Observation of Three Dimensional Micro-Scaled Structures Buried in Porous Alumina Layers Fabricated by Anodic Oxidation

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(Received 2 April 2008; Accepted 20 May 2008; Published 3 June 2008)

We have observed porous alumina layers fabricated by the anodic oxidation of aluminum sheets utilizing a selective etching. We have found that two types of 3-dimensional structures form inside the alumina layer during the oxidation process. One is dome-like micro-structures which have straight pores of approximately 100 nm in diameter, and the other tree’s root-like structures which grew in a radial manner. By using non-uniform etching conditions that the concentration of phosphoric acid is more than 20 wt%, those buried structures appear because the matrix is preferentially removed. Moreover, we have found that the position of the dome-like structures can be controlled by artificial scratches on the initial surface. [DOI: 10.1380/ejssnt.2008.147]

Keywords: Anodic oxidation; Porous alumina; Etching; Self-assembly; Surface structure, morphology, roughness, and topography

I. INTRODUCTION

Porous alumina prepared by anodic oxidation of an Al sheet exhibits a self-organized ordered nanohole array with a honeycomb arrangement [1]. The aspect ratio of the formed nanoholes is very high: the diameter is from 4 to 200 nm [2] and the depth is sub-micrometer to several tens micrometers. The hole diameter can be controlled by the applied voltage, and the typical inter-pore distance is 50–420 nm [3]. The fabrication process, moreover, is very simple. Therefore, this technique is promising to fabricate nano-space arrays in many applications. A perfectly ordered porous alumina structure in large area, moreover, can be fabricated by employing a two-step anodizing process [4] or an indentation technique using SiC molds [5, 6]. These techniques have been applied to fabrication of further complicated nanostructure arrays, such as fabrication of nanodot arrays using a porous alumina film as a mask [4], metal nanocomposites by depositing metal into the porous alumina pores [7], a porous structure of metals using a porous alumina as a template [2, 8], and direction-controlled carbon nanotube arrays [9, 10]. By anodic-oxidation of Al/Ti or Al/Si bilayers, membranes modified with the porous alumina patterns were fabricated on the Ti or Si substrates [11, 12]. Al nanostructures, such as nano-wires and nano-pillars were also fabricated from anodic alumina membranes [13]. The dimensions of the nanoholes are suitable for confinement of biological molecules. Therefore, porous alumina is expected to be a useful substrate for bio-sensors. In fact, DNA and protein patterning using porous alumina substrates have been reported [14, 15]. It is known that porous alumina layers fabricated by the anodic-oxidation have domain structures. The domain size is small at the early stage of the oxidation and then become larger with the oxidation time. In the previous studies, emphasis has been put on the fabrication of a uniform hole arrays on wide areas [5, 16, 17]. In actual applications such as bio-devices, however, isolated nano-space patterns are desirable because integration technique is more strongly required than discrete devices. Self-organized nano-space arrays that are isolated in micro-scale will be more useful in many applications than the uniform arrays in a large scale.

In this paper, we describe formation of three-dimensional micro-scaled structures buried in the bulk of the porous alumina layers. Those structures can be separated from the matrix of the porous alumina using selective etching and observed by a scanning electron microscopy. Since the formation process of such three-dimensional structures are closely related to the self-organization of nanohole arrays in the anodic oxidation of Al sheets, the observation of the buried non-uniform structures will be valuable to reveal the mechanism of the porous alumina self-organization process.

II. EXPERIMENTS PROCEDURE

Porous alumina layers were fabricated by anodic-oxidation for 1 h to investigate the domain structure formation process. We employed selective etching of the porous alumina layers to clearly demonstrate the three-dimensional structures buried in the bulk of the porous alumina layers.

Aluminum substrates of $0.5 \times 10 \times 20$ mm (99.99 % purity) were cleaned in acetone in an ultrasonic bath to remove contamination introduced from the air and soaked for a couple of second in 100 wt% phosphoric acid solution at $60^\circ$C to remove the aluminum oxide layers on the surfaces. The treated substrates were then oxidized in air at $300^\circ$C to form the oxide layer. To fabricate porous alumina layers, the Al substrates were soaked in oxalic acid solution (0.3 M) with stirring and anodization was performed at 40 volts for 1 h. The counter electrode was an Al sheet. To keep the temperature uniform, anode oxidation was performed in a constant-temperature water bath. The current becomes constant 30 mA after a short time of the initial fluctuation. After the anodization, the Al substrate was washed by deionized water to remove remaining oxalic acid solution on the surfaces. To fabricate a uniformly etched porous alumina, the etching was performed using a 8 wt% phosphoric acid solution at $60^\circ$C. To investigate the dependence of etching rate on

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ISSN 1348-0391 © 2008 The Surface Science Society of Japan (http://www.sssj.org/ejssnt) 147
concentration of the etching solutions, we used the phosphoric acid of 20 wt%, 40 wt%, 60 wt%, 80 wt% and 100 wt%. The etching time was 5 min, and 15 min. After etching, the substrates were washed in a deionized water. The surface morphology was observed by a field emission-scanning electron microscope (SEM) at glancing angles of 60° and 90° with respect to the surfaces.

### III. RESULTS

Figure 1(a) shows a porous alumina surface just after anodic oxidation in oxalic acid solution (0.3 M) at 40 volts for 60 min. Nanohole arrays were observed on the surface but the arrangement of the nanoholes were irregular. Figure 1(b) shows the porous alumina surface after etching in phosphoric acid solution (8 wt%) at 60°C for 30 min. The etching depth was approximately several micrometers. On this surface, regularly ordered nanohole arrays with a domain structure were observed. The pitch of nanoholes was approximately 100 nm. In this case, the etching process uniformly proceeds and the resulting surface was flat even though the anodized layer is not a uniform material as shown later.

To investigate the domain structure formation process from the early to the late stages of anodic oxidation, we observed the morphology of the porous alumina layer after non-uniform etching using several different concentrations of phosphoric acid solution. By controlling the etching solution concentration, unique structures appeared as shown in Fig. 2. The anode-oxidation conditions were same as those in Fig. 1, and the etching condition was the only difference between the samples shown in Fig. 1 and Fig. 2. Figure 2(a) shows dome-like porous alumina micro-structures in which straight pores of approximately 100 nm in diameter formed. The pores grew vertically and the height of the domes was approximately 8 µm. The nanopores are grown continuously below the interface at the bottom of the dome-like structures as suggested in Fig. 1(b). Figure 2(b) shows a different type of alumina structures which grew from certain points in a radial manner to form tree’s roots shape (root-like structure), and Fig. 3 shows images of such root-like structures glanced from the top. These structures remained on the surface because the etching rate is much smaller than that of the matrix. The root part of this structure is observed even on above the nanoholes as shown in Fig. 3(b). We investigated the dependence of etching concentration and the dependence of etching time on the structures shown in Fig. 2.

Figure 4 shows SEM images of the alumina layers for different etching solution concentrations, where the phosphoric acid concentrations were 20 wt% in (a) and (b), 40 wt% in (c) and (d), and 60 wt% in (e) and (f). The etching time was 5 min. In our experiments, the etching rates around the periphery of the substrate (Figs. 4(a), (c) and (e)) were much faster than the center area (Figs. 4(b), (d) and (f)). From Fig. 4, it is found that the dependence on the phosphoric acid concentration is small for the concentrations above 20 wt% though the morphology is much different from that in Fig. 1. The intermediate structure between the dome-like and the root-like micro-structures appeared, in particular, in Fig. 4(b). On the used Al surfaces, scratches introduced during the polishing process exist. The observed direction in which the micro-structures are arranged coincides with the substrate scratch, suggesting that the ordered micro-structures can be fabricated by the patterning of the scratch on the substrate surface.
FIG. 3: (a) SEM image of the root-like structures observed from the top, and (b) its magnified image.

Figure 5 shows etching time dependence of the morphology using 100 wt% phosphoric acid where the dome-like and root-like micro-structures coexist. After 5 min etching shown in Fig. 5(a), the dome-like structure is higher than the root-like ones and the difference is enhanced after 15 min as shown in Fig. 5(b). This indicates that the etching rate of the dome is much smaller than the root-like structure, probably due to the difference in the stoichiometry of these structures.

Figure 6 shows an SEM image of the arrangement of the dome-like structures in wide area. This image was taken around the periphery of the substrate prepared by the etching using 20 wt% phosphoric acid for 5 min. An ordered dome-like structure array is observed and the direction of the order coincides with the scratch. The width of the structure is scattered, but the height is almost constant, approximately 6 µm.

IV. DISCUSSION

We will discuss the formation and etching processes of the three dimensional micro-structures formed by anodic-oxidation of aluminum substrates in oxalic acid solution (0.3 M). From the experimental results, the as-grown porous alumina layer is a non-uniform material and consists of dome-like structures, root-like structures, and the matrix, when roughly classified. The etching rate of these materials are comparable when the phosphoric acid concentration is 8 wt%, and the self-organized ordered nanopores appear on a flat surface. However, when the phosphoric acid concentration is larger than 20 wt%, the etching rate of the dome-like structure is very low, that of the matrix high, and that of the root-like structure intermediate. Figures 7(a), (b) and (c) show a model of as-grown porous alumina (a), the surface after the uniform etching (b), and that after the selective etching (c). At the early stage of the anodic oxidation, the current distribution may be non-uniform because the initial surface morphology is not perfectly flat, and high current density paths are formed at the regions with a high electric field on the surfaces. Generally, the etching rate
FIG. 5: SEM images of porous alumina surfaces which were etched using a 100 wt% phosphoric acid solution (a) for 5 min and (b) for 15 min.

FIG. 6: SEM image of the arrangement of the dome-like porous alumina structures.

FIG. 7: Model of anodic-oxidation of an Al sheet and etching of the porous alumina layer. (a) as-oxidized porous alumina, (b) after the uniform etching, and (c) after the selective etching.

is lowest when the material is perfectly stoichiometric. Oxidation along the high current density paths produces stoichiometric alumina (Al₂O₃) with nano-porous structure. The dome-like structure corresponds to the initially formed oxidation path and the etching rate is lowest. Outside the high-current density paths, non-stoichiometric alumina (AlOₓ) regions with higher etching rates form as the matrix. As the oxidation proceeds, the current paths are self-organized and uniformly distributed. During this self-organization process, directions of the current paths are bended from the vertical direction and the root-like structures are formed. Once the current paths are self-organized, oxidation proceeds uniformly in the micro-scale. In this model, the stoichiometric dome-like structures are formed from the high current density. When a scratch is formed on the substrate surface, the electric fields are enhanced along the scratch, and concentration of the current occurs around the scratch. Therefore, the ordered array of the dome-like structures of porous alumina are formed as shown in Fig. 6. In the future work, characterization of the stoichiometry of the oxides, for example using an X-ray photoelectron spectroscopy, is required.

V. CONCLUSION

We have observed three-dimensional porous alumina structures fabricated by the anodic oxidation of aluminum sheets utilizing a non-uniform etching. We have found that two types of micro-scaled structures are buried in the alumina layer. One is a dome-like micro-structure which has straight pores of approximately 100 nm in diameter, and the other a tree’s root-like structure which grows in a radial manner. By selecting an etching solution, a non-uniform alumina layer can be removed with a similar etching rate, and a flat surface with a regularly arranged nanohole array can be obtained. By using non-uniform etching conditions, however, those two structures can be selectively left on the etched surface after removal of the matrix. To further reveal the formation mechanism, studies on chemical states of the non-uniform alumina layers will be necessary.

The formation of those micro-scaled structures should be general in porous alumina formation because the anodic oxidation proceeds from non-uniform current distributions to ordered ones, and the ordered nanohole array requires a sacrificial surface layer of the alumina layer. We have found that ordered nanohole array also exist inside the dome-like structures which can be separated from the matrix by the selective etching. Moreover, the position of the dome-like structures can be controlled by scratches on the initial surface. Therefore, those structures will be promising in many applications as nanohole arrays separated in micro-scale.
Acknowledgments

We would like to thank Prof. Masuda, Prof. Tokeshi, and Prof. Niwano for valuable discussion. This work was partly supported by CREST/JST ant Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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