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Short communication

The missing nano-architecture found in the barrier layer of porous anodic alumina

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ABSTRACT

Hexagrams were revealed on the barrier layer of porous anodic alumina during chemical etching and ion milling, indicating non-uniform etching. Six-membered ring structure holes appear firstly around the center of each cell and subsequently merge into a primary circular opening. A new pore-opening mechanism is proposed, and the possible origin of the non-uniform etching rate is also discussed.

1. Introduction

The highly ordered and mutually parallel pore arrangement of porous anodic alumina (PAA) fabricated by a self-organization process in acid electrolyte has inspired scientific interest for decades [1]. In the past years, great efforts have been paid not only for its fabrication technique [2–4] but also for its numerous applications in different disciplines [5–7]. Among the applications, the PAAs are often required to open the barrier layer, forming a through-hole structure [8–10]. In some cases, such as masks for nanodot array deposition and membranes for molecule separation [11–14], it is desired to fabricate the PAAs with funnel-shaped pores for ease of the liquid and vapor through-flow. To realize this goal, one of the simplest ways is to control the opening of barrier layer precisely down to several nanometers [15,16]. However, although many strategies, including wet-chemical etching [17–19], ion milling [20], and plasma etching [21], have been tried, the morphology of the openings is always found deviating from a circle when their diameter is smaller than a dozen of nanometer, appearing an irregular shape. This phenomenon arouses a question: what is the actual nano-architecture of barrier layer?

In order to answer this question, recently, we systematically studied the barrier layer structure of PAAs by wet-chemical etching and ion-beam milling methods. Interestingly, the etching rate of barrier layer is found to be non-uniform. With the etching time increasing, the morphology of barrier layer evolves gradually from hemispherical dome to hexagram. Initial breaching is not located at the center of barrier layer dome as suggested before [17,18,20]. Instead, six-membered ring structure holes are formed firstly around the dome center, and subsequently, the residual dome collapses, appearing a primary circular opening. In this paper, the detailed experimental results are presented and discussed. We believe that the related information is much important in understanding the growth mechanism of PAAs and will be beneficial for the future applications.

2. Experimental

For convenience of the microscopic observation, PAAs with large interpore distance (D_{int}) were fabricated in phosphoric acid electrolyte. Prior to anodization, high purity (99.99%) aluminum sheets were degreased and then electropolished in a mixture of perchloric acid and ethanol (v/v 1:4) at 21 V and 1–5 °C for 5 min. Next, the Al sheets were anodized at 205 V and 1–5 °C for 6 h in 1 wt% H_3PO_4 electrolyte with 0.01 M $Al_2(C_2O_4)_3$ addition [22,23]. Subsequently, the PAA was completely removed in a mixture of H_3PO_4 (50 mL/L) and CrO_3 (30 g/L) at 70 °C. The second anodization was conducted for another 6 h under the same conditions. The optional pore widening of the as-anodized sample was performed after the two-step anodization, then aluminum substrate was removed completely in a saturated $CuCl_2$ solution.

To avoid the difference of anodization process, the obtained PAA was sliced into small pieces and thoroughly rinsed in deionized water as the experimental samples. Two methods were used to etch the barrier layer from the bottom side [17–20]. The first was wet-chemical etching in 5 wt% H_3PO_4 at 40 °C. The second was ion-beam milling with the base pressure of 3×10^{-3} Pa, the Ar flux of 5 sccm, the ion current

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of 180 mA, the acceleration voltage of 260 V, and the grid voltage of 560 V. The incident Ar^{+} ion beam was perpendicular to the sample surface. The sample holder was rotated at 30 r/min. The morphologies of all the samples were observed using a LEO 1530VP field emission scanning electron microscope (FE-SEM).

3. Results and discussion

To etch the barrier layer of the as-fabricated PAAs by wet-chemical method with a fixed time interval of 7.5 min, the morphological evolution can be seen clearly. Initially, the fresh barrier layer is a hexagonal close-packed 2D array of domes (pore tips) (Fig. 1a). In the first 7.5 min, the top portion of the dome is etched faster, and a number of irregular voids appear at the cell boundaries as the dome shrinks (Fig. 1b). Subsequently, the cell walls buried under the crevices are etched more slowly and become more and more pronounced as the process proceeds (Fig. 1c–e), and a double hexagon pattern is observed on the surface (Fig. 1f–l). Interestingly, the triple cell junction sites dissolve more readily in the subsequent period (Fig. 1c–g), showing different properties from the other regions along cell boundary. After the inner layer of the dome completely dissolves, depressions are formed gradually at the region around cell junctions, and ridges are shown across the midpoints of cell boundaries (Fig. 1h). As the dome continues to shrink, the depressions and ridges become more prominent and converge towards the dome center, forming a pattern of hexagrams (Fig. 1j). The dome is breached before 75 min, and a primary circular opening appears at the center of the hexagram. The formation of hexagrams demonstrates that there is a hexagonal symmetrical distribution of etching rate within each cell, and the etching contrast (i.e. the variation of local etching rates) decreases from the cell boundary to the dome center. After the barrier layer is completely removed, the undulation on the surface is diminished gradually (Fig. 1l).

It is reasonable to infer that the hexagonal distribution of etching rate should be also reflected in the initial breaching of the barrier layer, since the ridges and depressions tend to converge at the center of each cell. As shown in Fig. 2, with the etching time increasing, the area and depth of depressions increase simultaneously (Fig. 2a and b). When the depth of depressions reaches the thickness of the barrier layer, the barrier layer is breached. If the etching contrast around the dome center is sufficiently high, the ridges will be strong enough to remain when the dome is breached at depression sites, then small holes will be formed subtending the intersection of neighboring ridges on each pore tip. Ideally, six-membered ring structure holes should appear symmetrically around the dome center (Fig. 2c). Further prolonging the etching time, the diameter of small holes increases, meanwhile the ridges become thinner. Eventually, the small holes merge and the residual dome collapses, resulting in the appearance of

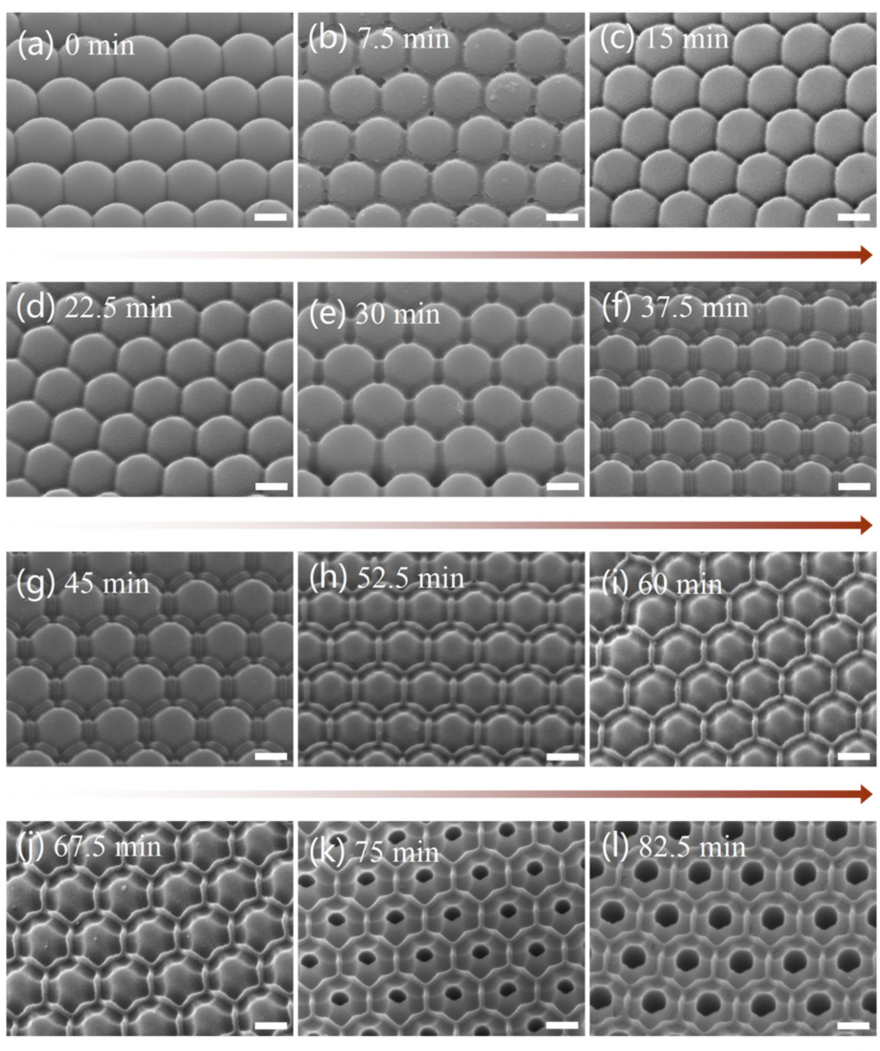

Fig. 1. Tilted FE-SEM images of the barrier layer in different stages of chemical etching. Scale bars are 250 nm.