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Fabrication of self-ordered nanoporous alumina for optical and structural characterization

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Resum

Presentem la fabricació, caracterització estructural i òptica de membranes d'alúmina nanoporosa autoordenada. Les mostres han estat fabricades per el procés de doble anodització. La morfologia de les membranes obtinguda mitjançant les diferents condicions d'anodització ha estat examinada amb un microscopi electrònic d'escombrat per tal d'estimar les seves propietats geomètriques. Les propietats estructurals estudiades mitjançant difracció de raigs X mostren que durant el procés de recuit termic, des de 600 ºC fins a 1200 ºC, l'alúmina nanoporosa ha cristal·litzat des de la fase amorfa fins a les formes gamma i alfa (cristal·lines). L'espectre de la transmissió òptica de les membranes d'alúmina porosa autoordenada va ser mesurat mitjançant un espectròmetre UV-VIS en el rang 300 - 1000 nm

Paraules clau: anodització · alúmina porosa · procés de autoordenació · difracció de raig X · espectre de transmissió

Abstract

We present the fabrication and optical and structural characterization of self-ordered nanoporous alumina membranes. The samples were fabricated using a two-step anodization process. The morphology of the membranes produced using different anodizing conditions was examined with a scanning electron microscope in order to estimate their geometrical properties. The structural properties studied by X-ray diffraction showed that nanoporous alumina is crystallized from amorphous phase to gamma and alpha (crystalline) forms during annealing at 600 ºC to 1200 ºC. The optical transmission spectra of the membranes were measured using a UV-VIS spectrometer in the range of 300 - 1000 nm.

Keywords: anodization · nanoporous alumina · self-ordering process · X-ray diffraction · transmission spectra

1. Introduction

Nanoporous alumina is one of the most promising nanomaterials in the area of nanotechnology. The fabrication of nanoporous alumina with unique properties provides a wide range of applications in different fields, such as nanotubes [1], nanowires [2] and photonic crystals [3]. The porous alumina with highly ordered nanopores can be prepared using a two step anodization of aluminum [4]. It is not necessary to use a lithography technique due to the self-organizing process. The morphology of the porous structure can be controlled by adjusting the anodizing parameters in order to obtain a nanoporous structure with interpore spacing between 40 - 400 nm and pore diameter from 10 to 300 nm [5].

The Porous Alumina Membranes (PAMs) used as a base material for the aforementioned applications require thermal stability at high temperatures. Therefore, in technological terms, it is necessary to study the structural properties of PAMs after high temperature treatment. Very few studies have been published to date focusing on the optical properties of porous alumina. Therefore, it is interesting to study the optical characterization of porous alumina membranes, which can provide useful information on their nanostructural properties for optical device applications. In this paper, we present the fabrication process of ordered porous alumina membranes using a 2-step anodization. We have measured transmission spectra of as-produced alumina membranes of different thicknesses. The transmission spectra in the UV-VIS range were measured for PAM samples of varying thicknesses in order to broaden the application field.

2. Experimental

High purity aluminum foils were used as the working substrates. The piece of foil is first cleaned in an acetone ultrasonic bath and the foil is later annealed at a high temperature to provide recrystalization that will increase the domain size in alumi-

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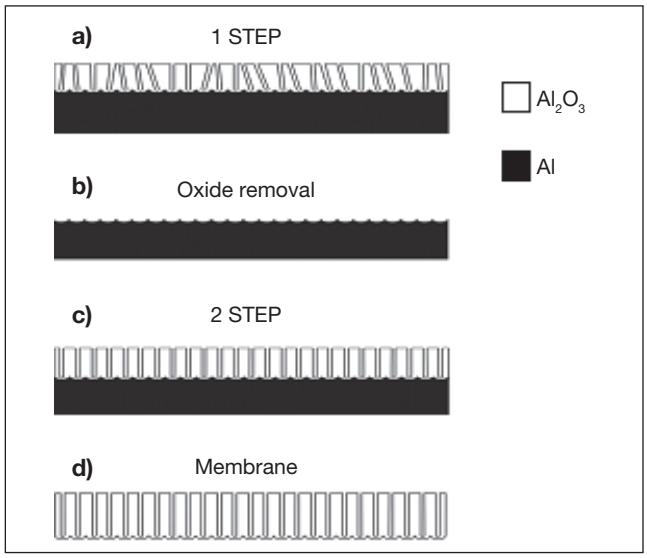

Figure 1. The scheme of experimental procedures for 2 step anodization.

num bulk. The foil is then used as an anode in the experimental setup for anodizing. Because pure aluminum has a very rough surface, it is necessary to polish the foil electrochemically in a mixture of ethanol and perchloric acid. This obtains a very smooth, mirror-like finish on the surface of the aluminum. We can then oxidize the aluminum via a two step anodization process. Anodization is first performed under specific conditions. In our work, we use 10 % sulfuric acid or 0.3 M oxalic acid as electrolyte at room temperature and we apply the voltage potentiostatically between 18-25 V for sulfuric solution or 40-60 V for oxalic solution. After the first anodization, a porous oxide grows on the aluminum substrate (Figure 1a) that is subsequently dissolved in a hot solution of chromic and phosphoric acid. This oxide removal leaves a pre-patterning on the surface of the aluminum that acts as a mask during the following step (Figure 1b). The second anodization is performed under the same conditions as the first, but the porous structure is self-ordered (Figure 1c). Finally, we can separate porous alumina from the substrate in order to obtain a free-standing membrane (Figure 1d). The detailed experimental preparation of porous alumina is described elsewhere [6].

3. Results and discussion

The morphology of porous alumina was examined by scanning electron microscopy (SEM). In Figure 2 there are two types of porous alumina: a) is porous alumina produced in sulfuric acid solution and b) is a sample prepared in oxalic acid. As we can see, the pore diameters of alumina prepared in oxalic acid are of around 30 nm. On the other hand, the sample prepared in sulfuric acid has a pore diameter of 15 nm. The distance (center to center) between pores is also different for each acid used for anodization. The pores of the samples prepared in oxalic acid are separated by a distance of 100 nm and for sulfuric acid the value is half that, at around 50 nm. The pore density is 10^9 and 4.10^9 pores per cm^2 for porous alumina prepared in

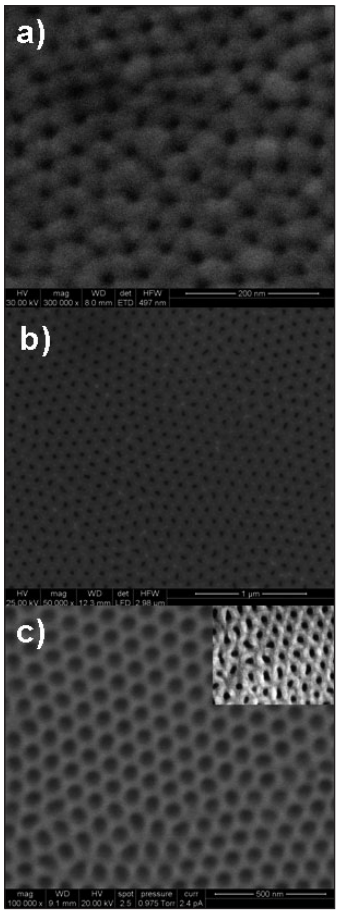

Figure 2. The SEM surface images of porous alumina produced in: a) sulfuric acid at 20 V, b) oxalic acid at 40 V and c) bottom image of alumina from oxalic acid, where the inset shows the opened pores.

oxalic and sulfuric acid, respectively. The aspect ratio (pore depth/pore diameter) of such a porous structure is very high, because the thickness of porous alumina can reach several hundreds of microns. Figure 2(c) shows the bottom of the porous alumina membrane covered by a thin barrier layer after detachment from the aluminum substrate. The inset in Figure 2c shows that this layer can be dissolved using a pore widening process and with this we can obtain pores throughout the layer.

As shown in Figure 3a, there is a strong linear dependence on interpore distance as well as of pore diameter on anodizing voltage. The increase in the applied voltage will produce a longer distance and also a larger pore diameter. Figure 3b represents the behavior of the oxide growth rate and porosity vs. voltage. The growth rate of the porous structure can be estimated from the anodizing time and total oxide thickness. This value is between 8 - 25 μm/h, depending on the anodizing voltage, as shown in Figure 3b. If we know the values of the interpore distance and pore diameter we can calculate the porosity using the following equation [7]:

$$P = \frac{2 \cdot \pi}{\sqrt{3}} \times \left(\frac{d}{2 \cdot D}\right)^2$$

Figure 3b shows that the porosity of porous alumina produced in oxalic increases slightly with anodizing voltage.

Figure 4 presents the x-ray diffraction spectra (using a Siemens D5000 diffractometer) of PAM annealed in-situ from room temperature up to 1200ºC. The diffraction spectra of

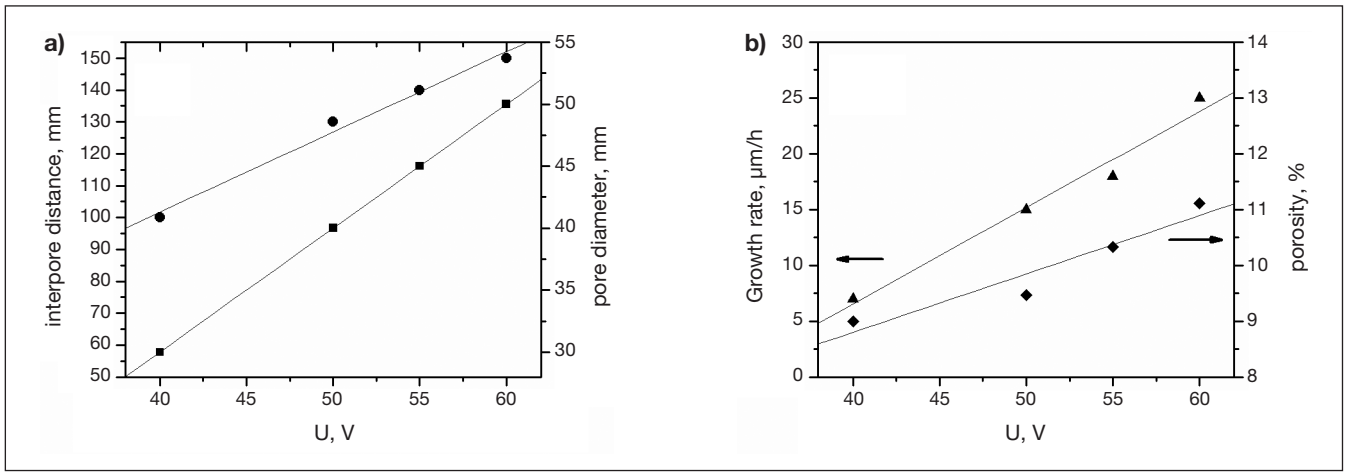

Figure 3. a) the dependence of interpore distance and pore diameter on the anodizing voltage, b) oxide growth rate and porosity vs. anodizing voltage using oxalic acid.

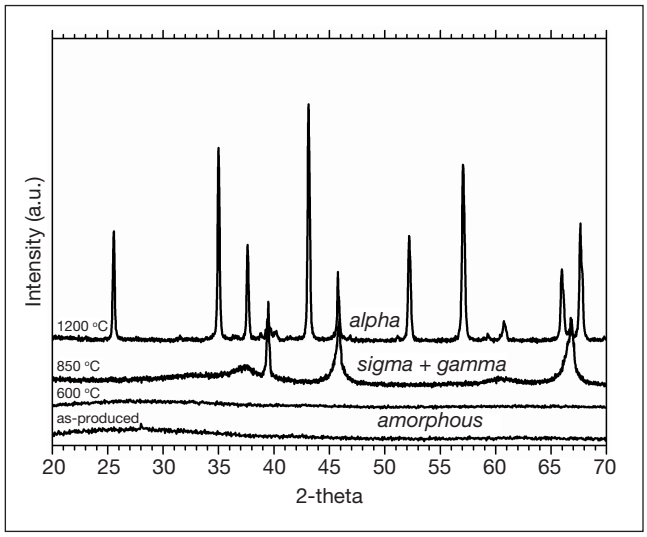

Figure 4. The X-ray diffract spectra analyzed for porous alumina annealed at different temperatures of 600 ºC, 850ºC and 1200 ºC.

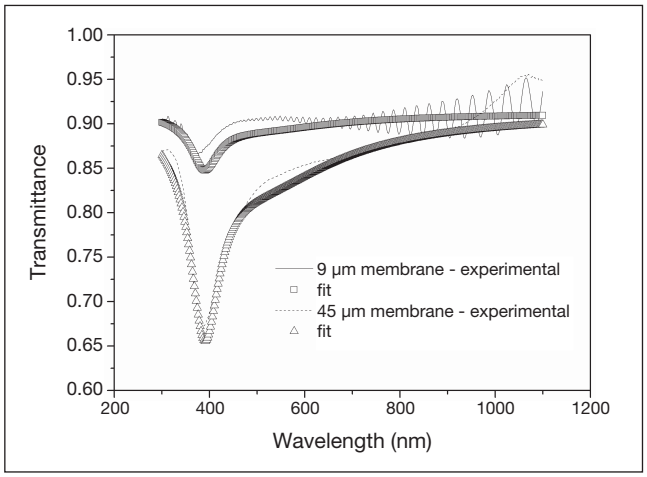

Figure 5. The transmission spectra measured in the wavelength of 300 nm to 1100 nm for porous alumina membranes with thicknesses of 9 μm and 45 μm.

room temperature and annealed PAM at 600 ºC revealed an amorphous structure. The annealing temperatures in the range of 850 to 1000 ºC transform the PAM structure into a mixture of γ- and σ - phases. However, as the temperature increases, more γ- alumina peaks appear, while the σ - form is suppressed. The crystallization of PAM to a-phase begins at 1100 ºC and ends at 1200 ºC, when relatively pure α-alumina is obtained.

Porous alumina membranes with different thicknesses (9 and 45 μm) were analyzed using a spectrophotometer with a SpectraPro-150 monochromator from ARC Inc. in the wavelength range from 300 to 1000 nm.

The measurements were analyzed using a standard optical characterization method [8]: the transmittance spectra were least-squares fitted to simulated spectra that assume that a sample consisted of a slab of porous alumina whose refractive index and extinction coefficient follows the Lorentz Oscillator dispersion with two oscillators and whose thickness is that determined by SEM. The two spectra for the two different thicknesses were considered simultaneously in the fitting. With this, the fitting considers that all the samples are made of the same material with the same optical properties.

Figure 5 shows the results of the measurements together with the best fit obtained. This best fit corresponds to two oscillators centered at 389 nm and 507 nm. The transmittance spectra have an almost constant value of 85% - 90% in the wavelength of 500 nm - 1000 nm for the three samples. However, in a region around 400 nm there is a clear absorption peak which increases with the porous alumina thickness.

4. Conclusions

In conclusion, we are able to fabricate nanoporous membranes with a tunable pore diameter as well as interpore distance. These membranes have a wide range of possible applications, such as active layers, masks or templates. The ordered porous alumina membranes (PAMs) were fabricated using 2-step anodization. The structural properties of PAMs were analyzed by X-ray diffraction. The crystallization starting from amorphous phase at room temperature, passing

through γ˜-alumina between 800 - 1000 ºC and finally reaching a-alumina form at 1200 ºC was observed. The optical characterization using optical spectroscopy showed that porous alumina has a large absorption peak in the wavelength around 400 nm.

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