Two-dimensional porous anodic alumina for optoelectronics and photocatalytic application

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Abstract. Fabrication of porous anodic alumina film structures using anodizing, sol-gel synthesis and photolithography is reported. The structures receive interest as planar waveguides due to strong photoluminescence of the embedded trivalent lanthanides. Mesoporous structures comprising sol-gel derived titania in porous anodic alumina play a role of effective catalyst for water purification.

1. Introduction

Microstructured film pattern with different configuration in accordance with the photomasks on the porous anodic alumina (PAA) thin films (less than 5 μm) can be produced by the photolithography. Microstructures manufacturing requires the protective oxide metal mask formation on the surface which is technologically complicated and rather expensive operation. It is possible to use xerogels films as a metal mask alternative to planarization surface. The xerogels can be produced by the sol-gel method or dip-coating followed by the heat treatment [1]. For example, titanium oxide, silica, alumina, yttrium-aluminum composites and other xerogels may be used as masking materials. The selective etching of lithographic masks and windows helps to create a structure with the etched groove configuration like a waveguide. Xerogels doped with different luminescense ions expands the range of possible application.

There are operations which are implemented for the microstructured films manufacturing:

- higly ordered PAA fabrication;
- xerogel deposition to obtain the planar surface;
- photomask deposition and photolithography to form a pattern according to the photomask;
- chemical etching throught the lithographic mask windows using selective etchants;
- removal of the photoresist.

This paper presents the results of the morphological analysis of microstructure of PAA formed using electrochemical anodization, sol-gel synthesis, photolithography and chemical etching and discussed the route of manufacture of such structures and their perspectives for optoelectronics and photocatalytic application.

2. Experimental part

The following operations were perfomed to produce the microstructured PAA:

I. Synthesis of the PAA with the required morphology in various modes of the anodizing process. Two-stage anodic oxidation process was used for increasing regularity of oxide film in various

electrolytes: orthophosphoric acid with a concentration of 9.8%, oxalic acid with a concentration of 3.6% and a mixture of sulfuric and oxalic acids.

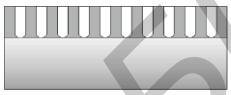
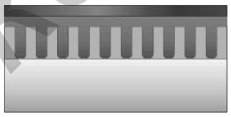
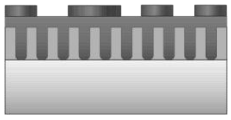
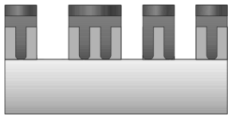
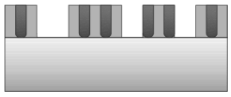
II. The xerogel formation on the surface of anodic oxide: sols were deposited by spinning with intermediate drying of each layer in air at 100-200 ° C, thus 8-10 layers were deposited to full closure of the pores mouthes surface planarization.

III. Photomask deposition and photolithography.

IV. Anisotropic etching throught the photolithographic mask windows: the choice of etchant and the process parameters were done. The etchants based on the solution of chromic anhydride and phosphoric acid, ammonium fluoride solution in hydrochloric acid, solution of hydrofluoric acid were investigated.

Table 1 illustrates of the steps of synthesis the described microstructured films.

Table 1. The sequence of operations forming a microstructured porous anodic alumina film

№	Operation and its graphical representation	
1	Higly ordered PAA fabrication	
2	Xerogel deposition for the: – surface planarization – filling the mouth of the pores;	
3	Photomask deposition	
4	Photolithography	
5	Anisotropic etching through the mask windows	
6	Photomask removing	

2.1. PAA and xerogel fabrication

PAA films was prepared by electrochemical anodization of aluminum foil, the process occurs in two stages. Anodic oxide obtained on the first stage was selectively vented in the solution containing chromic anhydride and phosphoric acid at a temperature of 60-70 ° C. The second anodizing stage took place in the conditions identical to the first. There are the prefered modes of the anodization process: for phosphate electrolyte the temperature was maintained at 10-12 ° C at a voltage of 100 V; for oxalic electrolyte 12-15 ° C the temperature was kept at 30 V and for combined electrolyte the temperature was maintained 12-15 ° C at a voltage of 20 V. Anodic films were finally dried in air at 100 ° C for one hour.

Titanium dioxide xerogel was deposited onto the PAA by sol-gel method using titanium ethoxide $Ti(OC_2H_5)_4$ as a titania precursor in ethylene glycol and citric acid; pH value of the sol equal to 1.0 was adjusted with concentrated nitric acid [2]. Sols were deposited on a substrate by spinning (rate

2700 rev / min, the duration of the operation for 30 seconds), each layer was dried in air at 100-200 ° C for 10-15 min, and then the next layer was formed. The structures xerogel/PAA were finally annealed for 30 minutes at a temperature of 400-500 ° C.

Protective mask with a pattern of grooves was formed on the alumina surface by the contact photolithography using the positive photoresist S 1813. The photoresist mask was removed in an organic solvent after the aluminum anodization in the open areas had made. Selective etching of alumina in the photolithography mask windows was carried out for 3 to 6 minutes depending on the type and temperature of the etchant.

The resulting structures were investigated by scanning electron microscopy (SEM).

3. Results and discuttion

In the phosphoric acid under the above conditions were obtained the porous oxide with a sufficiently large (90-100 nm) pore diameter, which hampers film xerogel formation because the pores were not filled after deposition more than 10 xerogel layers. Anisotropic etching of the structure through a mask of the photoresist leads to formation the grooves walls with the many defects due to he etchant flowing under the photomask. A partial penetration of photoresist into the pore channels complicates its removal during subsequent photolithography (Figure 1).

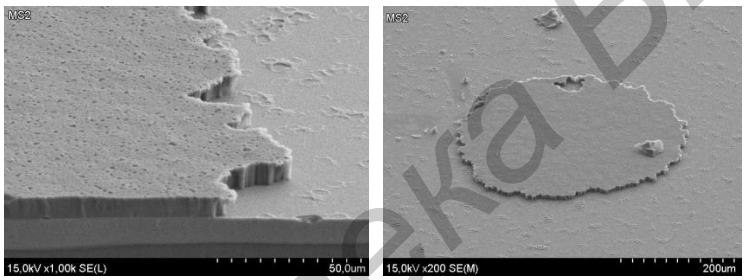


Figure 1. Titania xerogel on the PAA formed in phosphoric electrolyte after the photolithography, anisotropic etching and photomask removing

Anodic film formed in the various electrolytes may have pore diameter in the range of 30-50 nm (oxalate electrolyte) and 20-30 nm (combined electrolyte) that allows planarized oxide surface by the formation 8 layers of titania xerogel. Figure 2 shows SEM images of the PAA films obtained in the combined electrolyte (10-15% sulfuric acid with the addition of 2-5% oxalic acid) after photolithography and etching in a solution containing chromic anhydride and phosphoric acid. But etchant wicking under photoresist the mask is still observed on the PAA with smaller pore diameter.

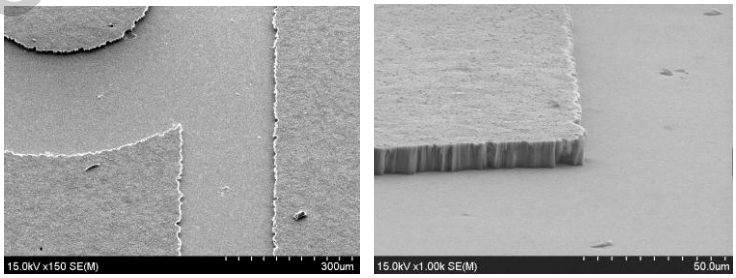


Figure 2. Titania xerogel/PAA structures after the photolithography, anisotropic etching and photomask removing

For the alumina film with smaller pore diameters a flat vertical wall of etched groove may be obtained. The use of selective etching agents containing fluoride ions also gives good result as compared to chromium containing etchants (SEM images are presented in Figure 3).

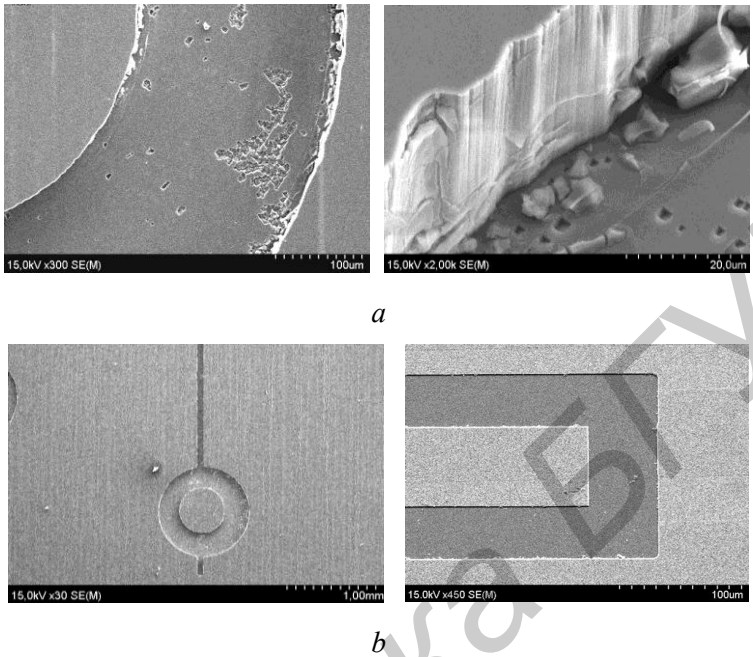


Figure 3. Titania xerogel/PAA structures formed in the combined electrolytes after the photolithography, anisotropic etching in the fluoride ions containing (*a*) and chromium ions containing (*b*) etches and photomask removing

Thus for an effective planarization PAA surface by the titania xerogel the PAA with diameter of the pores less than 50 nm are preferable. Vertical walls of the etching grooves with fewer defects obtained after the etching through a photomask in the ammonium fluoride solution in hydrochloric acid compared to the etching solution of hydrofluoric acid etchant or chromic anhydride and phosphoric acid etchant.

4. Microstructured films for the photocatalytic water purification

Titania in the anatase phase on the PAA structures with the longituginal etching grooves, in our view, are promising for environmental photocatalysis due to the developed surface which increases the contact plane between the titania and contaminated solution [3, 4].

Figure 4 shows SEM images of the structures containing more layers of titanium oxide. The xerogel is formed on the surface of the sample and in the etching grooves. Figure 5 presents the results of the photocatalysis with the microstructured PAA/titania. Photocatalytic degradation of the Rhodamine C was performed in double-walled glass reactor transmitting UV light at wavelength above 320 nm. Titania xerogel/PAA samples were placed in the reactor containing dye aqueous solution with the initial concentration of 0.04 mmol/l and were illuminated by the light for 2 h. The concentration of the dye was *in situ* monitored by recording absorption spectra of the dye solution at λ = 551-554 nm every 20 minutes.