Materials Letters 85 (2012) 146–148

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Formation of dense alumina nanowires from anodic alumina membranes

L.A. Meier, A.E. Alvarez, D.R. Salinas [1,2], M.C. del Barrio *

Instituto de Ingeniería Electroquímica y Corrosión (INIEC), Departamento de Ingeniería Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:
Received 12 April 2012
Accepted 23 June 2012
Available online 2 July 2012

Keywords:
Alumina nanowires
AAO
Anodizing
SEM

ABSTRACT

Dense alumina nanowire arrays were formed by a method that consists in a partial dissolution of the anodized aluminium oxide (AAO) membrane by chemical attack in 2 M H_3PO_4 during 45 minutes, as a step immediately following the second anodizing. During this procedure the pore walls are partially dissolved by a controlled acid attack and the alumina nanowires arise as a consequence of this process, being the vertices of the hexagonal pores the origin of them. The thickness of them ($\approx$ 40 nm) is slightly smaller than the diameter corresponding to the triple junction point of the membrane. By controlling the dissolution time it is possible to obtain alumina nanowires covering virtually the entire surface with lengths similar to the thickness of the AAO membrane that exceeding 10 μm. The steps of nanowires formation are discussed as follows.

1. Introduction

In the last years, nanostructures such as nanodots, nanowires and nanotubes have been of considerable attention due to their chemical and physical properties and its various applications.

In particular, one-dimensional nanostructures (1-D) of alumina are of special interest due to their dielectric and catalytic properties. They offer promising technological applications, which are attributed to their high strength, corrosion resistance, chemical stability, low thermal conductivity and good electrical insulation [1]. Moreover, alumina nanowires have become a thrilling field of study because they are useful for water purification filter technology owing to their large surface area and highly electropositive surface [2,3].

The chemical etching of a porous anodic alumina membrane is considered as an easy and cost effective way to fabricate uniform diameter alumina nanowires [2]. In this sense, several groups of authors reported different alumina nanostructures that were fabricated via a simple etching method in NaOH [4–7] or in a chromic and phosphoric acid solution [1,7]. Alternatively, Mei et al. [8] produced alumina nanotube and nanowire arrays by etching the AAO in 5%w phosphoric acid solution and subsequent thermal treatment. The diameter of the nanowires is about 30–40 nm, which corresponds to the thickness of the wall between the nanopores. These authors concluded that the formation of one individual nanowire can be attributed to the splitting of walls surrounding three nanopores.

On the other hand, McGrath et al. [9] formed alumina nanowires in a one-step anodization process using a 0.1 M phosphoric acid solution. These authors proposed that while the pores grow by the anodization, the pore walls are slowly attacked by chemical dissolution, thus widening the pores and generating nanowires of about 50 nm in diameter.

All the previously mentioned authors agree on the steps of alumina nanowires formation. The dissolution starts in the thinnest parts of the alumina membrane walls causing nanorods formed by three adjacent pores. In other words, by etching the alumina membrane, the pore walls are first dissolved because they are the thinnest regions but the vertices remain on the surface resulting in alumina nanowires.

In our previous work [10], we demonstrated that a complete dissolution of the AAO template can be achieved by immersing the membrane in a 2 M H_3PO_4 acid solution. During this study we observed that prior to the complete dissolution, alumina nanowires were formed. The main objective of this paper is to present a simplified and virtually free of pollutants method for the formation of alumina nanowires. The time required to form these nanostructures is considerably shorter than the reported by other authors. The morphologies obtained were observed by Scanning Electron Microscopy (SEM).

2. Experimental procedure

The templates were fabricated from high purity (99.99%) aluminium foils by applying a two-step anodizing process [1,10,11]. Anodization was conducted under constant cell

* Corresponding author. Tel./fax: +54 291 4595101x3611.
E-mail address: mcdb@uns.edu.ar (M.C. del Barrio).

[1] ISE member.

[2] Professor Salinas died during the development of this paper.

0167-577X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2012.06.085

potential of 40 V in a 0.3 M oxalic acid electrolyte. A platinum mesh was used as counter electrode. The alumina nanowires were formed by chemical attack in a 2 M H_3PO_4. All the electrolytes were prepared from supra-pure chemicals (E. Merck, Darmstadt) and fourfold quartz-distilled water. Also, they were deaerated by bubbling highly purified nitrogen prior to each experiment. This procedure was performed at a temperature $T=25$ °C. SEM studies were carried out using an EVO 40 XVP (LEO) microscope, with an accelerating voltage of 20 keV. The surface was coated with a thin conducting Au film.

3. Results and discussion

The alumina membrane surface morphology, generated by two anodizing steps [1,10,12], shows the typical regular and uniform structure, constituted by an array of highly ordered hexagonal pore domains with columnar channels in the cell centre (Fig. 1a). The hexagonal shape of the pores can be perfectly distinguished, being the pore diameter between 60 and 75 nm, while the wall thickness is about 30–40 nm.

Fig. 1b shows a SEM image of the first step of the alumina nanowires formation after the chemical attack in a 2 M H_3PO_4 for a period of approximately 5 min. During the dissolution of alumina membranes, the thinnest regions are the first to be dissolved. It is important to highlight that the pore walls linking three neighbouring cells are thinner than the other regions. After 10 min of dissolution (Fig. 1c), the thinnest walls are broken and the triple-junction points are separated. This process starts from top to bottom of the membrane. Thirty minutes later, the walls are completely dissolved, only the triple-junction points which generate the nanowires remaining. This procedure is illustrated in Fig. 2a, which shows that nanowires are going out from the triple-junction points of the AAO. Finally, after 45 min of dissolution, the alumina membrane is completely dissolved and nanowires collapse under gravity, forming groups with the same orientation (Fig. 2b). The nanowires have uniform diameter with a typical thickness of 40 nm and their length exceeds 10 μm, which is proportional to the original thickness of the alumina membrane.

It is known that the AAO template is composed by amorphous alumina and during the alumina etching process the lateral dissolution of pores is faster than the vertical dissolution. This lateral dissolution is possibly due to a pH gradient along the pores that favours the dissolution from top to bottom. When the acid solution diffuses into the channels, the pore walls are dissolved by the active etching component H^+. The thinnest part of the wall between two neighbouring pores is etched away at first and, as a consequence, the acid attack produces alumina nanowires. The triple junction points may have a different crystal structure, less soluble, more resistant to attack than the rest of the porous AAO layer. This may be due to compressive stresses at the triple junction during the membrane formation [9,13,14]. The pH gradient quickly changes along the pores because the acid

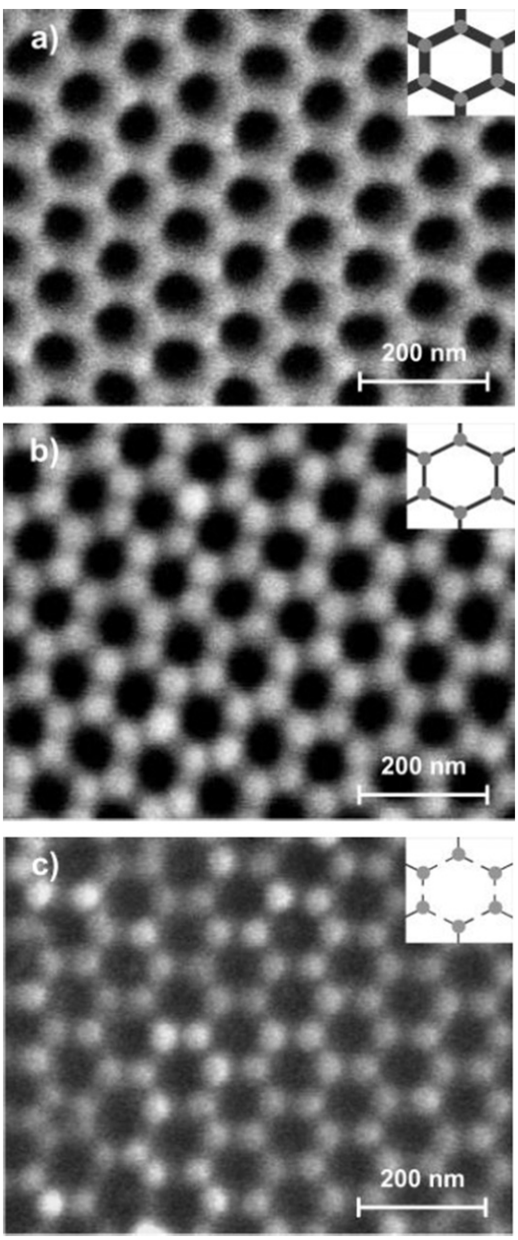

Fig. 1. SEM topographical images of the AAO obtained after chemical attack, in a 2 M H_3PO_4 at 25 °C during: (a) 5 min. (b) 10 min. (c) 15 min. Inset: schematic diagram of the corresponding step of the alumina nanowires formation process.

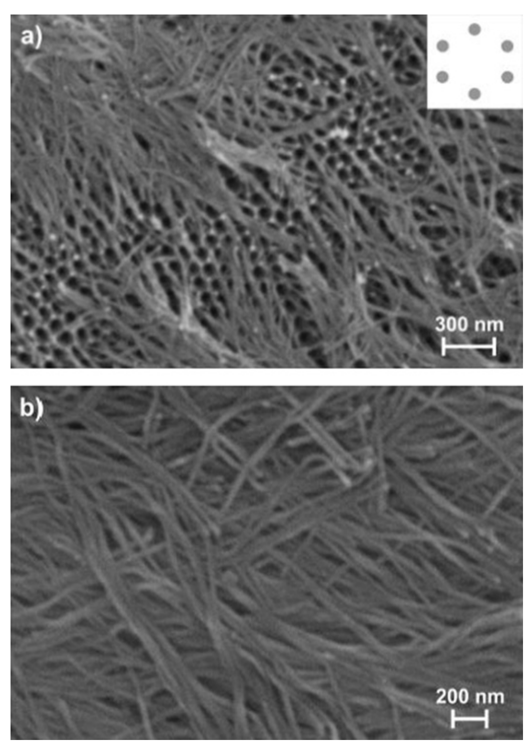

Fig. 2. SEM topographical images of the alumina nanowires: (a) coming out the triple-junction points of the AAO, (b) dense arrays after 45 min of dissolution.

solution can penetrate inside the pores while their walls disappear, forming the nanowires. This pH gradient permits the dissolution until it reaches the bottom of the membrane. The vertical dissolution of the nanowires cannot be discarded, but its rate is slower than the lateral dissolution. By controlling the dissolution time it is possible to obtain alumina nanowires with lengths similar to the thickness of the AAO membrane and slightly thinner than the one corresponding to the triple points.

This study has several advantages compared with what is already known in the literature. We can show that it is not necessary to apply annealed [14–16] for several hours to achieve membranes with highly ordered pores and nanowires with a relatively uniform size distribution [10]. To generate the AAO membrane we operate at room temperature unlike many authors who work at different temperatures [1,7,16–18] or/and higher constant cell potential [1]. Furthermore, relatively short periods of times are used both to obtain the AAO membrane and the nanowires.

4. Conclusions

This paper presents an alternative method to obtain both the AAO membrane and the nanowires in a relatively short period of time. The method used is simpler, milder and with low environmental impact. This technique consists in a partial dissolution of the membrane by chemical attack in 2 M H_3PO_4 during 45 min. It was found that controlling the dissolution time it is possible to obtain alumina nanowires with lengths similar to the thickness of the AAO membrane and slightly thinner than the one corresponding to the triple points. Alumina nanowires, of about 40 nm in diameter and with lengths exceeding 10 μm, cover virtually the entire surface, being the vertices of the hexagonal pores the origin of them.

The main advantages of this work can be summarized as follows:

- Not need to apply annealed for several hours (temperature range: 350–500 °C) as were used by other authors.
- The AAO membrane can be obtained working at room temperature and relatively low constant cell potential.
- Relatively short period of times are spent both to obtain the AAO membrane and the nanowires.
- A more clean, free of heavy metals method is used both to obtain the AAO membrane and the alumina nanowires.
- It is possible to obtain membranes with highly ordered pores and nanowires with a relatively uniform size distribution.
- We reported a much milder wet etching of AAO membrane using only the common H_3PO_4 solution instead of NaOH solution.

Acknowledgements

The authors wish to thank the Universidad Nacional del Sur (PGI24/M128) Argentina, for financial support of this work. L.A. Meier acknowledges a fellowship granted by CONICET. L.A. Meier, A.E. Alvarez and M.C. del Barrio especially grateful to D.R. Salinas for his direction, support and encouragement.

References

[1] Pancholi A, Stoleru VG, Kell CD. Nanotechnology 2007;18:215607.
[2] Kim J, Choi YC, Chang K-S, Bu SD. Nanotechnology 2006;17:355–9.
[3] Han JK, Kim J, Choi YC, Chang K-S, Lee J, Youn HJ, et al. Physica 2007;E36:140–6.
[4] Xiao ZL, Han CY, Welp U, Wang HH, Kwok WK, Willing GA, et al. Nano Lett 2002;2:1293–7.
[5] Liu SM, Zhang WD, Liu ZL, Liu LH. Appl Catal A 2005;287:108–15.
[6] Xu XJ, Fei GT, Zhu LQ, Wang XW. Mater Lett 2006;60:2331–4.
[7] Zhou J-h, He J-p, Zhao G-w, Zhang C-x, Zhao J-s, Hu H-p. Trans Nonferrous Met Soc China 2007;17:82–6.
[8] Mei YF, Siu GG, Fu RKY, Chen P, Wu XL, Hung TF, et al. Appl Phys 2005;97:034305.
[9] McGrath RS, Misra M, Sklar GP, LaCombe JC. Mater Res Soc Symp Proc 2005;876E R1.3.1.
[10] Meier LA, Alvarez AE, Salinas DR, del Barrio MC. Mater Lett 2012;70:119–21.
[11] Masuda H, Hasegwa F, Ono S. J Electrochem Soc 1997;144:L127–30.
[12] Thongmee S, Ding J, Jiabao Y, Pan H, Yi JB, Lin JY. Synth React Inorg Met–Org Nano-Met Chem 2008;38:469–74.
[13] Hu G, Zhang H, Di W, Zhao T. Appl Phys Res 2009;1:78–82.
[14] Tian M, Xu S, Wang J, Kumar N, Wertz E, Li Q, et al. Nano Lett 2005;5:697–703.
[15] Rana K, Kucukayan-Dogu G, Benju E. Appl Surf Sci 2012;258:7112–7.
[16] Xu XJ, Fei GT, Zhu LQ, Wang XW. Mater Lett 2006;60:2331–4.
[17] Zhao S, Chan K, Yelon A, Veres T. Nanotechnology 2007;18:245304.
[18] Gerein NJ, Haber JA. J Phys Chem B 2005;109:17372–85.