J Solid State Electrochem (2003) 7: 344–347
DOI 10.1007/s10008-002-0333-0

ORIGINAL PAPER

**Yan-Tao Pang · Guo-Wen Meng · Li-De Zhang
Wen-Jun Shan · Chong Zhang · Xue-Yun Gao
Ai-Wu Zhao · Yong-Qiang Mao**

Electrochemical synthesis of ordered alumina nanowire arrays

Received: 11 July 2002 / Accepted: 30 September 2002 / Published online: 27 November 2002

Abstract Ordered Al_2O_3 nanowire arrays embedded in the nanochannels of anodic alumina membranes (AAMs) were synthesized by electrodepostion at room temperature. Our synthetic route yielded large quantities of Al_2O_3 nanowires of uniform size and shape that are ~40 μm long with diameters of 70 nm. The Al_2O_3 nanowire structures were characterized by scanning and transmission electron microscopies, high-resolution transmission electron microscopy, energy dispersive spectroscopy and X-ray photoelectron spectroscopy.

Keywords Alumina nanowire · Electrodeposition · Anodic alumina membrane

Introduction

In recent years there has been increasing interest in the fabrication of one-dimensional nanostructures because of their potential application in electronic, magnetic, optical, and micromechanical devices. To obtain scaled-up functional devices, highly ordered nanowire or nanotube arrays are essential. The most common technique used to fabricate such nanostructures is the so-called template synthesis [1, 2, 3, 4]. This method has been used to prepare tubules and fibrils composed of metals [5, 6], semiconductors [7], and other materials such as carbon nanotubes [8]. Electrodeposition is cheap and fast in comparison with other methods, such as the sol-gel and CVD methods. In addition, the anodic alumina membrane (AAM) is a good choice for a template because the channel diameters are easily adjusted (down to 9 nm) to sizes enabling quantum confinement. Using AAM templates, well-aligned oxide semiconductor nanowire arrays, such as ZnO [7] and SnO_2 [9], have been fabricated by electrodeposition and oxidation.

Alumina whiskers and fibers are widely used in advanced materials such as metal matrix composites because of their higher temperature resistance and higher modulus values [10, 11]. Additionally, high-performance alumina fibers can be used as catalyst supports, radar-transparent structures, and antenna windows [12]. Recently, Al_2O_3 fibers [13] and nanopillars [14] have been produced. However, a high temperature was needed for both of these methods. Branched alumina nanotubes (bANTs) [15] and individual alumina nanotubes (ANTs) [16] were also reported for alumina oxide. Nevertheless, little has been reported about the fabrication of Al_2O_3 nanowire arrays. In this communication, we report the large-scale synthesis of ordered Al_2O_3 nanowire arrays embedded in the nanochannels of AAMs by electrodeposition at room temperature.

Experimental

Through-hole AAMs with ordered nanochannels was prepared via a two-step anodization process as described in detail elsewhere [17, 18, 19, 20, 21, 22]. The first anodization was conducted under a constant voltage of 40 V at 5 °C in 0.3 M oxalic acid solution, in a thermally isolated electrochemical cell for 4 h, during which the electrolyte was vigorously stirred using a pump system. Then the alumina layer produced was removed by wet chemical etching in a mixed solution of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 °C for 6 h. The second anodization was carried out under the same conditions as those in the first one for 12 h. After coating a protecting layer on the surface of the porous alumina film, the central aluminum substrate was removed in a saturated $HgCl_2$ solution, and the surrounding aluminum was retained as support. A subsequent etching treatment was carried out in a 6 wt% phosphoric acid solution at 30 °C for 70 min to remove the barrier layer on the bottom side of the AAM. A thin gold layer (about 200 nm) was evaporated onto the upper side of the AAM by

Y.-T. Pang (✉) · G.-W. Meng · L.-D. Zhang · W.-J. Shan
X.-Y. Gao · A.-W. Zhao
Institute of Solid State Physics,
Chinese Academy of Sciences, Hefei 230031, P.R. China
E-mail: ytpang@263.net

C. Zhang
Department of Chemistry,
Nankai University, Tianjin 300071, P.R. China

Y.-Q. Mao
Nanjing Institute of Geology and Paleontology,
Chinese Academy of Sciences, Nanjing 210008, P.R. China

using a JEE-4X vacuum evaporator in a vacuum of 2×10^{-5} Torr to serve as the working electrode in a two-electrode electrochemical cell. The electrolyte contained 30 g/L $AlCl_3$. The electrodeposition was carried out at a constant current density (0.5 mA/cm^2), with graphite serving as the counter electrode, at room temperature for 40–48 h.

After electrodeposition, scanning electron microscopy (SEM; JSM-6300), transmission electron microscopy (TEM; JEM-200CX), high-resolution transmission electron microscopy (HRTEM; JEOL-2010), energy dispersive spectroscopy (EDX; Oxford, Link, ISIS), and X-ray photoelectron spectroscopy (XPS; Escalab M K, Mg K_α X-rays as the excitation sources) were used to characterize the Al_2O_3 nanowire arrays.

Results and discussion

After the AAM was etched away by using a mixed solution of 6 wt% phosphoric acid and 1.8 wt% chromic acid, the remaining product was cleaned in an ultrasonic bath. SEM images (top view and cross-view) of the Al_2O_3 nanowire arrays are shown in Fig. 1a and b, respectively. It can be clearly seen that bulk quantities of Al_2O_3 nanowires with an equal height and a highly ordered tip array were formed. Figure 1a shows that the lengths of the Al_2O_3 nanowires are about 40 μm, which is similar to the thickness of the AAM template used.

Figure 2a shows the TEM image of a bundle of nanowires obtained after dissolving away part of the alumina template. The dark areas are Al_2O_3 nanowires. The nanowires are straight with relatively uniform diameters of 70 nm, which is nearly equal to the diameter of nanochannels in the AAM. Figure 2b shows the TEM image of a single Al_2O_3 nanowire with a diameter of 60 nm. The surface of the nanowire is not smooth, which could be caused by the rough surface of internal pores of the AAM. It should be pointed out that the dissolving rate is different between the alumina template and the electrodeposited alumina nanowires in the acid solution. The contact areas of the alumina template with the acid solution are larger than those of the alumina nanowires, so the dissolving rate of the alumina template is higher than the alumina nanowires in acid solution. When the alumina template was etched away by the acid

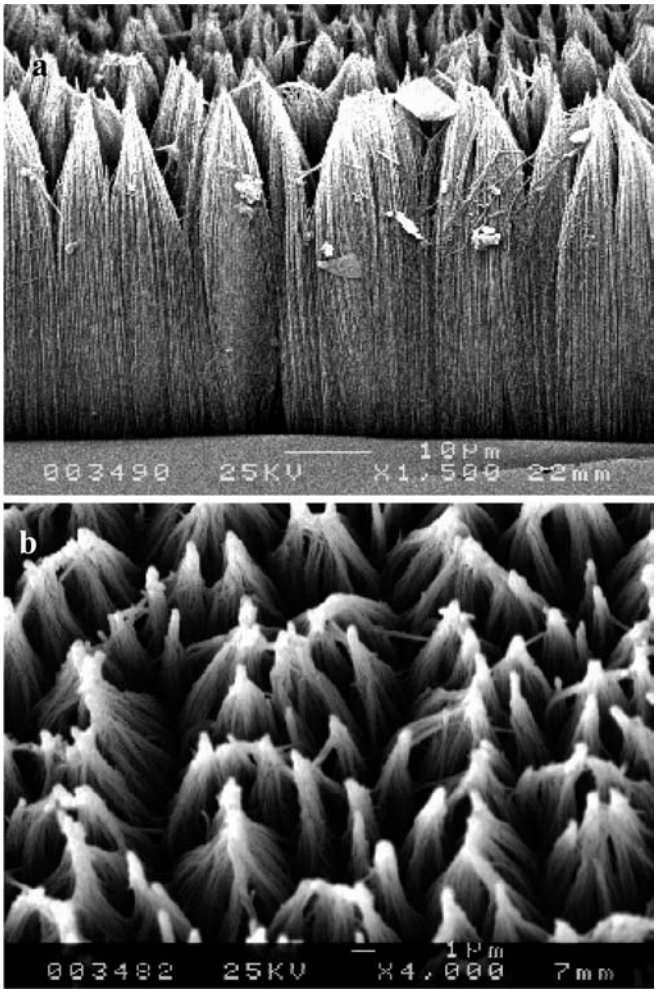

Fig. 1 SEM images of the resulting ordered Al_2O_3 nanowire arrays after removing the AAMs: **a** cross-section view and **b** top view

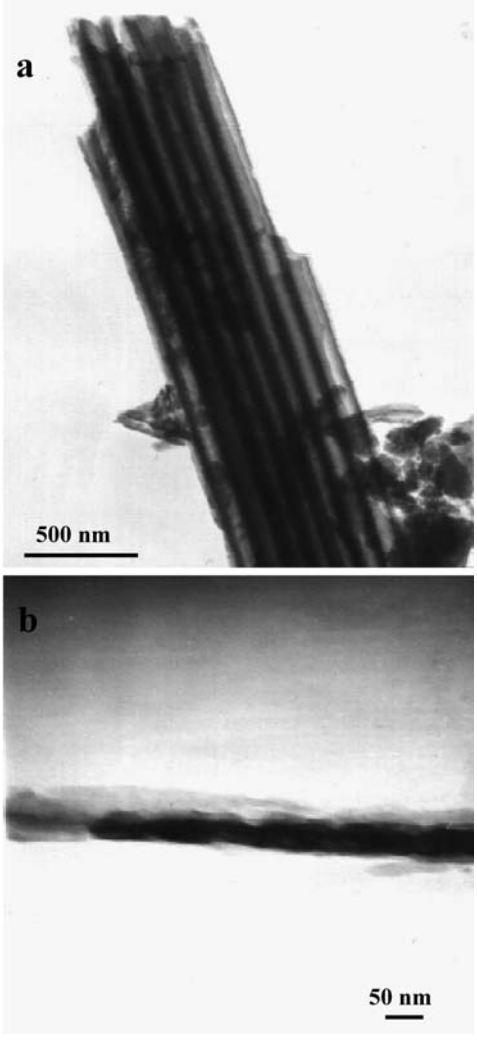

Fig. 2 TEM images of typical Al_2O_3 nanowires: **a** a bundle of Al_2O_3 nanowires; **b** a single Al_2O_3 nanowire

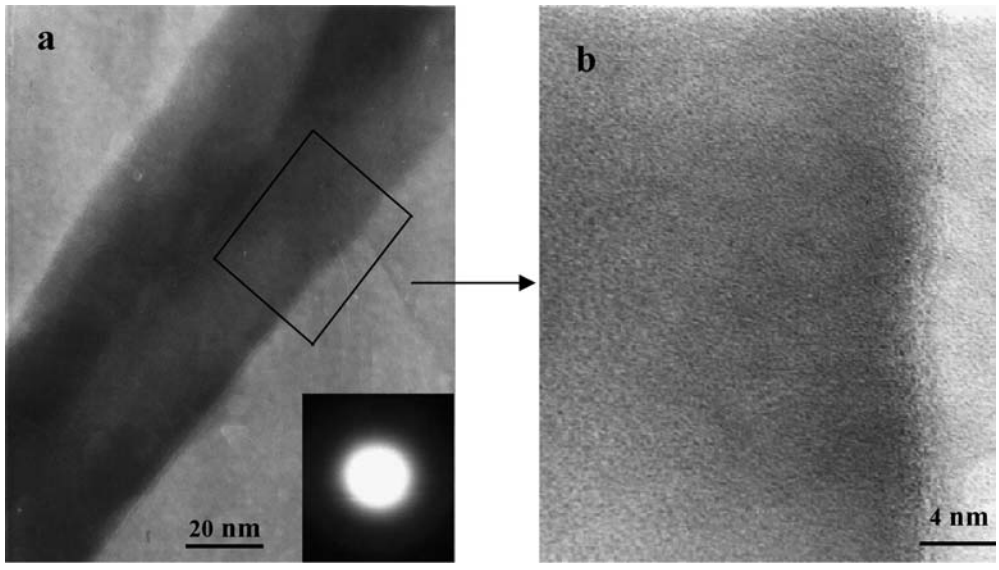

Fig. 3 **a** TEM image of a typical Al_2O_3 nanowire. *Inset*: SAED pattern taken from the nanowire showing some amorphous halo rings. **b** HRTEM image of a typical Al_2O_3 nanowire, showing the absence of crystal lattice planes, which further confirms its amorphous nature

solution, the outer surface of the alumina nanowires was also partially etched simultaneously. Thus the diameter of the Al_2O_3 nanowire in Fig. 2b is smaller than in Fig. 2a.

The selected area electron diffraction (SAED) pattern (Fig. 3a, inset), taken from a representative Al_2O_3 nanowire, reveals some diffusive rings, but no diffraction spots could be identified, indicating that the Al_2O_3 nanowire is amorphous. No crystalline fringes could be identified in high-resolution TEM (Fig. 3b) at the lattice-resolved scale, providing further confirmation of the amorphous nature of the wires.

The chemical composition of the nanowires was analyzed using EDX and XPS. EDX (attached to the HRTEM, not shown here) measurements made on representative nanowires detected only O, Al, and Cu atoms. The atom ratio of Al to O calculated from the quantitative analysis data is about 1:5, which is higher than 2:3 in bulk alumina. This may be caused by oxygen adsorption on the surface of the Al_2O_3 nanowires. It is obvious that Cu atoms were generated from the Cu grid.

The photoelectron spectra of Al_{2p} (Fig. 4a) and O_{1s} (Fig. 4b) are in good agreement with the data observed for Al_2O_3, revealing that the products are composed of Al_2O_3 nanowire arrays.

From the SEM images (Fig. 1), it is obvious that the alumina nanowires grew out of the nanochannels of the AAM. On the other hand, the TEM analysis reveals that the uniform alumina nanowire diameters are nearly equal to the diameter of nanochannels in the AAM. So, our experimental results are different from the alumina nanopillar arrays [14] fabricated by chemical etching AAMs in dilute NaOH solution. However, the growth mechanism of Al_2O_3 nanowires within the nanochannels of the AAMs is not clear at present and further investigation is still needed.

In summary, we have demonstrated the fabrication of dense, continuous Al_2O_3 nanowires, 40 μm long and with uniform diameters of 70 nm, by direct electrodeposition in the nanochannels of AAMs. Our experimental results demonstrate that the novel, simple route we used can produce bulk quantities of ordered amorphous Al_2O_3 nanowires and is likely to be of interest in future applications.

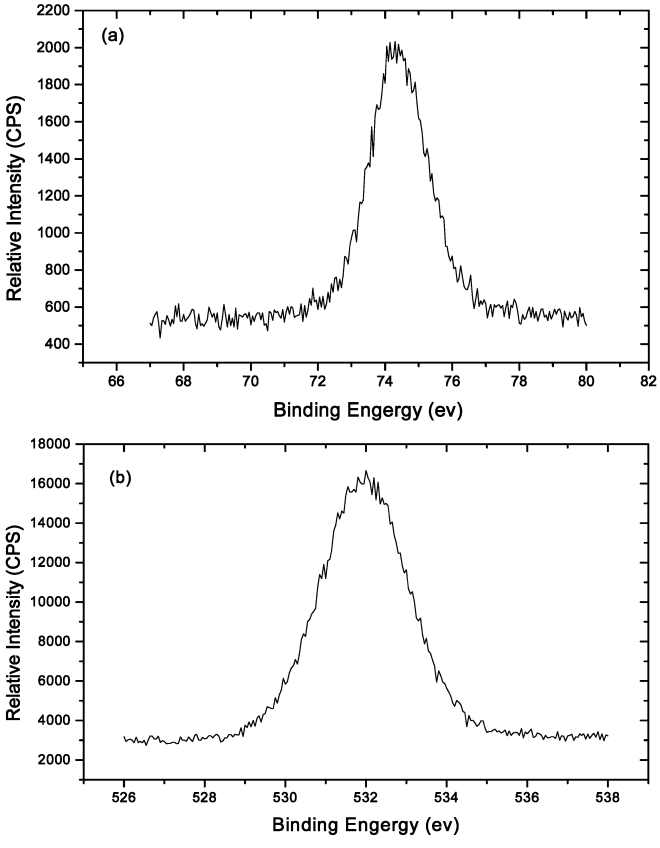

Fig. 4 **a** X-ray photoelectron spectrum for Al_{2p} in the product. **b** X-ray photoelectron spectrum for O_{1s} in the product

Acknowledgement This work was supported by the Ministry of Sciences and Technology of China and the Natural Science Foundation of China (grant no. 19974055).

References

1. Martin CR (1994) Science 266:1961
2. Parthasarathy RV, Phani KLN, Martin CR (1995) Adv Mater 7:896
3. Martin CR (1996) Chem Mater 8:1739
4. Martin CR (1997) Chem Mater 9:2544
5. Huber CA, Huber TE, Sadoqi M, Lubin JA, Manalis S, Prater CB (1994) Science 263:800
6. Nielsch K, Müler M, Li AP, Gösele U (2000) Adv Mater 12:582
7. Li Y, Meng GW, Zhang LD, Phillip F (2000) Appl Phys Lett 76:2011
8. Suh JS, Lee JS (1999) Appl Phys Lett 75:2047
9. Zheng MJ, Li GH, Zhang XY, Huang SY, Lei Y, Zhang LD (2001) Chem Mater 13:3859
10. Touratier M, Béakou A (1992) Compos Sci Technol 44:369
11. Dragone TL, Nix WD (1992) Acta Metall Mater 40:2781
12. Cooke TF (1991) J Am Ceram Soc 74:2959
13. Valcárcel V, Souto A, Guitián F (1998) Adv Mater 10:138
14. Yuan ZH, Huang H, Fan SS (2002) Adv Mater 14:303
15. Zou JP, Pu L, Bao XM, Feng D (2002) Appl Phys Lett 80:1079
16. Pu L, Bao XM, Zou JP, Feng D (2001) Angew Chem Int Ed 40:1490
17. Masuda H, Yada K, Osaka A (1998) Jpn J Appl Phys 37:L1340
18. Li AP, Müller F, Birner A, Nielsch K, Gösele U (1999) Adv Mater 11:483
19. Jessensky O, Müller F, Gösele U (1998) J Electrochem Soc 145:3735
20. Jessensky O, Müller F, Gösele U (1998) Appl Phys Lett 72:1173
21. Masuda H. Hasegawa F, Ono S (1997) J Electrochem Soc 144:L127
22. Li AP, Müller F, Birner A, Nielsch K, Gösele U (1998) J Appl Phys 84:6023