Arrays of ordered Pb nanowires with different diameters in different areas embedded in one piece of anodic alumina membrane

2002 J. Phys.: Condens. Matter 14 11729

(http://iopscience.iop.org/0953-8984/14/45/314)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11729–11736 PII: S0953-8984(02)53173-8

Arrays of ordered Pb nanowires with different diameters in different areas embedded in one piece of anodic alumina membrane

Y T Pang[1,3], G W Meng[1], L D Zhang[1], W J Shan[1], X Y Gao[1], A W Zhao[1] and Y Q Mao[2]

[1] Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[2] Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, People's Republic of China

E-mail: ytpang@263.net

Received 9 September 2002
Published 1 November 2002
Online at stacks.iop.org/JPhysCM/14/11729

Abstract

Nanochannel arrays with constant nanochannel density but varying nanochannel diameters in different areas in one piece of anodic alumina membrane are achieved. Using this type of membrane as a template, ordered Pb nanowire arrays with constant nanowire density but diameters decreasing radially were obtained by electrodeposition. Scanning electron microscopy and transmission electron microscopy (TEM) images taken from different areas of the Pb nanowire arrays show that we can control the growth of aligned Pb nanowires with different diameters in a single process at one time. The individual Pb nanowires have been characterized using selected-area electron diffraction and high-resolution TEM. Nanometre-scale fibrils, rods, wires, and tubules of metal, semiconductor, carbon, and other materials with the same density but different diameters in different areas can be fabricated using this type of template, in combination with other fabrication techniques. The simultaneous integration of ordered nanowire structures with different diameters embedded in a single anodic alumina membrane could be useful in nanodevice manufacture as well as electronics, optoelectronics, and magnetics.

1. Introduction

In the last decade, the template synthesis method has been playing an important role in the fabrication of many kinds of nanowire [1, 2] and nanotube [3, 4] because of its interesting and useful features. Recently, a self-ordered nanochannel material formed by anodization of

[3] Author to whom any correspondence should be addressed.

high-purity Al in an appropriate acid solution [5, 6] has attracted increasing interest as a key template for the fabrication of nanometre-scale structures [7, 8]. The anodic alumina membrane (AAM) possesses hexagonally ordered porous structure with channel density in the range 10^{10}–10^{12} cm^{-2}, and extremely high aspect ratio of the channels (depth divided by width). The pore diameter and interpore distance increase linearly with the applied anodization voltage; this can be controllably achieved in the ranges 4–200 nm [5] and 50–420 nm [9], respectively. The pore diameter can also be controlled by adjusting the pore widening time [10]. Using an AAM, nanometre-scale fibrils, rods, wires, and tubules of metal [1, 11, 12], semiconductors [13–15], carbon [16], and other solid materials with uniform diameters were successfully fabricated. However, it still remains a great challenge to control the growth of aligned nanowires with different diameters in different areas in one piece of AAM.

As a superconductor, Pb nanowire has long been the dominating material in electronics. Recently, Pb nanowires embedded in track-etched polycarbonate membranes were synthesized by electrodeposition [17]. In this communication, we report the fabrication of AAM with same nanochannel density but different nanochannel diameters (AAM-SNDDND) in three different areas, and arrays of Pb nanowires with different diameters but constant pore density embedded in the nanochannels of AAM-SNDDND by electrodeposition. This technique can be extended to fabricate nanowires with different diameters in different areas in one electrodeposition process, which was not possible previously.

2. Experimental procedure

The fabrication process involves three steps:

(1) electrochemical generation of AAM;
(2) chemical generation of AAM-SNDDND;
(3) electrodeposition of pure metal Pb nanowires embedded in AAM-SNDDND.

AAM templates were prepared by a two-step anodization process, as described previously [18–21]. Briefly, high-purity (99.999%) aluminium foils were used as the starting material. Prior to anodizing, the aluminium was annealed at 500 °C in order to obtain homogeneous conditions for pore growth over large areas. Anodization was carried out under a constant cell voltage of 27 V in a 0.3 M sulfuric acid solution at 0 °C for 4 h. The formed alumina was then removed by a mixture solution of phosphoric acid and chromic acid, and the Al sheet was anodized again under the same conditions as those in the first treatment for 8 h. After the anodization, the remaining aluminium was removed selectively in multiple steps in a saturated $HgCl_2$ solution (figures 1(a)–(d)). The central part of remaining aluminium, denoting as I (figure 1(b)), was removed first. Then drops of a 5 wt% aqueous mixture of phosphoric acid were dropped on this part at 30 °C for 10 min. This process makes the barrier layer of the part become thin. Subsequently, the remaining aluminium around the central part, denoted as II (figure 1(c)), was removed and the barrier layers of parts I and II were thinned under the same conditions as for part I in the first treatment. Finally, the outer part of remaining aluminium, denoting as III (figure 1(d)), was removed and then the whole bottom part of the AAM was dipped into 5 wt% aqueous mixture of H_3PO_4 for 20 min. The surrounding aluminium was retained as the support. In order to fabricate an array of Pb nanowires, a layer of Au film was deposited as an electrode on one side of the AAM-SNDDND using a vacuum evaporation apparatus. The electrolyte contained a mixture solution of 30 g l^{-1} $PbNO_3$ and 45 g l^{-1} H_3BO_3 and was buffered to pH = 2.5 with nitric acid. The electrodeposition was carried out at a constant current density (2.5 mA cm^{-2}), with carbonate serving as the counter-electrode at room temperature for 8 h.

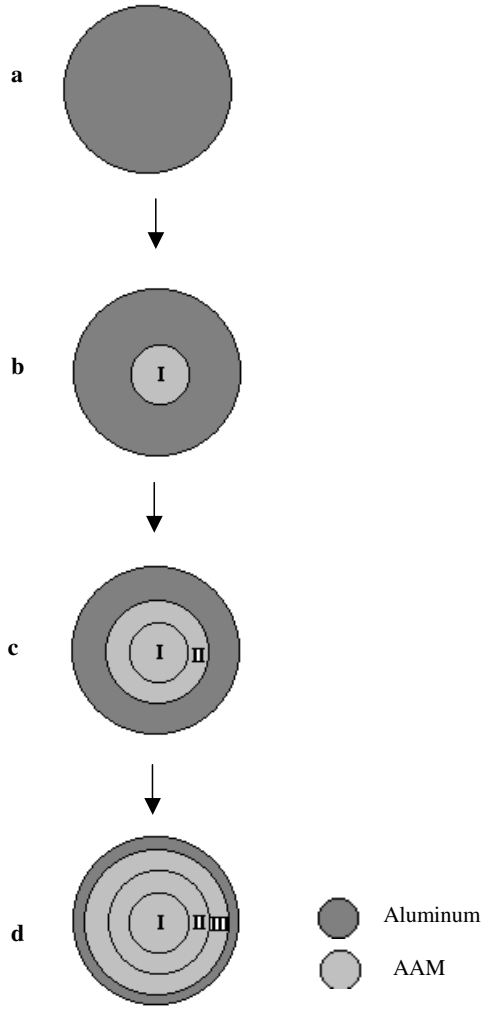

Figure 1. A schematic outline of the procedure for producing AAM-SNDDND.

The Pb nanowire arrays embedded in AAM-SNDDND were characterized by x-ray diffractometry (XRD, MXP18AHF, D/Max-rA) with Cu Kα radiation ($\lambda = 1.5405$ Å), scanning electron microscopy (SEM, JSM-6300), transmission electron microscopy (TEM, JEM-200CX), selected-area electron diffraction (SAED), and high-resolution electron microscopy (HREM, JEOL-2010). For SEM observation, a piece of AAM-SNDDND embedded with Pb nanowires was eroded in 5% NaOH solution at 30 °C for 30 min to remove the AAM-SNDDND partially and then attached to the SEM stub after careful rinsing with de-ionized water. A thin gold layer was evaporated to form a conducting film for observation. Specimens for TEM and HREM observations were prepared by dissolving away the AAM-SNDDND completely, which was accomplished by placing a small piece of Pb/AAM-SNDDND in the same solution as for SEM observation for 60 min. The solution was then slowly removed using a syringe and was carefully replaced with distilled water to rinse the products. The rinsing process was repeated three times. The remaining black solid

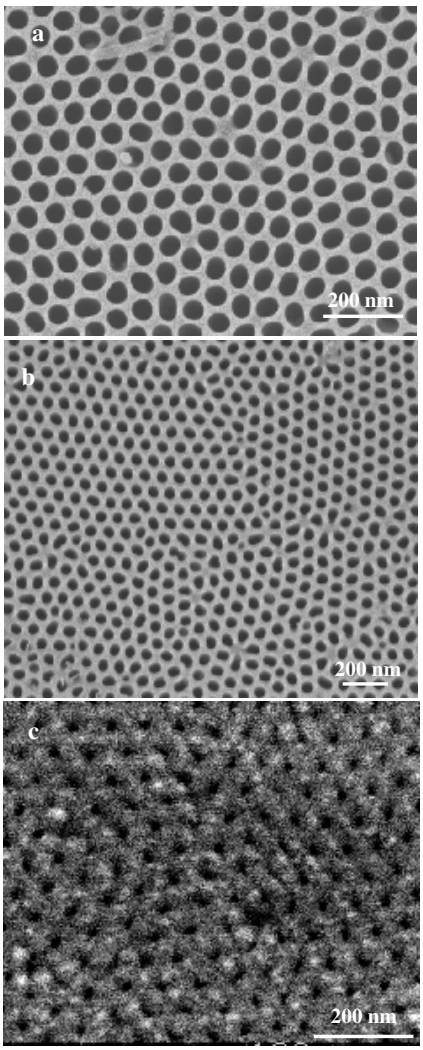

Figure 2. SEM images of the ordered AAM-SNDDND. (a) The top view of part I; (b) the top view of part II; (c) the top view of part III.

was collected and ultrasonically dispersed in 1 ml of ethanol. A drop of the suspended solution was placed on a carbon grid and allowed to dry prior to electron microscope analysis.

3. Results

Figure 2 shows the SEM images of AAM-SNDDND. The images of (a), (b), and (c) were taken from the parts I, II, and III (figure 1) with nanochannel diameters of about 50, 35, and 20 nm respectively. The interpore distances are the same (about 70 nm).

A typical XRD pattern for a prepared Pb/AAM-SNDDND sample is shown in figure 3. The peaks are found to be very close to (111), (200), (220), (311), (222), and (400) for bulk Pb, indicating that the structure of bulk Pb is preserved in AAM-SNDDND.

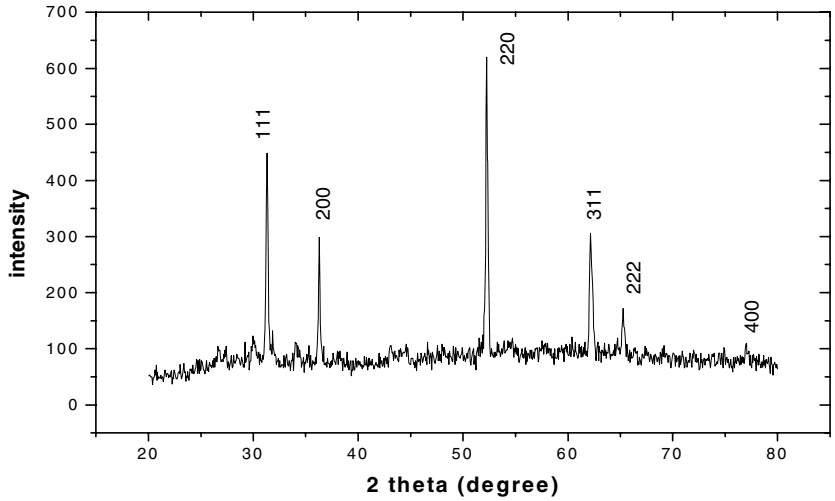

Figure 3. The XRD spectrum of the Pb nanowire arrays embedded in AAM-SNDDND.

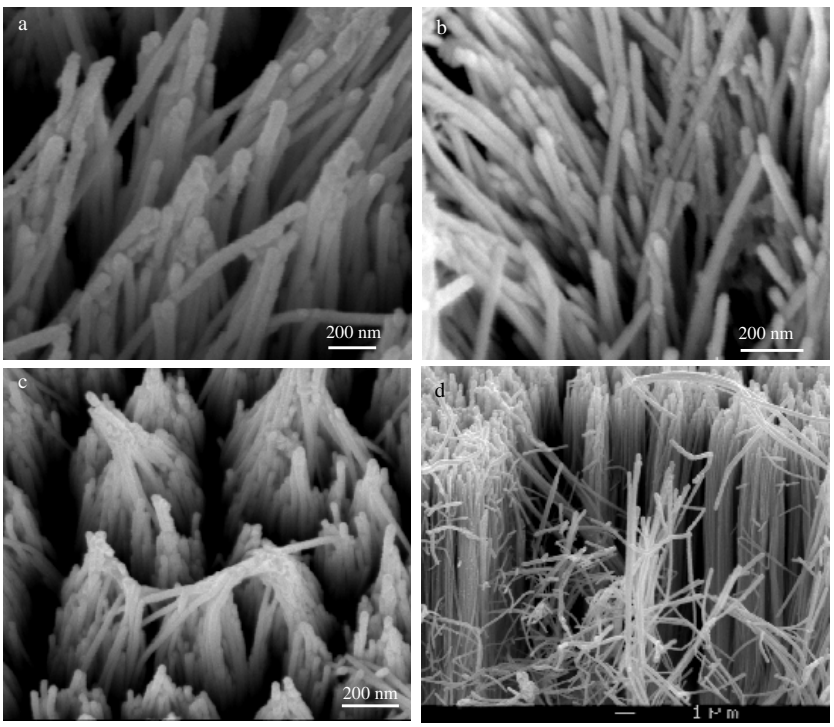

Figure 4. SEM images of the resulting ordered array of Pb nanowires. (a), (b), and (c) are images of parts I, II and III, respectively. The ordered Pb nanowires with average diameters of 55, 40, and 25 nm can be clearly seen in (a), (b), and (c); (d) a cross-sectional view of part III.

Figures 4(a)–(c) show SEM images of the Pb nanowire arrays, which were taken from parts I, II, and III (figure 1), respectively. The diameter distribution of the nanowires was obtained using the statistical results for ten wire diameters per part from SEM images. The

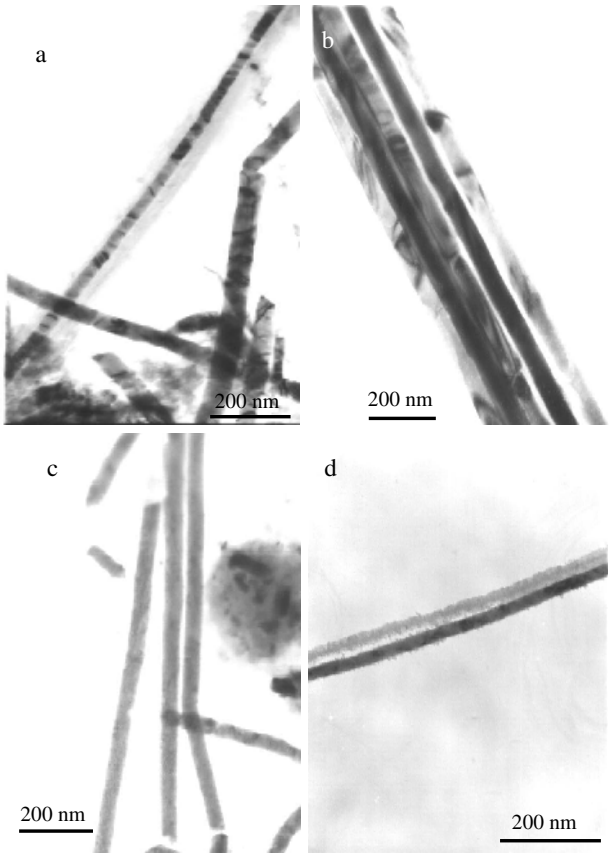

Figure 5. TEM images of Pb nanowires. (a) An image taken from parts I, II, and III together. (b), (c), (d) Images of Pb nanowires with average diameters of 50, 35, and 20 nm taken from parts I, II, and III, respectively.

Table 1. Diameter data for wires grown in AAM-SNDDND.

		Average diameters (nm)	
Parts	Wires	SEM	TEM
I	10	55	50
II	10	40	35
III	10	25	20

statistical results (table 1) show that Pb nanowires with average diameters of 55, 40, and 25 nm were obtained in parts I, II, and III, respectively. Figure 4(d) shows a cross-sectional SEM view of part III. The lengths of the Pb nanowires are about 15 μm, which is in good agreement with that for the AAM-SNDDND template used.

The TEM technique was employed to get more details of the Pb nanowire morphology and structures. Highly magnified TEM images of the prepared sample (figure 5) show a number of nanowires with different diameters. Figure 5(a) was taken from the sample including parts I, II, and III together. Figures 5(b), (c), and (d) were taken from parts I, II, and III, respectively. The diameter distribution of the nanowires was obtained using the statistical results for ten

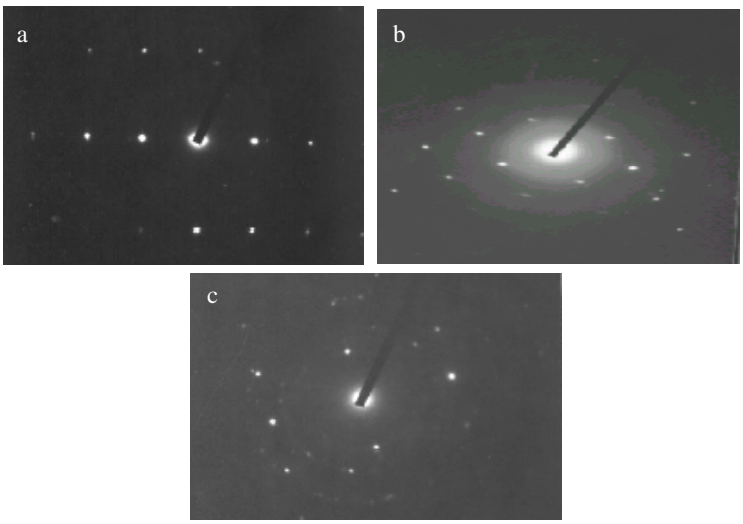

Figure 6. SAED patterns of the Pb nanowires with different diameters of (a) 50 nm, (b) 35 nm, and (c) 20 nm.

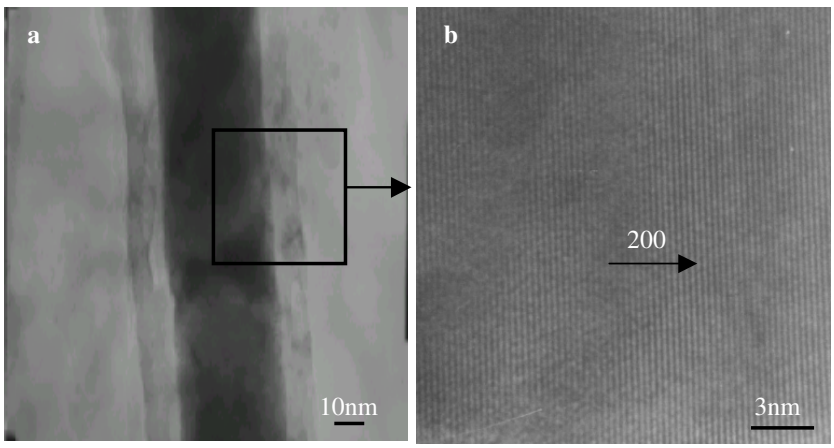

Figure 7. A HREM image of a single Pb nanowire with the diameter of 35 nm. The lattice spacing is about 0.251 nm.

wire diameters from TEM images. The statistical results (table 1) show that Pb nanowires with average diameters of 50, 35, and 20 nm were obtained. The average diameters of Pb nanowires from TEM images are smaller than those from the SEM images, which may be caused by the Au layer evaporated in SEM sample preparation.

The crystalline structures of the individual Pb nanowires with different diameters were investigated by means of SAED and HREM. Figures 6(a) and (b) show the SAED patterns of the Pb nanowires with diameters of 50 and 35 nm, respectively. Many individual nanowires were characterized, and we always observed a single set of diffraction spots in the SAED patterns, indicating that the Pb nanowires with diameters of 50 and 35 nm are essentially single crystal. The single-crystal structures of the Pb nanowires with diameters of 50 and 35 nm were further confirmed by HREM images. The HREM images (figure 7) clearly show

the single-crystal structure of an individual Pb nanowire with the diameter of 35 nm. However, SAED patterns from the Pb nanowires with the smallest diameter (20 nm) are different from those in figures 6(a) and (b). The SAED patterns (figure 6(c)) reveal that Pb nanowires with polycrystalline structures have been prepared.

4. Conclusions

In addition, the smaller diameter in the ordered Pb nanowire arrays is a result of the anodization conditions such as the electrolyte, voltage, and temperature of anodization [22], and the larger diameter could be controlled within the interpore distance of the AAM-SNDDND template by adjusting the pore widening time [10]. Therefore, the diameter ratio of the Pb nanowires can be changed in some range.

In summary, we report the fabrication of AAM with diameters radially decreasing and, using it as a template, we obtained ordered Pb nanowire arrays with constant wire density but different diameters in different areas embedded in one piece of AAM-SNDDND. These nanowires with selectable diameters and lengths provide the possibility of comparing nanometre-scale characteristics for various diameters with respect to size confined, and will be useful for the study of the electric properties of Pb nanowires and have potential applications in electric devices. In addition, the method is easily applicable to fabricate other metal nanowire arrays and nanotube arrays. The simultaneous integration of ordered nanowire structures of different diameters embedded in a single AAM-SNDDND could be useful in nanodevice manufacture as well as electronics, optoelectronics, and magnetics.

Acknowledgments

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

References

[1] Huber C A, Huber T E, Sadoqi M, Lubin J A, Manolis S and Prater C B 1994 *Science* **263** 800
[2] Whitney T M, Jiang J S, Searson P C and Chien C L 1993 *Science* **261** 1316
[3] Hoyer P 1996 *Adv. Mater.* **8** 857
[4] Li J, Papadopoulos C, Xu J M and Moskovits M 1999 *Appl. Phys. Lett.* **75** 367
[5] Masuda H and Fukuda K 1995 *Science* **268** 1466
[6] Masuda H and Hasegawa F 1997 *J. Elecrochem. Soc. Interface* **144** L127
[7] Saito M, Kirihara M, Taniguchi T and Miyagi M 1994 *Appl. Phys. Lett.* **55** 607
[8] Routkevich D, Bigioni T and Moskovits M 1996 *J. Phys. Chem.* **100** 14037
[9] Li A P, Müller F, Birner A, Nielsch K and Gösele U 1998 *J. Appl. Phys.* **84** 6023
[10] Almawlawi D, Coombs N and Moskovits M 1991 *J. Appl. Phys.* **70** 4421
[11] Nielsch K, Müller F, Li A P and Gösele U 2000 *Adv. Mater.* **12** 582
[12] Evans P R, Yi G and Schwarzacher W 2000 *Appl. Phys. Lett.* **76** 481
[13] Xu D S, Xu Y J, Chen D P, Guo G L, Gui L L and Tang Y Q 2000 *Adv. Mater.* **12** 520
[14] Suh J S and Lee J S 1999 *Appl. Phys. Lett.* **75** 2074
[15] Wei P H, Li G B, Zhao S Y and Chen L R 1999 *J. Electrochem. Soc.* **146** 3536
[16] Varol H S and Himsch A 1996 *Energy Mater. Sol. Cells* **40** 27
[17] Yi G and Schwarzacher W 1999 *Appl. Phys. Lett.* **74** 1746
[18] Masuda H, Yada K and Osaka A 1998 *Japan. J. Appl. Phys.* **37** L1340
[19] Li A P, Müller F, Birner A, Nielsch K and Gösele U 1999 *Adv. Mater.* **11** 483
[20] Jessensky O, Müller F and Gösele U 1998 *J. Electrochem. Soc.* **145** 3735
[21] Jessensky O, Müller F and Gösele U 1998 *Appl. Phys. Lett.* **72** 1173
[22] Diggle J W, Downie T C and Goulding C W 1959 *Chem. Rev.* **69** 365