

New Application of AAO Template: A Mold for Nanoring and Nanocone Arrays

Shiyong Zhao,^{*,†,‡} Helene Roberge,[†] Arthur Yelon,[‡] and Teodor Veres[†]

Functional Nanomaterials Group, Industrial Materials Institute, National Research Council Canada, 75 de Mortagne Boulevard, Boucherville, QC, J4B 6Y4, Canada, École Polytechnique de Montréal, Département de Génie Physique et Regroupement Québécois sur les Matériaux de Pointe (RQMP), CP 6079, Succursale Centre-ville, Montréal, Québec, H3C 3A7, Canada

Received March 29, 2006; E-mail: shi-yong.zhao@cnrc-nrc.gc.ca

Nanostructured materials have great potential in microelectronics, optoelectronics, magnetic storage, and sensors because they display novel physical and chemical properties.¹ In particular, ordered arrays of nanoparticles, nanowires, nanotubes, and nanodots have recently attracted much attention.² Template deposition^{3–13} has been used in order to make ordered arrays of nanoscale objects. Anodized aluminum oxide (AAO) has been extensively used in the past few years as an easy way to prepare nanowires and nanotubes by electrodeposition.^{4,8–12} Many kinds of ordered arrays of nanoparticles, with different diameter and shape, such as disks, hemispheres, hemiellipsoids, cones, and even rings have also been made using ultrathin alumina masks (UTAMs).^{14–16} However, the UTAMs are very thin (80–640 nm) and fragile and are difficult to handle. Here we report the use of an AAO film as a mold for preparing ordered arrays of nanodots. The material was deposited onto the large conical opening of the nanopore in the as-prepared AAO film by sputtering or e-beam evaporation. After removal of the AAO film, an array of nanodots with the pattern of the AAO film was obtained.

The electrochemical oxidation of Al has a very long history.^{17–19} Since Masuda and Fukuda's study of self-ordered porous alumina membranes by a two-step replicating process,²⁰ AAO films have become one of the most prominent template materials for the preparation of nanostructured materials. For convenient observation via scanning electron microscopy (SEM), the pores are usually enlarged in phosphoric acid. This treatment by acid solution fragilizes the AAO film. In addition, the initial morphology of the as-prepared AAO film is lost.²¹ Here, we report a new method for preparing and detaching the AAO templates which not only leads to less fragile and easier-to-handle surfaces but also permits template transfer onto metal surfaces. After anodization of high purity Al (99.999%) by the two-step process (0.3 M oxalic acid, 1 °C, 40 V), the sample was anodized in a solution of HClO₄ (68%) and (CH₃CO)₂ (98%) (v/v = 1:1) at a voltage of 45 V for 3 s. An open-through AAO film with the as-anodized initial morphology was thus immediately separated from the substrate.^{21,22}

The morphologies of the as-prepared AAO films were characterized by SEM (Hitachi S-4700). Figure 1a shows the SEM image of the top surface of an AAO film detached by the electrochemical method from the Al substrate. Hexagonally ordered pore arrays with an interpore distance of around 100 nm have been obtained. The inset in Figure 1a is the cross-sectional view of the as-prepared AAO film. It is clear that the pores have a large conical opening with a smaller bottom rim of 13 nm diameter, after which the pores become larger with all channels at a uniform diameter of 40 nm (as indicated by the white lines). Figure 1b is the SEM image of the bottom surface of the AAO film detached by the electrochemical

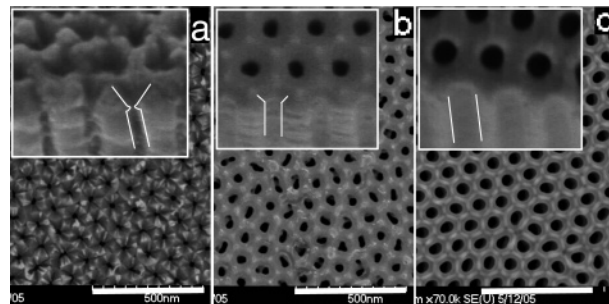


Figure 1. SEM images of AAO film as-detached by electrochemistry method from Al substrate with the cross-sectional view (insets). The scale bar is 500 nm, and the magnification in the inset is twice that of the original image: (a) top surface; (b) bottom surface; (c) top surface after pore-enlarging.

method from the Al substrate. The pore diameter of 40 nm and the interpore distance of 100 nm are both consistent with that shown in Figure 1a. Every nanopore has a conical opening as shown in the inset of Figure 1a. However, the diameter of the bottom rim is larger (34 nm) and the height of the conical opening is shorter compared with those on the top surface. If the pores are enlarged by a wet chemical method, the conical opening of both surfaces is no longer visible. Figure 1c shows the top surface of the AAO film after a pore-enlargement process was carried out in 5 wt % H₃PO₄ solution for 30 min at 30 °C. The diameter of the pores has been increased to 70 nm, and the opening has the same diameter as the channel. The uppermost layer of the AAO film in which the conical opening existed has been removed during the pore-enlarging process. Thus, the conical opening has become very short, as shown in Figure 1c.

Little attention has been paid to the conical opening, since it is the long tube which is used as a template for nanowires or nanotubes. Here, we use the conical opening as a mold to prepare metal nanodots in a well-ordered array. This method can be used for other kinds of materials such as oxides and semiconductors.

Sputtered metal films were deposited onto the three kinds of AAO film surfaces of Figure 1. This metal film can be detached from the AAO film directly or after immersing the sample in a solution of 1 M NaOH for 5 min. Figure 2 shows the SEM images of our results. Figure 2a is the SEM image of an Ag film sputtered onto and subsequently detached from the top surface of an as-prepared AAO film. The nanodot array was hexagonally ordered on a continuous metal film. The period of the nanodot array is 100 nm, which is consistent with the period of the AAO film. In the center of every nanodot (or “nanoring”) is a small hole of diameter about 12 nm. Using the bottom surface of the AAO film as a mold, an ordered Ag nanoring array was also obtained by sputtering, as shown in Figure 2b. The resultant Ag nanoring arrays have similar

[†] National Research Council Canada.

[‡] École Polytechnique de Montréal.

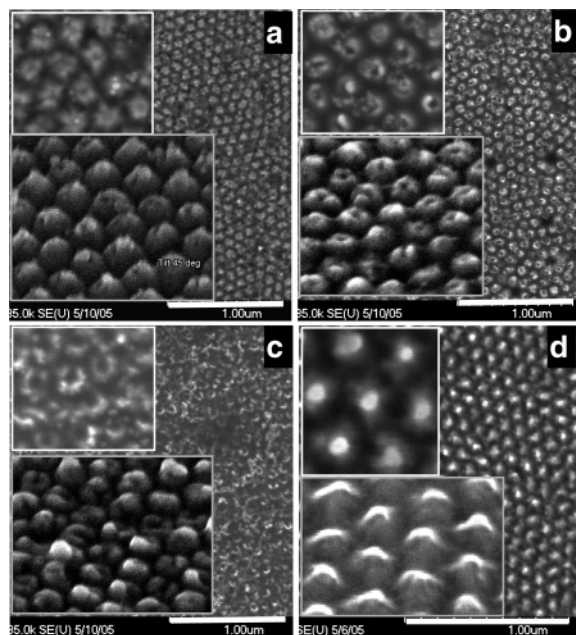


Figure 2. SEM images of Ag films sputtered onto the surface of as-prepared AAO film and detached from the AAO film: (a) top surface; (b) bottom surface; (c) top surface after pore-widening. Panel d shows SEM image of Pd film e-beam evaporated onto the top surface of as-prepared AAO film and detached from the AAO film. The upper insets are the normal view with higher magnification, and the lower insets are the corresponding 45° oblique view. All the scale bars are 1 μm and the magnification in the insets are three times that in the original images.



Figure 3. Preparation process of ordered nanoring arrays: (a) beginning of metal deposition on AAO film; (b) thicker metal film was deposited; (c) metal film with ordered arrays of nanorings after removing AAO film.

morphologies to those made using the top surface as a mold, except that the center hole is larger, of diameter about 21 nm. If the pore-enlarged AAO film was used as mold, the resulting nanorings were shorter and not as clearly defined, as shown in Figure 2c. The central hole in the nanoring is larger, about 31 nm.

In addition to nanorings, nanocone arrays can also be made using this AAO mold. Figure 2d is a SEM image of Pd film e-beam evaporated onto an AAO template and detached from it. The nanodot, or “nanocone”, has no hole in the center. The period of the nanodots is 100 nm, which is consistent with the period of the AAO film. The lower insets in Figure 2 are the 45° oblique views. The 3-D structures are clear, and the heights of the nanorings and nanocones, calculated from these images, are about 40, 30, 25, and 50 nm in Figure 2 a, b, c, and d. The central hole in the nanoring can be seen in Figure 2 a, b, and c but not in Figure 2d, as expected.

AFM measurements further support the conclusions of the SEM study (Figure S1, Supporting Information). The central holes in the nanorings are also seen. The heights of the nanorings and nanocones, measured from the cross-sections, are about 30, 25, 25, and 50 nm in Figure S1-a, b, c, and d, in reasonable agreement with the results from SEM. Energy-dispersive X-ray spectroscopy (EDX) (Figure S2) and X-ray diffraction (XRD) (Figure S3) measurements show that the nanorings and nanocone consist of Ag or Pd metal, as expected.

The proposed mechanism of growth of the nanodots is shown in Figure 3. At the beginning of the deposition, the metal deposits onto the top surface of the AAO film, including the surface of the

opening of the pores, as well as into the nanopores through the bottom rim of the opening. The metal film consists of many nanorings with holes in their centers. As the deposition progresses, the hole in the nanoring becomes smaller, until it finally closes. Thus, a nanoring with a hole in the middle is formed. After the AAO film was removed, a metal film with ordered arrays of nanorings on the surface was obtained. The diameter of the hole in the nanoring depends on the diameter of the bottom rim of the conical opening. As shown in Figure 1a, b, c, the diameters of the bottom rims of the openings are 13, 34, and 70 nm, respectively. Correspondingly, the diameters of the holes are 12, 21, and 31 nm as shown in Figure 2 a, b, c. If the rate of deposition is low, the pore is closed early, and the hole in the nanoring is very small and a nanocone is obtained instead, as shown in Figure 2d, an image of Pd deposited by e-beam evaporation at a low rate of about 0.1 nm/s (compared with the rate of 0.3 nm/s for the sputtered Ag film).

In summary, we have developed a new application of AAO films for the preparation of ordered nanoring and nanocone arrays. In particular, Ag nanoring and Pd nanocone arrays with morphologies transferred from AAO templates were fabricated. This method can be easily used for other materials such as metals, oxides, and semiconductors. Deposition can be performed via evaporation, sputtering or other methods. By depositing more than one layer of material on the AAO film, a nanodot array (such as Ag) standing on another substrate (such as SiO_2) can be obtained.

Acknowledgment. The authors would like to thank Bo Cui and Francois Normandin for their assistance with the sample preparation and analysis. This research has been supported by the National Sciences and Engineering Research Council of Canada (NSERC) and the National Research Council of Canada (NRC).

Supporting Information Available: Experimental details, AFM images, EDX and XRD patterns of all four samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.
- (2) Wilson, O.; Wilson, G. J.; Mulvaney, P. *Adv. Mater.* **2002**, *14*, 1000.
- (3) Martin, C. R. *Science* **1994**, *266*, 1961.
- (4) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61.
- (5) Mansky, P.; Harrison, C. K.; Chaikin, P. M.; Register, R. A.; Yao, N. *Appl. Phys. Lett.* **1996**, *68*, 2586.
- (6) Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.
- (7) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gosele, U. *Science* **2002**, *296*, 1997.
- (8) Yang, B.; Wu, Y.; Zong, B.; Shen, Z. *Nano Lett.* **2002**, *2*, 751.
- (9) Nielsch, K.; Muller, F.; Li, A.-P.; Gosele, U. *Adv. Mater.* **2000**, *12*, 582.
- (10) Prieto, A. L.; Martin-Gonzalez, M.; Keyani, J.; Grönsky, R.; Sands, T.; Stacy, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 2388.
- (11) Wang, Y.; Ye, C.; Fang, X.; Zhang, L. *Chem. Lett.* **2004**, *33*, 166.
- (12) Qin, J.; Nogues, J.; Mikhaylova, M.; Roig, A.; Munoz, J. S.; Muhammed, M. *Chem. Mater.* **2005**, *17*, 1829.
- (13) Ferain, E.; Legras, R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *208*, 115.
- (14) Masuda, H.; Yasui, K.; Nishio, K. *Adv. Mater.* **2000**, *12*, 1031.
- (15) Lei, Y.; Chim, W.-K. *Chem. Mater.* **2005**, *17*, 580.
- (16) Lei, Y.; Chim, W.-K. *J. Am. Chem. Soc.* **2005**, *127*, 1487.
- (17) Thompson, G. E.; Furneaux, R. C.; Wood, G. C.; Richardson, J. A.; Goode, J. S. *Nature* **1978**, *272*, 433.
- (18) Furneaux, R. C.; Rigby, W. R.; Davidson, A. P. *Nature* **1989**, *337*, 147.
- (19) Thompson, G. E. *Thin Solid Films* **1997**, *297*, 192.
- (20) Masuda, H.; Fukuda, A. *Science* **1995**, *268*, 1466.
- (21) Yuan, J. H.; He, F. Y.; Sun, D. C.; Xia, X. H. *Chem. Mater.* **2004**, *16*, 1841.
- (22) Lira, H. de L.; Paterson, R. *J. Membr. Sci.* **2002**, *206*, 375.

JA062148+