solution at area of 0.1–0.2 mm^2. The duration of the first anodization was 12 h. Then formed oxide layer was selective dissolved in H_3PO_4/CrO_3 solution (T = 70–80 °C). Second anodization has duration of 5 min and was conducted under the same conditions as the first anodization. Then sample was rinsed with distilled water.

Surface of obtained samples was investigated by AFM Ntegra Therma (NT-MDT) and SEM Quanta 3D 200i (FEI Company). The tapping mode AFM was used (Fig. 111.1). The intermittent tapping mode was developed [8–10] in order to overcome the limitations of contact mode (Fig. 111.2). Here the cantilever was allowed to oscillate at a value close to its resonant frequency. When the oscillations occur close to a sample surface, the probe will repeatedly engage and disengage with the surface, restricting the amplitude of oscillation. As the surface is scanned, the oscillatory amplitude of the cantilever will change as it encounters

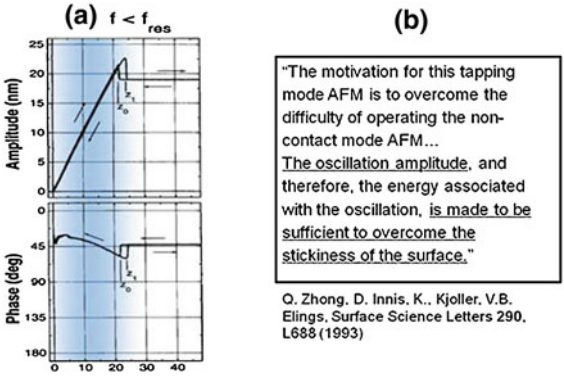


Fig. 111.1 Principle of tapping mode

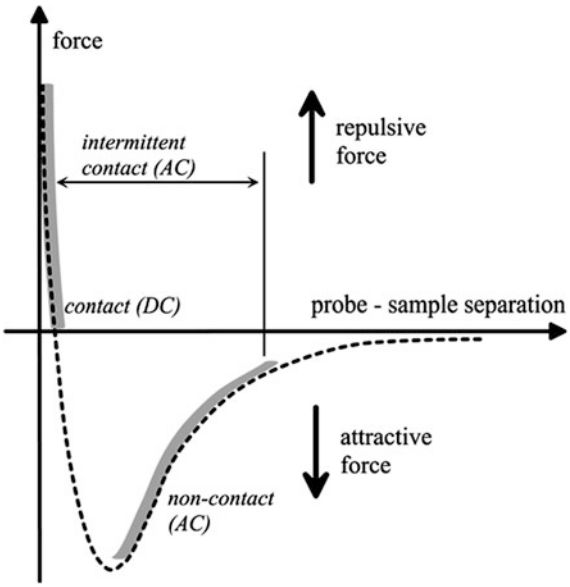


Fig. 111.2 Principle of contact and non-contact modes

differing topography. By using a feedback mechanism to alter the z-height of the piezocrystal and maintain constant amplitude, an image of the surface topography may be obtained in a similar manner as with contact mode imaging [11, 12].

111.3 Results and Discussion

Figure 111.3 shows the topography image of samples after the first anodization. The size of the grains determined by AFM was found in the range from 50 to 100 nm.

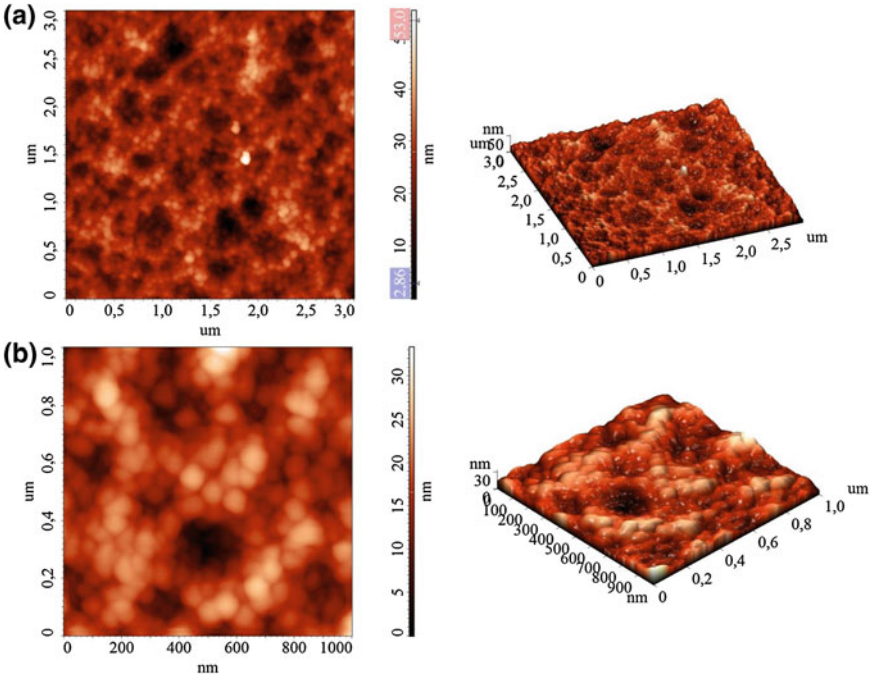


Fig. 111.3 AFM images of the sample surface with an area scan 3 × 3 μm (**a**) and 1 × 1 μm (**b**) after the first anodization

After selective dissolution of the formed oxide layer in H_3PO_4/CrO_3 solution uniformly distributed pores are appear on the sample surface. The average size of pores is about 50 nm (Fig. 111.4).

We also used phase mode (Fig. 111.5) for studying of samples surface. The principle of phase mode consist in the following: if the phase lag of the cantilever oscillation relative to driving signal is recorded in a second acquisition channel during imaging in intermittent contact mode, noteworthy information on local properties, such as stiffness, viscosity, and adhesion, can be detected that are not revealed by other AFM techniques. It is good practice to improve interpret the images obtained. For this mode it was used probes which have resonant frequency of 87–230 kHz. If we have high resonant frequency of probe we can get better phase contrast image.

Figure 111.6 shows the topography image of samples after the second anodization. We assessed the size of nanopores using the software of our microscope for surface morphologies of samples, as shown in Fig. 111.6.

Figure 111.7 shows SEM image and analysis of the elemental composition of Al_2O_3 surface after first anodization.

As it is shown in Fig. 111.4, there are many large grains allocated against the even background produced as a result of anodization. Elemental analysis (Fig. 111.8) revealed that these grains are not remnants of alumina, but the pure aluminum.

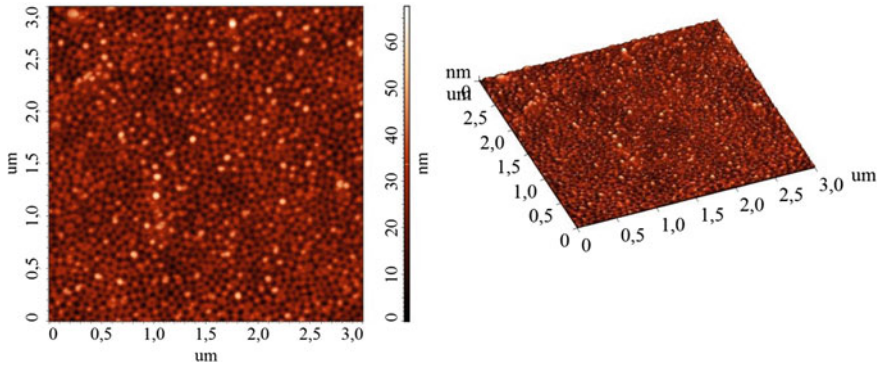


Fig. 111.4 AFM image (3 × 3 μm) of the surface after the first anodization and removing of the oxide layer

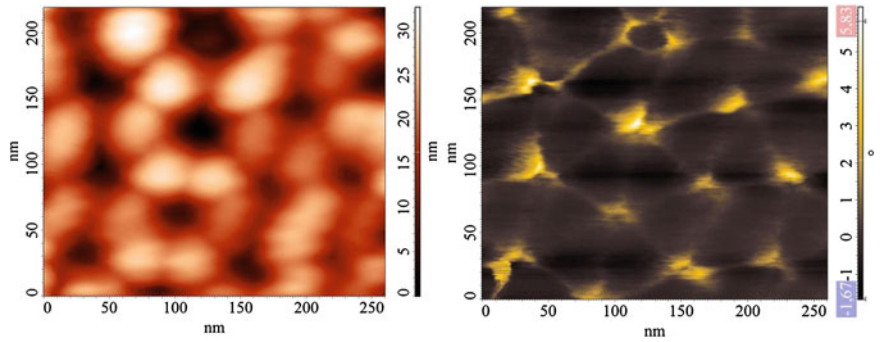


Fig. 111.5 AFM image and phase contrast image of the surface after removing of the oxide layer (3 × 3 μm)

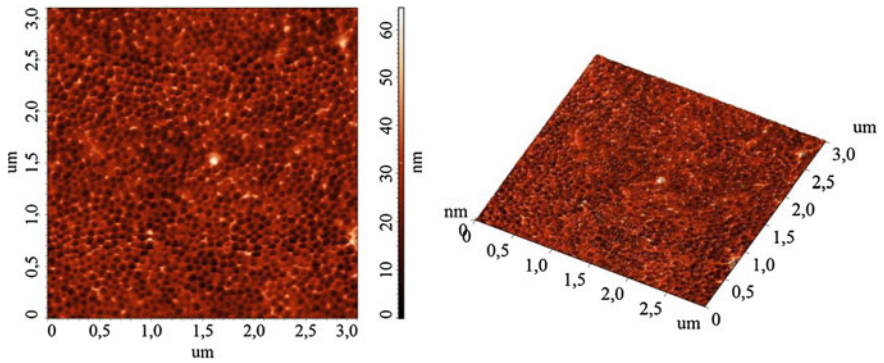
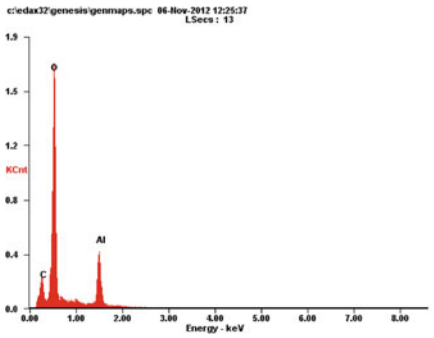


Fig. 111.6 AFM scans after the second anodization during 5 min: **a** AFM image and surface section profiles (3 × 3 μm), **b** 3D image



Element	Wt%	At%
OK	46.83	59.77
AlK	53.17	40.23
Matrix	Correction	ZAF

Fig. 111.7 Elemental analysis of Al_2O_3 sample obtained after first anodization

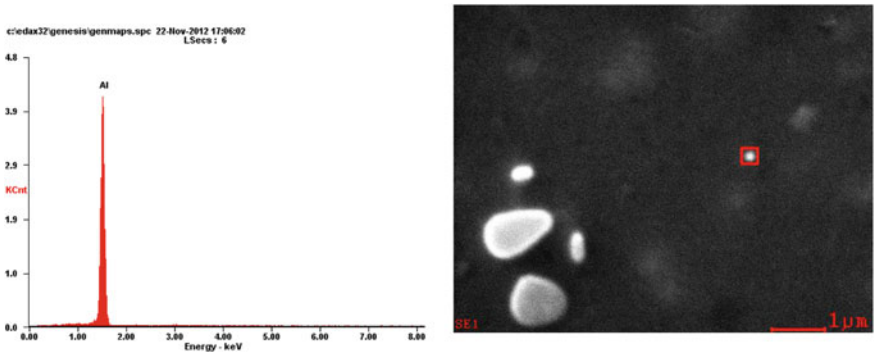


Fig. 111.8 SEM image and elemental analysis of the surface after removal of the oxide layer

111.4 Conclusions

We have obtained nanoporous alumina films in two-stage process of anodization using oxalic acid. A special electrochemical cell was made for etching experiments. The morphology of nanoporous alumina was studied by atomic force microscopy and scanning electron microscopy. The size of pores and the interpore distance is coinciding with the known literature data [13]. The AFM is the proper research method for study of morphology of nanoporous alumina surface and allow to develop methods of nanoporous alumina synthesis which is promising matrix to produce different nanostructured materials.

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