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Electrochimica Acta 53 (2008) 2109–2114

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Fabrication and structural control of anodic alumina films with inverted cone porous structure using multi-step anodizing

T. Nagaura [a,*], F. Takeuchi [b], S. Inoue [a]

[a] National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
[b] Department of Materials Science, Tokyo University of Science, Noda, Chiba 278-8510, Japan

Received 27 July 2007; received in revised form 24 August 2007; accepted 3 September 2007
Available online 14 September 2007

Abstract

Porous anodic alumina (PAA) film has recently attracted much attention as a key material for the fabrication of various nanostructures. In this study, a multi-step anodization and leaching process was employed to produce three-dimensional nanometer scale structured film. During the leaching process, the porous alumina film was dipped in phosphoric acid solution for pore widening. Each anodization process was followed by this leaching process. This method produced alumina film with multi-step structure. Meanwhile, with five-step film production, the structure showed inverted cone structure. We produced the low aspect ratio pores of this structure, which would be applicable for fabrications of nanomaterials. In addition, the aspect ratio was controlled by changing the anodization duration.

Keywords: Anodization; Porous alumina; Three-dimensional nanostructure; Aluminum substrate; Multi-step nanostructure

1. Introduction

PAA film has attracted considerable attention in the nanotechnology field, and has been applied to various functional nanomaterials, such as nanorods, nanodots, nanotubes and nanomembranes made from magnetic, photocatalytic, semiconductive or electronic materials [1–18]. PAA film produced by the anodization technique has a nano-scale porous structure in mass production and the pore height and diameter are controllable. The structure has a huge number of nano-scale holes whose cell diameter (pore to pore) can be controlled from about 10 nm by using sulfuric, oxalic, phosphoric or other acid solutions as the anodization solution. In recent research, the maximum cell size was increased to 1 μm by using a citric acid solution and high anodizing voltage [19]. With these films, the pore diameter can be increased within the cell size by employing a pore-widening process, which involves dipping the sample in an appropriate acid or alkaline solution after anodization.

It is easy to produce straight pores in PAA film, but researchers have also realized structures with other shapes. AC anodization in sulfuric acid produces unique PAA films with tortuous pores [20]. These films have good resistance to corrosion and are suitable for applications related to structural materials because of their thick and dense porous structure. Other research developed new structures that included pore joining and termination or pore branching beneath the cylindrical pores [21,22]. This approach uses two different anodizing voltages. The first is used to fabricate straight pores as in the conventional method. In the next step, a second voltage is employed. If a higher voltage is applied, the current increases gradually and the pores are joined or terminated according to the change in cell size. In contrast, when a lower voltage is applied, the current decreases suddenly to 0 mA, and recovers gradually to shape small pores at the bottom of holes. Also, Diggle et al. proposed a film with a different cell size [23]. This film was designed by using a voltage increase formation process. These techniques were recently utilized to produce Y-junction carbon nanotubes and porous cellular ceramic membranes [24,25]. Moreover, in recent research, 3D-shaped PAA films were developed with other anodization methods, in which two different voltages are applied under different conditions to achieve porous layers with different diameters [26]. Films with different pore diameters in the pore depth direction were also developed by employing two-step replication or heat treatment [27,28]. Yanagishita et al. fabricated ordered

* Corresponding author. Fax: +81 29 854 9060.
E-mail address: NAGAURA.Tomota@nims.go.jp (T. Nagaura).

0013-4686/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.electacta.2007.09.016

conical pores by repeated anodization and pore-widening treatment, and produced antireflection polymer surface using this film as molds [29].

This work focused on the fabrication and structural control of multi-step and inverted cone structure. In particular, employing the alternate repetition of the combination process of anodization and pore-widening treatment [29,30], we study the structural change by changing a number of repeating cycles of the combination process. Furthermore, this work also focused on the fabrication of the inverted cone structure with low aspect ratio (cone height vs. cone diameter), e.g. 1–5. At the previous nanomaterials using PAA film, the deposited materials in the pores easily drop, get together or lean on each other after chemical etching of PAA film [31]. These low aspect ratio structures would be tolerant to these problems, and thus suitable for the fabrication of functional nanomaterials. Also, these films can be mass produced and have advantage in productivity in contrast to laser processing or other process, since this fabrication process is the combination of the conventional anodization techniques and requires only simple equipments.

2. Experimental

A highly pure aluminum sheet (99.99%, 100 mm × 20 mm × 1.0 mm, Wako Pure Chemical Industry Ltd.) was used as a working electrode in the anodization process, and a carbon electrode was employed as a counter electrode. The anodization was conducted in a 2 vol.% phosphoric acid solution at 10 °C with appropriate magnetic stirring. The anodizing voltage was increased from 0 to 120 V in the first 60 s to prevent over-dissolution of aluminum, and then maintained at 120 V for 40–590 s in each process. A high-output dc power supply (PVS 600-2, Kikusui Electronics Corp.) and a large water bath were employed to apply a high voltage at a constant low temperature even when the power consumption was high, and a PC was connected to the power supply to control the anodizing voltage and monitor the current density. After anodization, the sample was dipped in a 5 vol.% phosphoric acid solution at 30 °C for 12.5–40 min to widen the holes in the PAA film during the leaching process. In order to produce the intended multi-step structures, each anodization was followed by a leaching process with various dipping durations.

The cross-sectional morphology of the PAA films produced under different conditions was observed with a field-emission electron microscope (FE-SEM: S5000, Hitachi Ltd.) after the films had been coated with a thin platinum layer.

3. Results and discussion

3.1. Fabrication approach

Fig. 1 shows the fabrication procedure with cross-sectional schematics of the PAA films. An aluminum sheet is anodized in phosphoric acid solution to fabricate cylindrical holes (Fig. 1A), and the pores are widened with a leaching process (Fig. 1B). This pore structure is equivalent to conventional film, and the thickness depends on the duration of the anodization process. After

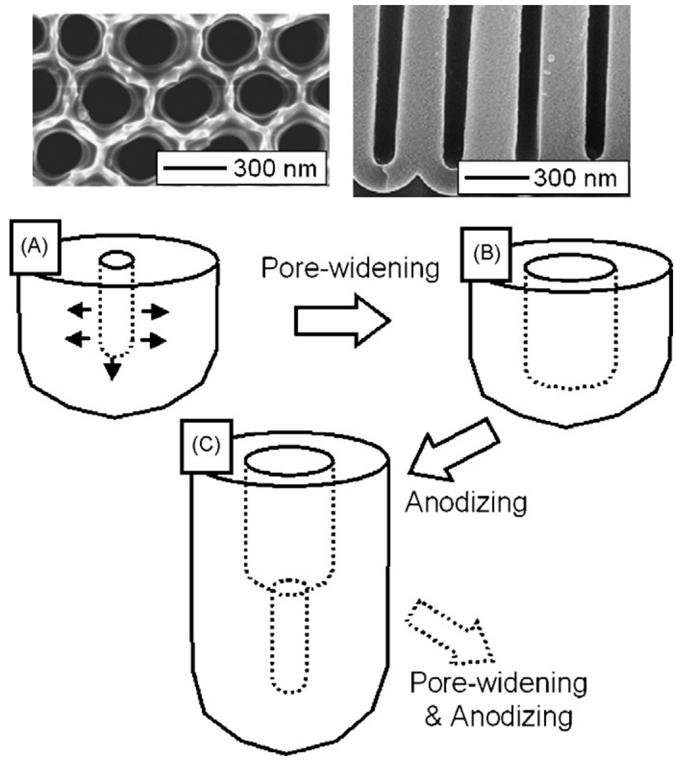

Fig. 1. Surface and cross-sectional image of PAA film, and schematic diagram of fabrication process for multi-step structure in single pore. (A) Nanoporous alumina with narrow cylindrical holes is formed by anodization. (B) Pores are widened by chemical dissolution. (C) The sample is anodized again to form new narrow pores beneath the first ones to produce a two-step stair structure.

the pores have been widened, the film is anodized once again to fabricate new narrow pores beneath the widened holes by the same voltage (Fig. 1C). The different pore diameters, which result from the pore-widening process employed between the first and second anodization, produces a two-step stair structure. With the other film production technique, the film with this two-step stair structure is subjected to more anodization and leaching process to fabricate the three- and five-step films. Each multi-step film is subjected to different pore-widening durations in the leaching process: 40 min for two-step film, 22.5 min × 2 for three-step film and 12.5 min × 4 for five-step film. During the production of these films, as the number of the stairs is increased, each pore-widening duration is decreased, so that the difference between the adjacent diameters becomes small.

Furthermore, we intend to fabricate the inverted cone structure with low aspect ratio. To obtain different cone height, anodization duration was changed during the production of the five-step film. Using anodization duration of 100, 150, 250, 480 and 650 s, we consider the aspect ratio control by the anodization duration.

3.2. Three types of multi-step structures

Three types of films with multi-step structures were achieved by repeating the anodization and pore-widening process. Fig. 2 shows cross-sectional FE-SEM images of specimens formed