Technical Article

Anodized Aluminum Oxide Membranes As Templates for Nanoscale Structures

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Fig. 1—The geometry of porous anodic alumina can be schematically represented as a honeycomb structure which is characterized by a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate. (a) Top view of AAO membrane. (b) Side view of the typical alumina structure fabricated using bulk aluminum.

Porous anodic aluminum oxide (AAO) membranes have attracted significant interest during recent years because AAO can be made conveniently and inexpensively. Yet they are extremely useful in nanoscience studies. Pore diameters (5 to 300 nm), and pore-topore distances (25 to 500 nm) can be easily controlled by varying the anodizing conditions. Highly ordered, straight nanopores in hexagonally close-packed arrays with domain sizes of approximately $2.5 \times 2.5 \ \mu m^2$ and aspect ratios as high as 1000:1 can be achieved. The nanopores within the AAO membranes are used as templates for fabricating various nanoscale structures, such as the first successful fabrication of superconducting lead nanowires with diameters of 60 and 200 nm. Lead was electrodeposited into the nanopores of AAO, and bismuth quantum nanotubes

Nuts & Bolts: What This Paper Means to You

A major facet of the future of the surface finishing industry lies in nanomaterials, that is, materials developed on the scale of nanometers. Much of the work to date has dealt with building the deposits from the ground up, by plating. Here, the reverse approach, working into a surface, has yielded some very original and useful results. Dr. Han and her colleagues have looked into controlling the nature of the pores produced during the anodizing of aluminum to produce "nanopores." This creative way of thinking has opened up new avenues for nanomaterials.



were fabricated, utilizing a newly developed hightemperature sintering method. It is also possible to construct highly ordered anti-dot arrays by coating the surfaces of the porous AAO membranes with magnetic materials. Significant enhancement of the critical field in superconducting Pb nanowires and an abnormal magnetoresistance in Ni magnetic anti-dot arrays are found in these samples. The preparation and characterization of AAO and its application in fabricating various nanowires, nanotubes and nanoscale antidots will be presented.

The fabrication of functional, nanostructured arrays in a well-controlled way is one of the exciting frontiers in today's science and technology. In recent years, numerous methods have been utilized, with varying degree of success, to fabricate nanostructures with smaller size, higher regularity and reliability because of the potential applications in electronic, optical and magnetic nanodevices. Compared to conventional lithographic techniques such as UV, x-ray, electron beam or scanning probe lithography, template methods, based on self-organized nanoporous arrays, present an inexpensive, high throughput and efficient process for achieving nanosize periodic structures with high aspect ratio over a large area.

Anodic films on aluminum, formed by anodization, have been used commercially as keying layers for the retention of organic coatings and the protection of Al substrates against

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Technical Editor's Note: Contrary to the common style used in this journal, <u>most</u> units in this paper, excepting temperature, are expressed in metrics only. In nanotechnology discussions such as what follows here, the scale is so small that English units are irrelevant. For example, "nano-inches" would just not be common usage – JHL.



Fig. 3—(a) A 2D false color image of small angle x-ray scattering intensities of a highly ordered AAO thin film. Due to a minute mismatch between the membrane and the incident beam direction, the scattering intensity is concentrated along a line corresponding to intersection of the membrane and the plane perpendicular to the beam. (b) A plot of averaged 1D spectrum showing scattering intensity as a function of scattering vector. The scattering peaks have been assigned based on a 2D hexagonally close packed model. The unit cell can be extracted from the slope of a $q^2 vs. (h^2+k^2+hk)$ plot. For this sample, hole-to-hole distance is 116.8 nm. (c) SEM of AAO membrane anodized at 50V showing a degree of ordering comparable to sample anodized at 40V.

corrosion and abrasion for at least 80 years.1 The anodic aluminum oxide (AAO) membranes formed in acidic solutions have a porous structure and mainly consist of amorphous Al₂O₃. The geometry of porous anodic alumina can be schematically represented as a honeycomb structure that is characterized by a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate (Fig. 1). Only an approximately hexagonal arrangement of these pores with low periodicity had been produced through conventional anodization in the past 70 years.² Recently however, AAO films with a perfect hexagonal pore arrangement over several μm², have been achieved through a two-step anodization process.³⁻⁸ Films created through this technique display a high degree of hardness and wear resistance, have excellent corrosion resistance and a high pore density and are thermally stable. The pore diameter, pore-to-pore distance and pore depth can be easily controlled by choosing appropriate anodizing conditions such as temperature, type and concentration of electrolyte, anodizing voltage and duration of the anodization.9 All these merits make AAO membranes an attractive template for the fabrication of ordered arrays of nanowires,⁷ nanodots, anti-dots and nanotubes. The pores can serve as a host to other material classes, such as magnetic or thermoelectronic materials. The integration of porous oxides with these other classes of materials allows for the rapid and inexpensive fabrication of complex composite materials.

Experimental



High purity aluminum foil (99.998%) with a thickness of 250 to 500 μ m was first degreased in acetone for 10 min and dried at

100°C (212°F), annealed at 500°C (932°F) under an argon atmosphere for 4 hr to enhance the grain size, and electropolished in a solution of $HClO_4$ (60 wt%) and EtOH (1:8 by volume) at a current density of 10 A/dm² (0.65 A/in²) and a temperature of 0°C (32°F) for 10 min to generate a smooth surface.

The anodization was carried out under constant anodizing voltage, in 0.3M aqueous solutions of either oxalic or sulfuric acid at 3°C (37°F) for 24 hr (Fig. 2). The resulting 70- μ m thick, porous alumina layer was stripped away from the Al substrate by etching the sample in a solution containing 6 wt% phosphoric acid and 1.8 wt% chromic acid at 60°C (140°F) for 12 hr. After removal of the initial AAO film, the anodization was repeated under the same conditions for a time





Fig. 5—Two identical AAO films grown simultaneously on both sides of Al substrate. (a) Rear layer backside. (b) Rear layer topside. (c) Front layer backside. (d) Front layer topside.



sufficient to reach the desired film thickness (typically on the order of hours). A freestanding AAO membrane with a highly ordered array of nanopores can then be obtained by selectively etching away the unreacted Al in a saturated HgCl, solution or a mixture of 0.1M CuCl, and HCl (37 wt%) in a 4:1 volume ratio. The pore array was studied by field emission scanning electron microscopy (SEM),** atomic force microscopy (AFM)*** and small angle X-ray scattering (SAXS).**** A dome-shaped aluminum oxide layer, with a thickness of 10 to 30 nm, depending on the anodizing voltage, forms at the bottom of each single nanopore during anodization (Fig. 1b). To remove this barrier layer, a protective polymer layer was first coated on the top surface of the AAO membrane to prevent etching of the surface structure and uneven diffusion of acid into the nanopores. The membrane was then immersed in 200 mL 5.0 wt% phosphoric acid at 30°C (86°F) for varying periods of time, rinsed with distilled water and dried under ambient conditions. The barrier layer removal and pore widening process was then studied by AFM and SEM.

Results & Discussion

Although the electropolishing process yields a surface with a roughness of less than 10 nm over a 5- μ m area, there are still small pits and bumps with densities as high as 10^{12} /cm², which could act as nucleation centers for pore growth.² The pore density is very high and the pore initiation sites spread randomly over the Al surface at the beginning of anodization. Ordering of the cell arrangement increases with anodizing time after the steady state growth of the porous structure is established.³ Therefore, at least two steps of anodization are needed to produce a membrane with highly ordered pore arrays. Long time first-step anodization and stripping of the resulting AAO film from the Al substrate not only removes the disordered AAO membrane but also leaves a highly ordered dimple array on the aluminum surface. Each dimple will initialize a new pore during the second anodization step, which is carried out under the same conditions as the first.³

We have carried out two-step anodizations at 10, 15, 20 and 25V in 0.3M sulfuric acid, and 10, 30, 40, 50, 60 and 80V in 0.3M oxalic acid at 3°C (37°F). In the past, SEM and AFM had been used exclusively as characterization tools for AAO membranes.¹⁰ While these techniques are ideal for local characterization of the structure and morphology of an AAO film, their bulk characterization abilities are

^{**} Hitachi S-4700II Field Emission Scanning Electron Microscope, Hitachi, Ltd., Tokyo, Japan.

^{***} DI Dimension 3000 with Nanoscope IIIA controller, Digital Instruments (now Veeco Instruments), Woodbury, NY.

^{****} Advanced Photon Source at Argonne National Laboratory, Argonne, IL.



Fig. 7—SEM images of the nickel antidot arrays on AAO membrane. Thickness of deposited nickel layers are (a) 5 nm, (b) 50 nm and (c) 100 nm. The inset in (c) is the side view of the 100-nm thick antidot array.



Fig. 8—Magnetotransport of 100-nm-thick nickel on (a) glass and (b) AAO membrane. Comparison of the magnetization of both samples is shown in (c). The inset in (c) shows the low field magnetization on expanded scales.

limited. Because of the insulator behavior of alumina, its characterization by SEM can be very difficult, and only information on the surface structure can be obtained. AFM has a very limited penetration into the pores and thus is not suitable to characterize the pore structure of thick films. SAXS has been used for the first time in our lab to characterize the cell configuration of films with thicknesses up to 100 μ m (~ 4 mil). The advantage of using SAXS is that, as a bulk characterization technique, it can be used to determine the average morphology over large areas and through the whole depth of the nanochannel as the X-ray beam is 200×400 μ m² in area (covering ~200 domains) and penetrates the film completely.

Two pieces of information can be obtained from SAXS data: pore-to-pore distance and the degree of pore ordering (Figs. 3a & b). SAXS data show that self-ordering takes place at 25V in sulfuric acid, 40 and 50V in oxalic acid solution, corresponding to pore-pore distances of 63, 100 and 125 nm respectively. Longer first-step anodization times increase the size of ordered domains in AAO only under these specific anodization voltages and little or no ordering was observed without the appropriate voltage conditions. The ordered structure at 50V anodization has never been reported before. This has been verified through SEM (Fig. 3c) and AFM imaging.

SAXS data also show that the pore-to-pore distance increases linearly with anodizing voltage no matter what type of electrolyte is used. The cell size increases by 2.2 nm for every volt (Fig. 4). SEM data shows that the pore diameter at the channel opening is independent of anodizing voltage, which is 10 nm in 0.3M sulfuric acid and 35 nm in 0.3M oxalic acid. It is mainly decided by the pH value of the electrolyte that determines the dissolution rate of alumina.

Perhaps unsurprisingly, the AAO films grow simultaneously on all aluminum surfaces expos/ed to electrolytes unless covered with an insulating polymer layer. Both the electrolyte and the aluminum are highly conducting while the Al₂O₃ is highly insulating. Thus, the potential throughout either the solution or the metal is essentially constant, and the gradient is normal to the surface and its magnitude independent of location (only depends on oxide thickness and porosity). This means that complicated 3D porous AAO structures can be formed by anodizing Al with any predefined shape. In the case of anodizing a thin aluminum foil, AAO films formed on both sides, and they can be separated by selectively etching away the aluminum substrate sandwiched between them in saturated $HgCl_2$ aqueous solution. The cell regularity is almost identical for the two films, with the backside of the AAO films containing fewer defects than the topside (Fig. 5).

A semispherical shell with homogeneous thickness known as the barrier layer (Fig. 1b) develops at the bottom of every single nanopore during the anodization process. This hasn't attracted much attention in the applications literature. However, removal of the barrier layer is required, when through-hole AAO membranes are needed. Examples for such applications include using AAO membranes for energy-efficient gas-separating membranes and pattern-transfer masks for e-beam evaporation,3 reactive ion etching11 or molecularbeam epitaxial growth.¹² Three methods had been used to open the barrier oxide layer: chemical etching,3 ion milling13 and plasma etching.11 Ion milling and plasma etching require expensive equipment and can only work on one small area at a time and thus are cost and time intensive. Chemical etching, on the other hand, is inexpensive, fast, convenient, reliable and can be used to etch samples with large dimensions. Very little study has been done in the past to reveal the barrier layer opening process. Our experimental results show that if the chemical etching is done properly, holes in the barrier layer from less than 10 nm in diameter up to 90% of the cell size can be obtained (Fig. 6c thru f). Once there is an opening in the barrier layer, the etching solution can diffuse into the pore and expand the pore along its entire length. Figure 6g shows the rate of opening as a plot of hole diameter with respect to time. Such a plot should prove useful in controlling the size of the opening in the barrier layer under a fixed poreto-pore distance. This is an interesting finding since highly ordered pore arrays with sub-10-nm diameter has not been demonstrated by self-assembly. More importantly, very interesting and unique nanostructures generated before the complete removal of the barrier layer had been observed by AFM imaging, which have potential application as templates to grow nanostructured thin films (Fig. 6a thru d).

Nanostructures including nanowires, nanotubes and antidots are promising subjects for research into the novel phenomena



Fig. 9—a) SEM top view of Ni nanowires (200 nm diameter, 0.05 M NiCl₂ in DMSO) with AAO templates partially removed.
(b) SEM cross-section view of Ni nanowires (60 nm diameter, 0.1 M NiSO₄ in H₂O) imbedded in AAO.
(c) SEM of Ni nanowires (60 nm diameter, 0.05 M NiCl₂ in DMSO) with AAO template completely removed.

(c) SEM of NI handwires (oo him alameter, 0.05 M NICI2 in DMSO) with AAO temptate completely removed

(d) Magnetization hysteresis of 2 to 3 μm long Ni nanowires with 200 nm diameter imbedded in AAO. The easy axis is perpendicular to the nanowires.
 (e) Magnetization hysteresis of 30 μm long Ni nanowires with 60 nm diameter imbedded in AAO. The easy axis is parallel to the nanowires.

induced under confined geometries and have potential applications in nanoscale devices. One approach in fabricating these nanostructures is the so-called "template synthesis" that utilizes nanopores in porous membranes as templates. The ultra-high-density magnetic antidot array, a promising candidate for magnetic storage applications, was prepared by depositing nickel onto AAO membranes by DC magnetron sputtering at 25°C (77°F) under 10⁻⁴ Pa.⁸ The antidot arrays made on AAO membrane with 100 nm pore-to-pore distance have pore density of 10¹⁰/cm², which corresponds to a storage density of 10 Gbits/cm² (Fig. 7). FESEM showed the pore size decreases with increasing thickness of deposited nickel.

The magnetotransport and magnetization data measure at 280°K for the 100-nm-thick film are summarized in Fig. 8. Whereas the transverse magnetoresistance shows similar overall behavior and magnitude as seen in the continuous film (Fig. 8a), unusual nonmonotonic behavior is observed in the longitudinal magnetoresistance (Fig. 8b), which we attributed to the inhomogeneous rotation of magnetic moments with respect to the applied filed and current directions. The magnetization curve of the antidot array exhibits a loop with enhanced values of coercive field and remnant magnetic moment, whereas the continuous film made by depositing nickel onto a glass slide has an almost reversible magnetization. We attribute this to the interplay of shape anisotropy and inhomogeneous magnetization caused by the nanoscale patterning of the magnetic film (Fig. 8c).

We prepared magnetic Ni nanowires with diameters as low as 60 nm imbedded in AAO by electrodeposition with both aqueous and dimethylsulfoxide (DMSO) solutions of metal salts (Figs. 9a, b, c). A 400-nm layer of gold was sputtered on one side of the AAO membrane to act as a cathode during the electrodeposition. Nickel nanowires were prepared with both DC and AC electroplating. We found that there is a limitation in the length of the nanowires (3 to 5 μ m) under DC electroplating, but this problem was solved by utilizing AC electrodeposition. Better quality nanowires with higher filling

percentages and narrower length distributions were made with AC electroplating. These nanowires exhibited a variety of novel properties, including localization, magnetic anisotropy, enhanced coercivity and giant magnetoresistance. The magnetization hysteresis of 2 to 3- μ m long nickel nanowires with a 200 nm diameter imbedded in AAO is shown in Fig. 9d. The easy axis is perpendicular to the nanowires. On the other hand, in 30- μ m long nickel nanowires with a 60-nm diameter imbedded in AAO (Fig. 9e), the easy axis tends to be parallel to the nanowires due to geometric anisotropy of this high aspect ratio structure. Such nanostructures have significant potential applications as high-density perpendicular recording media and field sensing devices, as well as being useful in fundamental scientific studies of nanomagnetics.

Superconducting lead nanowires were made by electrodepositing Pb into the nanopores from a 0.07M Pb(NO₃)₂ aqueous solution. The experimental set up is the same as shown in Fig. 2. The SEM image, obtained after dissolving the AAO membrane with a 1M NaOH aqueous solution, shows the uniform length and diameter of the lead nanowires (Fig. 10a). Transport measurements show an enhancement of the critical field (Fig. 10b).

Polymer nanotubes were made by first wetting the AAO membrane in a 1 wt% polyethylene solution in acetone, and then dried at 100°C (212°F) for 1 hr (Fig. 11a). SEM images were then recorded after dissolving the AAO templates with a 1M NaOH aqueous solution. The outer diameter of the polymer nanotubes is controlled by the AAO pore diameter and the length of the nanotubes is determined by the thickness of the AAO membrane. These nanotubes can be used as a protective insulating layer for metal nanowires.

Bismuth nanotubes were made by a high temperature sintering method. A bismuth layer was first electrodeposited on AAO by using a thin layer of gold as electrode. After sintering the sample at 450 to 650°C (842 to 1112°F), Bi nanotubes with a wall thickness of 10 nm were observed (Fig. 11b).

Fig. 10—(a) Superconducting lead (Pb) nanowires electrodeposited into the nanopores. The SEM image was obtained after dissolving the AAO membrane with NaOH aqueous solution. (b) Transport measurements

show an enhancement of the critical field.







Fig. 11—(a) Polyethylene nanotubes after dissolving AAO template.
(b) Bismuth nanotubes made by a high temperature sintering method.

Conclusion

We have established several electrochemical anodization procedures for synthesizing a new generation of anodic aluminum oxide (AAO) membranes containing large-area periodic arrays of uniform pores. The process converts aluminum foil, with thicknesses between 0.25 and 1 mm, into aluminum oxide by anodizing the foil in an acid solution. The self-organized pore diameters and pore-to-pore distances can be adjusted by changing the anodization voltage and the acid concentration. We have succeeded in synthesizing porous AAO membranes with pore diameters ranging from 10 to 200 nm by anodizing aluminum in oxalic and sulfuric acids under various reaction conditions. By utilizing the nanopores of AAO membranes as templates, we synthesized magnetic nickel and superconducting lead (Pb) nanowires with diameters down to 10 nm by electrodeposition. Polyethylene nanotubes and bismuth quantum nanotubes were synthesized with AAO membranes using a high temperature sintering method. Highly ordered antidot (hole) arrays of magnetic nickel prepared by coating the surfaces of the porous membrane show an abnormal magnetoresistance, attesting to the exciting physics of these novel nanostructures created utilizing the AAO templates.

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