



## Regular Article

## Impurity-driven formation of branched pores in porous anodic alumina

Byeol Kim<sup>a,1</sup>, Yong Youn<sup>b,1</sup>, Yi-Seul Park<sup>a</sup>, Dal Nim Moon<sup>a</sup>, Kyungtae Kang<sup>c</sup>, Seungwu Han<sup>b</sup>, Jin Seok Lee<sup>a,\*</sup><sup>a</sup> Department of Chemistry, Sookmyung Women's University, Seoul 140-742, South Korea<sup>b</sup> Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, Seoul 151-755, South Korea<sup>c</sup> Department of Applied Chemistry, Kyung Hee University, Yongin, Gyeonggi 446-701, South Korea

## ARTICLE INFO

## Article history:

Received 21 April 2016

Accepted 17 May 2016

Available online 2 June 2016

## Keywords:

Anodic aluminum oxide

Impurity

Branched pore

Electric-field distribution

Current-density distribution

## ABSTRACT

Understanding of pore formation in porous anodic alumina is prerequisite for realizing its potential applications in the field of nanofabrication. Here, we explored the impurity-driven pore formation of porous anodic alumina via a two-step anodization process in acid solution with various applied voltages. We varied the purity of Al foil, and found that the branching and bending of pores displayed by low-purity Al foils are originated from an electric-field imbalance that results from the presence of impurities. Also, the pore formation mechanism and characteristic geometry induced by the impurities within the Al foil were investigated using experimental and simulation models.

© 2016 Elsevier Ltd. All rights reserved.

Owing to the unique self-ordering properties in nanometer scale, porous anodic aluminum oxide (AAO), typically formed by the electrochemical oxidation of Al in acidic solutions, has been extensively investigated for application in the field of nanofabrication [1–3]. It is generally believed that the anodization current during the steady-state growth of the porous film is mainly related to the movement of ionic species ( $\text{Al}^{3+}$ ,  $\text{O}^{2-}$ , and  $\text{OH}^-$ ) through the oxide layer at the bottom of the pores for the pore formation. While  $\text{Al}^{3+}$  ions are directly injected into the electrolyte, the oxide film is formed at the metal/oxide interface, due to the migration of  $\text{OH}^-/\text{O}^{2-}$  species. As a result of the incorporation of the electrolyte species, an anion-contaminated layer is formed [4–7]. This field-assisted dissolution model suggests that the development of a porous film results from the equilibrium established between the formation of the oxide at the metal/oxide interface and the field-enhanced dissolution at the oxide/electrolyte interface [8,9]. The evolution and development of porous films arise from the viscous flow of alumina from the bottom of the pores toward the cell walls, which is driven by film growth [4,5].

A porous anodic alumina film with hexagonally close-packed pores is typically obtained through a self-organized two-step anodization process [10]. The stress placed on the anodic film during pore formation is evenly distributed over the entire film area [11,12]; consequently, the resulting porous film exhibits a self-ordered, hexagonal close packing of the pores. And, the characteristic parameters of porous anodic alumina, such as pore diameter ( $D_p$ ), inter-pore distance, and oxide-film thickness can be controlled by adjusting the anodizing conditions,

including the type of electrolyte, temperature, applied potential, current density, and duration of the first anodization process [13–18]. Additionally, the anodization response is highly dependent on the purity of the Al foil employed; impurities contained within the Al foil can change the flow of ions during the electrochemical reactions that lead to pore formation [19–24]. Recent studies have investigated the migration of anion species into the oxide film formed on the surface of the Al substrate during anodization that leads to a considerable accumulation of impurities in the barrier layer [21]. The local accumulation of alloying elements in a given region of the metal/oxide interface can change the local rates of pore formation [19,20]. Moreover, it has been reported that impurities at the metal/oxide interface—the primary location of oxide growth—may inhibit the formation of the aluminum oxide [21, 22]. Consequently, changes in the oxidation reactions due to impurities can ultimately result in the formation of non-uniform oxidation cracks and flaws on the film surface [24].

In this work, we present a comparative study of the characteristic geometry of porous anodic alumina films prepared from three Al foils of different purity (99.999%, 99.5%, and 99.0%) via a two-step anodization process in oxalic acid solution at various applied voltages. To explore the effect of impurities in low-purity Al foil on the electrochemical reaction rates, oxidation, and dissolution, we investigated the structural features of the anodic alumina films using experiments and simulation models to confirm the growth mechanism induced by the impurities within the Al foil.

To fabricate a porous alumina membrane, three types of Al foils of different purity (99.999% ( $\text{Al}_{99.999}$ ), 99.5% ( $\text{Al}_{99.5}$ ), and 99.0% ( $\text{Al}_{99.0}$ )) were anodized via a two-step process in 0.3 M oxalic acid solution at an applied voltage of 40 V and a temperature of 10 °C (see the experimental details in supplementary information). The scanning electron

\* Corresponding author.

E-mail address: [jinslee@sookmyung.ac.kr](mailto:jinslee@sookmyung.ac.kr) (J.S. Lee).<sup>1</sup> These authors contributed equally.

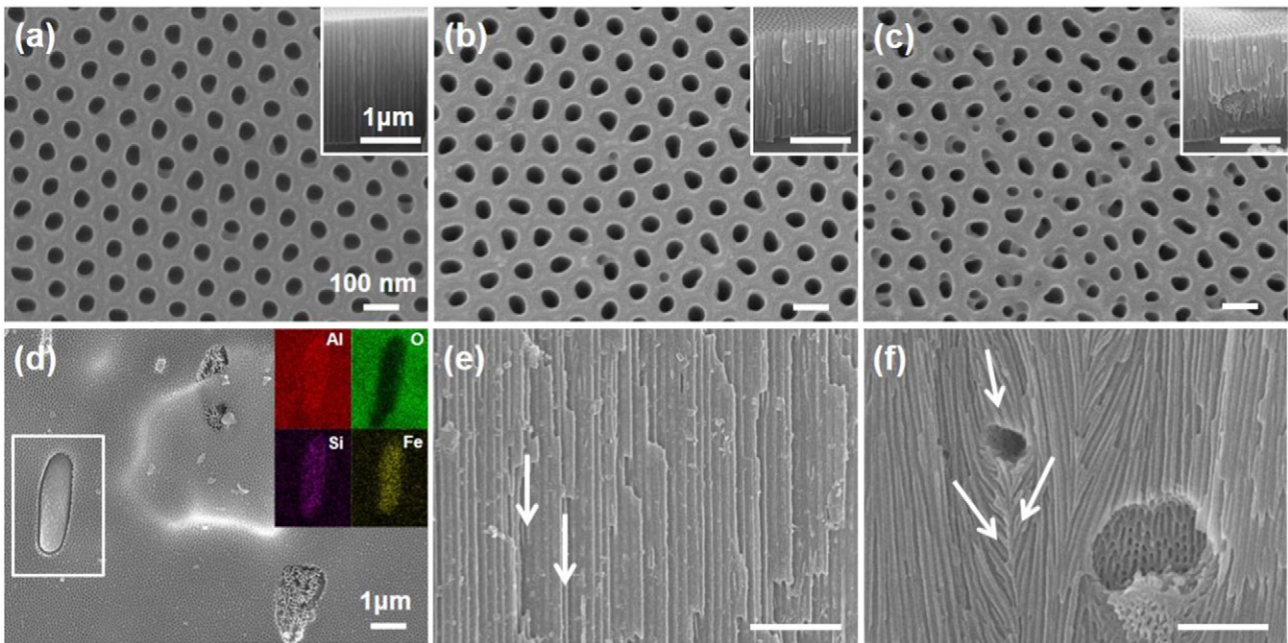
microscopy (SEM) images in Fig. 1a–c show that the anodized alumina film obtained from Al<sub>99.999</sub> has a hexagonally ordered pore array with most of the pores being circular in shape, but, when the Al purity is reduced, the array regularity and the circularity of the pores are degraded. In particular, anodized alumina film using Al<sub>99.0</sub> exhibits a disordered pore array featuring distinctly non-circular pore shapes; these appear to overlap with adjacent pores, resulting in a sub-pore structure alongside the main pore array.

Previous studies have shown that the presence of impurities can influence the local rates of oxidation and consequently affect the oxide morphology [19,20]. Interestingly, even a tiny amount of impurities in the Al foil can exert a strong effect on the alumina film morphology, including defects,  $D_p$ , and film thickness. Here, we define defects as the irregular pores, which are not circular. As the purity of the Al foil decreased, the defect percentage increased (Fig. S1a) and the  $D_p$  values decreased (Fig. S1b). The alumina film resulting from the anodization of Al<sub>99.0</sub> showed a high defect percentage of ~60%, a slightly smaller pore diameter of ~41 nm, and a relatively large standard deviation as a consequence of a greater number of elliptical pores. Generally, for anodization with a conventional potentiostatic system, the  $D_p$  values of an anodic alumina film increase linearly with the applied potential, at a rate of ~0.9 nm V<sup>-1</sup> [25]. However, the present study indicates that the  $D_p$  values can be also affected by the purity of the employed Al foil. The final morphology of the alumina films depends on the impurities, which introduce disordered pore arrays and non-uniform pore shapes, resulting in an irregular  $D_p$ . The occluded impurities in the Al foil induce an unbalanced local chemical reaction rate [19,20], which triggers disordered pore formation and causes the formation of defects in the alumina film; this in turn reduces its growth rate. The side-view SEM images of the alumina films with different impurity (insets of Fig. 1a–c) confirm the changes in film thickness, which shows the alumina film thickness after anodization as a function of the purity of the Al foil. In particular, the thickness of the anodized film decreased from 2.07 μm for Al<sub>99.999</sub> to 1.78 μm for Al<sub>99.0</sub> (Fig. S1c). Therefore, it supports that the presence of impurities at the metal/oxide interface can effectively retard the growth of the oxide. Impurities in the Al foils may not be evenly distributed, and can aggregate to form “islands of impurities”.

In order to confirm this hypothesis, low-magnification SEM images of the anodized alumina samples were analyzed. In particular, the top-view image of the anodized alumina film obtained with Al<sub>99.0</sub> reveals a large number of defects as well as a putative lump of impurity (Figs. 1d and S2). Energy-dispersive X-ray spectroscopy (EDX) mapping data shows that the main impurity components of this “island of impurities” are Si and Fe, which are concentrated in the tubular island; this suggests that the occluded impurities can block the electrochemical reactions related to the pore formation. These findings indicate that impurities are locally distributed and can trigger a change in the anodic alumina formation [24].

In the side-view image of the alumina film displayed in Fig. 1f, a very large void (white arrow), which corresponds to a defect, can be observed. We can thus assume that the impurities are degraded on the anodic alumina film and have a significant effect on local pore morphologies, thereby inducing transformations in the pore structure. Moreover, if located inside the bulk Al, the impurities can affect the formation of a straight pore channel. Fig. 1e–f shows the directions along which pores were formed on porous alumina films prepared with Al foils of different purity. Anodized films derived from the low-purity Al<sub>99.0</sub> foils exhibited tilted arrays of pore channels progressed along a specific direction to avoid the impurity [26], while the high-purity Al<sub>99.999</sub> foil showed an upright pore channel perpendicular to the bulk Al; this behavior may be due to the local position of the impurities. In this study, these impurity driven branching and transformation of pore arrays have often been observed at the pore bottom even after anodizing for 10 h.

Based on our initial results and preliminary hypotheses, we then investigated the effect of the electric field as the main driving force on the pore growth during anodization as well as the effect of the impurities on the direction of the electric field. The branched pore-growth mechanism in the impurity-laden film was investigated with an ion-current simulation model [4,24,27]. Anodization during the steady-state growth of the porous alumina involves a cross transport of ionic species for pore formation. Fig. 2a–c shows the simulated electric-field distribution and ionic-current density, based on the geometric parameter of produced pore channel (Fig. S3). It is seen that a small lump of impurities (circle)



**Fig. 1.** SEM images of porous anodic alumina anodized using Al foils of different purity: (a) 99.999%, (b) 99.5%, and (c) 99.0%. Insets show side-view SEM images of the corresponding alumina films. (d) Top-view SEM image of the porous alumina anodized using 99.0% Al foils. Inset shows EDX analysis of the impurity composition in the area outlined by the white square. (e, f) Side-view SEM images of porous anodic alumina anodized using (e) 99.999% and (f) 99.0% Al foil, respectively. White arrows indicate the direction of pore arrays.

Download English Version:

<https://daneshyari.com/en/article/7911821>

Download Persian Version:

<https://daneshyari.com/article/7911821>

[Daneshyari.com](https://daneshyari.com)