

In-depth study of self-ordered porous alumina in the 140–400 nm pore diameter range

Jaime Martín ^{*}, Cristina V. Manzano, Marisol Martín-González ^{*}

IMM-Instituto de Microelectrónica de Madrid (CNM-CSIC), Isaac Newton 8, PTM, E-28760 Tres Cantos, Madrid, Spain

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ABSTRACT

The growth of self-ordered anodic aluminum oxide (AAO) templates with pore diameters in the 140–400 nm range is achieved by anodization in phosphoric acid at low temperatures ($-4\text{ }^{\circ}\text{C}$). The procedure used in this study is able to completely avoid the “burning” of the oxide, highly frequent in anodizations in phosphoric acid solutions at high voltages. The current density measured during the anodizations is rather low, $0.6\text{--}0.7\text{ mA/cm}^2$; therefore, low growth rates have been also measured ($<2\text{ }\mu\text{m/h}$). AAO templates present a relatively low porosity value of 8.4%. However, a considerable pore-enlargement-rate ($v_{\Delta d} = 0.636 \pm 0.101\text{ nm/h}$) has been observed as a consequence of the chemical dissolution of the pore walls during the anodization. Thus, the results reported here constitute an exhaustive study on the preparation of large-diameter-pore self-ordered AAO templates that enables both to access to pore diameters up to now inaccessible and to efficiently overcome the difficulties of their fabrication process ascribed to its aggressive reaction conditions.

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1. Introduction

Orderly structured materials with nanoscale lateral dimensions are being strongly demanded in several modern technologies. Thus, self-ordered anodic aluminum oxide (AAO), consisting of an ordered array of nanopores, has become one of the most habitual platforms for nanostructure fabrication [1–3]. It is highly versatile with respect to the diameter and length of the pores, of relatively low cost, has a high long-range ordered architecture, and uniform tailored pores with hexagonal symmetry. These aspects allow the preparation of both one-dimensional materials and nanostructured surfaces comprised of arrays of a variety of nanoelements, such as dots, pillars, holes or tubes [4–7]. Moreover, due to its physico-chemical properties and high stability, nanostructures of any chemical nature can be templated by this approach, from metals and semiconductors to biomacromolecules [3,4,8–10].

Self-ordered anodic aluminum oxide (AAO) covers a broad range of pore diameters (d_p), typically from 20 to 400 nm, by carrying the anodization out in different conditions (Fig. 1 [11]) [6,12–14]. The low diameter region, up to 100 nm, has been traditionally the most studied one and few attentions have been paid on the relatively hardly controlled high-voltage anodizations, which lead to large diameters (from 100 to 400 nm). However, in recent

years, the “large-diameter-pore” AAOs have attracted increasing interest since enables the application in: 2D photonic crystals to modify electromagnetic waves [10,11], tissue engineering [15] or fabricating soft-matter nanotubes [7,16,17], for example. However, two points are still challenging in relation to well-ordered “large-diameter pore” AAO templates. (i) On the one hand, the aggressive conditions of reaction required for their synthesis frequently induces the breakdown or “burning” of the oxide film as a consequence of local current concentrations. (ii) Despite the effort made in the last years, there is still a gap in the accessible diameter values between 80 and 180 nm for ordered AAOs obtained under Mild Anodization conditions [18] (dark background region in Fig. 1). This diameter range is just the appropriate for investigating confinement effects on many processes with length scales of the order of tens of nm, such as large-scale dynamical processes of polymers and biomacromolecules [19,20], and thus, to establish the crossover point from a bulk-like behavior to a confined-behavior. Moreover, been able to completely cover the whole diameter region from 20 to 400 nm is crucial for developing tailored and well defined porous membranes for fractionation and filtration.

However, the reaction conditions for achieving self-ordered AAO templates with such diameter values have not been up to now described, to the best of our knowledge. It is well known that the pore diameter (d_p) and the interpore distance (D_{int}) are connected through the ratio $d_p/D_{int} \approx 0.35$ for of self-ordering in Mild Anodization conditions [21]. Thus, the interpore distances of the AAOs with diameters between 80 and 180 nm should be between

^{*} Corresponding authors. Tel.: +34 91 806 07 00; fax: +34 91 806 07 01.

E-mail addresses: jaimemartinp@imm.cnm.csic.es (J. Martín), marisol@imm.cnm.csic.es (M. Martín-González).

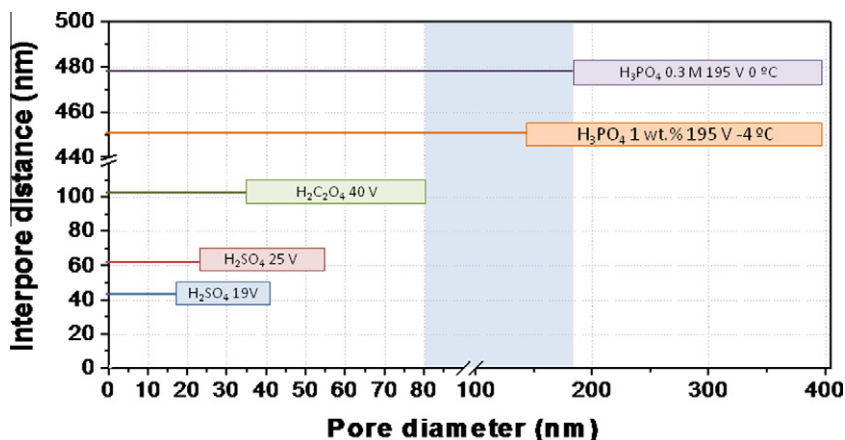


Fig. 1. Summary of pore diameters and corresponding inter-pore distances accessible with ordered AAO anodized in mild conditions. The different line corresponds to in H₂SO₄ 10 wt.% under 19 V [14] (blue line), in H₂SO₄ 0.3 M under 25 V [13] (pink line), in H₂C₂O₄ 0.3 M under 40 V [6] (green line), H₃PO₄ 0.3 M under 195 V (purple line), and H₃PO₄ 1 wt.% under 195 V (the anodization performed here, orange line). The colored background represents the non-accessible diameter pore range with self-ordered AAO, until date. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

230 and 460 nm. On the other hand, the D_{int} is known to be directly proportional to the applied voltage (V), being the proportionality parameter ζ equal to 2.5 nm/V [18]. Therefore, the voltage needed for achieving that D_{int} range should be in the range between 110 and 185 V. These relatively high voltage values require phosphoric acid (H₃PO₄) as electrolyte, but, to the best of our knowledge, the conditions for the periodic pore arrangement for anodization in H₃PO₄ acid solutions have not been found below 195 V. On the other hand, one could also get pores with diameters above the lower limit of the inaccessible diameter range, *i.e.* 80 nm, by widening originally smaller diameter pores. This fact could allow carrying the anodization out at voltages slightly lower than 110 V and thus in less aggressive electrolytes, such as oxalic acid (H₂C₂O₄). However, again, the self-ordering conditions for anodizations in H₂C₂O₄ are far away from 110 V (in Mild Anodization conditions), being for the moment, impossible to cover the diameter range between 80 and 180 nm following this approach either.

An additional limitation associated with the use of phosphoric acid as electrolyte is the strong chemical dissolution of pore walls that promotes the increase in the pore sizes [22]. According to literature, Masuda's pioneering synthetic procedure leads to pores of 160–180 nm in diameter [12,23–25], however, due to solvent effect of the electrolyte, pore diameter significantly increases as anodization goes by. Therefore, also from this point of view, it would be interesting to reduce the diameter of pores of the original AAO so a broader diameter range will be covered.

The pioneering synthetic procedure of “large-diameter-pore” AAO was reported by Masuda et al. [12]. The paper described the anodization of an aluminum foil using 0.3 M phosphoric acid as electrolyte, under an applied voltage of 195 V, and at 0 °C. However, this procedure requires highly efficient heat dissipation for the exothermic reaction, which, from a practical point of view, it is not so easy to achieve. Roughly, only one out of four samples was successfully obtained using the previous conditions in our lab. The localized increases of temperature on the anodic layer promote high current flow and the breakdown of the oxide films (“burning”), which leads to a loss of uniformity and ordering of the pore array. Several approaches have been tried in order to avoid the “burning”: (i) A reduction of the applied voltage; nevertheless, the obtained pores were more inhomogeneous and less ordered [14]. (ii) The addition of organic compounds [22,26] and (iii) the exchange of the first anodization by a lithographic process, which substantially increases the cost and the complexity of the procedure [27]. (iv) Finally, Li et al. reported an anodization in sim-

ilar conditions of Masuda's, but at lower temperature [28]. This last approach nicely works; the breakdown of the AAO films is efficiently avoided, and well ordered pore arrangements are obtained. However, in that paper little information about the anodization was reported.

In this work, we report an exhaustive study on AAO with 140 nm in diameter pores obtained by anodizing at 195 V under very low temperature –4 °C. Therefore, we are able to reduce in 40 nm the upper limit of the non-accessible diameter range. The anodization is completely stable and the “burning” of the oxide is completely avoided. Also, methanol was added to prevent the electrolyte from freezing at such a low temperature. Moreover, some of the most relevant aspects to facilitate the preparation of self-ordered AAO templates with pores around 140 nm such as the growth rate, the current density, and the optimized first anodization length, are shown together with the most important morphological characteristics of the obtained nanostructure, such as, the pore diameter (d_p), the inter-pore distance (D_p), the porosity (P), and the length of the ordered domains.

2. Materials and methods

Ordered AAO templates have been prepared by a two-step electrochemical anodization of aluminum [6,28]. Firstly, ultrapure (99.999%) aluminum foils (Advent Research Materials, England), were cleaned and degreased by sonication in acetone, water, isopropanol, and ethanol. The used aluminum foils were disks with 3 cm diameter (an area of approx. 7 cm²) and had a thickness of 0.5 mm. The anodized area was also circular with 2 cm of diameter.

Foils were then electropolished in a solution of perchloric acid/ethanol (1/3) under a constant voltage of 20 V, and after that, the first anodization was achieved. A phosphoric acid/methanol/water mixture (1:10:89, weight proportions) was used as electrolyte, under a constant potential of 195 V and at –4 °C. Ten weight percent of methanol was added to the electrochemical bath in order to avoid the electrolyte from freezing. The total volume of electrolyte was 500 ml. The electrochemical cell consisted of a jacketed glass cylindrical reactor with a volume of approximately 700 ml. The refrigeration liquid was an ethylene glycol/water mixture (50/50) which in turns is cooled by a circulating cooling bath. The electrolyte was vigorously stirred (approx. 600 rpm) by means of a mechanical stirring set up, with a four bladed PTFE stirrer. To avoid completely the breakdown, the anodization began at an applied

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