Nanoporous Self-organized Anodic Alumina Templates

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Abstract

We describe the set-up recently implemented at IFIMUP to grow nanoporous self-organized alumina templates using anodic aluminum. The parameters controlling large-area orderliness are presented and the influence of anodizing voltage is discussed. We show that the pore size and interpore depend on the applied voltage. We were able to show that the interpore distance depends on applied voltage, and to obtain the ideal conditions (temperature, voltage, electrolyte concentration, …) to fabricate ordered structures with ordered pores around 30 nm interpore distance.

Introduction

Nanoporous materials have gained much importance in the last 20 years due to their potential industrial and technological applications for nanometric device fabrication. In fact, because the existent nano-lithographic techniques like e-beam, X-ray or focused ion beam are expensive and have a low throughput, new assembling methods are needed for the large scale, inexpensive, production of nanodevices. Nanoporous alumina templates, which are well known to the chemical industries and can be readily obtained by common electrochemical processes, offer the prospect of a self-assembling method to achieve the required nanodimensions. Compatibility with existing semiconductor microfabrication technologies, together with their unique properties and relatively easy and low-cost processing makes the Anodic Aluminum Oxide (AAO) a promising candidate for growth of custom made nanostructures. Application examples such as functional electrodes, solar cells, carbon nanotubes, photonic crystals, electroluminescence displays or components for magnetic storage devices, are examples that evidence the versatility and potential of these nanostructures. The arrangement and shape of the pores are dependent of the applied anodization voltage, temperature, type and concentration of the electrolyte. Highly-ordered hexagonal lattices have been already successfully prepared by a two-step anodization process [1] and structures with pore diameters in the 24–158 nm range and interpore distances between 66 nm and 500 nm were demonstrated [2]. Square and triangular pores lattices arrangements are also achievable by means of pre-patterning techniques [3].

In this work we present recent results on the fabrication of nanoporous alumina templates using a home-made anodization set-up, which is now available at IFIMUP. We study the dependence of anodization voltage on the interpore distances, as well as in the orderliness of the produced nanostructures. The influence of electrolyte temperature on this electrochemical process is also discussed.
Materials and methods

In order to fabricate nanoporous alumina templates using anodic aluminum, we implemented an anodization set-up, schematically depicted in figure 1. This set-up is constituted by a Teflon cell were a Platinum (Pt) mesh (99.999%) works as a cathode and the aluminum substrate as an anode, being able to anodized substrate areas around ∼30 mm². The Current density transients j(t) are monitored during the anodization process using a Keithley 2400 Sourcemeter.

Nanoporous alumina films are obtained by electrochemical oxidation of high-purity (>99.997%) aluminum foils. Prior to anodization, several cleaning treatments are employed. The substrate is first degreased in ethanol, followed by soft chemical polishing in sodium hydroxide solution (1M), which removes the native oxide layer, being then rinsed in deionized water.

A two-step anodization procedure [1], is used in order to achieve the desired organization of pore structure.

In the work here presented, the first anodizations were performed at constant voltages of 15V, 20 V and 25 V during 2 hours. As electrolyte a 0.3 M sulfuric acid solution was used and the temperature was kept constant within 12 ± 2°C. The resulting porous-oxide layer was then etched away in 0.5 M phosphoric/0.2 M chromic acids mixture at 60°C for 15 minutes. Scanning Electron Microscope (SEM) analysis confirmed the presence of dimples in the bottom aluminum foil, originated from the nanoporous alumina layer.

A second anodization of the aluminum (with an encarved hole structure) was then carried out in the same conditions as the first one.

In some cases, only the alumina film was needed. In order detach the alumina membranes from the aluminum foil/substrate underneath, a saturated solution of copper(II) chloride was used. This solution dissolved the aluminum resulting in a free-standing alumina membrane.

Morphology characterization of the nanoporous alumina films and aluminium substrates (after alumina removal) was done using FEI Quanta 400FEG SEM. In addition, the orderliness of the porous structure was characterized by numerically calculating power spectrum (square modulus of the Fast Fourier Transform) of single domain SEM images.

Figure 1 a) Schematic view of the anodization set-up implemented in this work. b) SEM micrographs of the backside of an alumina membrane of the first anodization after removed aluminium, formed in 0.3M H₂SO₄ (12°C), reflecting the highly organized pore structure developed. Inset fig. 1b) Fast fourier Transform of the SEM picture.
attributed to a different stage of porous structure formation [4]. On the other hand, in figure 1 b) we present a SEM picture of the back side of a membrane produced using anodic aluminum, after a long first anodization. Notice the formation of a regular hexagonal array, which constitutes the negative of the pore structure engraved on the aluminum foil. This clearly shows the essence of the two step anodization method. After the long first anodization, the anodization front, at the interface between aluminum and alumina is highly regular, thus by removing this Alumina layer, the second anodization can proceed in a highly ordered pore structure. In the inset of figure 1 b) we show the Fourier transform of the SEM micrograph depict in figure 1 b) attesting the high ordeness of the porous membrane produced.

The formation of porous-type or a barrier-type alumina layers is immediately reflected in the potentiostatic current density [j(t)] transients. For porous-type alumina, j(t) profiles, shown in figure 2, typically evolve in four levels, as described below, each one attributed to a different stage of porous structure formation [4]. On the other hand, when a barrier-type film grows, a continuous decay of j(t) is observed (not shown). The four stages of pore formation are pointed out in figure 2 a1). Initially, j(t) decreases rapidly corresponding to the formation of a barrier-type alumina layer [fig. 2 a1] before tA] i.e. there exists a non-conductive oxide coverage of the entire surface of the aluminum foil exposed to the electrolyte solution. From tA to tb j(t) slows down, and passes through minimum value. This is due to the competition, in certain conditions of
field and temperature, between barrier formation and enhanced oxide dissolution by the 
focusing effect of the electric field in surface depressions. If pores start to nucleate and 
to grow \( j(t) \) increases, achieving a maximum value. Subsequently, \( j(t) \) slightly decreases 
[fig. 2 \( a_1 \) from \( t_c \) to \( t_b \)] due to growth competition among the pores. Finally, \( j(t) \) arrives 
at a constant value indicating a constant growth rate [fig. 2 \( a_1 \) above \( t_b \)]. In this way, 
monitoring the \( j(t) \) transients during anodization process we are able to predict the 
formation of an ordered domain structure.

Figure 2 \( c_i \) shows the behaviour of the current of anodization at different temperatures, 
12°C (C1) and 14°C (grey). In the anodization at 14°C, after the formation of the pores, 
there is an accented increase of the current density, which was confirmed to correspond 
to the appearing of micro cracks. The local heating causes an inhomogeneous electric 
field distribution at the bottom, leading to local (di)electrical breakdown of the oxide. In 
fact, cracks on the oxide film are generated if porous alumina is formed without 
temperature controlling.

In figures 2 \( b_1 \), \( b_2 \) and \( b_3 \) we show aluminum substrates after removal of the first 
anodization alumina layer, grown at applied potentials of 15V, 20V and 25V, 
respectively. Comparing the three anodizations and for the time employed in this work 
– 2 hours – we can conclude that an applied potential of 25 V gives the best conditions 
for the appearance of organized patterns, as it is clealy seen in the FFTs in the insets. 
Notice however the confinement of pore order to the aluminium grains. A similar 
ordered state could be obtained with 15 V and 20 V if longer anodization times were 
employed. It also can be seen the anodization at a 25V voltage give the largest interpore 
distance in the aluminium (~30nm), in agreement with the literature [4].

From SEM analysis, we can conclude that an anodization in 0.3M H2SO4 solution at 
12°C, carried out at a potential of 25V for 2 hours, gives the best conditions, suitable for 
the appearance of a long-range hexagonal-pattern organization. After subsequent 
removal of the alumina layer, these craved dimples in the aluminium substrate will act 
as nucleation sites for \( 2^{\text{nd}} \) anodization pore structure growth. The field-enhanced 
dissolution will occur preferentially at the bottom of the holes, where the pore will start 
to form. An optimized (hexagonal lattice) transfer patterned, from a \( 1^{\text{st}} \) anodization step, 
is thus required, in order to obtain an excellent nanoporouous alumina template from the 
\( 2^{\text{nd}} \) anodization step.

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