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# ADVERTISEMENT



## Highly ordered nanochannel-array architecture in anodic alumina

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The development of the ordered channel array in the anodic porous alumina was initiated by the textured pattern of the surface made by the molding process, and growth of an almost defect-free channel array can be achieved throughout the textured area. The long-range-ordered channel array with dimensions on the order of millimeters with a channel density of  $10^{10}$  cm<sup>-2</sup> was obtained, and the aspect ratio was over 150. The master for molding could be used many times, which makes it possible to overcome problems in the conventional nanolithographic technique, such as low through-put and high cost. © *1997 American Institute of Physics*. [S0003-6951(97)03145-8]

Nanochannel-array materials, which have fine, uniform channels of nanometer dimension, have stimulated considerable interest in recent years due to their utilization as a host or template structure for nanometer devices, such as magnetic, electronic, and optoelectronic devices.<sup>1,2</sup> The most characteristic feature of these materials has been emphasized with the extremely high aspect ratio of their channels (depth divided by width) which is difficult to achieve with conventional lithographic techniques. Anodic porous alumina, a typical self-ordered nanochannel material formed by anodization of Al in an appropriate acid solution, has recently attracted increasing interest as a key material for the fabrication of nanometer-scale structures.<sup>3,4</sup> The structure of anodic porous alumina is described as a close-packed array of columnar cells, each containing a central pore of which the size and interval can be controlled by changing the forming conditions.<sup>5</sup> We reported previously that anodic porous alumina with relatively long-range order can be obtained in oxalic acid<sup>6</sup> and sulfuric acid<sup>7</sup> under an appropriate anodization condition, in which the pores are organized spontaneously into close-packed hexagonal arrays. However, the defect-free area of naturally occurring ordering appears in a domain structure and is limited to the size of several micrometers.

Here, we propose a novel approach for precise control of the growth of the channel array in the anodic porous alumina, which enables us to fabricate the long-range-ordered channel-array architecture on the millimeter scale. Our approach was motivated by the idea that if the development of the hole is guided by the appropriate texture of the surface at the initial stage of anodization, and an appropriate condition is maintained for the self-ordering, the long-range-ordered channel-array architecture can be expected to grow spontaneously. This process has two points of interest:

- shallow ordered textures (array of concaves) which can be easily prepared with a standard lithographic process can introduce the development of pores<sup>8</sup> and can guide the growth of channels with an extremely high aspect ratio, and
- (2) a molding process using an appropriate master has been

The molding process is the simplest way to produce a textured surface but is rarely applicable in the nanometer scale. Very recently, a process for the fabrication of microstructures of polymer material was reported.<sup>9</sup> However, to our knowledge, the application to a metal substrate has not been reported in nanometer dimensions. Introduction of the molding process is favorable for texturing the Al surface, because Al has sufficient plasticity to be deformed by mechanical molding. In contrast to the orientation-dependent anisotropic wet etching of Si,<sup>10</sup> the anodizing process of Al is independent of the restriction of the orientation of the crystal, because the main driving force in the formation of the channel in the anodic alumina is the electric field rather than the crystal direction. This allows the fabrication of the initiation point by a mechanical deformation process and continuous growth of the ordered channels without being affected by crystal orientation.

The fabrication procedure of the ordered channel-array structure is schematically shown in Fig. 1. An Al sheet (99.99% purity) was annealed at 400 °C for 1 h to facilitate deformation in the molding process, and was polished electrochemically. The master which has a hexagonally arranged array of convexes was fabricated with the use of conventional electron beam (EB) lithography. The substrate for the master requires enough mechanical strength and suitably for EB lithography on the nanometer scale. We examined several kinds of substrates and found that the SiC single-crystal wafer satisfies these requirements. The size of the SiC master was typically  $4 \times 5$  mm, on which the array of convexes was fabricated in the area of  $3 \times 0.6$  mm. The largest SiC mold fabricated was 3 mm×3 mm in textured area.

The master was placed on an Al sheet and pressing was carried out using an oil press at room temperature. This process generated the array of concaves on the surface of Al, which was the replicated negative of the convexes of the master. The appropriate pressure, at which the pattern was fully transferred to the Al surface, was approximately 5

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introduced for texturing the surface to offer the high through-put mass production which can overcome the bottle neck in the conventional nanolithographic process.

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FIG. 1. Process for the ordered channel array; SiC mold with hexagonally ordered array of convexes (a), molding on the Al (b), textured Al (c), anodization and growth of channel architecture (d), removal of Al and barrier layer (e).

ton  $cm^{-2}$ . Under that pressure, the master could be detached from the patterned Al and reused.

The anodization of Al was conducted in an oxalic acid solution under the constant-voltage condition. To clarify the cell configuration, the specimen was dipped in a 5 wt % phospholic acid solution at 30 °C for pore-widening treatment after the anodization. For the observation of the cell configuration from the bottom part of the oxide film, called the barrier layer, the Al layer was removed in a saturated HgCl<sub>2</sub> solution and then the barrier layer was subsequently removed by etching treatment in a phosphoric acid solution.

Figure 2 illustrates the surface view of the anodic porous alumina by a scanning electron microscope (SEM), half of which (right-hand side) was pretextured by molding. Channels arranged in a two-dimensional hexagonal configuration were observed only in the pretextured area, while the arrangement of the channels was disordered in the untreated area. The interval between channels, in other word, the size of the cells, corresponded to that of the pretextured pattern (150 nm in the case of the array shown in Fig. 2). The result shown in Fig. 2 confirms that the predetermined pattern formed by mechanical deformation can act as initiation points and guide the growth of channels in the oxide film.



FIG. 2. SEM micrograph of surface view of anodized Al; pretexturing interval was 150 nm. Anodization was conducted in 0.3 M oxalic acid of 17 °C at 60 V for 36 min. Pore widening was carried out in 5 wt % phosphoric acid at 30 °C for 70 min.



FIG. 3. Cross-sectional view of channel array of anodic alumina; pretexturing and anodization conditions are the same as in Fig. 2. Pore widening was carried out in 5 wt % phosphoric acid at 30 °C for 60 min. The SEM observation was carried out without removal of Al and barrier layer of the oxide film.

The cross-sectional view in Fig. 3 demonstrates the high-aspect-ratio appearance of the channel in the anodic alumina. From this photograph, the growth of straight parallel channels perpendicular to the substrate can be confirmed. The most characteristic feature of the present method is that shallow predetermined concaves can initiate the pores and guide the growth of the long channel (16  $\mu$ m in the case of Fig. 3). The depth of each concave formed by molding was  $\sim$ 20 nm, as determined by the profile analysis using an atomic force microscope. This shallow pattern generated the long-channel architecture with an almost ideal configuration over 15  $\mu$ m in depth (aspect ratio of as much 150). The cell size of the anodic porous alumina is proportional to the forming voltage<sup>5</sup> (2.5 nm for a specific applied voltage). If the anodization condition did not satisfy the requirement dictated by the relationship between the cell size and forming voltage, ordered growth could not be maintained.

The ordered configuration of the channel can be confirmed from the view of the barrier layer of the film (Fig. 4). The almost defect-free configuration in the area shown in Fig. 4 verifies that all channels grew straight, parallel to each other. When the whole specimen is viewed, some defects could be observed in the cell configuration at the present stage. The development of defects was affected by the surface condition of the Al after molding. Defects in the texture, which were due to imperfections in the pattern of the master or dust at the surface, may generate the defects in the cell configuration. The ratio of the defects was also dependent on the depth of the channel in the oxide film. The number of the defects tended to increase as the film grew.

Figure 5 summarizes the obtained channel-array architectures of the anodic alumina with different intervals. These architectures were formed using the predetermined pattern of concaves with periodicity identical to that of formed cells,

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FIG. 4. SEM micrograph of cell configuration in barrier layer; anodization condition was the same as that for Fig. 2. Al was removed in saturated  $HgCl_2$  solution after pore-widening treatment in 5 wt % phosphoric acid at 30 °C for 30 min, and the barrier layer was removed by dipping the sample in the phosphoric acid solution for 75 min.

with subsequent anodization at the corresponding voltages. In the smallest architecture formed at 40 V, the channel diameter was 70 nm, and the interval was 100 nm, which corresponds to the packing density of  $10^{10}$ /cm<sup>2</sup>.

In the previous studies of naturally occurring ordering of the cell configuration without the assistance of the predetermined texture, the degree of self-ordering was strongly dependent on the applied voltage which was determined by the solution used for the anodization.<sup>6,7</sup> In the case of anodiza-



FIG. 5. SEM micrographs of cell configuration in barrier layer with different intervals of 100 nm (a), 150 nm (b), and 200 nm (c). Anodization voltage were 40 V (a), 60 V (b), and 80 V (c). Anodization was conducted in 0.3 M oxalic acid of 17 °C for (a) and (b), and 0.04 M oxalic acid of 3 °C for (c). Thickness of the oxide films was approximately 3  $\mu$ m.

tion in the oxalic acid solution, the most appropriate voltage for the ordering was  $\sim 40$  V; the cell configurations were less ordered above 60 V. However, with the aid of surface texturing, no distinct difference in the degree of ordering of the cell configuration could be observed within the range of anodizing voltage from 40 to 80 V used in the present experiment, in so far as the anodization condition obeyed the relationship (2.5 nm/V) described above. It is thought that this difference in the voltage dependence of the ordering between these two growth modes, that is-the growth with and without pretexturing, originates in the difference in the readiness of the ordering of cell configuration. The naturally occurring ordering is presumably strongly dependent on the applied voltage compared to the growth using pretexturing, because the rearrangement of the cell configuration through growth must take place, in contrast to the ordering with texturing in which the pore can develop orderly in the initial stage of anodization.

Our experiment shows that the present process will be suitable for the mass production of restrictedly ordered nanochannel array architectures with a high aspect ratio. The nanochannel array with long-range order will be a powerful tool in the development of nanodevices. For example, longrange periodicity is promising for the fabrication of huge data storage systems in which the long-range ordering is essential for tracking in read and write operations.

The ordered channel array obtained with the present process can produce the highly ordered channel array in a variety of materials, such as metals and semiconductors using a two-step replication process.<sup>8,11–14</sup> Air-hole array architectures replicated with high-refractive-index materials will be a candidate for realizing the photonic band structure in the visible wavelength region.

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