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Fabrication and characterization of porous alumina membranes

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Abstract

Porous alumina membranes are often used as templates for synthesizing nanowire arrays due to their well-defined pore structures, high pore densities and uniform pore sizes. In this study, porous alumina with pore diameters of 15-135 nm was prepared via a two-step anodization process using sulphuric acid and oxalic acid as electrolytes. The anodization process was carried out in the voltage range of 15 V to 60 V, using pure aluminum foil as anode and platinum as cathode. Pore diameters, pore depths and the spacing between adjacent pores were carefully controlled by the anodizing conditions used. The morphologies and pore structures of the templates produced were studied using plan-view and cross-sectional scanning electron microscopy (SEM).

Keywords: Porous alumina, anodization, templates.

1. Introduction

In recent years, low-dimensional nanostructures such as nanowires, nanotubes and nanoribbons have been intensively studied. In comparison to bulk materials, these nanostructures offer new properties that have been confirmed experimentally; e.g. superconductivity and enhanced magnetic coercivity. Low-dimensional nanostructures have many potential applications in various fields like sensors, lasers, field-effect transistors, optical waveguides, resonators, cantilevers and generators. In order to realize their potentials, it is important to explore the techniques used for synthesizing this class of materials. Some of the methods are expensive and require high temperature or high vacuum for synthesis, e.g. chemical vapor deposition [1], high temperature catalytic processes [2], magnetron sputtering or top-down e-beam lithography. Others produce tangled mixtures of nanowires having uncontrollable lengths, diameters and morphologies. Electrodeposition, in comparison, offers many advantages including precisely controlled operation at near-room temperatures, low energy requirement, rapid deposition rate, low cost and easy scalability, environmentally friendly and flexibility in geometry designing [3]. Generally, two techniques used to produce low-dimensional nanostructures via electrodeposition, namely, template-assisted electrodeposition and template-free electrodeposition [4]. In template-assisted electrodeposition, low-dimensional nanostructures are commonly electrodeposited using templates like porous alumina and track-etched polycarbonate membranes.

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2. Experimental

In this work, a two-step anodization process was employed for the fabrication of porous alumina membranes. The effects of anodizing electrolytes and anodization conditions on pore structures of the membranes were systematically studied. High purity aluminum foil (Al 99.995%, thickness 0.11 mm) was first purged with acetone in an ultrasonic cleaner to degrease its surface. The sample was subsequently etched in 1 M NaOH followed by rinsing with ultrapure water. Electrochemical cell for the anodization process consisted of a platinum plate as cathode and an aluminum foil as anode. The aluminum foil was anodized for 1 hour under constant voltages of 15-25 V and 40-60 V using 1.8 M sulfuric acid and 0.3 M oxalic acid as electrolytes respectively. After the first anodization, a strip-off process was carried out in a mixture of 1.8% chromic acid and 6% phosphoric acid to remove the aluminum oxide formed, leaving behind nanosized and well-ordered concave patterns on the aluminum foil. This would act as the self-assembled mask for the subsequent anodization process. The second anodization process was performed using the same conditions as first anodization for 4 hours. After the second anodization, remaining aluminum foil was removed in a mixed solution of $CuCl_2$ and HCl. The bottoms of the pores, closed by barrier layer, were opened using 5% H_3PO_4 solution. Microstructural characterizations on the template produced were subsequently performed using scanning electron microscope and X-ray diffraction to elucidate its morphology and microstructure.

3. Results and Discussion

As shown in Table 1, the current density increases slowly with increasing applied anodization potential.

Table 1: Applied potentials and corresponding current densities for aluminum anodised in oxalic acid at same temperature and electrolyte concentration, with constant agitation of the electrolyte (500 rpm)

Anodisation potential (V)	40	55	60
Current density (mA cm^{-2})	5.66	11.32	16.98

The formation rate of the alumina was determined experimentally by measuring the thickness of porous alumina membrane produced. Formation rates of between 86 nm min^{-1} to 146 nm min^{-1} were achieved at applied potentials of between 40 V and 60 V. Temperature was found to have a significant influence on the growth of porous alumina membranes. Growth rates of porous alumina (anodized in oxalic acid at 55 V) were 90 nm min^{-1} and 120 nm min^{-1} at 10°C and 20°C respectively. Theoretically, there is an approximate factor of two for volume expansion from aluminum to alumina. Nevertheless, actual thickness of alumina after anodization could be much thinner, especially at lower temperatures, when the anodising rates are slow due to chemical dissolution of alumina during anodization. The dissolution rate is a function of anodizing solution composition and operating temperature [5].

Fig. 1 shows the typical SEM images of porous alumina membranes which have been anodised in 0.3 M oxalic acid at 10°C. As shown in Fig. 1(a), most of the pore channels in the porous alumina membranes are regularly aligned with little or no tilt with respect to the surface normal and without lateral branching. The porous alumina membranes exhibit regular well-ordered honey-comb pore morphology as exemplified in the plan-view SEM image in Fig. 1(b). Prolonged pore widening process tends to suffer from the undesirable effects of irregular pore enlargement, merging of neighbouring pores and damage of the upper surface of porous alumina membranes as shown in Fig. 1(c). Quantitative image analysis performed on pore density and porosity shows that the porous alumina templates produced have pore densities of 10^{10} pores cm^{-2} and porosities of between 0.2-0.3. Inter-pore distance and pore diameter could be precisely tuned by carefully controlling the anodization potential. Working range of anodization potentials varied according to the types of electrolytes used. For sulphuric acid, anodization was carried out at 15 to 25 V as stable anodization potentials above 25 V were difficult to maintain due to the occurrence of surface pitting. Typical anodisation voltages for oxalic acid were 40-60 V for interpore distances of 90-135 nm. Fig. 2 shows the graph of experimentally measured inter-pore distance against anodization potential at 20°C. Inter-pore distance of the lattice was found to increase linearly with voltage for both the sulphuric acid and oxalic acid electrolytes used, with a slope of 1.90 nm V^{-1} which is slightly smaller than what have been previously reported [6]. The difference may be attributed to the purity of the aluminum foil used and the number of defects present on the foil.

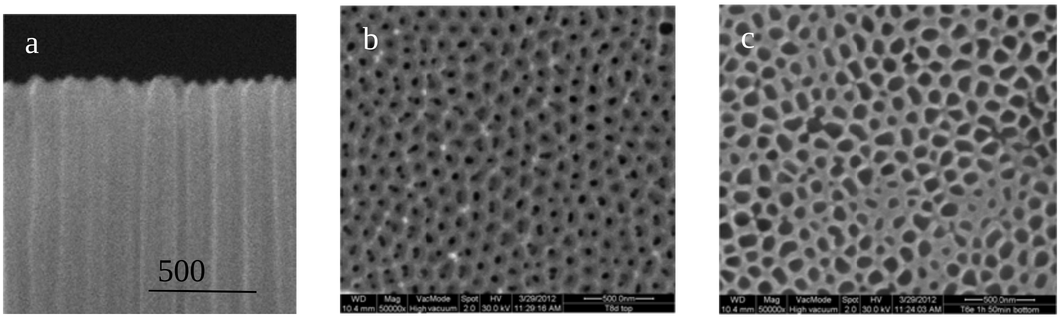

Fig. 1: SEM images of porous alumina membranes anodised in 0.3 M oxalic acid at 10°C. (a) Cross-sectional view and (b) top-view of porous alumina membrane exhibiting regular pore morphology after pore widening. (c) Top-view of the membrane showing defected pore walls after prolonged pore widening.

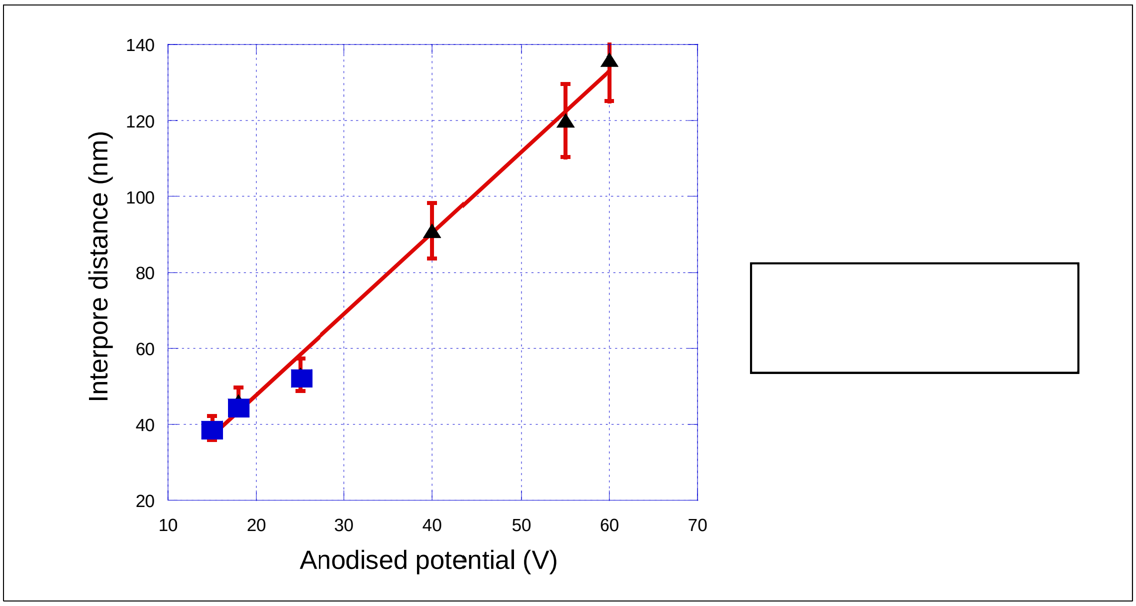

Fig. 2: Graph of inter-pore distance against anodization potential at 20°C.

4. Conclusion

Porous alumina membranes having well-ordered self-assembled pore structures with pore diameters of between 15-135 nm were successfully fabricated using a two-step anodisation process. Pore diameter and length could be controlled precisely via suitable selection of anodizing conditions such as electrolyte composition, operating temperature and applied potential. The effect of anodising condition on pore formation rate was carefully studied and the constant ratio between anodisation potential and interpore distance for the porous alumina membranes was established.

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