Nanocomposite material based on nanoporous oxide of aluminum with additives of silver and gold nanoparticles

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Abstract. Porous films of anodized aluminum oxide with pore sizes of 50-60 nm were obtained. Silver nanoparticles in porous alumina have been synthesized by the method of controlled single-jet crystallization. The synthesis of gold nanoparticles in the pores was carried out by the reduction of $HAuCl_4$ with NaOH alkali in the pores of aluminum oxide.

1. Introduction

Due to theunique porous structure, the parameters of which (diameter, length and distance between neighboring pores) can be varied during the synthesis, porous alumina films can be used as inorganic membranes [1–3], calibration grids, a templating material for the synthesis of nanowires or nanotubes with a controlled diameter and high geometric anisotropy [4–6], as well as 2D photonic crystals [7, 8].

At present, the greatest use of porous aluminum oxide films has been found as matrices for the synthesis of ordered arrays of anisotropic nanostructures of various compositions. Magnetic materials, such as Fe, Co, Ni, obtained in the channels of porous Al_2O_3, are promising for the creation of a magnetic information storage medium. In this case, the possibility of changing the geometric anisotropy of nanostructures by varying the charge missed during the electrodeposition of the metal makes it possible to control the magnetic properties of nanowires [9].

Membranes of anodic aluminum oxide are a promising material for the creation of high-tech devices operating at elevated temperatures [10]. The coefficient of thermal conductivity of aluminum oxide films is 1.6 W/m×K, which is much higher than the thermal conductivity of polymeric materials and glasses used as solid-state matrices for dye lasers [11–13]. If the pores are filled with laser dyes, then such a system can be used as an active medium for a tunable laser.

2. Method of experiment

The following reagents were used to prepare porous alumina films: Al (0.5 mm thick sheet, 99.99%), oxalic acid $(COOH)_2$, H_3PO_4 conc., CrO_3, $CuCl_2$, HCl, ethanol C_2H_5OH (96%). In order to increase the size of Al crystallites, remove microstresses, and then achieve better ordering of the pores, aluminum substrates were annealed in air for 10 hours at 550 °C in a muffle furnace. For the preparation of solutions, double filtrated and deionized water is used on the AquaMax 360 Basic water purifier. The specific resistance of water was 18.2 MΩ / cm.

An important characteristic of metallic aluminum, which affects the process of ordering of a porous structure, is the roughness of its surface. The alignment of the aluminum surface was carried out by electrochemical polishing in a pulsed mode. Before polishing, the surface of the aluminum plate is cleaned with acetone. For the electrochemical polishing of the aluminum surface, an electrolyte is

used, which has the following composition: CrO_3 (185 g/l) and H_3PO_4 (1480 g/l.). The aluminum plates were immersed in a 500 ml heat-resistant dish with the prepared solution at an electrolyte temperature of 80 °C and mixed with a magnetic stirrer (IKAMAG RET control-vise). For electrochemical polishing the following parameters were chosen: voltage - 11-13 V, current - 1.2 A. The polishing time of the aluminum surface lasted 15-20 minutes. Quality control of electrochemical polishing was evaluated by the appearance of the aluminum surface. The temperature of the mixer was 80 ° C, and the temperature of the solution was controlled by a thermocouple. A plate of aluminum (of the same composition and larger in area) was attached to the negative electrode, and a plate of aluminum for polishing was placed on the positive electrode. The current source was Agilent technologies N8740A 150V, 22A, 3300W. The following parameters were set: voltage limits of 11-12 V, current 1.2 A. After that, the samples were washed in distilled water and dried in air. It is noted that an increase in the duration of electropolishing leads to smoothing of the unevenness, but is accompanied by a significant dissolution of aluminum and a decrease in the thickness of the metal plate. Anodic oxidation of aluminum was carried out in a two-electrode electrochemical cell using direct current sources. The resulting porous aluminum oxide matrices were separated from the aluminum base by selective dissolution of the latter in a solution of 0.25 M $CuCl_2$ in water.

Synthesis of silver nanoparticles in porous alumina was carried out by the method of controlled single-jet crystallization. The method is based on the reduction of the silver ammoniac complex by a reducing agent, which was formic acid. To 25 ml of an aqueous solution of silver nitrate with a concentration of 0.4%, 1 pea of NaOH is added. The solution becomes muddy. After deposition of silver on the bottom of the glass, gently drain the top of the solution and wash 2-3 times with distilled water. To the resulting precipitate add 5 ml of deionized water. Then 400 μl of concentrated ammonia are added to the resulting solution and mixed, and the solution becomes clear as a result. In the resulting solution, preliminarily heated to 60 °C aluminum oxide film is dropped and 400 μl of formic acid is added. The reaction is carried out for 4-5 minutes, then the liquid is drained, the alumina film is washed with distilled water and dried at a temperature of 60 °C. The synthesis of different concentrations of nanoparticles in the film was carried out by varying the volume of formic acid added during the reaction.

For the synthesis of gold nanoparticles (AuNPs), we used solutions of $HAuCl_4$ (1 ml of Au solution per 9 ml of deionized water) and NaOH (1g NaOH per 25 ml of water). For the synthesis of AuNPs in aluminum oxide, the pH of the gold solution (initial pH = 1.5-1.95) it is necessary to bring to 10, adding a solution of NaOH (1N) dropwise. Then, the porous alumina film is immersed in a solution of $HAuCl_4$ (pH = 10) and heated at 80 °C for 2 hours. After this time, the color of the film changes from white to raspberry-pink (if the $HAuCl_4$ solution is concentrated, respectively, violet). This is a sign that the gold nanoparticles have formed in the pores. The synthesis of different concentrations of nanoparticles in the film was carried out by varying the volume of NaOH solution added during the reaction.

The synthesized nanostructures were studied using a Tescan Mira 3 LMU microscope at a 15 kV accelerating voltage and a working distance of 7 mm. Information on the local chemical (element) composition was obtained using an energy-dispersive detector, excited by fast electrons of characteristic X-ray radiation

3. Result and discussion

Figure 1 shows the current characteristic for the production of an oxide layer in oxalic acid. The formation of the first pores in the oxide film is most likely to occur in some defective places, for example, at the boundary of the crystallite, in the film cracks. Simultaneously with the growth of pores, the alumina layer begins to grow from the outer part of the film at the film-metal interface, the individual cells of which have the form of a hemisphere.

From these studies, it was found that changes in the current density are observed throughout the anodization process. There are three stages of changes in the current dependence:

Stage 1. When the current is turned on, there is a sharp increase in the current density due to the presence of a thin oxide film on the aluminum surface. At this stage, the thickness of the oxide layer increases.

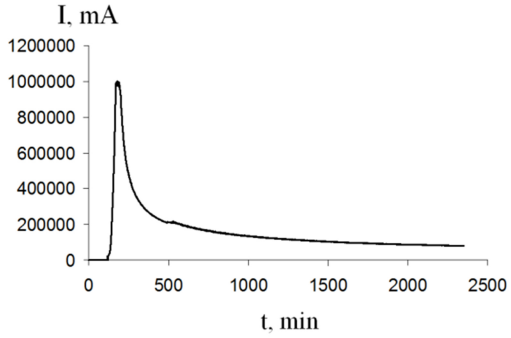
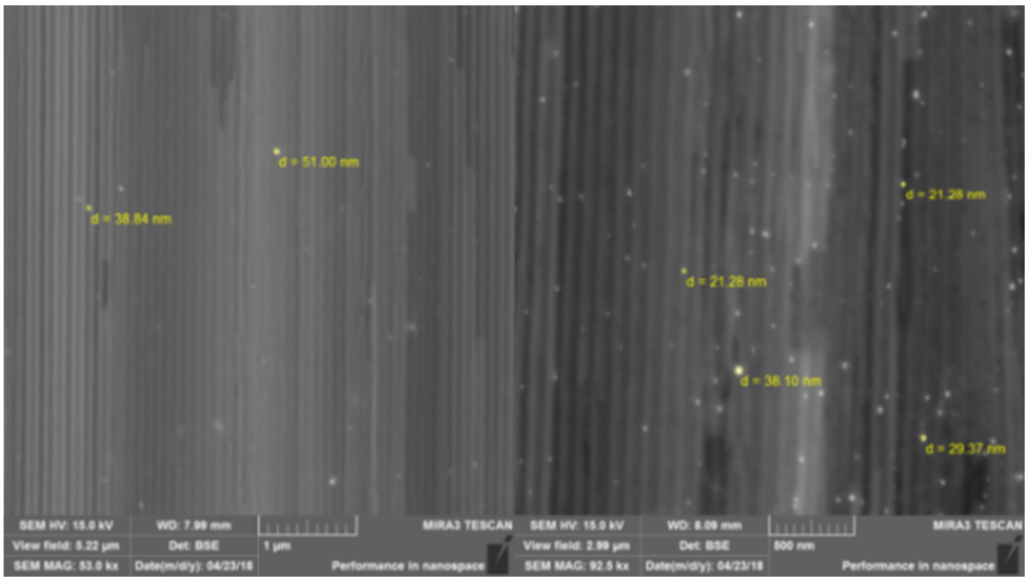


Figure 1. Current characteristic of the process of anodizing aluminum.

Stage 2. The value of the current density starts off fall. At this stage, the porous structure of anodized aluminum is formed, followed by an increase in the pore depth.

Stage 3. The value of the current density passes through a maximum and the current decreases. This occurs in connection with the achievement of the ultimate thickness of the porous alumina layer and the rupture of the upper pore layers.

SEM images of transverse cleavages of the samples and the results of determining the content of chemical elements on the surface of aluminum oxide are shown in figures 2 and 3, respectively. It can be seen that nanoparticles of silver (figures 2 a, 3 a) and gold (figures 2 b, 3 b) are formed on the walls of pores of nanoporous alumina.



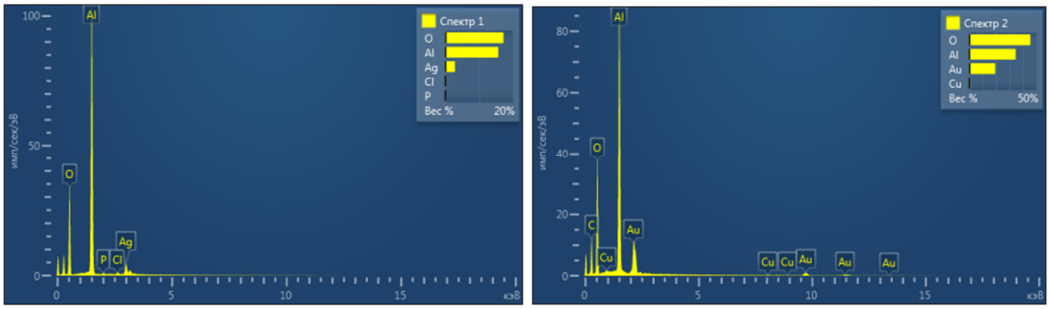
(a)(b)

Figure 2. SEM image of the transverse cleavage of an aluminum oxide film.

Figure 4 a shows absorption spectra of silver nanoparticles of different concentrations in a film of nanoporous alumina. It is seen from the figure that the absorption band of silver nanoparticles in the matrix has a maximum at a wavelength of 387 nm. The appearance of an absorption band with a maximum at wavelength 387 is indicative of the formation of nanoparticles in pores. The half-width of the spectrum is 43 nm, with a change in the concentration of nanoparticles in the film it was 36 nm.

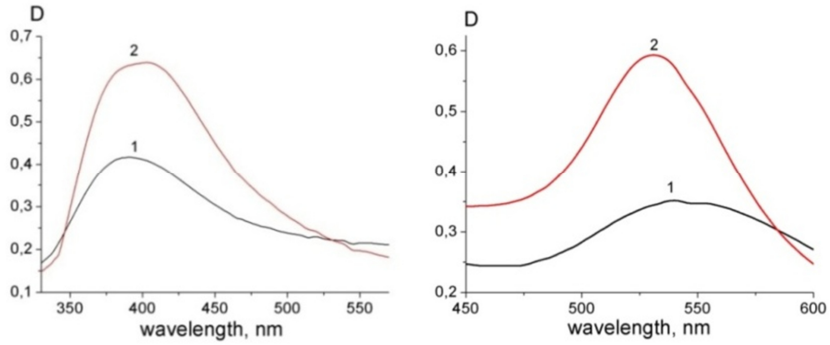
The same figure (figure 4 b) shows the absorption spectra of gold nanoparticles of different concentrations in a film of nanoporous alumina. The appearance of an absorption band in porous

aluminum with a maximum at a wavelength of 534 nm is indicative of the formation of gold nanoparticles in pores. It can be seen from the figure that the absorption band of gold nanoparticles in the matrix has a maximum at a wavelength of 534 nm. The half-width of the spectrum is 52 nm, with a change in the concentration of nanoparticles in the film, the half-width of the absorption spectrum was 42 nm.



(a) (b)

Figure 3. Energy dispersive spectrum of elements on the surface of an aluminum oxide film.



1-C_{Ag}=2•10^{12}mol/m^2;
2-C_{Ag}=7•10^{13}mol/m^2

1-C_{Au}=6•10^{11}mol/m^2;
2-C_{Au}=2•10^{13}mol/m^2

(a) (b)

Figure 4. Absorption spectrum of silver (a) and gold (b) nanoparticles in the matrix of nanoporous alumina.

4. Conclusion

Thus, as a result of the experiments, porous films of anodized aluminum oxide with pore sizes of 50-60 nm were obtained. The synthesis of silver nanoparticles in porous alumina was carried out by the method of controlled single-jet crystallization. The synthesis of gold nanoparticles in pores was carried out by restoring $HAuCl_4$ with alkali NaOH in the presence of a porous alumina film.

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