

GROWTH SEQUENCES OF HIGHLY ORDERED NANO-POROUS ANODIC ALUMINUM OXIDE

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Ordered nano-channel array materials have attracted increasing attention in recent years due to their utilization as templates for nanostructures, such as magnetic, electronic, and optoelectronic devices. The growth of porous aluminum oxide films has been known for years [1,2] and has been recently developed to highly ordered nanoporous anodic aluminum oxide (AAO)[3]. For the improvement of nano-pore arrangement two types of process have been studied; naturally occurring long-range ordering and ordering with ideally arranged hole configuration using prepattern aluminum. Self-organization of nano-pore domains, leading to a densely packed hexagonal pore structure, recently observed by Masuda et al.[3]. In this technique, highly ordered hexagonal pore arrays are formed under two-step anodizing in acidic solutions [4-7].

To fabricate ordered nanopore arrays, a similar two-step anodization process was used. The high purity aluminum (99.99%) plates were anodized in a 0.3M oxalic acid electrolyte under anodic potential equal to 40 V. In this work, we utilized ex-situ contact-mode atomic force microscopy [8] and scanning electron microscopy to promote the topographical properties of AAO membranes. The sequence of ordering growth of AAO membranes is seen in Figure 1. During the first step anodization process, the pores nucleate at the surface at almost random positions, and as a result pores on the surface occur randomly and have a broad size distribution (Fig 1b). After removing the oxide layer, formed during the first step, the remaining periodic concave patterns can be seen on the aluminum substrate (Fig. 1c). An ordered nanopore array is obtained after anodizing for the second time by using the same parameters as in the first step (Fig. 1d). In fact, the concave pattern acts as self-assembled masks for the second anodization process [6]. Moreover, based on the ex-situ AFM and SEM studies, the ordered domains show a typically linear growth behavior by increasing the duration of first anodization step as: $D = 0.55 t$, where D is the domain size in square micrometer and t is the first anodizing step time in hr. However, the extension of the second-step anodizing time increases the AAO membrane thickness without affecting the through pore arrangement. Figure 2 illustrates the through pore arrangement of AAO membranes with different thicknesses.

It is concluded that an almost ideally arranged hexagonal cell configuration with a pore size of approximately 40 nm and appropriate through pore arrangement is achieved. It is obvious that the concave patterns, formed after removing the first oxide layer, cause to develop the ordered nanopore domains, which are separated from the neighboring domains with different lattice orientations by grain boundaries and show polycrystalline structures.

References:

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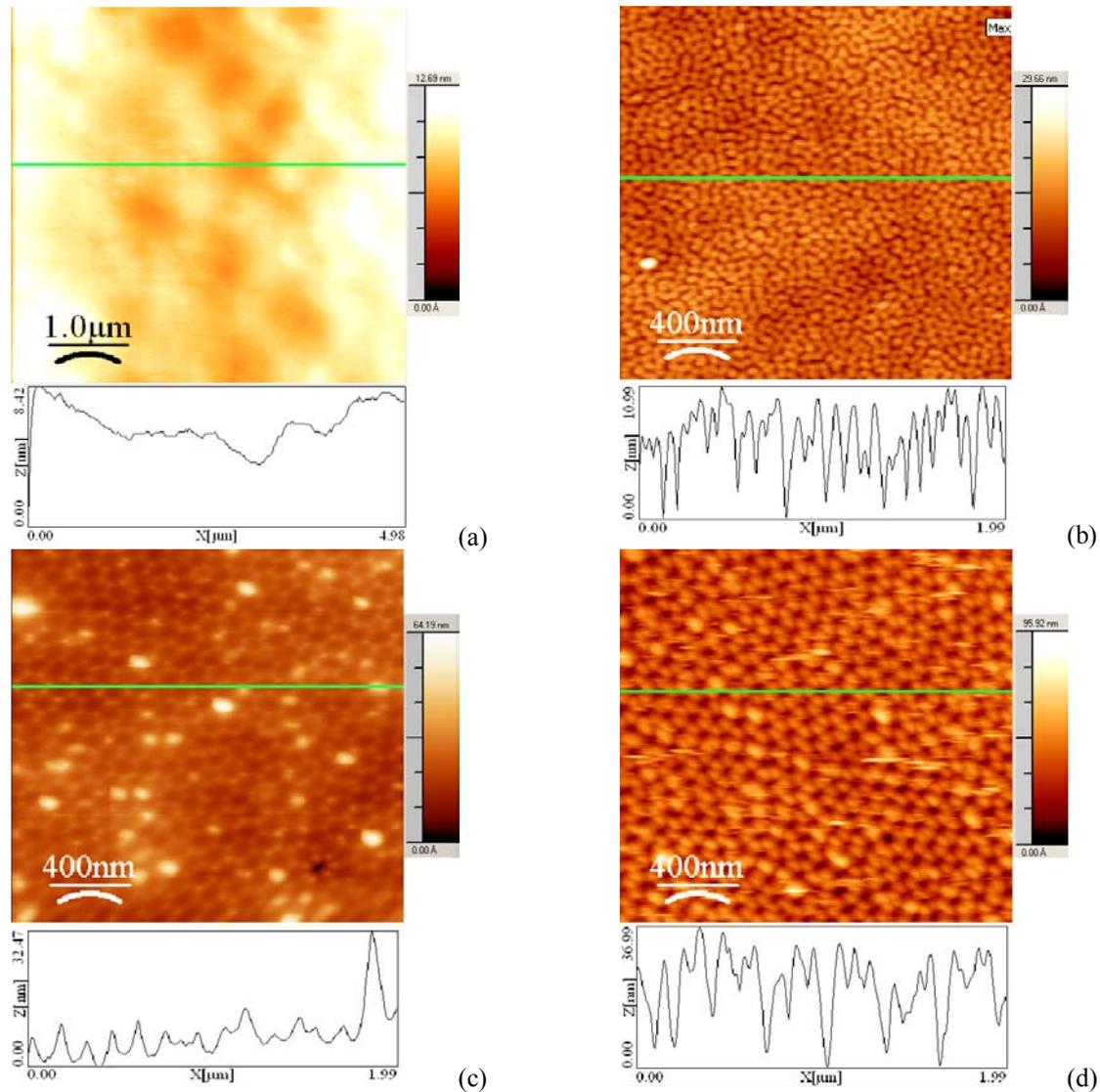


Figure 1. Topographies of surfaces, obtained after (a) Electropolishing in 4 C₂H₅OH: 1 HClO₄ for 15 min below 10°C, (b) Anodizing for 6 hr in 0.3M oxalic acid under 40V below 2°C, (c) Dissolving the oxide layer, formed during the first step anodizing, in a mixture of 0.2M H₃PO₄ and 0.2M H₂Cr₂O₄ at 60°C, (d) Two-step anodizing in 0.3M oxalic acid under 40V for 6hr and 45 min in the first and second steps, respectively (pore widening for 30 min in 5% wt H₃ PO₄ at 35°C).

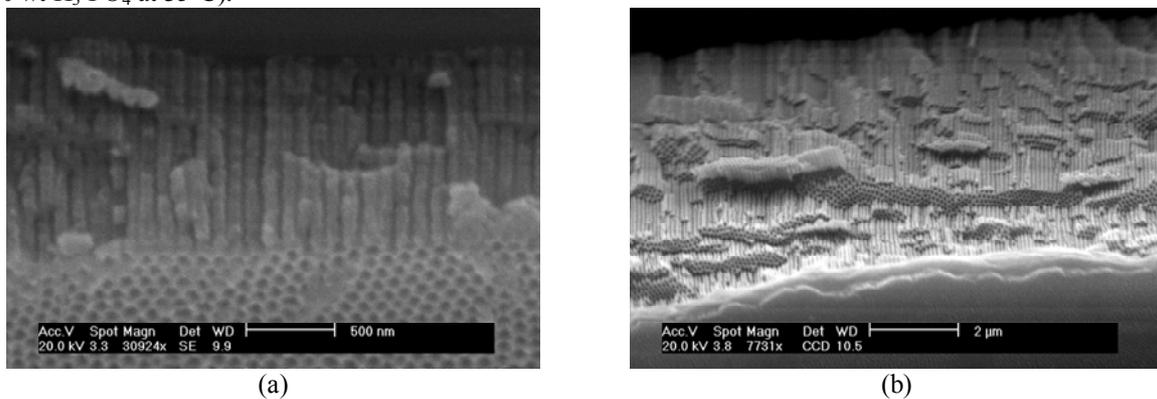


Figure 2. SEM images of fracture surfaces of AAO membranes, obtained with the two-step method after 6 hr anodizing in the first step and 45 min (a) and 6hr (b) in the second step.