Study of electric parameters of thin porous anodic alumina layers

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Abstract. Currently, the study of the electric parameters of porous anodic alumina (PAA) layers is of interest for sensor applications (humidity, DNA, etc.). PAA layers are synthesized using electrochemical anodizing of aluminum foil in potentiostatic mode with an aqueous solution of sulfuric acid and glycerin as an electrolyte. The surface morphology of the layers was studied by atomic force microscopy. The electric characteristics were studied using impedance spectroscopy at room temperature and under heating. An increase in the impedance of the heat-treated PAA sample was found, as well as an increase in the impedance with an increase in the measurement temperature. The results are explained by the influence of adsorbed water molecules on the electric characteristics of porous layers.

1. Introduction
Thin films based on porous anodic alumina (PAA) are of great interest to various applications due to its biological inertness, durability and unique ordered structure [1, 2]. In recent years the development of semiconductor sensors encourages the active study of electric properties of such materials. Nanoporous layers are of interest for gas-selective membranes [3] and sensors for reducing gases, mesoporous layers can be used for humidity sensors, and microporous layers are prospective for water filters and DNA sensors [3-5].

Anodic alumina layers were studied using impedance spectroscopy in [6]. It was found that PAA layers combine a small capacitance and a small loss tangent with excellent field strength and low leakage current. The revealed variation of the permittivity within 10% and the presence of loss peaks on the temperature and frequency dependences of $\tan \delta$ indicate the influence of the ion relaxation mechanism on the polarizability of dielectrics with characteristic times from 10 to 145 μs, depending on the type of dielectric. The influence of the technological parameters of anodizing on the electric parameters of PAA layers is shown in [7]. Electric strength of layers decreases with increasing anodizing voltage, electrolyte concentration and film thickness. The determining factor in this case is the diffusion of oxidant ions through the growing oxide to the substrate surface.

The electric characteristics of porous membranes are greatly influenced by water adsorbed on the surface. Previous studies [8] have shown that water molecules form fractal aggregates on the surface of porous materials. In [9], porous thick films of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ ceramic materials were investigated as moisture sensitive materials. The effect of the anodic alumina pore size on the characteristics of the humidity sensor is shown in [10].

The aim of this work was to study the electric parameters of PAA thin films and membranes using impedance spectroscopy.
2. Experiment
The PAA layers were formed by electrochemical anodizing of aluminum foil using a special laboratory complex designed and constructed in our laboratory. The complex consists of three key blocks (Fig. 1): a personal computer, a synthesis device, and a power supply unit. The synthesis was carried out in a fluoroplastic single-chamber electrochemical cell of a vertical type with a cooling system.

![Figure 1. The setup for the synthesis of PAA layers.](image)

Aluminum foils (50 and 100 μm) were used as initial materials. Anodizing was carried out in a potentiostatic mode, which was provided by an ATN-1351 power supply. An aqueous solution of sulfuric acid with the addition of 15% glycerin was used as an electrolyte. The technological conditions for the synthesis are shown in Table 1.

| Sample No | Al thickness, μm | U, V | T, °C | t, min | Heat treatment | PAA type |
|-----------|-----------------|------|-------|--------|----------------|----------|
| 1 (270C)  | 100             | 22   | -2    | 30     | T = 400 °C, 4 hours | layer    |
| 2 (261C)  | 50              | 23   | 5…-1 | 125    | no             | membrane |
| 3 (252C)  | 50              | 22   | -7…-13| 221    | no             | layer    |

In capacitor structures with thin nanoporous PAA layers, the aluminum part of the substrate, which did not react with the electrolyte, was the lower electrode. Upper aluminum electrodes with a diameter of 2 mm were formed on PAA surface by magnetron sputtering. When studying the parameters of membrane, the lower aluminum electrode was also applied to the entire surface of the membrane using magnetron sputtering.

PAA samples were studied by atomic force microscopy (AFM) using NTEGRA-Therma probe nanolaboratory (NT-MDT, Zelenograd, Russia) in tapping mode. NSG 01 series probes with a cantilever in the form of a rectangular beam with a resonance frequency of 150 kHz were used.

The frequency dependences of the complex resistance module and the phase shift angle between the current and voltage in the capacitive circuit were measured in the frequency range from 5 kHz to 500 kHz using the Z500P impedance meter (Elins, Chernogolovka, Russia). All three samples were examined at room temperature, and sample 1 was additionally measured at various temperatures from 20 °C to 255 °C. To process the experimental impedance data, the complex plane method was used, in which the impedance, like any complex number, was represented as the dependences of the real and imaginary components of the complex resistance.
3. Results and discussion

Figure 2 shows the surface morphology of PAA samples 1 and 2. As can be seen from the presented AFM images, when using a foil with a thickness of 100 µm for electrochemical anodizing, rolling lines have a great influence on the morphology of the sample, and when using a thinner foil, their influence decreases. In general, both samples are porous materials with pore sizes of approximately hundreds of nanometers.

![AFM images of PAA samples 1(a) and 2 (b). Scan area size is 5×5 µm. Pores are marked with arrows.](image)

The Nyquist plots for the samples, whose synthesis conditions are specified in Table 1, are shown in Fig. 3. For samples 2 and 3, the curves are almost identical, while for sample 1 the real and imaginary components of the complex resistance are much larger, so the curve in Fig.3 is located higher.

![Nyquist plots for PAA samples at room temperature.](image)

The results showed that the type of PAA (layer or membrane with similar thicknesses) does not significantly affect the electric parameters, in contrast to the additional synthesis conditions. A comparison of the curves shows that the determining factor that makes the greatest contribution to the complex resistance of PAA layers is heat treatment.

Figure 4 shows the results of the study of sample 1 at different temperatures. It was found that the radius of the semicircle approximating the experimental data increases with increasing temperature.
Figure 4. Nyquist plots for sample 1 at different temperatures.

The experimental results can be explained by considering the effect of adsorbed water molecules on the conductivity of PAA layers and membranes. It is known that the effect of electronic conductivity in the bulk of PAA is parallel to the effect of surface conductivity, which is affected by the adsorbed water layer. This bulk conductivity process dominates only at extremely low humidity values, when there are only a few adsorbed molecules. The nature of the impedance in the low-frequency region is a consequence of the migration of ions in the adsorbed layer to the electrodes. This migration leads to the accumulation of ions (space charge formation) on the electrodes. Since the relaxation time of ion migration is longer than that of charge transfer, it is observed only at low frequencies. Therefore, there is no pronounced maximum in the studied frequency range on the Nyquist plot.

The fundamental mechanism of the influence of humidity on the electric parameters of porous materials is the physical absorption of water molecules on the initially chemisorbed layer of electrolyte ions [11]. The anodizing process leads to the capture of a certain amount of electrolyte anions in the pores. Even in low humidity conditions, the presence of these anions on the surface provides a high charge density for easy physisorption of water molecules. As a result, a network of fluid is formed inside the pores. Impurity anions also act as proton donors through a dissociative mechanism, attaching to the protons of water molecules.

Both the heat treatment and the increase in the measurement temperature result in the removal of the chemisorbed electrolyte molecules and a decrease in the concentration of the adsorbed water molecules in the pores. Consequently, the effect of surface conductivity in the adsorbed water layer is reduced. Chemisorbed hydroxyl ions increase the electrical conductivity of the material, either by transferring electrons to the conduction band of the base material, or by jumping protons between neighboring hydroxyl groups when an electric field is applied.

4. Conclusion

The results showed that the type of PAA (layer or membrane with similar thicknesses) does not significantly affect the electric parameters, in contrast to the additional synthesis conditions. A comparison of the curves shows that the determining factor that makes the greatest contribution to the complex resistance of PAA layers is heat treatment.

Thus, the paper shows the effect of heat treatment and measurement temperature on the impedance of the PAA layers. The heat treatment of the PAA layer is a key factor affecting its electric performance and leads to an increase in the impedance. As the measurement temperature increases, the electric characteristics of PAA also change greatly, with an increase in the radius of the semicircle.
approximating the Nyquist plot. The obtained dependences are explained by the change in the conductivity in the water layer adsorbed on the PAA surface.

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