Polycrystalline nanopore arrays with hexagonal ordering on aluminum

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Nanopore arrays with $6\times10^{8}-5\times10^{10}$ cm^{-2} pore densities were fabricated by self-organized anodization on aluminum. A two-step anodization process was used to oxidize aluminum in oxalic, sulfuric, and phosphoric acid solutions. Hexagonally ordered pore arrays were obtained within domains of a few micrometers, which are separated from neighboring domains with different orientation of the pore lattice by domain boundaries, i.e., the nanopore arrays show characteristics analogous to two-dimensional polycrystalline structure. The interpore distance can be controlled by changing the electrolyte and/or the applied voltage. © *1999 American Vacuum Society.* [S0734-2101(99)20304-1]

I. INTRODUCTION

Nanochannel-array materials have attracted considerable scientific and commercial attention due to their potential utilization in magnetic, electronic, and optoelectronic structures, and devices.[1,2] Self-organizing structures have been proposed to fabricate such nanoscale structures due to their potentially low cost and relative ease of fabrication.[3–5] Anodic porous alumina, which has been studied extensively over the last five decades,[6] has recently been reported to be a typical self-ordered nanochannel material.[7,8] Self-organization during pore growth, leading to a densely packed hexagonal pore structure, has been reported in oxalic, sulfuric, and phosphoric acid solutions.[7–10] However, the ordered pore arrangements are formed under some specific anodizing conditions after a long anodization time, and as a result, they can only be observed on the bottom part of the films. Masuda and Satoh first showed that straight nanoholes could be formed in a thin membrane of porous alumina by stripping away the thick oxides obtained from the first long anodization and subsequently anodizing it for a short time.[11] However, ordered nanopore arrays with high aspect ratio (ratio of diameter and depth) have not yet been prepared, and the arrangement morphology of the arrays has not been studied. In this article, we report regularly arranged and parallel nanopore arrays with high aspect ratio in anodic alumina, and show the arrangements of the ordered nanopore arrays in differently oriented domains.

II. EXPERIMENT

High purity (99.999%) aluminum foils were used for anodization. The aluminum substrates were degreased in acetone and cleaned in a mixed solution of HF, HNO_3, and HCl acids, and then annealed under nitrogen ambient at 400 °C to remove mechanical stresses and recrystallize. Metallographic examination showed the grain sizes of the annealed foils to be 100–200 μm. To smooth the surface morphology, the substrates were electropolished in a mixture of $HClO_4$ and C_2H_5OH. The mean roughness of the polished surface was measured by atomic force microscopy (AFM) to be 3 nm over a 3 μm square scan area.

Anodization was conducted under constant cell potential in three types of aqueous solutions, sulfuric, oxalic, and phosphoric acid as an electrolyte. The aluminum foils were mounted on a copper plate serving as the anode and exposed to the acid in a thermally isolated electrochemical cell. During anodization, the electrolyte was vigorously stirred or recycled using a pump system. The values of voltage, current, and temperature were recorded via computer.

During the 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. However, under some specific anodization conditions,[7–10] hexagonally ordered pore domains can be obtained at the bottom of the layers. To facilitate the observation of pore arrangements at the bottom, the remaining aluminum substrate was removed in a saturated $HgCl_2$ solution after anodization, and the pore bottoms were subsequently opened by chemical etching in 5 wt % aqueous phosphoric acid. This etching process also leads to some pore widening, so the observed pore diameters do not reflect the intrinsic properties of the anodization process. On the other hand, this etching process can also be used to adjust the ratio of pore diameter and distance in a certain range, especially for the thin porous membranes.

To fabricate ordered nanopore arrays in which the holes are straight and regularly arranged throughout the film, a two step anodization process similar to that reported by Masuda and Satoh[11] was used. In the first anodization process, the hexagonally ordered pores were formed at the bottom layer by the self-organization process. Subsequently, the oxide layer is removed by wet chemical etching in a mixture of phosphoric acid (6 wt %) and chromic acid (1.8 wt %) at 60 °C. The remaining periodic concave patterns on the aluminum substrate act as self-assembled masks for the second anodization process. An ordered nanopore array is obtained after anodizing for the second time by using the same parameters as in the first step. The structures of the nanopore arrays of anodic porous alumina were observed using a scanning

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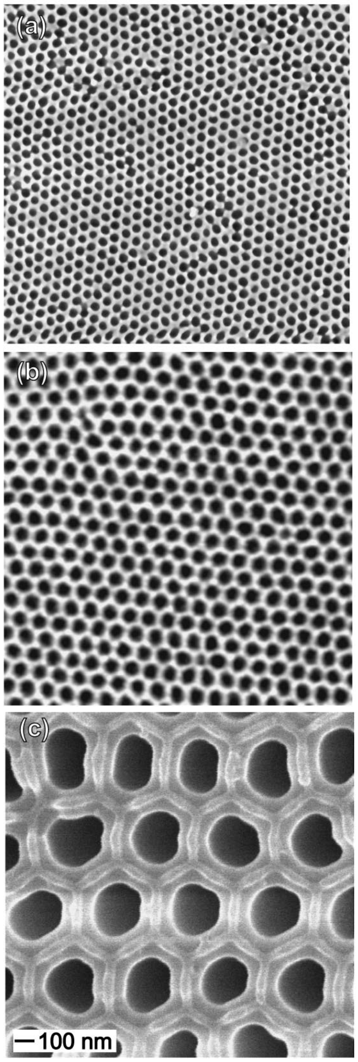

FIG. 1. SEM bottom view of porous alumina layers with hexagonally ordered pore structures after opening the pore bottoms. The anodic alumina layers were prepared by anodizing in 0.3 M sulfuric acid at 10 °C at 25 V (a), 0.5 M oxalic acid at 5 °C at 40 V (b), and 10 wt % phosphoric acid at 3 °C at 160 V (c). Pore opening was carried out in 5 wt % phosphoric acid at 30 °C for 30 min (a), 35 °C for 30 min (b) and 45 °C for 30 min (c).

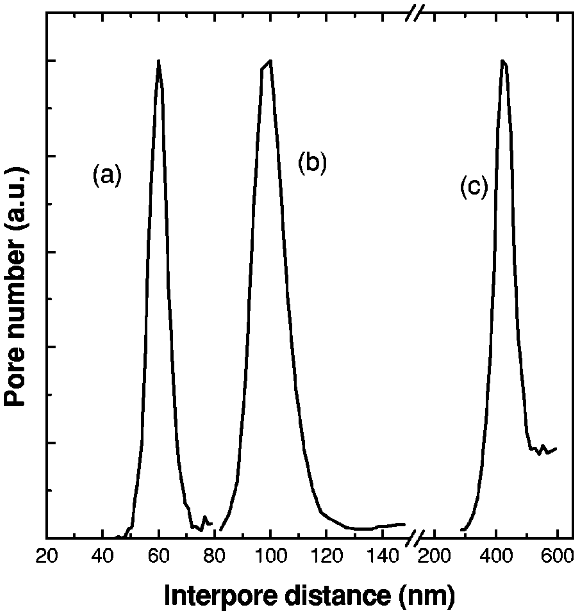

FIG. 2. Distributions of interpore distances for the ordered porous alumina which were anodized in sulfuric (a), oxalic (b), and phosphoric acids (c) using the same parameters as in Fig. 1. Numbers of pores contributing to the analysis are 790, 2530, and 5505, respectively.

electron microscope [(SEM), JEOL JSM-6300F] and atomic force microscope [(AFM), Digital Instruments, NanoScope 5000]. The analyses using AFM were performed in tapping mode in air and the scan rate was kept at 1 Hz.

III. RESULTS

Figure 1 shows SEM micrographs of the pore arrangements with the same magnification, where the films were anodized in sulfuric, oxalic, and phosphoric acid solutions under potentials of (a) 25, (b) 40, and (c) 160 V, respectively. Almost perfect hexagonally arranged pore domains can be seen. In the domains, hexagonally ordered pores are surrounded by six hexagonally ordered columnar oxides, which are interconnected to form a network structure. The interpore distances, i.e., the center-to-center distance between neighboring pores, and their distribution are shown in Fig. 2. The mean interpore distances are 60, 100, and 420 nm, and the full-widths at half-maximum of the size distributions are 6, 11, and 70 nm, respectively. The increases of the curves on the high distance side come from the overlaps of the second peaks which correspond to the second nearest neighbor pore distance. It shows that the hexagonally ordered nanopore arrays with a narrow size distribution can be extended to a wide spacing range by a self-organization process although the arrays anodized in phosphoric acid have a more disordered structure than those anodized in oxalic or sulfuric acids.

To observe the orientation of ordered domains, Fig. 3

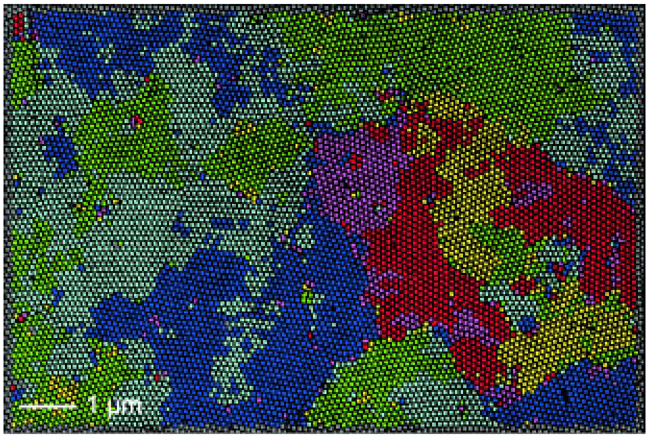

FIG. 3. Polycrystalline pore arrangement of the ordered porous alumina. The analysis was based on the SEM bottom view of a porous alumina layer. Different orientations of the pore lattices are shown in different colors. The pores adjacent to the image edge shown in gray are not taken into account. Anodization was conducted in 0.3 M oxalic acid at 1 °C at 40 V, and pore opening was carried out in 5 wt % phosphoric acid at 35 °C for 40 min.

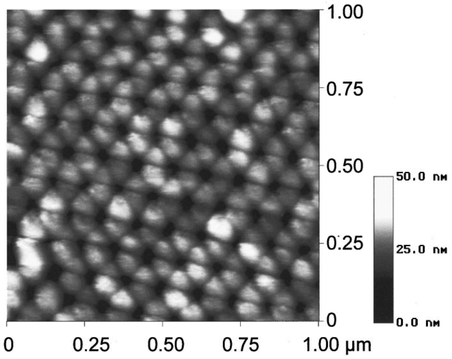

FIG. 4. AFM top view of nanopore arrays in anodic alumina prepared by two step anodization. Anodization was conducted in 0.5 M oxalic acid at 5 °C at 40 V, and the first and second anodization time are 22 and 99 h, respectively.

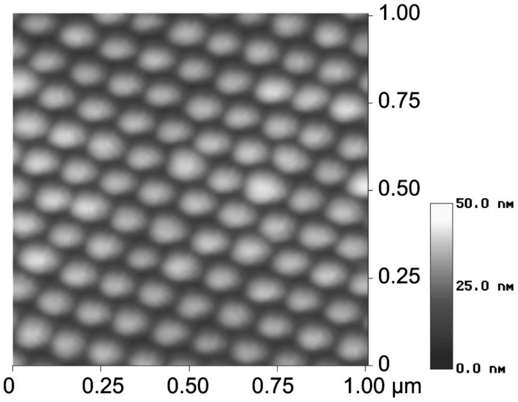

FIG. 5. AFM bottom view of nanopore arrays in anodic alumina prepared by two step anodization before pore opening. The pore bottom is covered by an oxide layer.

gives the domain morphology where the domains with different orientation of the pore lattice are shown in different color. The analysis is based on a SEM micrograph of porous alumina which was anodized under 40 V in oxalic acid. A detailed description of the analysis method for the image will be given later. The ordered domains are in a range of 1–5 μm, which are separated from neighboring domains with different orientation of the pore lattice by domain boundaries, i.e., the ordered pore arrangements show a domain structure analogous to a two-dimensional polycrystalline structure. Some defects, i.e., pores which are not hexagonally arranged, are marked in different color from the surrounding. Anomalous features are observed at the domain boundaries, and the domains are randomly oriented and of random shape. The ordered domains have no correlation with the crystalline grains of the aluminum since the latter are about two order of magnitude larger.

The self-organization mechanism of the hexagonally ordered porous alumina was discussed previously.[9,10] It was suggested that the repulsive forces between the neighboring pores caused by mechanical stress at the metal/oxide interface promote the formation of hexagonally ordered pore arrangements. And the best ordering is achieved for a moderate expansion factor (relative ratio of thickness of the grown alumina layer and the consumed aluminum layer) of 1.4, independent of which electrolyte is used. Based on this explanation, we changed anodization parameters, e.g., anodic electrolyte and voltage, while controlling the expansion factor and prepared ordered arranged pore structures with interpore distances of 50, 60, 100, 150, and 420 nm, which corresponds to a pore density range of $6\times10^{8}-5\times10^{10}$ cm^{-2}.

After the formation of the hexagonally ordered pores, the oxide layer was stripped away and a second anodization process was conducted. Nanopore arrays with high aspect ratio and straight holes were prepared by using this two step anodization process. Figure 4 shows an AFM top view micrograph of the nanopore array. The two steps of anodization were conducted in 0.5 M oxalic acid under 40 V and 5 °C, and the anodization time of the first and second processes were 22 and 99 h, respectively. The dark parts in Fig. 4 correspond to the pores. The period of the pore arrangement or interpore distance is about 106 nm. The roughness of the surface results from the second anodization process and the chemical etching for removing of the oxide layer.

After coating a handling and protecting layer on the surface of the porous alumina film, the remaining aluminum substrate was removed in saturated $HgCl_2$ solution. The thickness of the free standing porous alumina layer was measured under an optical microscope to be about 170 μm for this sample. Figure 5 shows an AFM bottom view exhibiting the morphology of the porous alumina. The pore bottom is covered by a layer of oxide aluminum called barrier layer. The bright parts in Fig. 5 correspond to the pore bottoms. The period of the pore arrangement or interpore distance is about 110 nm, almost the same as that at the surface of the arrays. The aspect ratio is more than 1500. When varying the second anodization period from 1 to 100 h, the ordered pore and domain structures do not change. This means that a nanopore array grown from a patterned aluminum surface yields ordered pore structures which closely resemble the pattern on the aluminum surface from which they grew. This implies that the nanopore arrays can also be grown from a prepatterned aluminum surface by means of electron beam lithography or nanoimprint techniques. The feasibility to pattern the aluminum surface by a molding process and to prepare ordered nanopore arrays in the anodic porous alumina have already been shown recently.[12] Our group is now working on direct prepatterning aluminum surface by an electron beam lithography technique and fabricating monocrystalline nanopore arrays on aluminum.

IV. CONCLUSIONS

We have fabricated nonlithographic nanopore arrays in anodic alumina with areal pore densities in the $6\times10^{8}-5\times10^{10}$ cm^{-2} range. A two-step anodization process was used to oxidize aluminum. Self-organized hexagonal pore arrangements were formed at the end of the first anodization process. After removing the irregular upper part, the densely ordered pits at the bottom of the anodic layer act as natural masks, and the nanopore arrays were fabricated by the second anodization process. Perfect ordered pore arrays were obtained within domains of a few micrometers, which are separated from neighboring domains with different orientation of the pore lattice by grain boundaries, i.e., the nanopore arrays show polycrystalline structure. The pore distance can be controlled by changing the anodic electrolyte and voltage.

ACKNOWLEDGMENTS

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