



A clean method to obtain a porous alumina template

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, Avda. Alem 1253, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:

Received 10 June 2011

Accepted 30 October 2011

Available online 29 November 2011

Keywords:

AAO

Alumina template

Anodisation process

SEM

ABSTRACT

The formation of a porous anodic alumina template using a two-step anodisation process and solutions free of Cr ions was studied. Anodising was conducted under a constant cell potential of 40 V in a 0.3 M oxalic acid electrolyte at 298 K. The chemical dissolution of the first anodising step was carried out in a 2 M phosphoric acid solution, at 298 K. Each step of the template formation was observed by SEM (scanning electron microscopy), evaluating the structural characteristics of the corresponding surfaces. The resulting template has rounded pores (≈ 65 nm) that are aligned forming small domains. Although the membrane obtained does not contain fully hexagonal pores, such as those obtained using chromic acid as an attack agent between the two anodising steps, it is equally useful for the finally purpose of producing a template for the growth of nanowires.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Anodised aluminium oxide (AAO) membranes are of considerable importance due to their application as a template for nanowires growth. In the deposition attended by templates, the chemical stability and the mechanical properties of the template used are important, as well as the diameter, uniformity and density of the pores. The template is obtained after two-step anodisation process that consists in a first anodisation in an acid solution, followed by a chemical etching to remove the oxide layer previously formed. Then, a second anodisation is performed under similar conditions as used at the first one. The obtained film has a uniform thickness and presents a regular hexagonal arrangement of parallel channels perpendicularly aligned to the surface, with a high mechanical and corrosion resistance, good chemical stability, low electric and thermal conductivity, but high ionic conductivity. [1–5].

In the last years, numerous works have been published about the steps of the anodisation process. Almost all authors employed a mixed solution of H_2CrO_4 and H_3PO_4 to dissolve the first anodisation step. It is known that this solution is hazardous and environmental unfriendly. Stein et al. [6] proposed an alternative and friendly method to dissolve the first anodising step, and monitored the structural characteristics of the template formed by in situ spectroscopic ellipsometric combined with electrochemical measurements. These authors showed an AFM (atomic force microscopy) topographical image of an anodised

aluminium electrode after a chemical dissolution in 2 M H_3PO_4 , but do not study the subsequent formation of the alumina membrane.

The aim of the present work is to form and characterise aluminium oxide templates that will permit the subsequent electrodeposition of metallic nanowires, by dissolving the first anodisation layer in a free Cr ions solution.

2. Experimental procedure

The templates were obtained by anodic oxidation of high purity (99.99%) aluminium foils. These foils, of 0.5 mm in thickness with an exposed area of 1 cm², were subjected to a sequence of mechanically and electrochemically polished in a solution of HClO_4 and 2-butoxyethanol [7] until a mirror-like finished surface was obtained. Following each polishing treatment, the electrode was rinsed in fourfold quartz-distilled water. Finally, the edges of the electrodes were coated with epoxy resin to prevent current leakage. A two-step anodisation process [2,8] was employed to form the AAO templates. Anodising was conducted under a constant cell potential of 40 V in a 0.3 M oxalic acid electrolyte at 298 K. After the first anodisation, a chemical attack was performed in order to etch of the oxide layer previously formed. This chemical dissolution was carried out in a 2 M phosphoric acid solution, at 298 K, as was proposed by Stein et al. as an alternative method [6]. The second anodisation was developed under the same condition as used at the first one. All the electrolytes were prepared from supra-pure chemicals (E. Merck, Darmstadt) and fourfold quartz-distilled water and were deaerated by bubbling highly purified nitrogen prior to each experiment. All the steps were developed at 298 K. A platinum mesh was used as counter electrode. Each step of the template formation was followed by SEM, using an EVO 40 XVP (LEO) microscope with an accelerating voltage of 15 keV and the samples surface was coated with a thin conducting Au film.

* Corresponding author. Tel.: +54 291 4595101x3611; fax: +54 291 4595182.

E-mail address: mcdb@uns.edu.ar (M.C. del Barrio).

¹ ISE member.

² Professor D.R. Salinas died on 15th July 2011, during the procedure of publication of this paper.

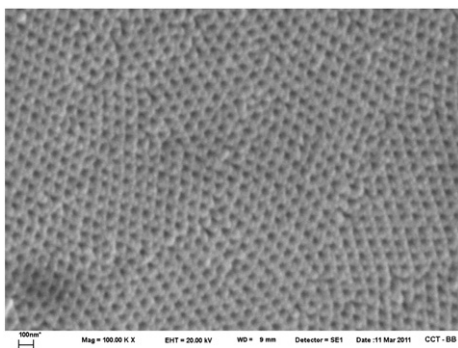


Fig. 1. SEM topographical image of the anodic aluminium oxide template obtained after the first anodisation step, in a 0.3 M oxalic acid for 3 h at 40 V and 298 K.

3. Results and discussion

Two step anodisation process involves, as a first step, the growth of an oxide layer that must be subsequently dissolved. The resulting aluminium oxide free surface acts as a substrate for the growth of a new more ordered oxide layer, during the second anodising step.

Fig. 1 shows a SEM image of the AAO surface after the first anodising step. The pores are of approximately 40 nm in diameter and are aligned forming small domains. The wall thickness is large. In order to dissolve this oxide layer, a chemical attack in 2 M phosphoric acid solution during 2 h, at 298 K, was performed.

Fig. 2 displays a SEM topographical image of the aluminium oxide free surface, which corresponds to the inter-phase between the aluminium metal and the barrier layer. The image shows a relatively uniform structure of rounded pits, forming small domains randomly distributed. The pits exhibit a size of approximately 70 nm in diameter

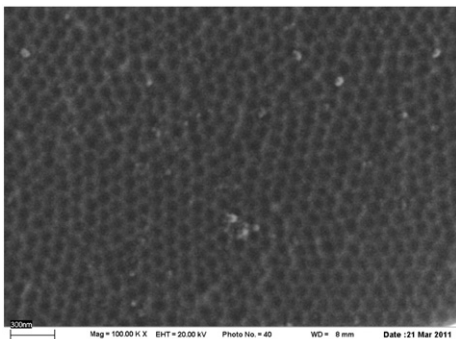


Fig. 2. SEM topographical image of the aluminium surface after removing the first oxide layer. The chemical dissolution was carried out in a 2 M phosphoric acid at 298 K.

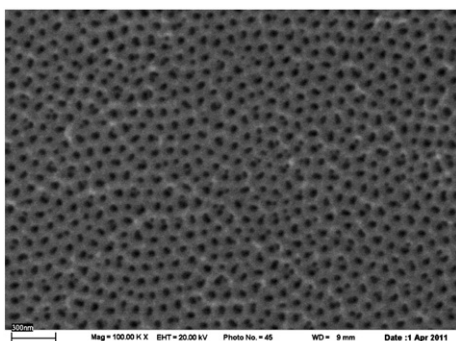


Fig. 3. SEM topographical image of the anodic aluminium oxide template obtained after the second anodisation step, in a 0.3 M oxalic acid for 3 h at 40 V and 298 K.

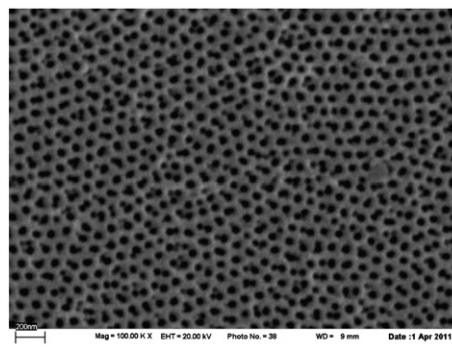


Fig. 4. SEM topographical image of the anodic aluminium oxide template obtained after a pores widening in a 0.5 M phosphoric acid at 298 K.

and seem to be arranged following a quasi-hexagonal order. In order to analyse the porous layer formed from this pre-structured surface, a second anodisation process was performed. The image obtained after this procedure is shown in **Fig. 3**. This topology is similar to that reported using a chromic acid solution [3,8–14] and is constituted by an ordered nanopore array (≈ 50 nm in diameter). In our case, the pores are rounded and are aligned forming small domains. Because the wall thickness is relatively large (≈ 60 nm) and in order to expand the diameter of the pores, the electrode was immersed in a 0.5 M phosphoric solution, during 45 min (**Fig. 4**).

As a consequence, the wall thickness decreases considerably (≈ 40 nm) and pores reach a diameter of approximately 70 nm. The location of the pores is in accordance with the pre-structured surface shown in **Fig. 2**. This implies that the porous layer formed during the second anodising step grows following the concave pattern created after the dissolution of the first porous oxide layer. It is important to note that some walls seem to be dissolved joining neighbouring pores, but this dissolution only occurs in the outermost surface and it is equally useful for the finally purpose of producing a template for the growth of nanowires.

Further work is required to verify the proper growth of the nanowires in such template, which is now in progress.

4. Conclusions

In this paper, the formation of a porous anodic alumina template using a two-step anodisation process and solutions free of Cr ions was studied. Each step of the template formation was observed by SEM, evaluating the structural characteristics of the corresponding surfaces. The resulting template has rounded pores (≈ 65 nm) that are aligned forming small domains. Although the membrane obtained does not contain fully hexagonal pores, such as those obtained using chromic acid as an attack agent between the two anodising steps, it is equally useful for the purpose of producing a template for the growth of nanowires.

Acknowledgements

The authors wish to thank the Universidad Nacional del Sur (PGI 24/M110) Argentina for financial support of this work. Lorena 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] Bhushan B, editor. Springer handbook of nanotechnology. New York: Springer; 2007.
- [2] Masuda H, Hasegawa F, Ono S. *J Electrochem Soc* 1997;144:L127–30.
- [3] Li AP, Müller F, Birner A, Nielsch K, Gosele U. *J Appl Phys* 1998;84:6023–6.
- [4] Hurtado MJ, Capitán MJ, Alvarez J, Fatás E, Herraste P. *Port Electrochim Acta* 2007;25:153–62.

- [5] Pribat D, Cojocaru CS, Gowtham M, Marquardt B, Wade T, Wegrowe JE, et al. *C R Phys* 2009;10:320–9.
- [6] Stein N, Rommelfangen M, Hody V, Johann L, Lecuire JM. *Electrochim Acta* 2002;47:1811–7.
- [7] Salinas DR. PhD Thesis, Universidad Nacional de Sur, Argentina, 1989.
- [8] Pancholi A, Stoleru VG, Kell CD. *Nanotechnology* 2007;18:215607.
- [9] Ghorbani M, Nasirpour F, Irajizad A, Saedi A. *Mater Des* 2006;27:983–8.
- [10] Li F, Zhang L, Metzger R. *Chem Mater* 1998;10:2470–80.
- [11] Mozalev A, Magaino S, Imai H. *Electrochim Acta* 2001;46:2825–34.
- [12] Pang YT, Meng GW, De Zhang L, Shan WJ, Zhang C, Gao XY, et al. *Solid State Sci* 2003;5:1063–7.
- [13] Kim J, Choi YC, Chang K-S, Bu SD. *Nanotechnology* 2006;17:355–9.
- [14] Rahimi MH, Saramad S, Tabaian SH, Marashi SP, Zolfaghari A, Mohammadinezhad M. *Appl Surf Sci* 2009;256:12–6.