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Growth of ordered, single-domain, alumina nanopore arrays with holographically patterned aluminum films

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Highly-ordered, single-domain ($\sim cm^2$), alumina nanopore arrays with controlled symmetry were obtained by anodizing prepatterned aluminum films that were deposited on silica substrates. Holographic lithography, in conjunction with a conformal deposition process, was utilized to form nanoscale corrugations on aluminum film surface prior to anodization. Both the order and symmetry of pore arrays were found to be well controlled and guided by the periodic surface corrugations from the initial stage of pore growth. Ordered nanopore arrays grown on foreign substrates are promising as a host or template for forming various nanodevices and their on-chip integration. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1517719]

Fabrication of ordered nanostructures has recently received a great deal of attention due to their potential applications in various fields such as in electronic, photonic, magnetic, biochemical devices, etc. The methods currently being used in nanoscale patterning include electron-beam lithography, focused ion-beam etching, and scanning-probe-based writing. While these methods offer flexibility and controllability in generating arbitrary patterns, they have intrinsic drawbacks of low throughput and high equipment cost. As such, these methods are not considered practical for large area (i.e., chip or wafer scale) patterning. An alternative approach has been investigated utilizing the self-organization (or self-assembly) phenomena that are observed in some materials systems.[1–3] Anodic alumina is known as a typical nanoporous material that shows a tendency to form self-organized pore arrays of triangular symmetry, and has been extensively studied, especially with bulk aluminum foils.[3–7] Highly regular arrangement of pores, however, occurs only for a small process window, and the domain size is usually limited to a micrometer scale on bulk foils.[8–11] Alumina pores grown with aluminum films that are deposited on foreign substrates (such as silicon or silica) would potentially offer much broader application than those on bulk aluminum foils. Any attempt to grow ordered pore arrays with aluminum films, however, has not been successful so far, since it usually results in amorphous-like arrangement of pores.[12,13] The difficulty stems basically from the fact that aluminum films usually have much smaller grain sizes compared with polycrystalline or crystalline bulk foils, and any order development is disrupted by the randomly-distributed, densely-spaced grain boundaries from the initial stage of pore formation. As such, growth of ordered pore arrays with aluminum films has remained as a major challenge from the science and technology point of view.

We have investigated the behavior of pore growth with prepatterned aluminum films and discovered that the arrangement of pores (both the order and symmetry of pore arrays) can be well controlled and guided over macroscale area ($\sim cm^2$ or greater) by nanoscale surface corrugations of aluminum films. First, we briefly describe the method to form ordered nanopore arrays with aluminum films. Photoresist grating patterns were developed on silica substrates using a holographic lithography process.[14] The grating period was designed to be in the range of 300–400 nm. The thickness of photoresist layers was controlled to be 100–150 nm, and the exposure dosage and developing time were properly adjusted such that substrate surface is fully revealed for approximately half of the grating period.[15] For two-dimensional (2D) grating patterns, the photoresist was double-exposed with 60° or 90° of rotation between exposure for triangular or square symmetry, respectively. Figure 1(a) shows a scanning electron microscope (SEM) image of a square-symmetry, photoresist-grating pattern developed on a silica substrate. Circular holes (diameter of $\sim$250 nm) are revealed in the peak intensity region of the 2D exposure pattern. Aluminum films with thickness of 350–400 nm were then deposited on the grating patterned substrates, using a thermal evaporation method with 5N-purity aluminum source. The deposited film surface conformed to the corrugation profile of the photoresist-patterned substrate with nearly the same amount of corrugation depth ($\sim$100 nm) [Fig. 1(b)]. (The interface region around the photoresist grating layer is not clearly resolved in this cross-sectional image due to the poor cleavage property of aluminum.) Anodic oxidation was then carried out on the as-deposited aluminum films in dilute electrolyte ($H_3PO_4 + H_2O$ in 1:800 volume ratio) at room temperature using a Pt wire as a counter electrode. The anodization was conducted under a constant voltage mode for 40 min. The anodic voltage was chosen such that the expected pore distance matches the grating period, for example, 140 V for 350 nm grating period.[10] After anodization, the samples were treated with short-time (1–2 min) etching in a phosphoric acid solution (diluted with water in 1:3 volume ratio).

Figure 2(a) shows an SEM micrograph of alumina pores grown with a 1D grating-patterned aluminum film. The pores grew highly ordered along the grating vector direction, that is, aligned regularly at each concave bottom of the periodi-

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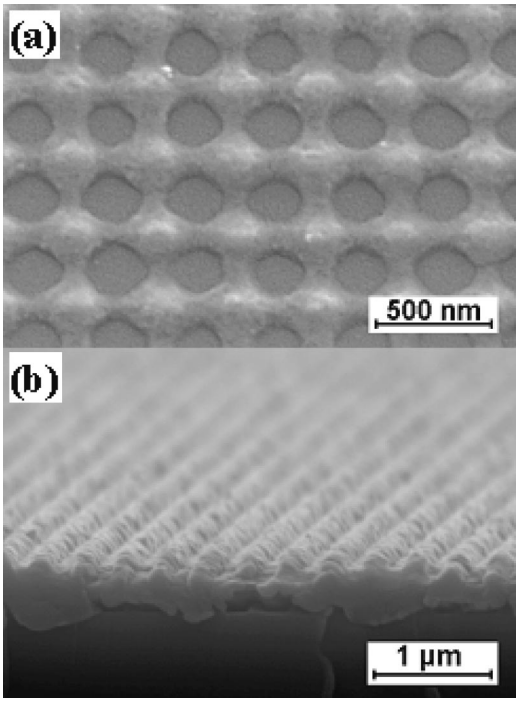

FIG. 1. SEM micrographs showing periodically corrugated surfaces of photoresist and aluminum films deposited on silica substrates. (a) Top view of a square-symmetry, 2D photoresist grating. (b) A 350-nm-thick aluminum film deposited on a 1D grating-patterned silica using a thermal evaporation method.

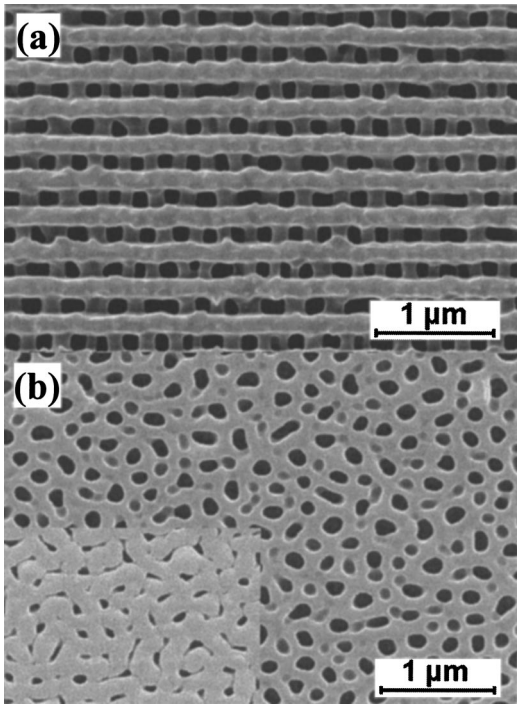

FIG. 2. SEM micrographs of alumina pores obtained from aluminum films that were deposited on silica substrates. (a) Alumina pores grown with a 1D grating-patterned aluminum film. (b) Alumina pores grown with a plain, unpatterned aluminum film. (The inset shows the as-grown alumina pores without any post-anodization etching.)

cally corrugated surface. In contrast, the pore arrangement along the grating line direction shows a significantly lower degree of order. The pores in each row are irregularly spaced along the grating line direction (some pores merged together) and do not show any coherency in their alignment between rows. The effect of surface prepatterning is further elucidated by comparing this image with that of an alumina pore sample that was prepared on a plain, unpatterned aluminum film [Fig. 2(b)], under the same anodization condition as the prepatterned case. The pore arrangement in the plain film's case looks amorphous without any order, and the pore shape and size are also irregular. Even more serious irregularity is observed from the pores that are as-grown without any post-anodization etching [the inset to Fig. 2(b)], and this indicates that pore nucleation was completely random in the unpatterned film case.

Pore growth was studied on the square-lattice 2D grating-patterned aluminum films (Fig. 3). Single-domain ordered arrangement of square-shaped pores was observed across the entire grating-patterned area ($1\ \text{cm} \times 1\ \text{cm}$). The domain size is currently limited by the grating pattern size and is scalable to larger values with proper change in optics. Pores show uniform depth (400 nm) and the pore bottom has a concave, hemispherical shape with barrier layer thickness of ~ 100 nm [Fig. 3(c)]. The pores grew well aligned to the center of corrugation bottom region. The result demonstrates that the nanoscale periodic corrugation of aluminum film surface can fully compensate the randomizing effect of grain boundaries in aluminum films from the beginning of pore formation, and can control/guide development of order throughout the pore growth process across the entire pattern area. In the case of self-organized pores formed on plain, bulk aluminum foils, the pore arrangement is limited to a triangular lattice due to the tendency to form the closest packing. The result in this study also demonstrates that this limitation can be overcome by introducing corrugation patterns of different symmetry to the surface of aluminum films.

Oxide dissolution in an anodic process is basically a field-assisted process, and occurs preferably on the concave surface region where the electric field is stronger than that in the flat or convex surface.[4] Pores thus nucleate and grow at these concave sites that are initially provided by the periodic

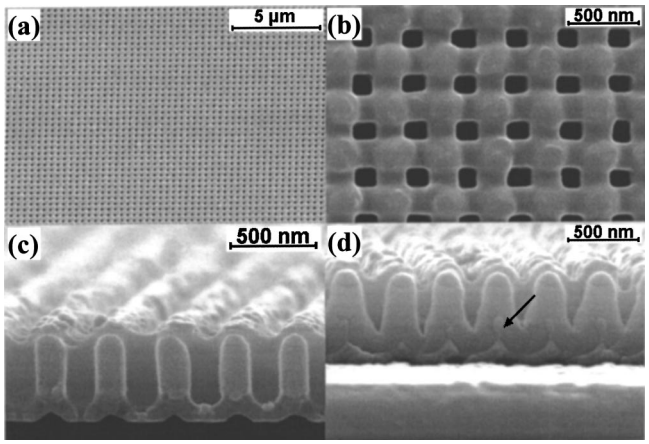

FIG. 3. SEM micrographs of alumina pore arrays obtained from square-lattice 2D grating-patterned aluminum films that were deposited on silica substrates. (a) and (b) Top-view images showing square-lattice arrangement of square-shaped pores. (c) Cross-sectional image showing that the pores grew well aligned to the center of the corrugation bottoms. (d) Cross-sectional image showing unanodized aluminum regions of a sample prepared with a two-step anodization process anodized first at 140 V for 30 min, and then at 70 V for 10 min.

surface corrugation. Oxide growth is also field-dependent, basically involving field-assisted migration of anions (such as O^{2-}) and cations (Al^{3+}) and reaction between them.[4,7] Once pores are seeded at the corrugation bottoms, oxide grows faster at the pore bottom regions than surrounding area, due to the minimum thickness of oxide, and therefore, to the maximum field strength in this bottom region. When aluminum becomes oxidized, the volume expands by approximately a factor of 2 due to the density difference between aluminum and alumina. The volume expansion at pore bottoms occurs mostly along the directions parallel to the hemispherical interface between metal and oxide, since the oxide in a concave region would be more constricted if it tries to expand along the thickness direction. The growing oxide is then pushed upward at the cross-points (i.e., cusps) of the neighboring hemispherical metal/oxide interfaces. This tendency is revealed in an SEM micrograph [Fig. 3(d)] of a sample that was prepared with a two-step anodization process (i.e., anodized first at 140 V for 30 min, then at 70 V for 10 min). The hemispherical profile of the aluminum/alumina boundary is clearly resolved. Elongated aluminum columns are also observed at some cusps [the region marked with an arrow in Fig. 3(d)]. This elongation is attributed to the reduction of the radius of hemispherical boundaries with the decrease in anodization voltage.[4] This image was obtained from a cross section that was cleaved slightly shifted away from the plane that exactly crosses pore bottoms. It is interesting to note that most pores show a square shape [Fig. 3(b)], although the photoresist grating shows circular opening in the bottom region [Fig. 1(a)]. The square shape of pores indicates a certain degree of in-plane anisotropy in oxide dissolution during pore growth. Considering the field-assisted nature of oxide dissolution, this image suggests that the in-plane component of electric field around the local field maxima (i.e., the pore bottoms) in the growing oxide may have higher field strength along the diagonal direction than that along the edge direction of squares. This anisotropic field distribution around the pore bottoms is attributed to the presence of aluminum spike regions that surround each pore with a square lattice and provide anodic potential to the barrier oxide. The electric field (and therefore oxide dissolution) will then be higher along this diagonal direction (due to the smaller thickness of barrier oxide along this direction), and this will induce each pore to develop/maintain a square shape during growth.

Alumina pores were also grown on triangular-lattice, 2D grating-patterned aluminum films (Fig. 4). A single-domain, triangular arrangement of pores was observed across the entire pattern area ($\sim cm^2$). The pore shape is considered a reflection of the grating pattern symmetry, similar to the square lattice case discussed above. Each concave bottom is surrounded by four corners, which form a rhombus-shape sublattice with two-fold symmetry. The in-plane radius of curvature at the corners of the major axis is smaller than that at the minor-axis corners. Therefore the electric field (and oxide dissolution) will be the strongest (fastest) along this major-axis direction. This is believed to induce the pores to take an elliptical shape. Overall, this study demonstrates that anodization of surface-corrugated aluminum films is a viable method to grow highly-ordered, single-domain, alumina nanopore arrays of controlled symmetry on large area of foreign substrates. The process developed in this work offers an efficient approach to integrating various nanostructured materials and devices on a single chip.

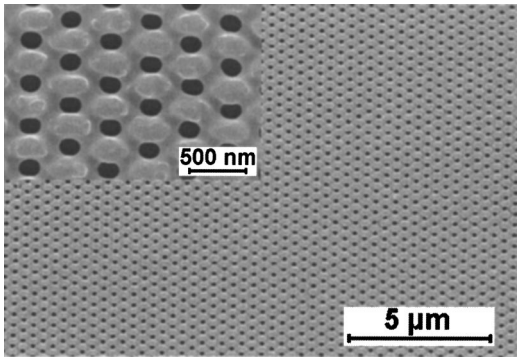

FIG. 4. SEM micrographs of alumina pores obtained from a triangular-lattice 2D grating-patterned aluminum film that was deposited on a silica substrate.

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[14] A He–Cd laser (325 nm wavelength, 15 mW output power) beam was expanded and collimated into beam diameter of 1–2 cm, and then split into two equal-intensity beams. The two beams were then recombined on a photoresist (Shipley 1805 positive photoresist diluted with thinner P solution in 1:1 volume ratio)-coated substrate forming a 1D grating pattern. The grating period was adjusted by changing the beam incidence angle.
[15] The presence of photoresist grating may reduce adhesion of the alumina layer to a substrate. This potential problem, however, can be overcome by transferring the grating profile to a substrate with an etching process and then removing the photoresist.