Thin Solid Films 552 (2014) 75–81

Contents lists available at ScienceDirect

Thin Solid Films

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

Preparation of self-ordered nanoporous anodic aluminum oxide membranes by combination of hard anodization and mild anodization

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ARTICLE INFO

Article history:
Received 25 March 2013
Received in revised form 13 December 2013
Accepted 13 December 2013
Available online 18 December 2013

Keywords:
Anodic aluminum oxide templates
Two-step anodization
Hard anodization
Mild anodization

ABSTRACT

Anodic aluminum oxide (AAO) is one of the most important templates for fabrication of nano-materials. In this paper, we present a fast two-step anodization method to prepare self-ordered AAO films. The first step is hard anodization (HA) in H_2SO_4 and the second step is mild anodization (MA) in $H_2C_2O_4$. HA in H_2SO_4 at a wide range of anodization voltage provided a fast formation of ordered arrays of pits on Al sheet, and in the second step, arrays of pits on Al substrate affected nucleation initially, and the anodization voltage of $H_2C_2O_4$ MA determined the degree of AAO later. Then the best anodization voltage of $H_2C_2O_4$ MA was validated to be around 40 V. The improved combination of HA and MA not only shortens the time of the first anodization step compared to conventional two-step anodization which was reported by Masuda and Fukuda (1995), but also keeps a highly ordered AAO within large area. Moreover, the relationship between the size of arrays of pits formed in H_2SO_4 HA and degree of order of AAO formed in $H_2C_2O_4$ MA was investigated in detail.

1. Introduction

Ordered nanochannel-array materials have attracted much attention over the last decades due to their broad applications in synthesis of nano-structured magnetic, electronic and optoelectronic materials [1–3]. Anodic aluminum oxide (AAO) films as templates have played an important part in preparing ordered nanochannel-array materials. Ordered AAO films have specific structure parameters with close-packed hexagonal cells, which can be controlled by changing anodization conditions. Many works have been done on fabrication of highly ordered AAO templates in the past decades [4–8]. Masuda H et al. employed the method of two-step mild anodization (MA) and etching to prepare a highly ordered AAO film in oxalic acid solution [4,5]. In the two-step anodization, it cost 10 or more hours at 40 V in oxalic acid solution to form a relatively thick AAO film on the Al substrate for the first step, and ordered arrays of pits were obtained after removing the AAO film. Secondly, the obtained Al sheet was anodized again and as a result a highly ordered AAO film with enough mechanical robustness and high aspect ratio was obtained due to the induction of the arrays of pits left on Al substrate. Without induced by ordered arrays of pits on Al substrate, it usually needs a very long time for self-adjustment from disordered to a highly ordered AAO. So, it takes a long time for the first step in Masuda H's two-step anodization. Meanwhile, the highly ordered cells appear only in a quite narrow voltage window, which leads the interpore distance or cell size to be confined to some fixed values in mild anodization (MA). For example, the best ordering anodization voltage in oxalic acid solution is about 40 V. Thus, there is a great limitation in Masuda H's two-step anodization process to form ordered arrays of pits on Al. In the method of etching, the area of a highly ordered AAO domain can only reach to square millimeter level and the aspect ratio of the formed AAO is low. The high cost and time consuming preparation process limited practical application of AAO.

The key of two-step anodization method is to obtain highly ordered arrays of pits on Al substrate. Chu et al. [6] employed high electric field to fabricate a highly ordered AAO rapidly in aged sulfuric acid solution. Lee W et al. [7–9] used a thin pre-existed film (about 400 nm in thickness) forming on the Al substrate to avoid local catastrophe, then prepared a highly ordered AAO film in oxalic acid or sulfuric acid solution through high electric field. High electric field led to rapid formation of self-ordered AAO. However, it also caused high mechanical stress in AAO, bringing the boundedness in practical applications. Fast fabrication of a highly ordered AAO in aged sulfuric acid solution by hard anodization (HA) provides an improved way for the first step to prepare highly ordered arrays of pits on Al substrate in two-step anodization process. In this work, we present a fast and improved two-step anodization method to prepare a highly ordered AAO. Fig. 1 shows the schematic diagram for the synthetic process. For the first step, HA in sulfuric acid is employed for less than 30 min to achieve ordered arrays of pits on Al substrate. For the second step, MA is conducted in oxalic acid. The relationship between the behavior of the second anodization step in oxalic acid and pits left on Al substrate after the first anodization step is also discussed. The improved combination of HA and MA not only shortens the time of the first anodization step compared to Masuda

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0040-6090/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.12.023

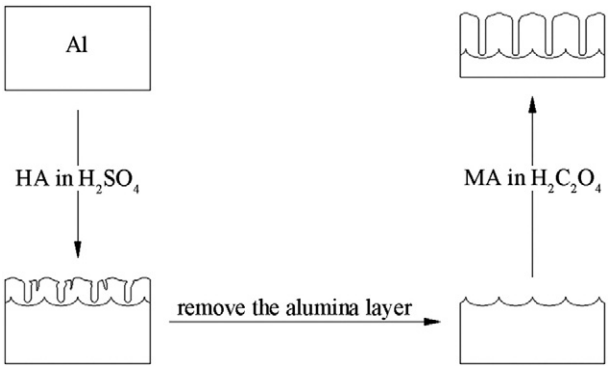

Fig. 1. Schematic diagram for the synthetic process.

H's two-step anodization [4] and keeps a highly ordered AAO within large area, but also decreases the high mechanical stress in AAO formed in HA. The process is characterized by low cost, time-saving and wide preparation parameter scope.

2. Experimental section

2.1. Fabrication of a highly ordered AAO in sulfuric solution

2.1.1. Pretreatment

High purity aluminum plates (99.999%, 20 mm × 10 mm × 0.5 mm, Beijing Research Institute for Nonferrous Metals, China) were used as working electrodes. Prior to anodization, all the Al sheets were degreased by ultrasonic in ethanol for 5 min and then electrochemically polished in a mixture solution of 65% $HClO_4$ and 99.5% ethanol ($V_{HClO_4}/V_{ethanol} = 1/4$) with vigorous stirring at 0 °C and 20 V for 5 min to achieve mirror finished surfaces in order to eliminate the influence of natural oxide film on the aluminum surfaces.

There are three methods to fabricate a highly ordered AAO in H_2SO_4 hard anodization (HA): (1) anodization under potentiostatic mode [6]; (2) anodization under galvanostatic mode [10]; and (3) anodization under potentiostatic mode of Al substrate with a thin pre-existed film (about 400 nm in thickness) [7,9]. Compared with methods (1) and (2), method (3) can avoid phenomena of burning and cracking, and the operation of method (3) is simpler. So method (3) was employed in this work.

2.1.2. Anodization

0.3 M and 0.04 M sulfuric acid solutions were employed under potentiostatic mode with U from 35 V to 70 V. For 0.3 M sulfuric acid solution the voltage was used below 40 V, and for 0.04 M sulfuric solution the voltage was used above 40 V. Anodization was performed in the corresponding sulfuric acid solution at 5 ± 2 °C with vigorous magnetic and compressed air stirring. A powerful cooling system and a large electrolysis bath (1 L) were used to maintain the low temperature needed for the high-field anodization. The aluminum sheets were anodized at 25 V (MA) for 10 min in the corresponding solution to generate a thin porous alumina surface layer which could avoid the burning or cracking in subsequent step. U was gradually increased to U_{target} of 35 V to 70 V at a rate of 0.1 V s^{-1}. Subsequently, the as-anodized sample was immersed into a mixture of phosphoric acid (6 wt.%) and chromic acid (1.8 wt.%) at 70 °C for 5 h to remove the alumina layer.

2.2. Fabrication of ordered AAO in oxalic acid solution

After removing the AAO formed in sulfuric acid, the second anodization step was conducted on the aluminum sheet in 0.3 M oxalic acid at 17 ± 2 °C with a voltage of 30 V, 32 V, 38 V, 40 V, 44 V and 52 V, respectively. Next, the sample was immersed in a mixture solution of 0.2 M $CuCl_2$ and 6.1 M HCl to remove the underlying Al substrate. Finally, a free-standing AAO film was obtained. The barrier layer and cross-sectional morphologies of the as-prepared AAO film were

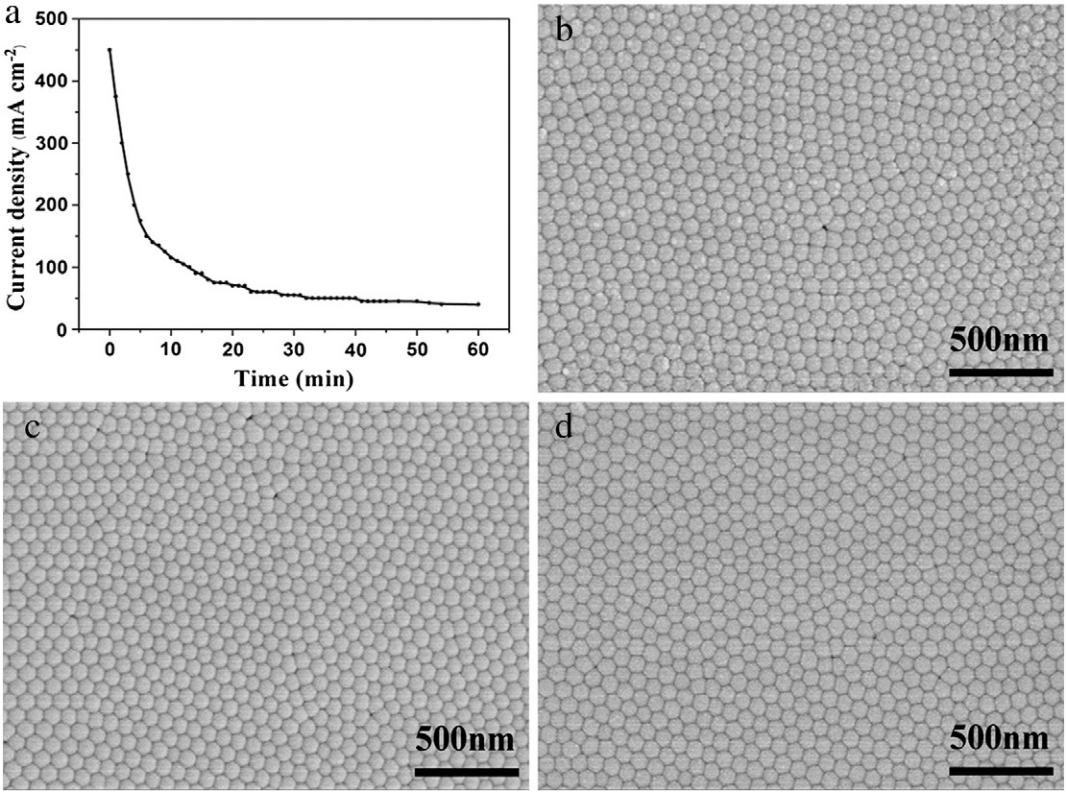

Fig. 2. FESEM images of the bottom surface of AAOs prepared in 0.3 M H_2SO_4 at 40 V for different time. (b) 10 min (j decreases to 125 mA cm^{-2}), (c) 30 min (55 mA cm^{-2}) and (d) 60 min (40 mA cm^{-2}). (a) is the relationship between current density and time in H_2SO_4 HA at 40 V.