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Ordering and modification of nanopores in porous anodic aluminum membranes

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ABSTRACT

Anodic aluminum oxide (AAO) has attracted significant intension for decades owing to its extensive applications in nanoscale science and technology. Novel structures, like nanoparticles, nanotubes, nanowires, etc., have been developed based on AAO templates and widely applied in optics, micro/nano electronics and microfluidic systems, etc. In this work, three approaches have been developed to control and modify the parameters and arrangement of nanopores in anodized alumina, including the change of electrochemical conditions, guiding the growth of nanopores by highly aligned line structure, and further modification of nanopores by physical vapor deposition. Moreover, highly oriented line structures used to guide the channel growth have been fabricated under optimal conditions and could be utilized as templates to form wrinkled membranes, nanowires, etc. We conclude that electrochemical anodization should be a very promising technique for the fabrication of various nanoscale structures leading to potential applications in optics, solar systems and micro/nano electronics.

1. Introduction

Anodic aluminum oxide (AAO) with naturally grown nano-sized and highly-ordered pores has successfully provided us with an alternative fabrication approach for various micro/nano structures, such as nano dots, nano tubes and nano wires [1–3]. In comparison with conventional techniques, such as E-beam lithography or FIB, AAO technique has the advantages of low cost and unique simplicity to fabricate ordered hole patterns with high aspect ratio of nanochannels.

In this work, we found that ultrasonic cleansing process, heated-up electrochemical polishing process and moderate time anodization under low voltage is capable of producing periodically distributed groove structures on the surface, guiding the growth of nanochannels at the valley between line structures. This approach to roughen the surface may contribute to the wrinkling process [4,5], which is currently attracting increasing attention. Furthermore, ordered honeycomb topography can also be obtained after long time anodization after the removal of the anodized alumina. Using this electrochemical technique, hexagonally arranged nanopores with high aspect ratio nanochannels in large area can be achieved. This technique should find potential applications in template-based synthesis of novel nano structures, optics, micro/nano electronics, microfluidic systems [6] and lab on chip.

2. Experiment

To fabricate AAO templates, pure aluminum (99.9%) foil was used as the anode and molybdenum as the cathode. The distance between the two electrodes was about 2 cm. Before anodization, the Al foil was degreased in ethanol ultrasonically and flushed with deionized water. Then the cleaned Al foil was electrochemically polished in a mixed solution of perchloric acid with ethanol (1:5 in volume) under a constant DC voltage of 18 V for 3 min [7]. The Al foil was anodized under different conditions to obtain AAO with pore diameters ranging from 20 to 180 nm. We used the conventional two-step anodizing process [8] by anodizing aluminum twice under the same condition. Aluminum was first anodized in a 0.5 M oxalic acid under 40 V at 3 °C for 3 h, followed by the removal of the first anodized alumina by soaking it in a mixed solution of 6 wt.% phosphoric acid and 1.8 wt.% chromic acid (1:1 in volume) at 85 °C for 45 min. In order to obtain the highly ordered pores, the aluminum with periodically distributed honeycomb pattern was anodized again under the same conditions as the first step. After specific time of second anodization, AAO template with highly ordered pores was formed.

In addition, with the same pretreatments and the normal two-step anodizing process we could fabricate AAO templates with much wider pore diameter in 8 wt.% phosphoric acid under 120 V at 3 °C. Moreover, under other optimal conditions we were able to alter the morphology of AAO by controlling pore parameters such as diameter and inter-pore distance. A unique way to achieve the specific morphology of highly oriented line structures with

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ordered channels beneath was to electrochemically polish the ultrasonically cleaned aluminum at ~50 °C, as opposed to the conventional anodization process, and then anodize it in acid under low voltage (20 V) at 3 °C for 20 min.

Meanwhile, by a physical vapor deposition the morphology of AAO could be further modified. Thin metal films of 25 nm in total were deposited onto the anodic alumina substrate via E-beam evaporation. To investigate the effect of deposition parameters on the morphology of AAO, metals in total thickness of 20 nm were evaporated onto the AAO sample fabricated under the same conditions.

3. Results and discussions

The anodization condition for AAO film with ordered pore distribution had been developed in this work. It was worth to note that the heat generation during anodization, especially under high voltage, would influence the growth of nanochannels. Both a magnetic stirrer and a cooling system were added to the whole anodic systems.

Samples fabricated in sulfuric acid, oxalic acid and phosphoric acid were characterized by a scanning electron microscopy (SEM) as respectively shown in Fig. 1a, b, and c. Obviously, AAO with pore diameters ranging from 20 to 180 nm were formed under specific conditions, of which some were listed in Table 1. The first way to control the morphology of AAO is to traditionally optimize electrolytic conditions to achieve the morphology controllability of AAO by changing the pore parameters.

An aluminum sheet was first polished at ~50 °C, higher than conventional polishing process, and then anodized in acid under low voltage for 20 min, periodically arranged wrinkles on the surface emerged as shown in Fig. 2. Watanabe et al. [9] reported that the processes of ultrasound cleansing and optimal anodization developed the highly aligned line structures, which was originated from the fiber-like structures left during the Al plate manufacturing process and then was implanted as a casting template to obtain line pattern of functional molecules. In contrast to their work, the unique features in this work include much more ordered line structures with the same height, electrochemically polished aluminum foil at ~50 °C before anodization, higher than the temperature of regular polishing process (room temperature), and linear nanochannel array grew at the valley of groove structures after anodization under 20 V for longer time. Compared to the sample that was polished at room temperature and possessed hexagonally distributed pores after same low voltage anodization in same electrolyte, it could be inferred that the unique highly-aligned wrinkle structures could be induced and further modified by the heated-up polishing process. Electrochemical polishing process at higher temperatures had preferential etching behavior in specific boundaries [10], leading to different dissolution rates from top to bottom

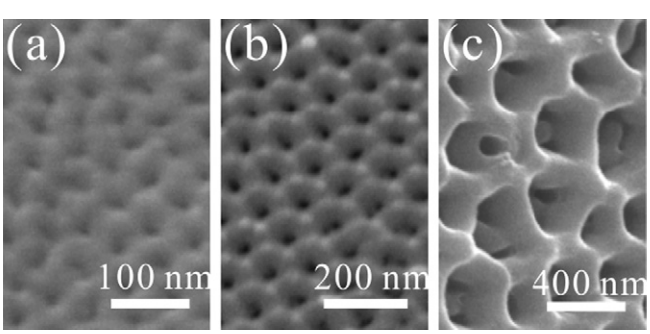

Fig. 1. SEM images of top surfaces of samples anodized in sulfuric acid (a), oxalic acid (b), and phosphoric acid (c). The pore diameters are about 20, 30, and 180 nm respectively.

Table 1
Some optimal experimental conditions for anodization and corresponding pore parameters.

Electrolyte	Concentration (wt.%)	Voltage (V)	Pore diameter (nm)
Sulfuric acid	2.8	25	~20
Oxalic acid	4.3	40	~30
Phosphoric acid	8	120	~180

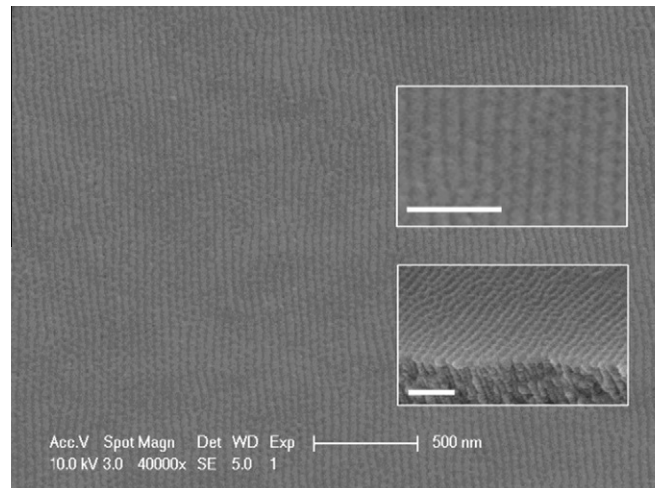

Fig. 2. SEM image of periodically arranged wrinkles formed after polishing at 50 °C and anodization under low voltage. The upright inset magnified the image to present the pores at the bottom of the valley; the inset below is the image of cross section. The scale bars in both insets are 200 nm.

of original fiber-like structures on the Al plate. Besides, during the heated polishing process the high temperature softened the Al electrode and rearranged the particles by changing the particle size and distribution [11], which might also roughen the surface and had an effect on the unique structures. Therefore, the heated polishing process together with the following process of anodization, inducing volume expansion after the formation of alumina, could be responsible for altering initial wrinkle structures with random width and depth into finer groove structure.

Furthermore, in our work another unique feature was the phenomenon that nanochannels could periodically grow at the bottom of valleys after 20 min electrochemical anodization. The upright inset in Fig. 2 magnified the wrinkled surface and weakly presented ordered pores at the valley, while the inset below showed the cross section so that one could clearly see both the highly oriented line features on the surface and ordered nanochannels beneath. Anodization in the electrolytes of both oxalic acid and sulfuric acid under 20 V could produce ordered wrinkles with linear pore at the valley between line structures, so to maintain the nanoscale groove structures with linear pore array required lower anodization voltage to make the curvature of the bottom of nanochannel match with that of the valley between line structures according to the widely accepted mechanism for pore formation [12]. As opposed to hexagonally distributed pore array grown on smooth Al surface polished at room temperature, the polished line structures influence the growth of nanochannel and guide the pores into linear array along the grooves between lines. In addition, 20 min anodization was longer than the time required to replicate and modify the wrinkle surface without nanochannel growth. Thus, highly oriented nanoscale grooves could benefit the final order of nanopores in anodized alumina and optimal anodization time could prolong the growth of nanochannels at the valley. As mentioned above, this kind of structures might also provide a new way to nano wrinkle pattern transfer.

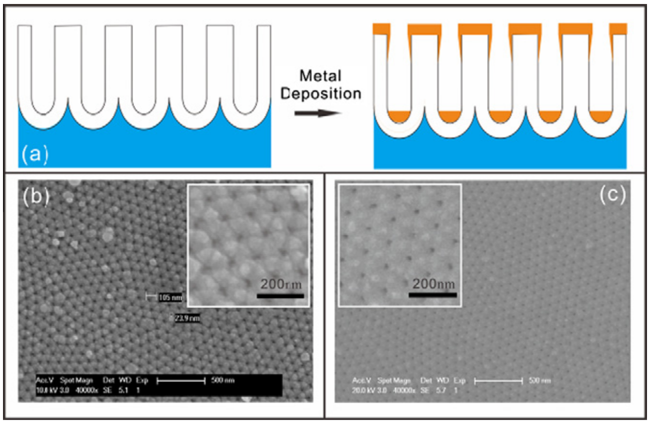

Fig. 3. (a) Schematic illustration of deposition onto porous alumina to adjust the diameter; (b) 25 nm metals deposited at a rate of 3 Å/s with pore diameter around 23 nm and (c) 20 nm metals deposited at a slower rate of 0.6 Å/s with pore diameter of 14 nm. Both insets in b and c show the enlarged images.

After the fabrication of porous alumina, E-beam evaporation was carried out to deposit different thickness of metals onto porous substrate at different deposition rates to investigate the influence on the morphology of AAO. Fig. 3a schematically depicted the principle of adjusting pore diameters by physical vapor deposition. During the E-beam evaporation process the films grown on the upper surface formed a network structure following the anodic alumina pattern. While the ones deposited into porous areas were disconnected and remained in the bottom of the pores due to the high aspect ratio. Therefore, the surface morphology of the deposited layers precisely imaged the upper surface pattern of the anodic alumina. During the deposition process the evaporated atoms entered into the channels and were partly deposited on the walls, leading to the decrease of the pore diameters. However, the results after the deposition demonstrated that the pore diameter was determined not only by the total thickness of the deposited material, but also by the deposition rate. Fig. 3b and c present the two same AAO templates after deposition of 25 nm metals at the rate of 3 Å/s and that of 20 nm metals at the rate of 0.6 Å/s, respectively, and the corresponding diameters after deposition were around 23 and 14 nm respectively, smaller than 30 nm of the original AAO pore diameter (Fig. 1b). Since thinner films deposited at slower rate have smaller pore diameter, the deposition rate might play a more important role in the morphology control of AAO than the total deposition thickness [13]. This could be used to precisely control the pore parameters of AAO template for applications with certain requirements on the controllability of pore pattern.

4. Conclusions

We have successfully demonstrated three ways to control and modify the arrangement of the pores on AAO by the change of electrolytic conditions, unique wrinkling process to guide pore growth, and physical vapor deposition to modify the parameters. Especially, the wrinkling process in this work provided a simple approach to directly obtain highly aligned line structures. On the other hand, the AAO templates could meet different requirements of applications on the pore diameters via traditional anodization under different optimal conditions, the wrinkling process, including heated polishing process and the process of anodization under low voltage, and physical vapor deposition. The processes comprising wrinkling as well as physical vapor deposition, developed in this work, to order and modify the nanopores should enable us to fabricate various micro/nano structures for broad applications in optics, mechanics, and fluidics.

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