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Synthesis of ordered Al nanowire arrays

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Abstract

Ordered Al nanowire arrays with the same nanowire density but the diameters decrease radially embedded in one piece of anodic alumina membranes were successfully fabricated by two-step synthesis: electrodeposition of Zn and replacement in $AlCl_3$ solution. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected-area electron diffraction techniques were used to characterize the Al nanowires obtained. SEM and TEM images taken from the different areas of Al nanowire arrays show that we can control the growth of aligned Al nanowires with different diameters in a single process at the same time. The investigation results not only have potential applications in photoelectric devices but also open up a new method for fabricating nano-scale materials.

1. Introduction

Recently, one-dimensional (1D) nanostructures have attracted considerable attention owing to their novel physical and chemical properties, and the potential applications in a new generation of nanodevices [1–3]. Template synthesis method has been playing an important role in the fabrication of many kinds of nanowires [4,5] and nanotubes [6,7] for its interesting and useful features. A self-ordered nanochannel material formed by anodization of high purity Al in an appropriate acid solution [8,9] has attracted increasing interest as a key template for the fabrication of nanometerscale structures [10,11]. The anodic alumina membrane (AAM) possesses hexagonal ordered porous structure with channel density in the range 10^{10}–10^{12} cm^{-2}, and extremely high aspect ratio of their channels (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 [8] and 50 to 420 nm [12], respectively. The pore diameter could also be controlled by adjusting the pore widening time [13]. Using AAM, nanometer-scale fibrils, rods, wires, and tubules of metal [4,14,15], semiconductors [16–18], carbon [19], and other solid materials with uniform diameters were successfully fabricated.

Al nanowires has been studied theoretically [20] and experimentally [21]. Recently, Huber et al. [22] and Tamada [21] reported the synthesis of aluminum nanowire arrays by injection and electron-beam direct-writing lithography, respectively. The fabricating process consist of very complicated apparatus such as high-temperature–high-pressure injection apparatus or electron-beam direct-writing lithography and the conditions are extraordinary strict in both the two methods. So a simply method of synthesis Al nanowire arrays is very important for practical applications. In this paper, we report the fabrication of Al nanowires with different diameters but identical nanowire density embedded in the nanochannels of AAM-SNDDND by two-step synthesis: electrodeposition of Zn [23] and replacement in the mixture solution which contained 0.1 M $AlCl_3$, 0.05 M EDTA and ammonia solution.

2. Experimental procedure

The fabrication process involves three steps: (i) electrochemical generation of AAM; (ii) chemical generation of AAM-SNDDND; (iii) electrodeposition of pure metal Zn nanowires embedded in AAM-SNDDND and replacement in $AlCl_3$ solution. AAM templates were prepared by a two-

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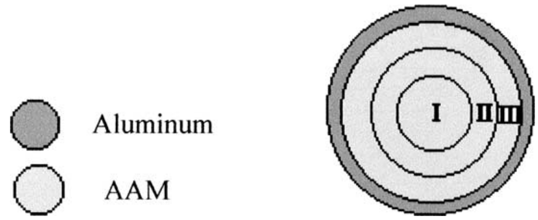

Fig. 1. A schematic outline of the AAM-SNDDND.

Table 1
Diameter data for wires grown in AAM-SNDDND

Parts	Wires	SEM, average diameters (nm)	SEM, average diameters (nm)
I	10	115	110
II	10	85	80
III	10	45	40

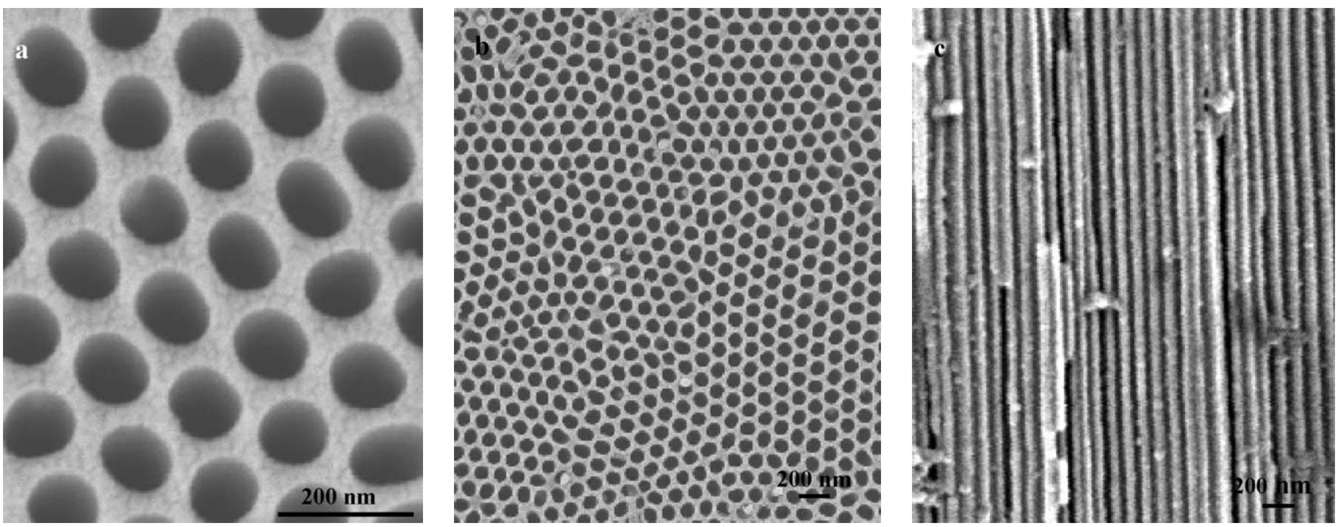

Fig. 2. SEM images of the ordered AAM-SNDDND. (a) The top view of the part I. (b) The top view of the part II. (c) The cross-section view of the part III.

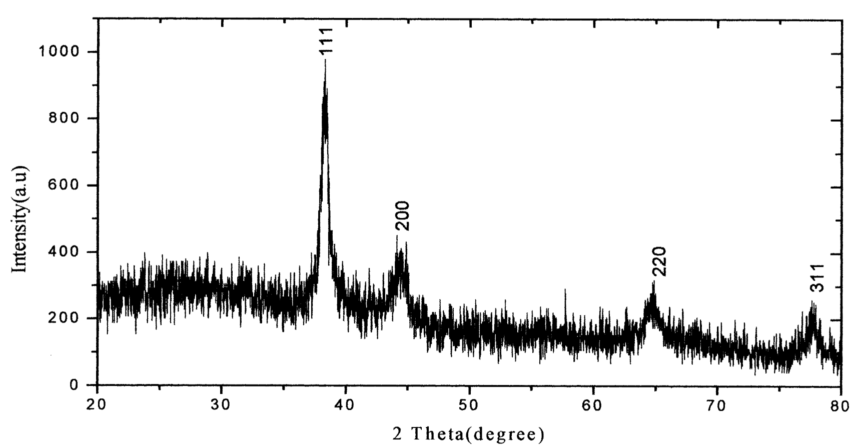

Fig. 3. XRD spectrum of the Al nanowire arrays embedded in AAM-SNDDND.

step anodization process. Anodization was carried out under a constant cell voltage of 50 V in a 0.3 M oxalic acid solution at 3 °C, as described previously [24–28]. For details on our techniques for preparing AAM-SNDDND, we refer the reader to our recent publications [29,30] and references therein. Fig. 1 shows the schematic outline of the AAM-SNDDND. The nanochannel density in the three parts (I, II, III) are identical but the nanochannel diameters are different. In order to fabricate an array of Zn 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 80 g l^{-1} $ZnSO_4$, and 20 g l^{-1} H_3BO_3 solutions and was buffered to pH = 2.5 with sulfuric acid. The electrodeposition was carried out at a constant current density (2.5 mA cm^{-2}), with graphite serving as the counter electrode at room temperature for 8 h. After electrodeposition, the sample surfaces were polished using a 50-nm SiC polishing sandpaper in order to get rid of the excess of Zn particles sticking to the surface. The sample was then washed with ethanol and deionized water in turn, and then dipped into replacement solution at 25 °C for 24 h. The replacement solution contained

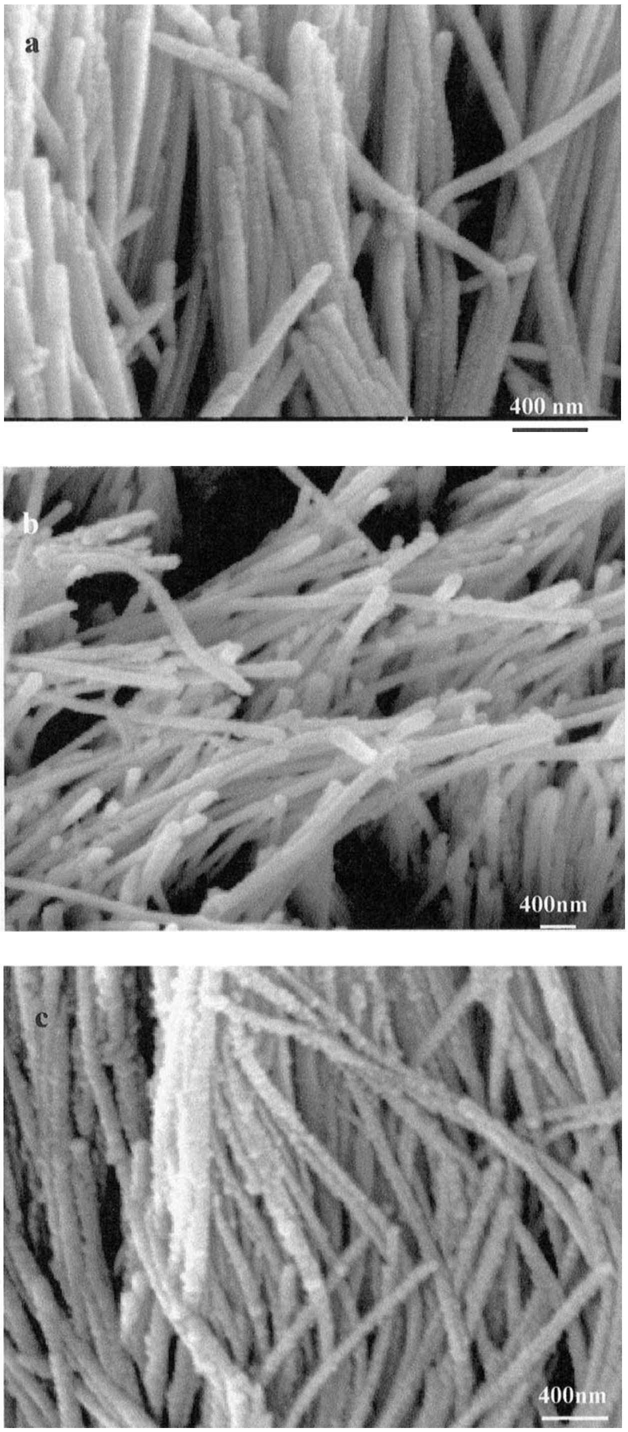

Fig. 4. High magnification SEM images of the resulting ordered array of Al nanowires. (a), (b) and (c) images of the part I, II and III, respectively. The ordered Al nanowires with uniform diameters of 115 nm, 85 nm and 45 nm can be clearly seen in (a), (b) and (c).

0.1 M $AlCl_3$, 0.05 M EDTA and was buffered to pH $= 7$ with ammonia solution.

Al nanowire arrays embedded in AAM-SNDDND were characterized by X-ray diffractometer (XRD, MXP18AHF, D/Max-rA) with Cu $K\alpha$ radiation ($\lambda = 1.5405$ Å), scanning

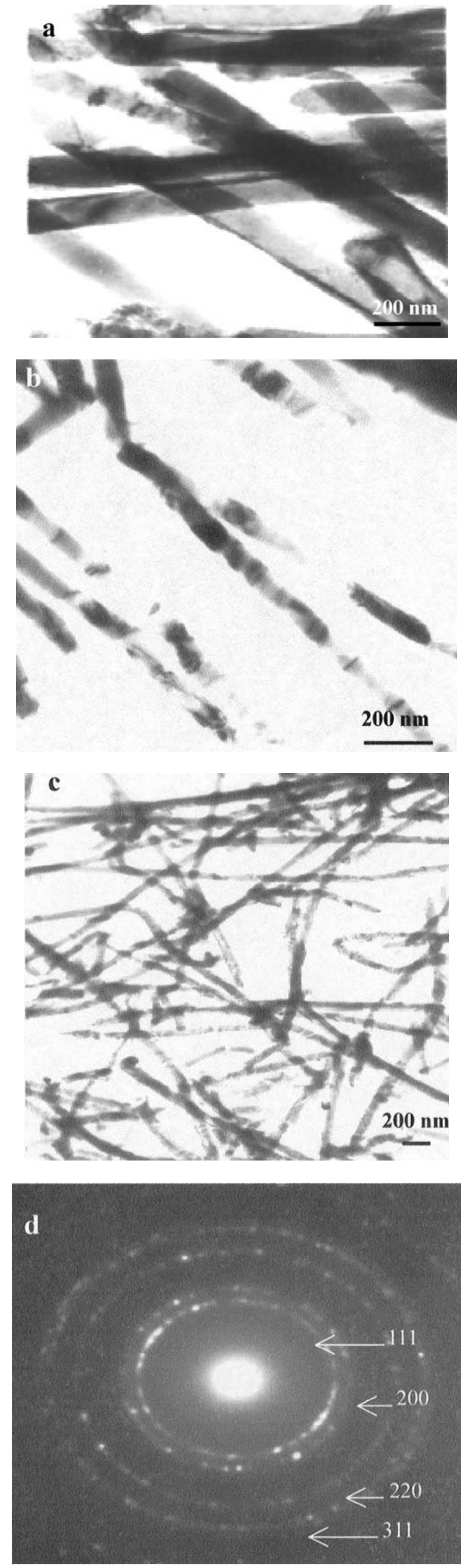

Fig. 5. TEM images of Al nanowires. (a), (b), and (c) images of Al nanowires with diameters of 110 nm, 80 nm, and 40 nm taken from the part I, II and III, respectively, (d) SAED pattern of the Al nanowires.

electron microscopy (SEM, JEOL, JSM-6300). Transmission electron microscopy (TEM, JEM-200CX) and selected area electron diffraction (SAED) were employed to characterize the individual Al nanowires. For SEM observation, a piece of AAM-SNDDND embedded with Al nanowires was eroded in a mixture solution of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) 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 observation were prepared by dissolving away the AAM-SNDDND completely, which was accomplished by placing a small piece of Al/AAM-SNDDND in the same solution 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 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 microscope analysis.

3. Result

Fig. 2 shows the SEM images of AAM-SNDDND. The images of (a), (b), and (c) were taken from the part I, the part II, and the part III (Fig. 1) with nanochannel diameters about 110 nm, 80 nm, and 40 nm, respectively. The interpore distance is the same (about 130 nm).

X-ray diffractometer (XRD) spectrum of the Al nanowires is shown in Fig. 3. The four peaks are found to be very close to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) of bulk Al, indicating that the structure of bulk Al is preserved in these wires. No peak associated with Zn and Al_2O_3 was found when the spectrum was taken immediately after Zn was replaced by Al, even after being exposed to air at room temperature for one week, there is still no Al_2O_3 peak in XRD spectrum. The top surface of the as-synthesized product was mechanically polished down by ~10 μm using the 50 nm SiC polishing sandpaper and then the sample were characterized by XRD again. The spectrum is identical with the first one, indicating that Zn deposited in the channels of AAM-SNDDND had been completely replaced by Al. In addition, the peak positions and their relative intensities are consistent with standard powder diffraction patterns of Al, indicating that there is no preferred orientation and that the Al nanowires in AAM-SNDDND channels were polycrystalline structure.

Fig. 4a–c shows SEM images of the Al 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 using the statistical results of ten wire diameters per part from SEM images. The statistical results (Table 1) show that Al nanowires with average diameters of 115 nm, 85 nm and 45 nm were obtained in the part I, the part II, and the part III, respectively.

The TEM technique was employed to get more details of the Al nanowire morphology and structures. High-magnified TEM images of the prepared sample (Fig. 5) show a number of nanowires with different diameters. Fig. 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 using the statistical results of ten wire diameters from TEM images. The statistical results (Table 1) show that Al nanowires with average diameters of 110 nm, 80 nm and 40 nm were obtained. The average diameters of Al 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. Furthermore, the highly crystalline nature of the Al nanowires was investigated by SAED measurements and many individual nanowires were characterized. The diffraction spots/rings (Fig. 5d) can be indexed as (1 1 1), (2 0 0), (2 2 0), and (3 1 1) reflections according to the bulk of Al. The appearance of diffraction rings/spots indicates the polycrystalline character of Al nanowires, which are consistent with our XRD results.

In addition, the smaller diameter in the ordered Al nanowires is determined by the anodization conditions such as the electrolyte, voltage, and temperature in the fabrication process of AAM [25], and the larger diameter could be controlled within the interpore distance of the AAM template by adjusting the pore widening time [13]. Therefore, the diameter ratio of the Al nanowires can be changed in some range.

4. Conclusion

In summary, we report the fabrication of anodic aluminum membrane with diameters radial decrease and using it as template, we obtained ordered Al nanowire arrays with same wire density but different diameters in different areas embedded in one piece of AAM-SNDDND. SEM, TEM and SAED investigation reveal that large scale Al nanowires was achieved. The simultaneous integration of ordered Al nanowire arrays with different diameters embedded in a single AAM-SNDDND not only open up a new method for fabricating nano-scale materials but also have potential applications in photoelectric devices such as wire-grid polarizer [21].

Acknowledgements

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