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Y.T. PANG[1,✉]
G.W. MENG[1]
W.J. SHAN[1]
L.D. ZHANG[1]
X.Y. GAO[1]
A.W. ZHAO[1]
Y.Q. MAO[2]

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

[1] Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, P.R. China
[2] Nanjing Institute of Geology and Paleontology, Chinese Academy of Sciences, Nanjing 210008, P.R. China

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ABSTRACT Nanochannel arrays with the same nanochannel density but different nanochannel diameters in different areas in one piece of anodic alumina membrane had been created. SEM observations on one piece of this type of anodic alumina membrane show that the nanochannel diameters radially decrease from 80 nm to 60 nm and to 40 nm along the radial direction. Therefore, using this type of membrane as a template, ordered Ag nanowire arrays with the same nanowire density but with diameters decreasing radially were obtained by electrodeposition. SEM and TEM images taken of different areas of the Ag nanowire arrays show that we can control the growth of aligned Ag nanowires with different diameters in a single process at the same time. Using this type of template in combination with other fabrication techniques, nanometer-scale fibrils, rods, wires, and tubules of metal, semiconductors, carbon, and other materials with same density but different diameters in different areas can be fabricated. 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.

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1 Introduction

In the last decade, the template synthesis method has played an important role in the fabrication of many kinds of nanowires [1, 2] and nanotubes [3, 4], because of its interesting and useful features. Recently, a self-ordered nanochannel material formed by anodization of high-purity Al in an appropriate acid solution [5, 6] has attracted increasing interest as a key template for the fabrication of nanometer-scale structures [7, 8]. The anodic alumina membrane (AAM) possesses a hexagonal ordered porous structure with a channel density in the range 10^{10}–10^{12} /cm^2, and an extremely high channel aspect ratio (depth divided by width). The pore diameter and interpore distance increases linearly with the applied anodization voltage, which can be controllably achieved in the ranges 4 to 200 nm [5] and 50 to 420 nm [9], respectively. The pore diameter can also be controlled by adjusting the pore widening time [10]. Using AAM, nanometer-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.

In this communication, we report the fabrication by electrodeposition of an anodic alumina membrane with the same nanochannel density but different nanochannel diameters (AAM-SNDDND), in three different areas and arrays of Ag nanowires with different diameters but identical pore density, embedded in the nanochannels of an AAM-SNDDND. 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

The fabrication process involves three steps: (1) the electrochemical generation of AAM; (2) the chemical generation of AAM-SNDDND; and (3) the electrodeposition of pure metal Ag nanowires embedded in AAM-SNDDND. AAM templates were prepared by a two-step anodization process, as described previously [17–20]. Briefly, high-purity (99.999%) aluminum foils were used as the starting material. Prior to anodizing, the aluminum was annealed at 500 °C in order to obtain homogeneous conditions for pore growth over large areas. Anodization was carried under a constant cell voltage of 40 V in a 0.3-M oxalic acid solution at 3 °C for 4 h. The formed alumina was then removed by a solution mixture of phosphoric acid and chromic acid, and the Al sheet was anodized again under the same conditions as those in the first, for 10 h. After the anodization, the remaining aluminum was removed selectively by multiple steps in a saturated $HgCl_2$ solution (Fig. 1a–d). The central part of the remaining aluminum denoted as I (Fig. 1b) was first removed. Then drops of a 5 wt. % aqueous mixture of phosphoric acid were dropped on this part at 40 °C for 5 min. This process made the barrier layer of the part become

✉ Fax: +86-551/559-1434, E-mail: ytpang@263.net

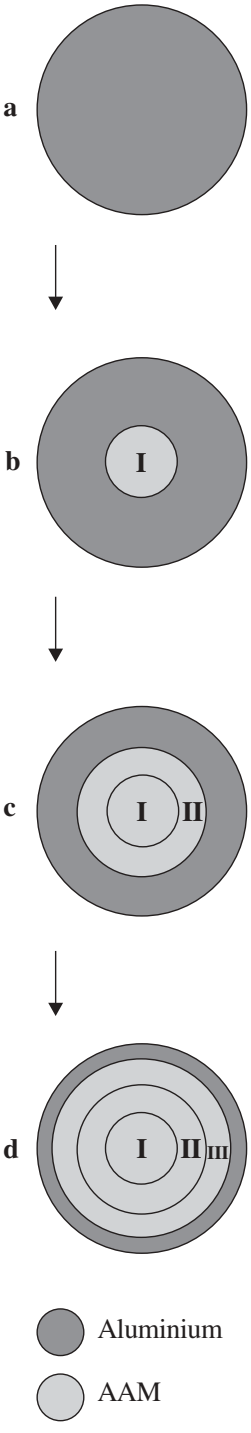

FIGURE 1 A schematic outline of the procedure for producing AAM-SNDDND. **a** before removing the aluminium; **b** the remaining aluminium of part I was removed; **c** the remaining aluminium of part II was removed; **d** the remaining aluminium of part III was removed

thin. Subsequently, the remaining aluminum around the central part denoted as II (Fig. 1c) was removed and the barrier layers of the part I and the part II were thinned under the same conditions as those for the part I the first time. Finally, outer part of the remaining aluminum, denoted as III (Fig. 1d), was removed and then the whole bottom of the AAM was dipped into a 5 wt. % aqueous mixture of H_3PO_4 for 20 min. The surrounding aluminum was retained as support. In order to fabricate an array of Ag 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 solution mixture of 300 g/l $AgNO_3$, and 45 g/l H_3BO_3 solutions 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) at room temperature for 8 h, with carbonate serving as the counter electrode.

The Ag nanowire arrays embedded in AAM-SNDDND were characterized by X-ray diffractometry [(XRD) MXP18AHF] (D/Max-rA) with Cu K_α radiation ($\lambda = 1.5405$ Å), scanning electron microscopy [(SEM) JSM-6300], and transmission electron microscopy [(TEM) JEM-200 CX]. For SEM observation, a piece of AAM-SNDDND embedded with Ag nanowires was eroded in 5% NaOH solution at 30 °C for 30 min to partially remove the AAM-SNDDND and then attached to the SEM stub after careful rinsing with deionized water. A thin gold layer was evaporated to form a conducting film for observation. Specimens for TEM observation were prepared by dissolving away the AAM-SNDDND completely, which was accomplished by placing a small piece of Ag/AAM-SNDDND in the same solution as that used 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

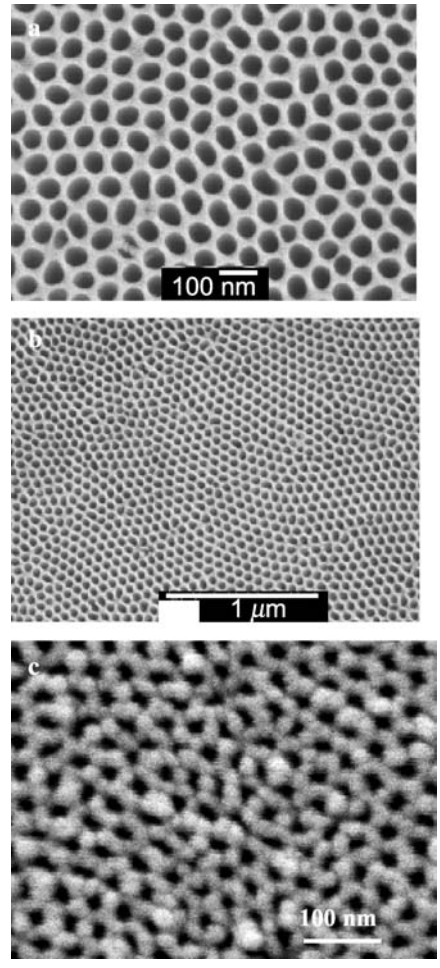

FIGURE 2 SEM images of the ordered AAM-SNDDND: **a** the top view of the part I; **b** the top view of the part II; and **c** the top view of the part III

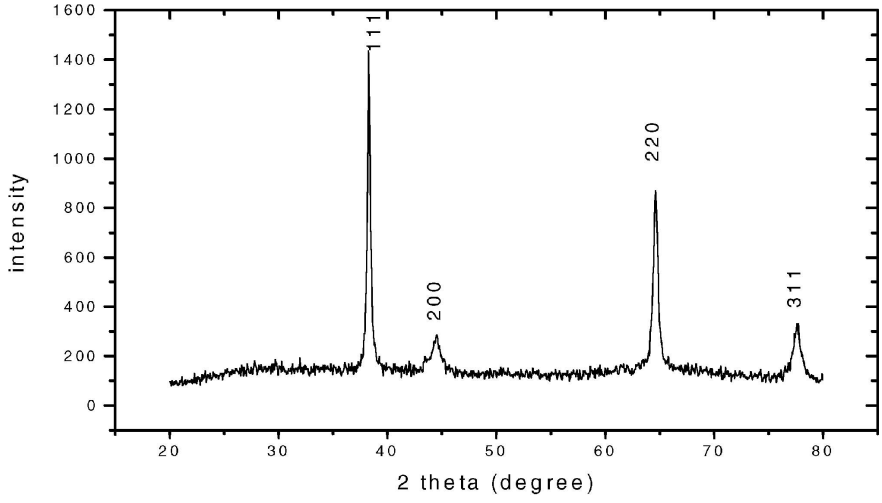

FIGURE 3 XRD spectrum of the Ag nanowire arrays embedded in AAM-SNDDND

rinse process was repeated three times. The remaining black solid 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 microscopy analysis.

3 Results and discussion

Figure 2 shows the SEM images of the AAM-SNDDND. The images (a), (b) and (c) were taken from the part I, the part II and the part III (Fig. 1) with nanochannel diameters about 80 nm, 60 nm and 40 nm respectively. The interpore distance was the same (about 100 nm).

A typical XRD pattern of the prepared Ag/AAM-SNDDND sample is shown in Fig. 3. The four peaks are found to be very close to the (111), (200), (220) and (311) peaks of bulk Ag, indicating that the face-center-cubic

Parts	Wires	Average diameters (nm)	Average diameters (nm)
		(SEM)	(TEM)
I	10	85	80
II	10	65	60
III	10	45	40

TABLE 1 Diameter data for wires grown in AAM-SNDDND

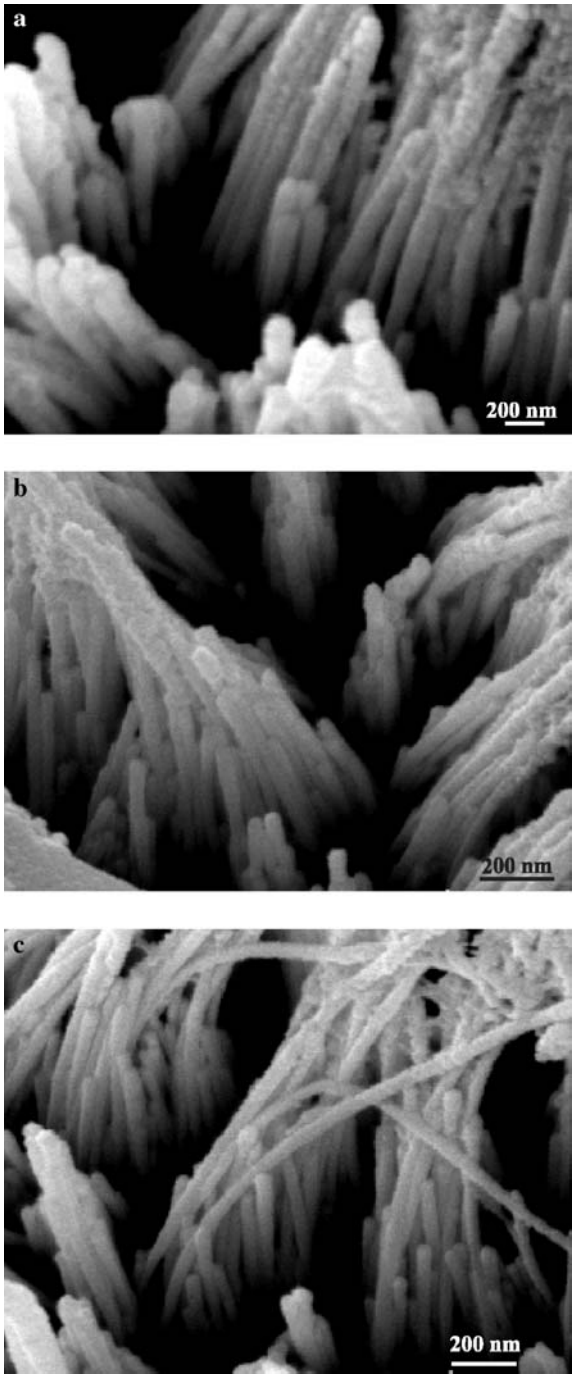

FIGURE 4 High-magnification SEM images of the resulting ordered array of Ag nanowires. **a**, **b** and **c** are images of the parts I, II and III, respectively. The ordered Ag nanowires with average diameters of 85 nm, 65 nm and 45 nm can be clearly seen in **a**, **b** and **c**

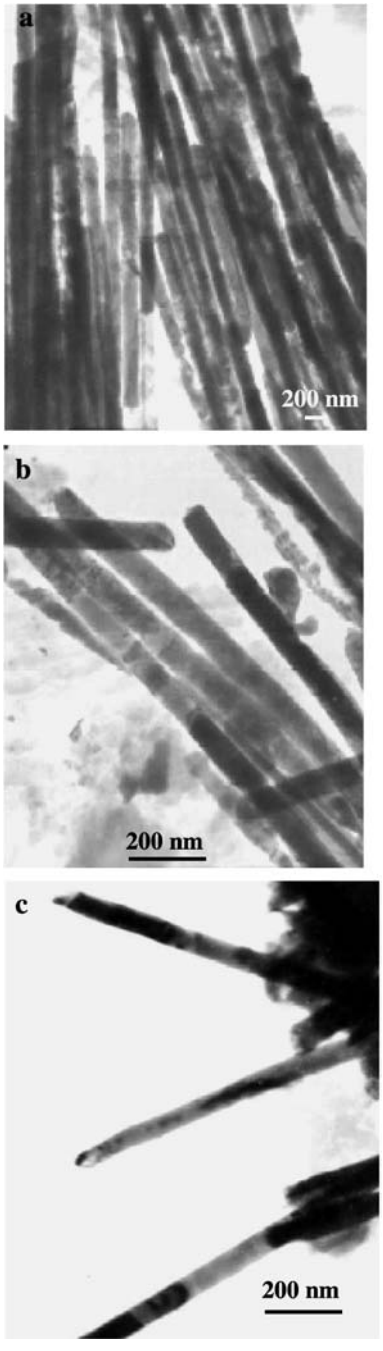

FIGURE 5 TEM images of Ag nanowires. **a**, **b**, and **c** are images of Ag nanowires with diameters of 80 nm, 60 nm and 40 nm, taken from the parts I, II and III, respectively

(fcc) structure of bulk Ag is preserved in these wires.

Figure 4(a–c) shows SEM images of the Ag nanowire arrays, which were taken from the part I, the part II and the part III (Fig. 1), respectively. The diameter distribution of the nanowires was obtained from SEM images using the statistical results of ten wire diameters per part. The statistical results (Table 1) show that Ag nanowires with average diameters of 85 nm, 65 nm and 45 nm were obtained in the part I, the part II and the part III, respectively.

The TEM technique was employed to obtain more details of the Ag nanowire morphology and structure. Highly magnified TEM images of the prepared sample (Fig. 5) show a number of nanowires with different diameters. Figure 5a, b and c were taken from the part I, the part II, and the part III, respectively. The diameter distribution of the nanowires was obtained from TEM images using the statistical results of ten wire diameters. The statistical results (Table 1) show that Ag nanowires with average diameters of 80 nm, 60 nm and 40 nm were obtained. The average diameters of the Ag nanowires from TEM images are smaller than those from the SEM images, which may be caused by the Au layer evaporated in the SEM sample preparation.

In addition, the smaller diameter in the ordered Ag nanowires is determined by the anodization conditions such as the electrolyte, voltage and temperature of anodization [21], 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 Ag nanowires can be changed in some range.

4 Summary

In summary, we report the fabrication of an anodic aluminum membrane with radially decreasing diameters and use it as template to obtain ordered Ag nanowire arrays embedded in one piece of AAM-SNDDND, with the same wire density but different diameters in different areas. These nanowires, with selectable diameters and lengths, provide the possibility of comparing the nanometer-scale characteristics of diameters with respect to their confined size, and will be useful for the study of the electric properties of Ag nanowires, and also have potential applications in electric devices. In addition, the method is easily applied to the fabrication of 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.

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