Simple fabrication of highly ordered AAO nanotubes

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In this paper, simple fabrication of hexagonally well-ordered Anodic Aluminium Oxide (AAO) nanotubes with high aspect ratio was reported. AAO nanotubes were obtained by two-step anodization. High purity aluminium foils were anodized in oxalic acid solution by applying 40 V constant voltage at 0 ^{0}C for 30 min. Removing of AAO barrier layer was discussed in details. AAO nanotubes were characterized by Scanning Electron Microscopy (SEM). SEM micrographs show that fabricated AAO nanotubes are approximately 70 nm in diameters and 9 μm in lengths with 90 nm interpore distances in a relatively large area of about 2 cm^2. Fabricated AAO nanotubes have high aspect ratio approximately 130.

Keywords: Anodization, Anodic aluminium oxide, AAO template, Nanotubes

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1. Introduction

Nanotechnology is a highly multidisciplinary field, drawing from fields such as computer technology, sensor technology, applied physics, materials science, colloidal science, chemistry and even mechanical and electrical engineering. Several nanofabrication techniques have emerged over the last couple of decades. Recently, template synthesis of functional nanomaterials by chemical self-assembly method has attracted considerable attention [1]. The template method has been accomplished using a variety of templates, which are polycarbonate membranes, nanochannel alumina and anodically grown aluminium oxide (AAO). AAO nanotubes have been extensively used as a template for the fabrication of nanowires and nanotubes as it possesses many desirable characteristics, including tuneable pore dimensions, good mechanical strength and thermal stability. It is used to prepare self assembled arrays of a variety materials, metals, alloys, and multilayers that can be incorporated into chemical sensors, solar cells and magneto-optic recording media [2]. AAO nanotubes can be synthesized with very high aspect ratios. High aspect ratio photonic crystals are expected to have many scientific and technological applications, such as tuneable filters, highly efficient lasers and in the measurement of the excited lifetime of molecules [1].

Masuda et al. in 1995 [3] and Jessensky et al. in 1998 [4] described how to fabricate AAO template on Al foil with ordered hexagonally parallel nanotubes using a two step anodization technique. The nanotubes are getting ordered form the bottom and up in the anodization process. To get them completely ordered all through the template it is necessary to introduce a pre-arranged pattern before anodization. They suggested that the anodization should be carried out in two steps. Several previous studies revealed that self-ordered AAO template can only be obtained under specific conditions. For example, structures with pore spacing of 50, 65, 100, 420 and 500 nm are fabricated at 19 V and 25 V in sulfuric acid, at 40 V in oxalic acid, and at 160 V and 195 V in phosphoric acid, respectively [3-5].

A simple approach to fabricate high aspect ratio AAO nanotubes on foil was reported in this study. A novel process for removing of alumina barrier layer was developed and discussed the process in details. Alumina barrier layer of AAO template was removed in $CuCl_2$ solution by chemical etching method as usual [4, 5]. On the contrary, alumina barrier layer of the nanotubes were electrochemically removed in KCl solution for several seconds.

2. Experimental

An electrochemical cell consisted of a two-electrode system; the platinum (Pt) sheet acting as the counter electrode and Al foil acting as the working electrode was used for anodization. High purity aluminium foils ($\geq$ 99.999%) were cleaned with acetone in an ultrasonic bath, annealed at 500^0 C for 3h and electrochemically polished in $HClO_4$:C_2H_5OH (1:5) solution for 2 min at 12 V. Then the samples anodized in 0.3 M oxalic acid ($H_2C_2O_4$) solution by applying 40 V constant voltage at 0^0 C for 30 min. Grown porous AAO film was chemically etched away in 6 wt. % phosphoric and 2 wt. % chromic acid mixture at 60^0 C for 5 min to form AAO nanotubes. Then, patterned AAO film was anodized under same conditions for 2.5 h and chemically etched away for 5 min in the second anodization.

The alumina barrier layer which is the bottom of the AAO nanotubes was removed by applying negative 2.75 V to the anode that consisted of 0.2M KCl solution for 160 s. This process is necessary to provide electrochemically deposition of metal nanowires into the AAO nanotubes for future studies.

The morphology of the fabricated AAO template was studied mainly by Scanning Electron Microscopy (SEM). SEM investigations were performed on a Jeol JSM 6335-SEM instrument operating at 15 kV. Before SEM analysis each samples were coated gold film with ca. 3 nm thickness using sputtering technique.

3. Results and discussion

Current–time transients during first and second anodization of AAO template are given in Figure 1. Current-time transients of anodization process were given in limited range as especially initial minutes of the process give important knowledge to explain the formation of AAO nanotubes. At the beginning of the oxide formation, both transients had an identical behaviour. During the first anodization process, the barrier type aluminium oxide film was grown, the current decayed from approximately 950 mA to 55 mA rapidly in a few seconds. After initial two minutes, while porous type aluminium oxide film growth was beginning, the following current decayed exponentially. Then, the transients passed through minimum constant value and increased to arrive at a maximum value. The time for AAO nucleation and AAO film growth for the first anodization was longer than in the second anodization. Subsequently, current slightly decreased again and a steady current remained. For the second anodization, the minimum current density was higher than for the first anodization. After first anodization and removing the initial aluminium oxide film, the surface was patterned with nanopits. The patterned surface remained at the bottom of each transient, where the resistance was the lowest and electric field was the highest, thus, the AAO nucleation was easier on a patterned surface.

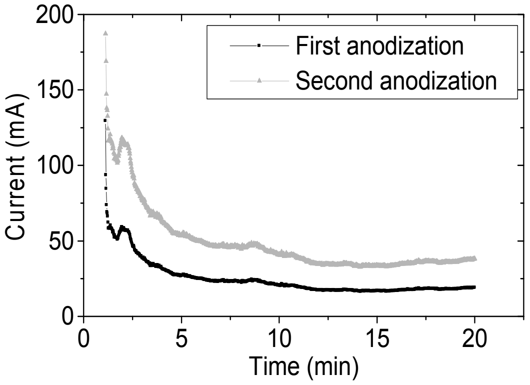

Figure 1. Current–time transients during first and second anodization of the AAO template

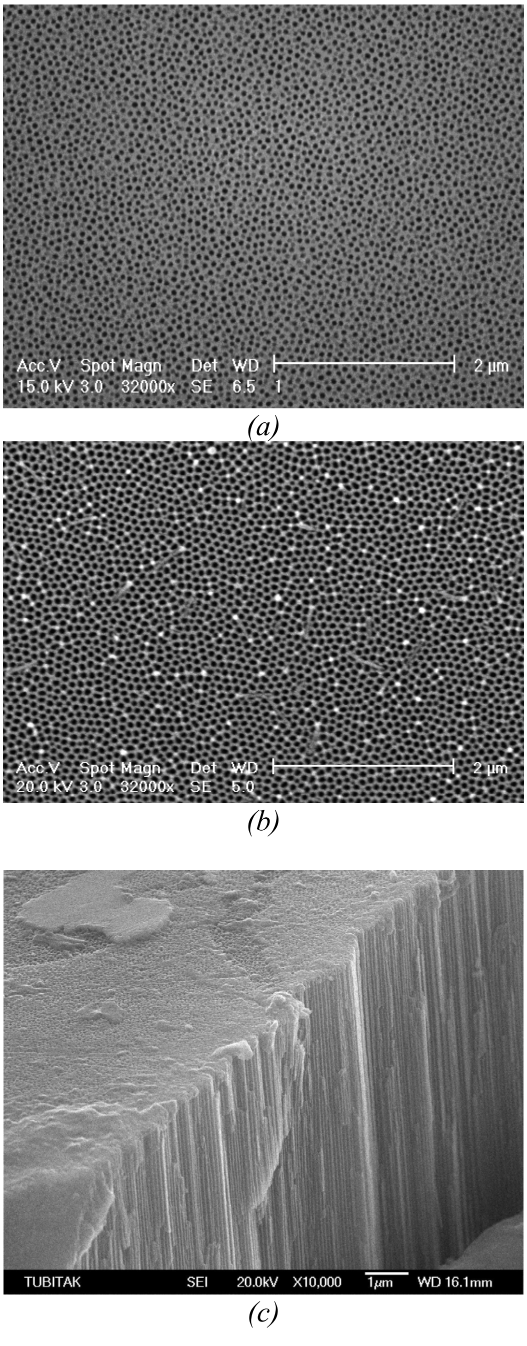

Figure 2. SEM micrographs of AAO nanotubes: (a) Top-view after first anodization; (b) Top-view after second anodization; (c) Cross-sectional view after second anodization.

Figure 2 shows typical top-views and cross-sectional view of the AAO nanotubes after first and second anodization. Alumina pores grow to the surface with equilibrium of field-enhanced oxide dissolution at the oxide/electrolyte interface and oxide growth at the metal/oxide interface. Oxygen containing ions (O^{2-} /OH^{-}) migrate from the electrolyte through the oxide layer at the pore bottom, Al^{3+} ions which simultaneously drift through the oxide layer are ejected into the solution at the oxide/electrolyte interface. Al^{3+} ions are lost to the electrolyte has been shown to be a prerequisite for porous oxide growth, whereas Al^{3+} ions which reach the oxide/electrolyte interface contribute to oxide formation in the case of barrier oxide growth. In addition, the thermal effects, high electric field and the change of the diffusion mechanism from planar diffusion to spherical diffusion accelerated diffusion rate of protons to the oxide/solution interface, which resulted in great acceleration of both the AAO barrier layer dissolution and the growth of tubes. Under constant potential, high current density in the second anodization caused to the large patterned surface area. Fabricated hexagonally straight AAO nanotubes were observed approximately 70 nm in diameters and 9 µm in lengths with 90 nm interpore distances. The initial pore arrangement was observed as irregular nanopits on the aluminium oxide surface due to repulsive forces between neighbouring pores gave rise to self-organization as shown in Figure 2(a). Final pore arrangement has a high regularity after the second anodization as shown in Figure 2(b). Also as shown in Figure 2(c), fabricated AAO nanotubes have a length to diameter ratio (called high aspect ratio) approximately 130. AAO nanotube density is approximately $1{,}2\mathrm{x}10^{10}\ \mathrm{cm}^{-2}$. (Nanotube density ($\rho$) = $(2/\sqrt{3}D_{\mathrm{int}}^{2})\mathrm{x}10^{14}$ cm^{-2}, where D_{int} is the interpore distance) [5].

The thickness of the template can be adjusted by changing the anodization time. The interpore distance as well as the pore diameters can be tailored by changing the anodization voltage. Figure 3 shows the length of the AAO template as a function of anodization time in oxalic acid solution at 40 V.

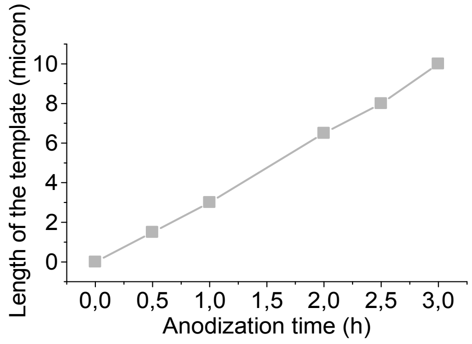

Figure 3. The length of the AAO template as a function of anodization time

Figure 4 shows current–time transient during the removing of alumina barrier layer of the AAO nanotubes.

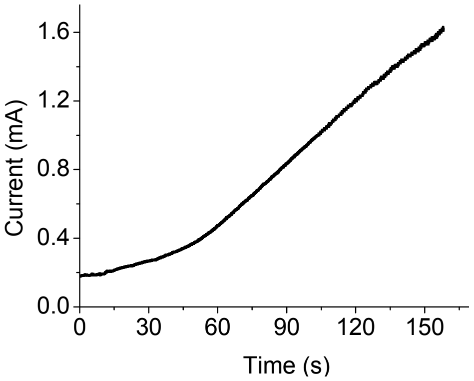

Figure 4. Current–time transient during the removing of alumina barrier layer

Alumina barrier layer which is the bottom of the Al foil based AAO nanotubes was removed by applying negative 2.75 V to the anode in 0.2 M KCl solution for 160 s. After applying of negative voltage to the AAO template, the alumina barrier layer was charged negatively and positive ions (H^+, K^+) of electrolyte present in the template move to the layer. The H^+ take an electron on the surface of alumina barrier layer and form H_2 gas that cause enrichment of electrolyte with KOH. As shown in Figure 4, the current curve as a function of time was increased while KOH was beginning to open up the blocked ends of the alumina barrier layer thus AAO nanotubes were connected to Al foil substrate. We found that alumina barrier layer must be removed in 160 s. Otherwise, if the current value rise up to 1.6 mA, the ordered AAO nanotubes is broken and have some cracks on the top of nanotubes due to influence of the increasing pH value as the OH^- ions are increasing in the electrolyte. Thus AAO nanotubes were obtained approximately 70 nm in diameters and 9 μm in lengths on Al foil with opened alumina barrier layer. This process required several seconds. In literature, some authors used chemical etching process for removing alumina barrier layer with $CuCl_2$ solution but, this process required several hours [4, 5].

Due to their low absorption coefficient and thermal stability, AAO nanotubes could be used for 2-D photonic crystals in the visible and infrared. The electronic band gap of alumina is 7- 9.5 eV. AAO could be used for metallodielectric photonic crystals associated with an increase in the width of photonic band gaps which may be realized [6]. Metallodielectric photonic crystal could show photonic band gaps for H polarization in all directions even though the dielectric constant of the AAO is as low as 2.8. The feasibility of the AAO as a dry etching mask has been introduced to fabricate photonic crystals integrated with semiconductors. This allowed the fabrication of GaAs nanotubes for 2-D photonic crystals [7]. Moreover, Du et al [8], obtained photoluminescence spectra of AAO nanotubes at room temperature. For AAO nanotubes, a blue band is seen in the wavelength range 400-600 nm. The AAO nanotubes were heated and the corresponding photoluminescence (PL) spectra obtained. It is found that, the intensity of the blue band is increase with increasing heat treatment temperature. The maximum intensity was obtained at approximately 500 ^{0}C.

4. Conclusions

Well-ordered hexagonal AAO nanotubes with high aspect ratio were fabricated by two-step anodization of high purity Al foil in oxalic acid solution. Obtained AAO nanotubes were approximately 70 nm in diameters and 9 μm in lengths with 90 nm interpore distances. This means the template has high nanotube density that enable to deposition of metal, alloy, multilayer nanowires with surface area for fabrication of especially chemical sensors, nanoelectronic, optoelectronic and magneto-optic devices. Also, we have described a simple electrochemical method for removing the AAO barrier layer. Alumina barrier layer was successfully removed in approximately 160s. We believe that the reported process has a strong impact on the prospect of developing the removal of the alumina barrier layer of the AAO template.

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