

Highly-ordered nanoporous anodic aluminum oxide films

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The samples of the nanostructured aluminum oxide films were obtained by anodic oxidation method (thickness is near 100 µm and d_{pores} = 42±4 nm). Two-stage aluminum oxidation was carried out in a two-electrode electrochemical cell at 0°C and the voltage value of 40 V. Oxalic acid solution was used as an electrolyte. The optimal heat treatment conditions, of the weak-luminescent films without destruction of the order structure have been proposed.

Образцы пленок наноструктурированного оксида алюминия толщиной 100 мкм и размером пор $d_{пор}$ = 42±4 нм получены при помощи метода анодного окисления. Двухстадийное окисление алюминия проводилось в двухэлектродной электрохимической ячейке при 0°C и напряжении 40 В, в качестве электролита использован раствор щавелевой кислоты. Выбраны оптимальные условия термообработки для получения оптически прозрачных образцов без нарушения высокоупорядоченной структуры.

1. Introduction

Nowadays, the obtaining of porous anodic aluminum oxide (AAO) from the various electrolytes has attracted the increasing of attention as a material for the development of new nanoscale objects with unusual and unique properties [1–3]. There are a number of properties such as the pores strict order at large surface areas, the narrow dispersion of the pores diameters and intervals between them, the controlled pore diameter, the ideal cylindrical shape and the strictly parallel channels needed to create new materials based on the nanosized objects. A possibility of the highly ordered composite materials obtaining like the carbon/AAO, the polymer/AAO, the metal/AAO, the semiconductor/AAO [4–9], together with their optical properties [10–12], permits to create some new optoelectronic devices. The anodic alumina films with a high degree of surface ordering are also used as two-dimensional photonic crystals [13], as cathodes for organic light-emitting diodes [14], humidity sensors [15,16].

In recent years, it has been developed many technologies for creating ordered porous layers of aluminium oxide, which are based on creation of the periodic structure on aluminum surface using different methods. Nanoimprint method [17], for example, involves creation of a stamp on aluminum surface with a matrix made on the silicon carbide basis with the following anodizing. Control of the periodic structure of aluminum oxide is then carried out by changing the time pattern of the matrix. This method allows creating the perfect ordered arrays of pores. Some other technologies involve a creation on aluminum surface of the artificial nanorelief with a scanning probe micro-

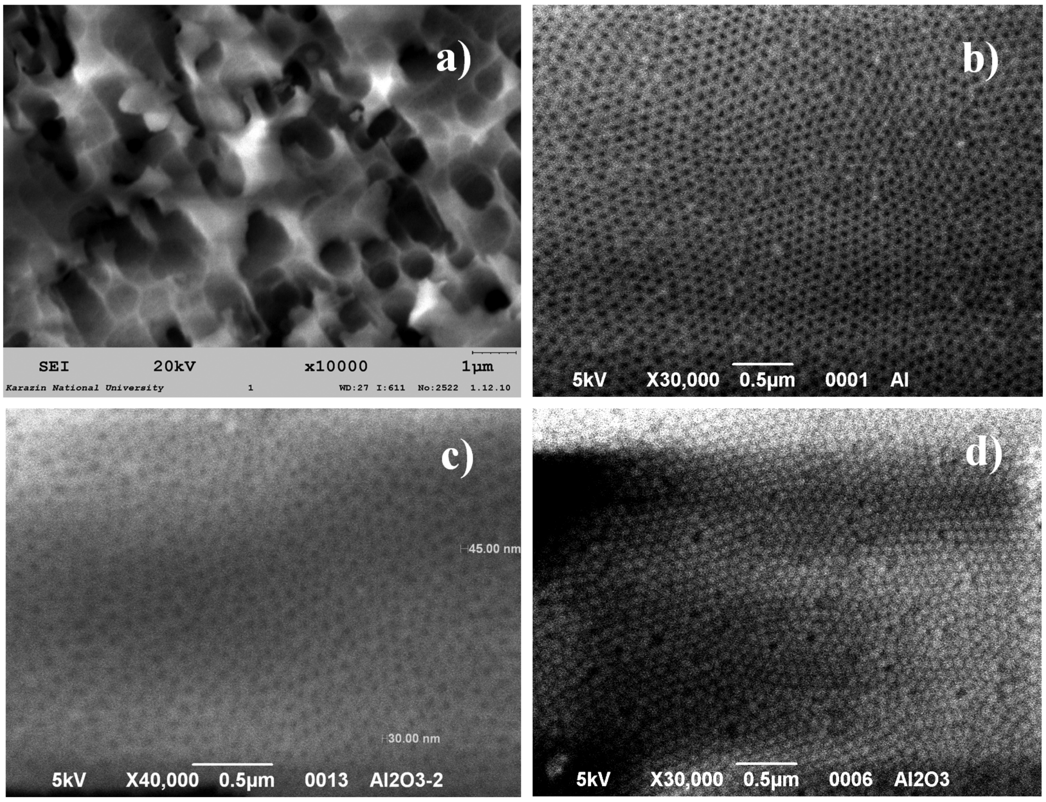

Fig. 1. SEM images of the structure AAO (a) the first stage of anodic oxidation of aluminum; (b) and (c) the second stage of anodic oxidation of aluminum; (d) barrier layer of AAO.

scope [18], which generates an array of the nanoscale pits orderly arranged, followed by anodic oxidation of the sample. However, these methods are complex, precise and also very continuous, that leads to high costs of technology and to its low output.

The aim of this work is obtain highly-ordered films on the basis of AAO for later use as a template for creating ordered composites of fluorescent nanomaterials of various compositions.

2. Experimental

Anodic aluminum oxide films were prepared by two-step electrolytic oxidation, the starting material was a high purity aluminum (99.999 %, the sheet thickness is 0.8 mm). The aluminum substrate were annealed on air for 24 h at 550°C to relieve tension in the metal and for increasing of the metal microcrystals size to achieve a better ordering of the structure. Then, the substrates were subjected to chemical etching in an aqueous sodium hydroxide (NaOH, 40 wt. %) solution at 80°C for 5 min. Further the chemical polishing of samples was carried out at 100°C for 3 min, in the solution of 72 % H_3PO_4 (ρ = 1.69 g/ml), 12 % H_2SO_4 (ρ = 1.84 g/ml), 8 % HNO_3 (ρ = 1.4 g/ml) and 8 % H_2O (by volume). As a result, we obtained the smooth surface substrates, which were subjected to anodic oxidation.

At the first stage aluminum electrolytic oxidation was carried out in a two-electrode electrochemical cell in electrolyte solution of oxalic acid $(COOH)_2$ with c = 0.3 mol/l under vigorous stirring, the electrolyte solution temperature was 0°C, the voltage value was 40 V. The aluminum anode-substrate mounted in the bottom of the cell, through which cooling was carried out using Peltier element. The stainless steel plate has been used as cathode.

After the first stage of anodizing during 48 h, the obtained oxide layer on aluminum surface was selectively dissolved in dilute solution phosphoric acid H_3PO_4 (5 %) with chromium oxide (VI) CrO_3 (c = 20 g/l) at 80°C. Aluminum substrates with an ordered roughness were received, after that they were subjected to repeated electrolytic oxidation at the same conditions. The second stage of anodizing held during 48 h too; a thickness of the porous aluminum oxide layer was approximately 100 μm.

The porous oxide films were separated from the aluminum substrates by their selective dissolution in 10 % methanol solution of bromine (Br_2) at 50°C. Then the films were washed with methanol and dried in air at room temperature. After that the samples were heat treated in the temperature range 350–950°C.

The structure of the samples was studied using a scanning electron microscope JSM-6390LV (SEM).

Luminescence spectra were recorded using spectrofluorimeter on the base of a grating monochromator MDR-23. Luminescence was excited by a He–Cd laser (λ = 325 nm).

3. Discussion

AAO samples investigation using SEM shows that the first stage of anodic oxidation leads to formation on the aluminum surface of irregularly arranged pores of different diameters (Fig. 1a). This fact illustrates the necessity of the repeated anodic oxidation of the sample with the prior removal of aluminum oxide layer, which was received at the first stage.

The AAO samples, which were obtained in the two-step aluminum anodizing, reveal an ordered porous structure with a perpendicular arrangement of pores channels relative to the sample surface. The structure of anodic films consists of domains (regions with strictly hexagonal arrangement of channels) with size of 5–10 μm, which is disoriented relative to each other (Fig. 1b). Mathematical treatment of the obtained by SEM data shows that the average pore diameter is 42±4 nm and the distance between their centers is 83±2 nm (Fig. 1c).

After the separation of AAO film from the aluminum substrate, the backside pores are closed by the barrier layer [10]. Reverse side of this film has hexagonally arranged hemispheres that formed from the barrier layer; the hemisphere center coincides with the channel pore center. According to the SEM data and further mathematical calculations, the average distance between the hemispheres is 83±2 nm (Fig. 1d).

In the luminescence spectrum of the unannealed AAO film sample demonstrates the broad band (λ_{max} = 460 nm) belonging to lattice defects [19] (Fig. 2, curve *1*). To remove these defects the films were annealed at different temperatures, which do not break the ordered structure of the films, for 3 h. It was found that the optimal annealing treatment is exposure of the sample for 3 h at T = 950°C resulting in a significant decrease of the defects luminescence intensity without disturbing the material structure (Fig. 2).

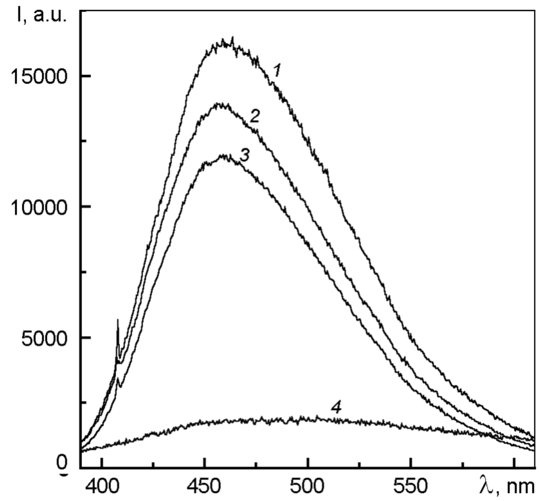

Fig. 2. Luminescence spectra of AAO films (λ_{exc} = 325 nm) at different annealing treatment during 3 hours: *1* — untreated film, *2* — 350°C, *3* — 550°C, *4* — 950°. T = 298 K.

4. Conclusions

In this work highly-ordered weak-luminescent porous anodic aluminum oxide films has been obtained. The thickness of the films is near 100 μm, the pore diameter is 42±4 nm and the average distance between their centers is 83±2 nm. Such films can be used as templates for creation of highly-ordered nanostructured composite materials of various composition and linear size.

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Високовпорядковані нанопористі плівки анодного окису алюмінію

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Зразки плівок наноструктурованого окису алюмінію товщиною 100 мкм та розміром пор $d_{пор}$ = 42±4 нм отримано за допомогою методу анодного окиснення. Двостадійне окиснення алюмінію проводилося у двоелектродній комірці при 0°C при напрузі 40 В, у якості електроліту використано розчин щавлевої кислоти. Обрано оптимальні умови термообробки для одержання нелюмінесцентних плівок без порушення високовпорядкованої структури.