research articles

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

Lukas Vojkuvka, Lluís F. Marsal*, Josep Ferré-Borrull, Trifon Trifonov, Josep Pallarés

NEPHOS group, Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, ETSE, Universitat Rovira i Virgili, Tarragona

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 °C fins a 1200 °C, 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 °C to 1200 °C. The optical transmission spectra of the membranes were measured using a UV-VIS spectrometer in the range of 300 - 1000 nm.

Keywords: anodization \cdot nanoporous alumina \cdot self-ordering process \cdot X-ray diffraction \cdot 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].

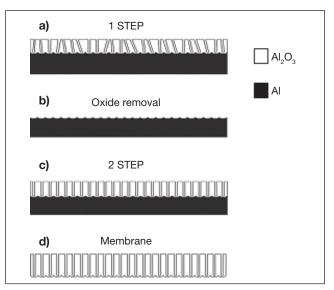
The Porous Alumina Membranes (PAMs) used as a base material for the aforementioned applications require thermal

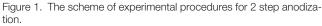
stability at high temperatures. Therefore, in technological terms, it is necessary to study the structural properties of PAMs after high temperature treatment. Very few studies have been published to date focusing on the optical properties of porous alumina. Therefore, it is interesting to study the 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 asproduced 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-

^{*} Corresponding author: Lluís F. Marsal. Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, ETSE, Campus Sescelades, Universitat Rovira i Virgili. Avda. Països Catalans 26, E-43007 Tarragona, Catalonia, EU. Tel. +34 977559625. Fax: +34 977559605. E-mail: Iluis. marsal@urv.cat





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 selfordered (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 cm² for porous alumina prepared in

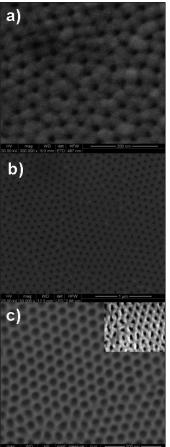


Figure 2. The SEM surface images of porous alumina produced in: a) sulfuric acid at 20 V, b) oxalic acid at 40 V and c) bottom image of alumina from oxalic acid, where the inset shows the opened pores.

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 μ m/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 1200°C. The diffraction spectra of

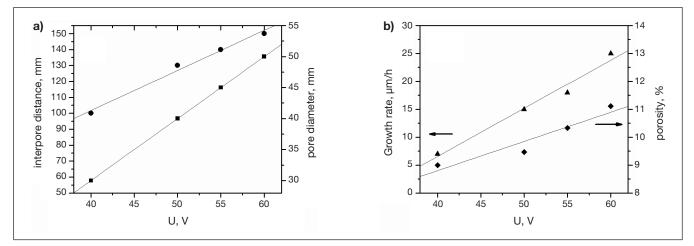


Figure 3. a) the dependence of interpore distance and pore diameter on the anodizing voltage, b) oxide growth rate and porosity vs. anodizing voltage using oxalic acid.

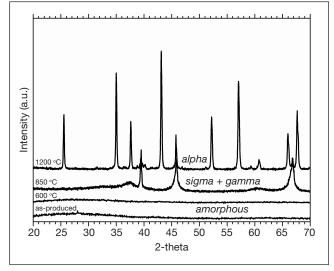


Figure 4. The X-ray diffract spectra analyzed for porous alumina annealed at different temperatures of 600 °C, 850°C and 1200 °C.

room temperature and annealed PAM at 600 °C revealed an amorphous structure. The annealing temperatures in the range of 850 to 1000 °C 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 °C and ends at 1200 °C, when relatively pure α -alumina is obtained.

Porous alumina membranes with different thicknesses (9 and 45 μ m) 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,

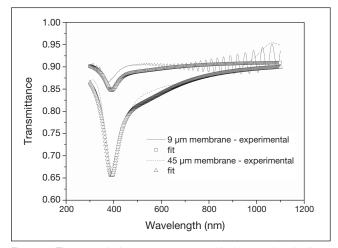


Figure 5. The transmission spectra measured in the wavelength of 300 nm to 1100 nm for porous alumina membranes with thicknesses of 9 μm and 45 $\mu m.$

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 °C and finally reaching a-alumina form at 1200 °C 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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About the authors

Lluís F. Marsal received B.S. and M.S. degrees from the Universitat de Barcelona, in 1991, and a Ph.D. degree from the Universitat Politècnica de Catalunya, in 1997, all in physics. His doctoral research was a contribution to the noncrystalline silicon-carbon alloys on crystalline silicon heterojunctions. In 1991, he joined the Department of Electronic Engineering, Universitat Rovira i Virgili, Tarragona, where he became Assistant Professor in 1994 and Associate Professor in 2000. His research interests are mainly devoted to the characterization and modeling of advanced electronic and photonic devices, photonic crystals based on silicon and micro-nanostructures. He is co-author of about 100 reviewed scientific publications in international journals and conferences. He is member of the Optical Society of America (OSA) and senior member of the Institute of Electrical and Electronics Engineers (IEEE).

Lukas Vojkuvka obtained his Electrical engineering degree in 2004 at the Brno University of Technology (VUT), Czech Republic. At present, he is a PhD student at the Departament d'Enginyeria Electrònica, Elèctrica i Autom→tica, Universitat Rovira i Virgili; where he is working on his thesis entitled: Development of technology and applications of porous alumina membranes. He focuses on the fabrication and optical characterization of porous alumina nanostructures.

Josep Ferré-Borrull received his B.S and M.S. degrees in Physics from the Universitat de Barcelona, in 1993 and 1995, respectively, and his Ph.D. degree in Physics from the Universitat de Barcelona, in 1999. At present he is a Ramon y Cajal Researcher at the Department of Electronic, Electrical and Automatic Control Engineering, Universitat Rovira i Virgili. His main research interests are the characterization of advanced photonic and electronic devices and photonic crystals, characterization methods and simulation tools for micro- and nano-photonic structures.

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Trifon Trifonov received M.S. degree in Laser Physics in 1996 from Sofia University (Bulgaria). From 2000 to 2005 he worked on his Ph.D. degree at the Electrical Engineering Department of the Universitat Rovira i Virgili. His doctoral thesis dealt with numerical simulation and the fabrication of 2D photonic crystals by electrochemical etching of silicon. In 2006, he joined the Micro and Nano Technology group, Universitat Politècnica de Catalunya as a Postdoctoral Researcher. He is mainly involved in the fabrication and optical study of 2D and 3D photonic crystals based on macroporous silicon.

Josep Pallarès received a PhD degree in physics from the Universitat Politècnica de Catalunya, in 1997. He is currently an Associate Professor with the Electronics Engineering Department, Universitat Rovira i Virgili. His current research interests are the characterization and modeling of advanced electron devices and the study of photonic crystals.