

Periodic Holes with 10 nm Diameter Produced by Grazing Ar⁺ Milling of the Barrier Layer in Hexagonally Ordered Nanoporous Alumina

Tao Xu,[†] Giovanni Zangari,[‡] and Robert M. Metzger^{*,†}

MINT Center and Departments of Chemistry and Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama 35487-0336

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ABSTRACT

Long-term anodization of aluminum provides a hexagonally ordered array of nanopores with very uniform pore diameters (between 30 and 50 nm, depending on pH, acid, and potential) and pore spacings of 80 to 100 nm within a matrix of amorphous aluminum oxide. However, one often desires smaller diameters. Because the bottom of each pore is U-shaped, we can use this geometrical feature and gradually open the U-shaped bottom cap of the alumina nanochannel by controlled grazing angle Ar⁺ ion milling and thus form smaller pore apertures. In initial results, we prepared opened holes with a diameter as small as 10 nm. This opens the door to numerous applications that need small but hexagonally periodic features produced by inexpensive means.

Hexagonally ordered arrays of nanopores form in amorphous alumina when aluminum metal is anodized in certain acids. Their highly ordered and straight nanochannel structure and their high density allow electrodeposition of magnetic nanodisks or nanowires inside the pore. This facilitates the manufacture ultrahigh-density magnetic recording materials,^{1,2} nanowires of other metals, and even the growth of ordered arrays of multiple-wall carbon nanotubes.³ When the bottom of the nanopores is opened by chemical etching⁴ or by a focused-ion-beam, the resulting nanoholes can be used for energy-efficient gas-separating membranes⁵ and as a pattern-transfer nanomask.^{6,7} The nanopores can also be used as an ordered 2-D photonic crystal.⁸

The self-organized regular pore positions are formed during anodic oxidation of aluminum. Porous oxide growth on aluminum in various electrolytes under anodic bias has been studied for more than 40 years.^{9,10} A highly ordered structure of nanopores in alumina¹¹ is typically achieved by anodizing a pure aluminum sheet in 0.3 M oxalic acid solution at 40 V at 5 °C for at least 1 day.^{10,11} A homogeneous U-shaped barrier oxide layer, 20 to 30 nm thick and with high impedance,¹² known as the barrier layer, develops at the bottom of every single nanopore. Seldom, however, does this U-shaped bottom attract sufficient attention. Geometrically, if the U-shaped bottom is gradually and

evenly etched away, then the hole size can be enlarged systematically from 0 nm up to the diameter of the nanopore (Figure 1).

In this work, we used grazing angle Ar⁺ ion milling to open the U-shaped bottom cap by controlling the milling time. Since Al₂O₃ is one of the hardest materials to be milled by Ar⁺ ions, the milling rate can be controlled by varying the milling current and the angle of incidence of the Ar⁺ ions (relative to the surface normal).

A hexagonal highly ordered array of alumina nanopores was fabricated^{10,11} by anodic oxidation of 99.998% pure Al sheet (0.5 mm thick). Al sheets were degreased in KOH, electropolished, rinsed, and then anodized in 0.3 M oxalic acid (COOH)₂ at 40 V DC, 10 °C, for 24 h. The samples were then immersed in 0.2 M H₂CrO₄, 0.4 M H₃PO₄ mixed etching solution at 60 °C for 3 h, to remove the initial Al₂O₃ layer and leave an ordered porous Al template. A successive anodization was applied on these samples for another 6 h, to produce an ordered hexagonal Al₂O₃ pore array with defect-free areas up to 5 μm², pore diameter 40 nm, period 108 nm, and pore length ca. 25 μm. Typical AFM topographic images of the hexagonal porous structure are presented in Figure 2.

The remaining Al metal layer was removed by placing the sample carefully to float on the surface of a saturated mercury dichloride (HgCl₂) solution, with the aluminum metal side on the bottom. This flotation can be achieved due to the surface tension of the solution and is preferable to

* Corresponding author.

[†] MINT Center and Department of Chemistry.

[‡] Department of Metallurgical and Materials Engineering.

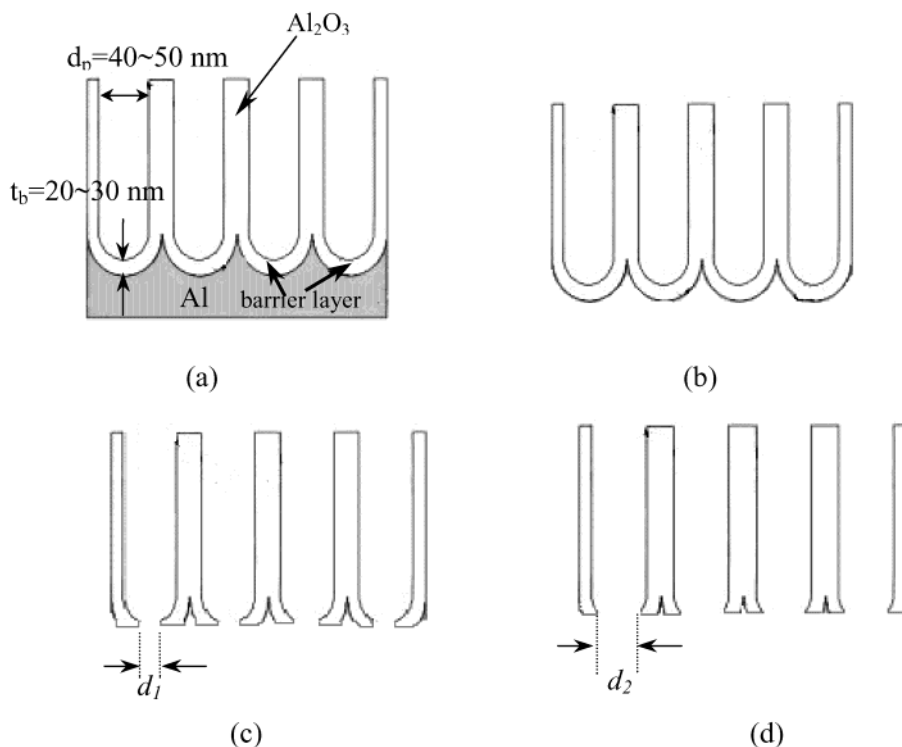


Figure 1. (a) Diagram of the ordered porous alumina structure, showing the nanopores (diameter d_p), the barrier layer (thickness t_b), and the Al metal. (b) Alumina nanopores and barrier layer after the Al metal is completely removed by using a HgCl_2 solution. (c, d) U-shaped Al_2O_3 barrier layer can be partially opened with hole diameter (d_1 or d_2), much smaller than the nanopore diameter d_p .

total immersion in the solution. After more than 10 h, the Al metal layer was dissolved completely, while the Al_2O_3 remained unharmed. The resulting alumina film was rinsed gently with pure water and desiccated in a vacuum over P_2O_5 . The bottom of the ordered porous alumina array is shown in Figure 3a. The U-shaped bottoms of the Al_2O_3 nanopores protrude from the base alumina by about 15 nm. A larger-scale image displays some grain boundary-like stages, shown in Figure 3b.

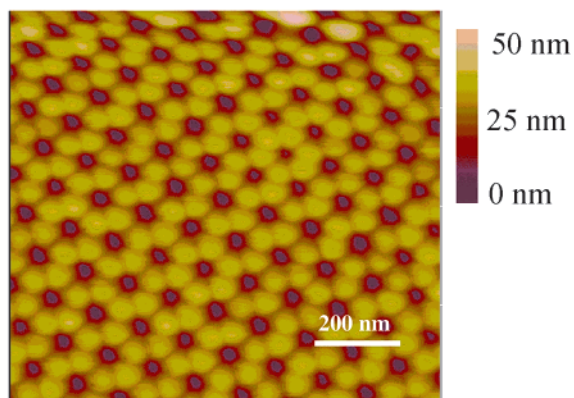
We tried two methods to open the bottom caps of the resulting ordered array of porous alumina nanotubes. The first method was etching by acid, as follows. The bottom caps were opened by setting the alumina film on the surface of a phosphoric acid or sulfuric acid solution, with the open side of the pores facing up, and the closed side of the nanopores (with the barrier layer) facing down and contacting the solution. The U-shaped bottom cap was successfully etched by acid, but this chemical etching results in a very irregular and nonuniform shape, and the etching rate was difficult to control. This nonuniform shape is shown in Figure 4, which is an AFM image of the alumina etched by 5 wt % phosphoric acid, viewed from the bottom (the side that was closed before etching).

The second method is etching by a reactive ion beam, which is more accurate and controllable.⁷ We opened the U-shaped bottom cap of alumina nanopores by Ar^+ ion milling, carried out on a Veeco Microetch ion miller. Clean nanoporous alumina samples were carefully placed on a rotary sample holder with a steel clip, with the bottom side facing the ion source. Al_2O_3 is one of the hardest materials to be milled by Ar^+ ion: the nominal milling rate for Al_2O_3

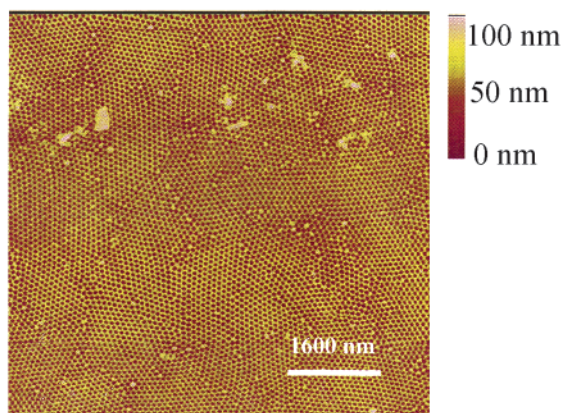
is 100 \AA min^{-1} at normal incidence for a 500 eV Ar^+ ion beam with current density of 1 mA cm^{-2} .¹³ To further slow the milling rate, the Ar^+ ion incident angle was tilted 60° from the surface normal. The Ar^+ ion current density was set at 0.5 mA cm^{-2} and the Ar^+ energy was set at 500 eV. During etching, the sample holder was rotated at 0.1 revolution per second, to ensure uniform milling. Samples were also neutralized by electrons ejected from a tungsten filament.

After 9 min of milling under the conditions stated above, we obtained a $1 \mu\text{m} \times 1 \mu\text{m}$ AFM bottom image (Figure 5a) of the pores viewed from the bottom: the pore diameter ranges from 8 to 14 nm; round holes are the dominant shapes, but some elongated holes can also be seen. Figure 5a shows 121 pore bottoms, with holes formed by ion milling; of these, 91 are circular holes, while about 30 are somewhat elongated holes. Figure 5b is a 3-D surface plot that shows that the pore bottoms are not all in the same plane. By manipulating the viewing angle, one sees that the some of the elongated or elliptical holes become round holes, while some round holes become elliptical. We believe that many of these holes appear elliptical because of the viewing angle. Some of the holes always appear to be elongated, independent of the viewing angle. These elongated holes are mostly likely due to either deformed pore bottoms or to the shadow cast by nearby pore bottoms that lie above the pore of interest. In general, the U-shaped bottom caps can be slowly and uniformly etched by Ar^+ ions over a larger area. Figure 5c is a $5 \mu\text{m} \times 5 \mu\text{m}$ AFM topography after 9 min milling.

Long-time milling leads to the disappearance of the protruding U-shape bottom caps and results in a hole



(a)



(b)

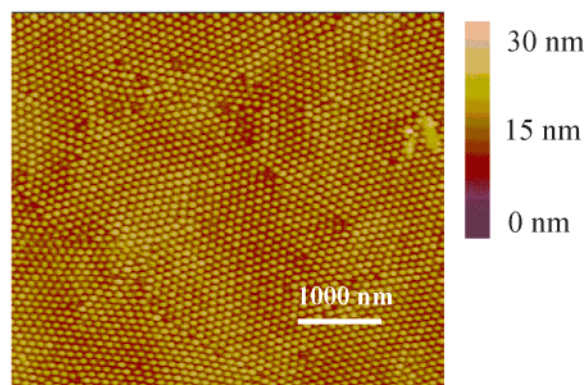
Figure 2. AFM images of hexagonally ordered array of alumina nanopores fabricated by anodization in 0.3 M oxalic acid at 10 °C, viewed from the top (Al metal is below the plane of the image). (a) $1\ \mu\text{m} \times 1\ \mu\text{m}$; (b) $8\ \mu\text{m} \times 8\ \mu\text{m}$.

diameter equal to the nanopore diameter. Figure 6a is a $1\ \mu\text{m} \times 1\ \mu\text{m}$ AFM topograph, showing the image of the opened holes after 35 min Ar^+ ion milling. The opened hole diameter is ca. 45 nm, which is about the diameter of the nanopores formed by anodization. This indicates that the U-shaped bottom cap has been etched away completely. The pore density of the Ar^+ milled side is $108\ \mu\text{m}^{-2}$, in agreement with that of the anodized side. This suggests that the nanochannels in alumina are very straight. Figure 6b shows a $5\ \mu\text{m} \times 5\ \mu\text{m}$ AFM topography, indicating the long-range trends. The open pores shown in Figure 6 are quite similar to those obtained by conventional anodization.

We have demonstrated that Ar^+ ion milling at grazing incidence can open the nanopores in alumite from the “closed side” in a controlled fashion, thus allowing the formation of hexagonally ordered periodic holes of diameter much smaller than afforded by extended anodization in acid. Such smaller hole diameters may be useful for exposing sub-10 nm diameter ordered cobalt particles as catalysts for preparation of ordered array of single wall carbon nanotubes, for organizing nanoscale electrodes for molecular electronic devices, and as a pattern transfer mask. While the cost of making hexagonally ordered nanopores is quite low, Ar^+ ion



(a)



(b)

Figure 3. AFM images of the barrier layer (bottom view), after removal of Al metal, showing the U-shaped caps of the nanopores (the open tops of the nanopores are below the plane of the image): (a) scale $1\ \mu\text{m} \times 1\ \mu\text{m}$; (b) scale $5\ \mu\text{m} \times 5\ \mu\text{m}$.

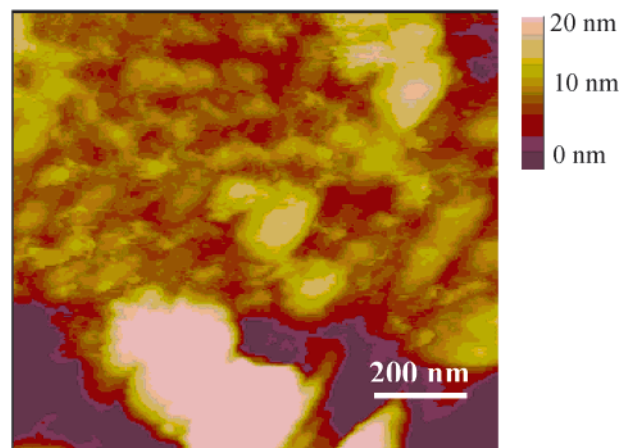
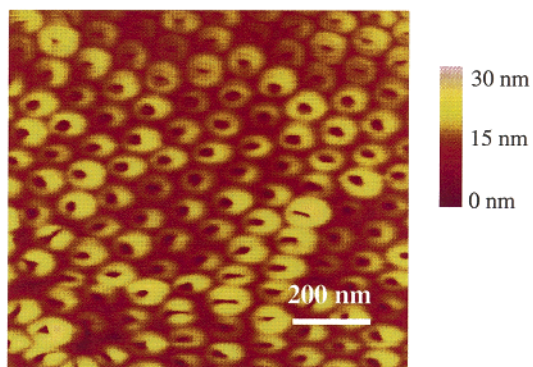
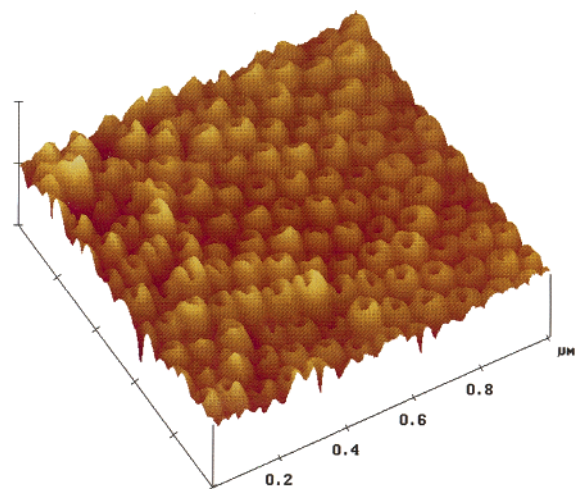


Figure 4. Results of chemical etching. AFM image of the barrier layer (bottom view), after etching in phosphoric acid. Some U-shaped caps of the nanopores are visible, but there is extensive disorder. Scale: $1\ \mu\text{m} \times 1\ \mu\text{m}$.

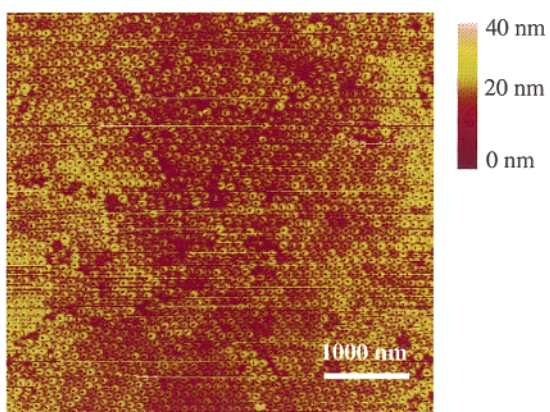
milling is a more costly procedure, but a procedure that may yield nanoscale features of the correct size for many applications.



(a)



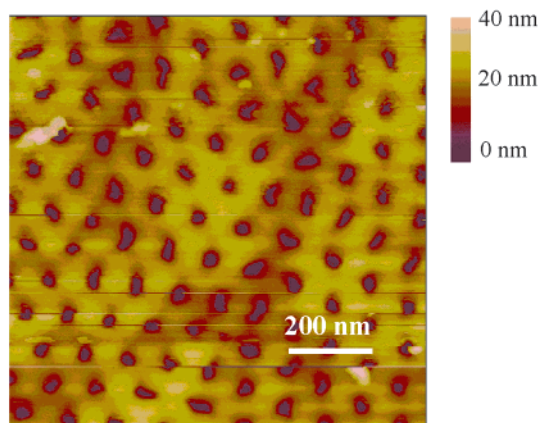
(b)



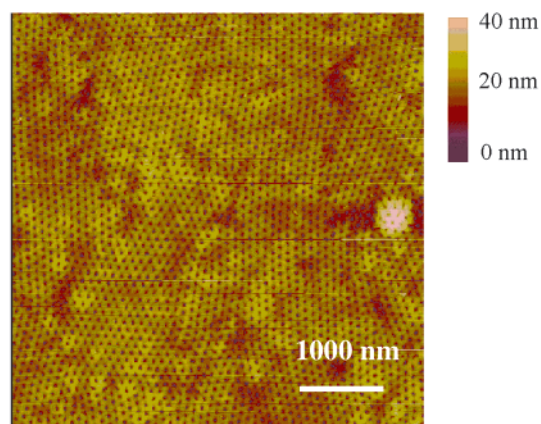
(c)

Figure 5. Results of shorter term Ar⁺ ion milling: AFM image of the barrier layer (bottom view), after 9 min Ar⁺ milling. (a) Scale, 1 μm × 1 μm; (b) 3-D surface plot mode of (a); (c) scale, 5 μm × 5 μm.

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(a)



(b)

Figure 6. Results of longer term Ar⁺ ion milling: AFM image of the barrier layer (bottom view), after 35 min Ar⁺ milling. (a) Scale, 1 μm × 1 μm; (b) scale, 5 μm × 5 μm.

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