High-speed focused-ion-beam patterning for guiding the growth of anodic alumina nanochannel arrays

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Long-range ordered arrays of anodic alumina nanochannels are grown by anodizing an aluminum covered with a patterned layer of polymethylmethacrylate (PMMA) resist. The two-dimensional hexagonal-closed-packed pattern is created by focused ion beam (FIB) exposure of the PMMA and transferred onto the aluminum surface by phosphoric acid etching. The required exposure time per channel is only $\sim 20 \mu s$, more than two orders of magnitude reduction in comparison with the previous method employing FIB direct sputtering of the aluminum surface. © 2003 American Institute of Physics. DOI: 10.1063/1.1555689

Recently, porous anodic alumina films (PAAF) with straight nanochannel arrays have attracted much attention for their potential use as templates of nanocomposites.1–5 Various arrays of nanorods, nanoparticles, zeolite, and carbon nanotubes have been grown into PAAF with different average channel spacing ($S$) and diameter ($D$), which depend linearly on the anodization voltage. Arrays of nanochannels with $S$ ranging from 10 to 500 nm (corresponding $D$ of $\sim 4 \sim 200$ nm) can be grown by simply varying the voltage from $\sim 4$ to $\sim 200$ V.6,7 However, such spontaneously grown PAAF have some undesirable features. Their $D$ and $S$ have large dispersion and channels are arranged irregularly. For a given anodization electrolyte, only when the anodization voltage lies with a small range, the channels can self-organize into domains of a hexagonally closed-packed (HCP) array, which also significantly reduces the dispersions in $D$ and $S$.7–9 For example, using oxalic acid as electrolyte, self-organized arrays can only be grown with a voltage between 30 and 60 V.10,11 By employing a two-step anodizing process under the earlier condition, PAAF with self-organized domains of a few microns have been demonstrated.9 However, such self-organized domains are randomly oriented with respect to each other. To draw an analogy to crystal growth, such PAAF with self-organized arrays is equivalent to a quasitwo-dimensional polycrystal with an average grain size of only $\sim 10$ lattice units. (In comparison, a small crystal of a few microns in size has $\sim 10$ 000 lattice units in each of its linear dimension.) For many applications such as photonic crystal,12,13 it is necessary to increase the size of a domain by several orders of magnitude. Therefore, various lithographic methods have been employed to pattern the Al before the anodization; and the pattern on the Al is then used to guide the growth of the nanochannels into an array with long-range order.14–16

We have previously employed focused ion beam (FIB) patterning of Al to achieve guided growth of long-range ordered alumina nanochannel arrays.16 Although effective and versatile, this guiding method of FIB direct-write can only be practically used to fabricate arrays of a few tens of million channels because its exposure time per channel has to be longer than a few milliseconds. In this letter, we report on a much faster (20 $\mu s$/channel) patterning method, which employs FIB patterning of an ultrathin polymethylmethacrylate (PMMA) resist and subsequent acid etching for transferring the pattern onto the underlying Al surface.

FIG. 1. Process for fabricating anodic alumina film with long-range ordered nanochannel arrays. (a) Aluminum polishing; (b) PMMA coating; (c) PMMA exposure by FIB; (d) PMMA development; (e) pattern transfer onto aluminum by acid etching; and (f) anodization and guided growth of a nanochannel array.

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The experiment procedure is shown schematically in Fig. 1. High purity annealed Al samples were prepared by electropolishing in a mixed solution of HClO$_4$ and C$_2$H$_5$OH (volume ratio 1:5) until the root mean square roughness of a $10 \times 10 \, \mu m^2$ surface area is $\sim 1 \, nm$, as measured by contact-mode atomic force microscope (AFM). A layer of PMMA (standard molecular weight of 950 K) mixed in anisole (2% by weight) was spun onto a polished Al substrate at a spin speed of 5000 rpm for 25 s and baked at 130 $^\circ$C for 1 h. The thickness of the PMMA was $\sim 70 \, nm$, and its root mean square roughness of a $4 \times 4 \, \mu m^2$ area was typically $\sim 2 \, nm$ after baking. A 50 keV Ga FIB with a diameter of $\sim 10 \, nm$ and beam current of 1.1 pA was employed to create pattern of HCP single-pixel dot arrays with various dwell time on the PMMA. The lattice constant of the array was set to 100 nm in order to match with the anodization electrolyte and voltage used in the experiments. The exposed PMMA were developed in 1:3 aqueous methyl isobutyl ketone and isopropanol alcohol mixtures to reveal the underlying Al surface. After the HCP array pattern on PMMA was transferred to the Al substrate as an array of concaves with depth of $\sim 3 \, nm$ [Fig. 2(b)]. (To be noted, both AFM images in Fig. 2 show the topography of typical samples before the anodization process.) Anodization of the patterned sample at 40 V led to the growth of a long-range ordered nanochannel array, as clearly shown by the AFM image of its barrier layer in Fig. 3(a). Compared to that of a self-organized array as shown in Fig. 3(b), the array grown by guided growth has not only increased range of order but also reduced dispersions in its spacing/diameter of the nanochannels. To quantitatively compare the increase in the range of the orientational order of the guided array, we can compare the Fourier transformation of the two images, as shown by the insets in Figs. 3(a) and 3(b). The guided array exhibits six prominent peaks; each has an angular spread of only $\sim 3^\circ$, while the self-organized array has an isotropic ring pattern, indicating the complete loss of its orientational order.

The PAAF with AFM, the remaining aluminum substrate was removed in a saturated HgCl$_2$ solution. When needed, the continuous barrier layer on bottom of the alumina was etched in a 5 wt% solution of phosphoric acid to obtain a free standing PAAF with arrays of through nanochannels.

A typical pattern on the PMMA created by the FIB with exposure time of 20 $\mu$s/pixel (corresponding dose on each pixel is $\sim 1 \times 10^{14} \, ions/cm^2$) is shown in Fig. 2(a). The pattern was transferred by phosphoric acid etching onto the Al substrate as an array of concaves with depth of $\sim 3 \, nm$ [Fig. 2(b)].

For samples that were exposed by the FIB with different

![FIG. 2. AFM images of the surface of PMMA resist on Al (a) after FIB exposure (20 $\mu$s/pixel) and development, (b) after acid etching in 10 wt% phosphoric acid at 25 $^\circ$C for 7 min.](image)

![FIG. 3. AFM images of the barrier layer for (a) a guided array of anodic alumina nanochannels and (b) a self-organized array. The insets show the Fourier transforms of the corresponding images.](image)
dwell time per pixel, concaves of varying depths were formed on the Al surfaces after a phosphoric acid etching for the same duration. Figure 4 shows the depths of the concaves as a function of FIB dwell time. The arrow in the figure indicates the threshold dose beyond which guided growth of a nanochannel array becomes effective. The corresponding threshold depth for the concaves is ~3 nm, which is essentially the same as that of the concaves for guided growth created by FIB direct-write, as demonstrated in our previous study. For comparison, Fig. 4 also includes the depths of the concaves created by FIB direct-write as a function of exposure time. The data clearly show that the PMMA-assisted guiding process is more than two orders of magnitudes faster than the FIB direct-write process.

Since the threshold depth for the concaves fabricated by the two different processes is the same, it is likely that guiding effect is controlled primarily by the surface morphology of the Al surface in the beginning of the anodization process. In other words, we believe that the electric field distribution on the electrolyte/Al interface, which is determined by the Al surface morphology, plays the most important role in pinning down the lateral positions of the nanochannels. Our conjecture is further supported by the observation that the PMMA resist was always removed after the prolonged anodization process. It suggests that the role of the PMMA was to withstand the phosphoric acid etching and allowed the creation of an array of concaves with enough depth to pin down the positions of the nano channels in the initial stage of the anodization. Once the guiding lattice of concaves and associated electric field distribution have been formed on the Al surface, the PMMA is no longer needed for guiding the growth of the nanochannels. (In fact, we have taken advantage of this interesting guiding behavior to avoid using a very thick resist and the resist-stripping step that are required in most photolithographic processes.)

In conclusion, we have demonstrated a high-speed lithographic method for creating a lattice of concave pattern on Al to guide the growth of anodic alumina nanochannels and fabricate arrays with long-range order. The method takes the advantage of the high sensitivity of PMMA to FIB exposure to expose a large array of pixels on a PMMA resist covering an Al sample. By transferring the pattern onto the underlying Al surface with phosphoric acid etching and anodization in appropriate conditions, the growth of long-range ordered nanochannel arrays is achieved. Compared with direct-write FIB patterning of Al, the method increases the writing speed by ~200 folds and makes possible the fabrication an array with hundreds of millions of channels in a practical time scale.

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