Electrochemistry Communications 12 (2010) 616–619

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Fabrication of through-hole TiO_2 nanotubes by potential shock

Yunkyoung Jo, Insoo Jung, Inhae Lee, Jinsub Choi *, Yongsug Tak *

Department of Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea

ARTICLE INFO

Article history:
Received 18 December 2009
Received in revised form 19 February 2010
Accepted 22 February 2010
Available online 1 March 2010

Keywords:
Titanium
Pore opening
Anodization
Barrier oxide

ABSTRACT

Through-hole nanotubular membranes of anodic TiO_2 were successfully prepared through the removal of the barrier layer using potential shock. The abrupt increase in the potential at the end of the anodization allowed the pores to homogenously open in the barrier layer within 10 s. The pore opening corresponded to the breakdown of the center of the barrier layer through the massive diffusion of the F^- ions, which were triggered by the significantly high potential (here, >80 V). The potential shock voltage and time were optimized based on the breakdown mechanism. This method is immediately applicable for preparing the through-hole membranes of anodic TiO_2 because it rapidly produces homogenous pore openings without the need for any complicated processes or dangerous chemicals.

1. Introduction

The fabrication of porous materials with straight channels, a small diameter distribution and highly self-ordered arrangements has attracted remarkable attention in past year because of various applications [1–3]. Among these methods and materials, the electrochemical anodization of aluminum and titanium under the appropriate conditions can provide a cost-effective preparation method for nanostructures with a controllable length and diameter through self-assembly behavior [4–6].

Hexagonally arranged pores can be formed on anodic aluminum oxide (AAO) in an acidic medium. The bottom of the pores has a barrier layer with a thickness that is linearly proportional to the anodizing potential, where the proportionality constant is around 1.25 nm/V [7]. Usually, this barrier layer can be removed from the bottom of the pores through chemical etching in weak acids, such as phosphoric acid and oxalic acid, after the AAO is detached from the aluminum substrate [8]. The barrier layer can homogenously be removed along the entire surface through the chemical etching because the thickness of the barrier layer is similar at each pore, and the barrier layer is uniformly dissolved by the weak acid. In addition, methods for detachments of AAO from the substrate were reported by several groups [9–11].

TiO_2 has much more attractive properties than AAO because it is intrinsically classified as a semiconductive material [12]. Therefore, TiO_2 is a useful active material for various electronics by itself [13]. AAO as an insulator is mainly used for template applications because of its inertness.

Anodic titanium oxide (ATO) takes on a hexagonally packed nanotubular morphology when it is prepared through anodization in an electrolyte containing fluoride ions [14–19]. Unlike AAO, the length of the nanotubes is strongly influenced not only by anodization time but also the electrolyte that is used [6,20]. Generally, shorter nanotubes are formed if the electrolyte has a lower pH value due to the dissolution of the formed oxide. Up until now, the TiO_2 nanotubes with a thickness of 1005 μm can be obtained through the anodization of titanium at 60 V in ethylene glycol containing 0.5 wt.% NH_4F and 3.0 wt.% water for 216 h [20]. Several methods have been developed to detach the ATO from the Ti substrate. For example, the ethanol immersion method [18,21] and the epoxy resin method [22] provide a fast and simple way to safely detach the ATO from the substrate. However, opening the pores in the barrier layer of ATO is still a challenge for many other applications. Even though chemical etching methods seem to work in opening pores [20], it does not provide the perfectly opened pores across the entire surface. Grimes's group claimed that a diluted hydrofluoric acid/sulfuric acid solution treatment is useful for the pore opening but the exact concentrations and procedures were not reported in detail [20]. Schmuki's group reported that the preferential condensation of HF vapor onto the barrier oxide of TiO_2 produces reliable pore opening [23]. Since this process is not adequate for mass production that involves pore opening, advanced method using methanol evaporation was developed to safely make a membrane without the use of corrosive solution [24]. Recently, Kant et al. showed that a stepwise reduction of the potential at end of the Ti anodization produces the through-hole structure of TiO_2 [25]. However, this method is not applicable for ATO at lower potentials (for example, 40 V). In this report, a method was investigated in order to open pores based on an abrupt increase in the potential within a few seconds instead of reducing the potential. This method provided reproducible and reliable results that showed that the pores in ATO prepared at various potentials (40 V–80 V) were homogenously opened. However, we focused on the optimization of

* Corresponding authors. Tel.: +82 32 860 7476, +82 32 860 7471; fax: +82 32 866 0587.
E-mail addresses: jinsub@inha.ac.kr (J. Choi), ystak@inha.ac.kr (Y. Tak).

1388-2481/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2010.02.013

potential shock methods in ATO prepared at 40 V in this reports because it provided basic principles, which can be applicable to ATO prepared at various potentials.

2. Experimental

The Ti foils (0.127 mm, 99.7% purity, Aldrich) were cleaned through sonication in acetone, isopropanol (or ethanol), and deionized water for 10 min during each step. The anodization solution was prepared with ethylene glycol (EG) containing 0.25 wt.% NH_4F and 1.0 wt.% deionized water. The power supply (Keithley SourceMeter 2400) was connected with 2 electrodes, consisting of the titanium foil as the working electrode and a Pt wire as the counter electrode, and this power supply was used for the anodization, which was carried out using a 2-step method. In the first step, titanium was anodized at 40 V and at room temperature for 2 h. Subsequently, the oxide that was formed was removed using the epoxy adhesive method [22]. A second anodization was carried out at 40 V and at room temperature for 3 h. Titanium oxide with a thickness of 10–15 μm was fabricated through this anodizatoin, and the pores were opened through an abrupt increase in the voltage. The morphologies and elements of the bottom were analyzed using a field emission scanning electron microscope (Hitachi, FE-SEM S-4300) and an X-ray photoelectron spectrometer (Thermo Electron U.K., XPS K-Alpha).

3. Results and discussion

The nanotubes prepared by anodization of Ti at 40 V in EG + 0.25 wt.% NH_4F + 1.0 wt.% H_2O were covered with a barrier layer. If the ATO bottom was chemically etched in a dilute HF solution, pores were inhomogeneously opened because some of the pores dissolved too much, resulting in a coarse dissolution surface. However, many of the other pores were not yet opened completely. Thus, the proper composition of etchant was very important for the homogenous pore opening using the chemical etching method. The pore opening process was very sensitive to the temperature and stirring speed because the fluoride ions very aggressively opened the pores. Thus, this chemical etching approach was not an adequate pore opening method because reliable results were not obtained.

Fig. 1 (a) shows the pore opening method based on the stepwise reduction potential suggested by Kant et al. [25], which showed that the stepwise reduction method was not applicable for ATO prepared at low potentials (here, 40 V). Instead, a potential increase after anodization led to the homogenous pore opening across the entire

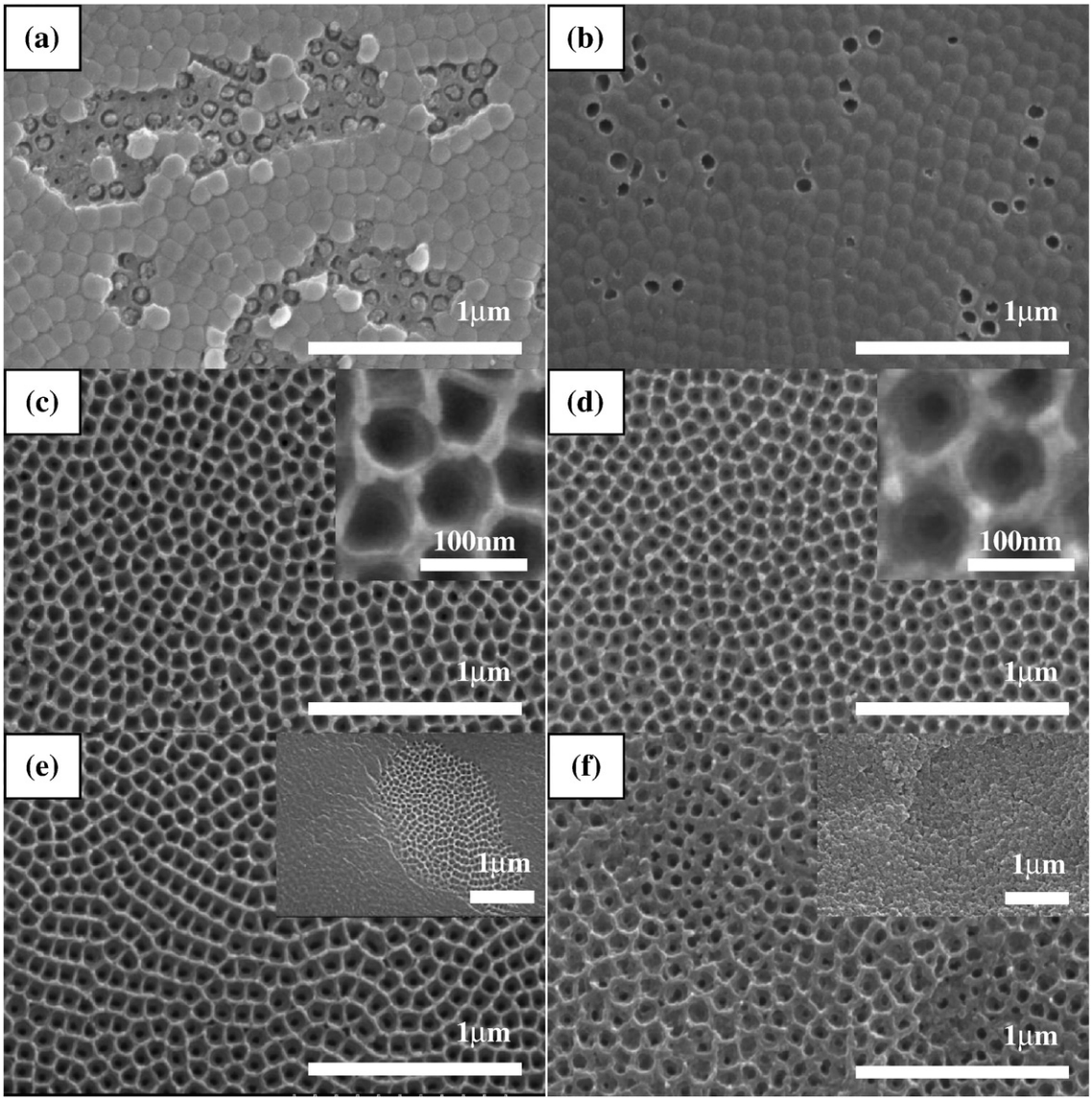

Fig. 1. FE-SEM images of the pore opening using (a) the thinning process suggested by Kant et al. (from 40 V to 10 V, 5 V/sec) and potential shock at (b) 60 V, (c) 80 V, (d) 100 V, (e) 150 V, and (f) 200 V. The potential shock was applied for 5 s.