A Simple Method for Synthesizing Copper Nanotube Arrays

Yinhai Wang,*[†,††] Changhui Ye,[†] Xiaosheng Fang,[†] and Lide Zhang[†]
[†]*Institute of Solid State Physics, Chinese Academy of Science, Hefei 230031, P. R. China*
[††]*Department of Physics of Anhui University, Hefei 230039, P. R. China*

(Received October 20, 2003; CL-030981)

A simple method to synthesize copper nanotubes in alumina membrane using the direct electrochemical deposition technique is presented. The method does not need a molecular anchor to treat the membrane in synthesizing the nanotubes. The diameter of the synthesized copper nanotubes is about 40 nm and depends on the pore size of the alumina membrane.

1-D nanoscale structures have drawn an increasing interest in research because of their unique thermal, electrical, magnetic, and optical properties that can be used to build the nanoscale devices.[1–3] Over the past few years, many methods have been developed for growing the nanoscale structures. Among those, the template-assisted synthesis with chemical deposition is one of the most popular techniques for the synthesis of nanoscale structures, particularly for metal and semiconductor nanowires.[4,5] Recently, the method of using the electrochemical deposition inside the alumina membrane has been widely employed in the growth of nanoscale fibrils and wires owing to the uniform pores array structure with each pore in a regular cylindrical shape in the membrane.[6–8] However, all current methods in synthesis of the nanotubes need to use the so-called "molecular anchor"[9,10] to prepare the alumina membrane. In this letter, we present the synthesis of copper nanotubes in alumina membrane using a direct eletrochemical deposition technique which does not need to employ the "molecular anchor" to treat the membrane.

The porous alumina membrane with ordered channel arrays was prepared from high-purity (99.999%) aluminum foil in 0.3 M oxalic acid by anodization.[11] A remaining aluminum layer at the bottom of the alumina membrane was removed in 1 M $CuCl_2$ solution. Subsequently, the pore bottoms were opened by chemical etching in 5 wt % phosphoric acid solution. A layer of Au was sputtered onto one side of the membrane served as an electrode. The electrochemical method was employed to deposit metal Cu into the pores of alumina membrane.[12] The electrolyte contained 0.2 M $CuSO_4{\cdot}5H_2O$ and 0.1 M H_3PO_4. The electrodeposition was carried out at a constant curent density (2.5 mA/cm^2) with carbonate serving as the counter electrode at room temperature for 2 h. The pH of the solution was controlled in the range 4.5 to 5.0 by adding 0.1 M H_2SO_4.

The sample with the nanotubes attached in the membrane was characterized by X-ray diffraction (XRD, MXP-18AHF) (see Figure 1). From the Figure 1, we can see that the diffraction peaks in the range $20^\circ < 2\theta < 78^\circ$ can be indexed as (111), (200), and (220) planes of the face-centered cubic structure of the metallic copper. The diffraction peak intensity of the (220) plane is much higher than those of the other two peaks, which indicates the Cu nanotubes in the alumina membrane are oriented along [110] direction. Figure 2a shows the scanning electron microscopy (FESEM, JSM-6700F) image of the Cu nanotubes after removal of the alumina membrane. The results display a highly ordered arrays of the Cu nanotubes. The diameter of the nanotubes is about 40 nm, in good agreement with the diameter of the alumina membranes. Figure 2b shows a top-view SEM image after removal of the top layer of the alumina membrane, denoting the open-ends of the Cu nanotubes.

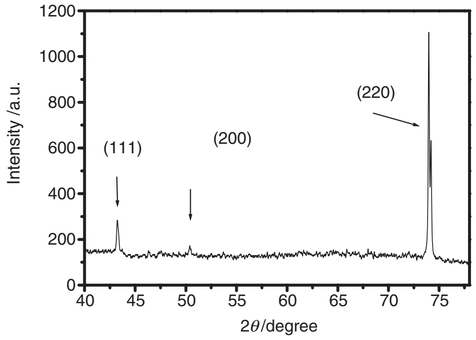

Figure 1. X-ray diffraction of Cu nanotubes embedded in alumina membrane. The diffraction peaks could be indexed as (111), (200), and (220) planes of face-centered cubic copper.

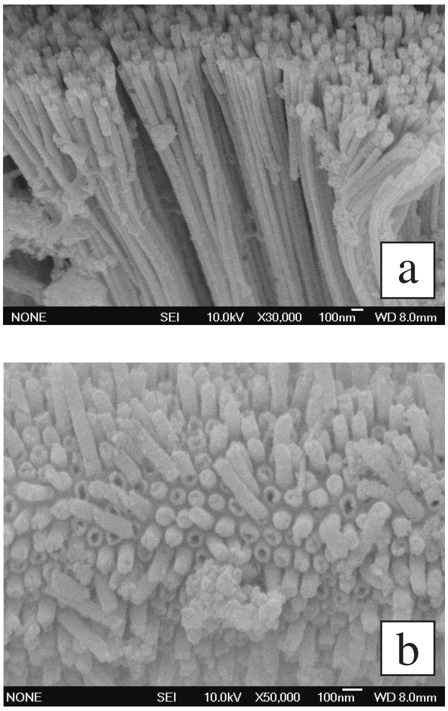

Figure 2. Scaning electron microscopy images of the Cu nanotube arrays after dissolution of the alumina membrane. (a) across-section image; (b) top-view image.

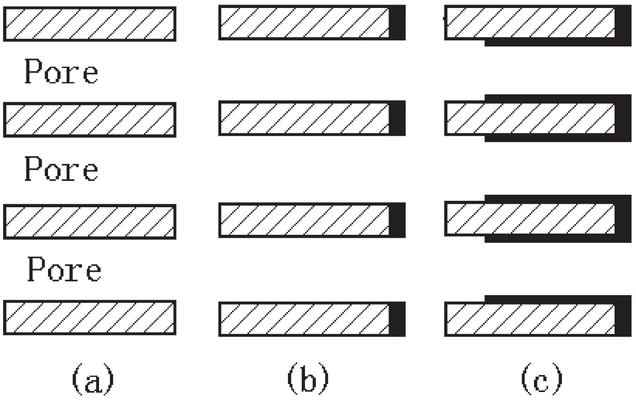

Figure 3. Schematic representation of the approach used to synthesize Cu nanotube arrays in alumina membrane. (a) Cross-section of alumina membrane; (b) Au layer sputtered on one side of the alumina membrane; (c) Cu nanotubes grown along the pore walls.

The common approach to obtain the nanotubes in the alumina membrane is to use the "molecular anchor" to treat the pore's walls in the membrane chemically so that the deposited metal can stick on the walls. For example, the alumina membranes for producing gold and nickel nanotubes were prepared by attaching the cyanosilane and methyl-γ-diethylenetriaminopropyldimethoxysilane to the pore walls inside the membranes as the "molecular anchors," respectively.[9,10] The selection of the "molecular anchor" usually plays an important role in synthesis of the different metal nanotubes. However, our method in producing the Cu nanotubes did not use any "molecular anchor." Instead, we controlled the thickness of the sputtered Au layer on the membrane carefully and find that it is a key factor for synthesizing the metal nanotubes. The Au layer should be thin enough not covering the opening ends of the pores in the membrane in order to produce the nanotubes. Otherwise the nanowires would be produced if the Au layer were too thick that it covers all opening ends of the pores. The thickness of the Au layer can be controlled accurately by controlling the sputtering time. Once a thin Cu layer attached on the pore walls in the alumina membrane, it creates a shielding to the applied electrical field to prevent the further deposition in the nanotubes. The process of the nanotubes growth is illustrated in Figure 3.

In summary, we present a simple method in synthesis of Cu nanotube arrays in alumina membrane using the direct metal deposition technique that does not need to employ any "molecular anchor" to treat the pore's walls in membrane. In the experiments, we controlled the thickness of the Au layer that served as an electrode accurately by controlling the sputtering time and find that it is a key factor for obtaining the nanotubes. We expect that this method can also be used in synthesis of the other metal nanotube arrays.

This work was supported by the National Major Fundamental Research Project of China (No. 19990645-1) and the Natural Science Research Projects of Anhui Province of China (No. 02022023 and No. 03044905).

References

1 S. Iijima, *Nature*, **354**, 56 (1991).
2 T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, *Nature*, **382**, 54 (1996).
3 E. W. Wong, P. E. Sheehan, and C. M. Lieber, *Science*, **277**, 1971 (1997).
4 C. A. Huber, T. E. Huber, M. Sadoqi, J. A. Lubin, S. Manalis, and C. B. Prater, *Science*, **163**, 800 (1994).
5 T. M. Whitney, J. S. Jiang, P. C. Searson, and C. L. Chien, *Science*, **261**, 1316 (1993).
6 X. Y. Zhang, L. D. Zhang, W. Chen, G. W. Meng, M. J. Zheng, and L. X. Zhao, *Chem. Mater.*, **13**, 2551 (2001).
7 X. Y. Zhang, L. D. Zhang, Y. Lei, L. X. Zhao, and Y. Q. Mao, *J. Mater. Chem.*, **11**, 173 (2001).
8 Y. Zhang, G. H. Li, Y. C. Wu, B. Zhang, W. H. Song, and L. Zhang, *Adv. Mater.*, **14**, 1227 (2002).
9 C. J. Brumlik and C. R. Martin, *J. Am. Chem. Soc.*, **113**, 3174 (1991).
10 J. C. Bao, C. Y. Tie, Z. Xu, Q. F. Zhou, D. Shen, and Q. Ma, *Adv. Mater.*, **13**, 1631 (2001).
11 Y. H. Wang, J. M. Mo, W. L. Cai, L. Z. Yao, and L. D. Zhang, *J. Marer. Res.*, **16**, 990 (2001).
12 Y. T. Pan, G. M. Meng, Y. Zhang, Q. Fang, and L. D. Zhang, *Appl. Phys. A*, **76**, 533 (2003).

Published on the web (Advance View) January 14, 2004; DOI 10.1246/cl.2004.166