Articles

Fabrication and Structural Characterization of Large-Scale Uniform SnO_2 Nanowire Array Embedded in Anodic Alumina Membrane

Maojun Zheng,*[,†,‡] Guanghai Li,[†] Xinyi Zhang,[†] Shiyong Huang,[†] Yong Lei,[†] and Lide Zhang[†]

Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, P. R. China, and Department of Applied Physics, University of Petroleum, Dongying, 257062, P. R. China

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Semiconductor SnO_2 nanowire arrays were fabricated by electrochemical deposition and thermal oxidizing methods based on highly ordered nanoporous alumina membrane. Their microstructures were characterized by X-ray diffraction, transmission electron microscopy, Raman spectrum, and scanning electron microscopy. The results indicate that the SnO_2 nanowire array with cassiterite polycrystalline structure is uniformly assembled into the hexagonally ordered nanochannels of anodic alumina membranes. There are three phases (Sn, SnO, and SnO_2) coexisting when the as-deposited assembly system is annealed at 823 K. However, only the SnO_2 cassiterite phase is detected when the assembly system is annealed at 923 K.

Introduction

In recent years, interest in the fabrication of quasi-one-dimensional nanostructural materials has been increasing because of their numerous potential applications in various areas such as materials sciences, electronics, optics, magnetics, and energy storage. Much effort has been made to fabricate one-dimensional nanostructural materials using a variety of nanofabrication techniques and crystal growth methods. Template synthesis is an elegant chemical approach for the fabrication of nanostructures, in particular for different kinds of nanowires. Carbon nanotubes and nuclear track polycarbonate membranes have been used as templates for fabrication of carbide nanorods, nitride nanorods, metal and semiconductor nanowires.[1−4] Recently, the anodic alumina nanoporous structure template has received considerable attention in synthetic nanostructure materials because of its several unique structural properties, such as controllable pore diameters, extremely narrow size distribution for pore diameters and their intervals, and the ideally cylindrical shape of pores.[5,6] They have been used extensively to fabricate nanometer-size fibrils, rods, wires, and tubules of metal,[7−9] semiconductors,[10−12] carbons,[13] and other solid materials by using a variety of methods.

Tin oxide is an important metal-oxide semiconductor. It has many important applications in the transparent conducting coating of glass, electrochemical modifiers on electrodes, solar cells, and gas-sensing devices.[14−16] It has been reported that nanocrystalline SnO_2 possesses excellent characteristics such as a high gas sensitivity and a short response time.[17,18] Up to now, studies on tin oxide have mainly focused on the preparations and physical properties of SnO_2 films and nanoparticles. Comparatively, very little work has been

[†] Chinese Academy of Sciences.
[‡] University of Petroleum.

(1) Zhang, Y.; Ichihashi, T.; Landree, E.; Nihey, F.; Iijima, S. *Science* **1999**, *285*, 1719.
(2) Dai, H. J.; Wong, E. W.; Lu, Y. Z.; Fan, S. S.; Lieber, C. M. *Nature* **1995**, *375*, 769.
(3) Han, W. Q.; Fan, S. S.; Li, Q. Q.; Hu, Y. D. *Science* **1997**, *277*, 1287.
(4) Whitney, T. M.; Jiang, J. S.; Searson, P. C.; Chien, C. L. *Science* **1993**, *261*, 1316.
(5) Masuda, H.; Fukuda, K. *Science* **1995**, *268*, 1466.
(6) Masuda, H.; Yamada, H.; Satoh, M.; Asoh, H.; Nakao, M.; Tamamura, T. *Appl. Phys. Lett.* **1997**, *71*, 2770.
(7) Huber, C. A.; Huber, T. E.; Sadoqi, M.; Lubin, J. A.; Manalis, S.; Prater, C. B. *Science* **1994**, *263*, 800.
(8) Nielsch, K.; Müller, F.; Li, A. P.; Gösele, U. *Adv. Mater.* **2000**, *12*, 582.
(9) Evans, P. R.; Yi, G.; Schwarzacher, W. *Appl. Phys. Lett.* **2000**, *76*, 481.
(10) Xu, D. S.; Xu, Y. J.; Chen, D. P.; Guo, G. L.; Gui, L. L.; Tang, Y. Q. *Adv. Mater.* **2000**, *12*, 520.
(11) Martin, C. R. *Science* **1994**, *266*, 1961.
(12) Cheng, G. S.; Zhang, L. D.; Zhu, Y.; Fei, G. T.; Li, L.; Mo, C. M.; Mao, Y. Q. *Appl. Phys. Lett.* **1999**, *75*, 2455.
(13) Suh, J. S.; Lee, J. S. *Appl. Phys. Lett.* **1999**, *75*, 2074.
(14) Wei, P. H.; Li, G. B.; Zhao, S. Y.; Chen, L. R. *J. Electrochem. Soc.* **1999**, *146*, 3536.
(15) Varol, H. S.; Hinsch, A. *Sol. Energy Mater. Sol. Cells* **1996**, *40*, 27.
(16) Kim, T. W.; Lee, D. U.; Lee, J. H.; Yoon, Y.S. *Solid State Commun.* **2000**, *115*, 503.
(17) Zuo, J.; Xu, C. Y.; Liu, X. M.; Wang, C. S.; Wang, C. Y.; Hu, Y.; Qian, Y. T. *J. Appl. Phys.* **1994**, *75*, 1835.
(18) Leite, E. R.; Weber, I. T.; Long, E.; Varela, J. A. *Adv. Mater.* **2000**, *12*, 965.

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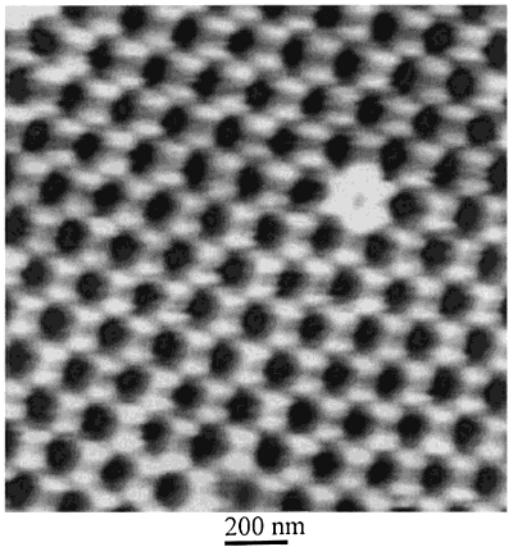

Figure 1. AFM image of alumina membrane.

conducted on the one-dimensional nanostructural SnO_2 system. In this article, we first report the preparation of a large-scale uniform SnO_2 nanowire array based on highly ordered nanoporous alumina membranes (AAM) by electrochemical deposition and thermal oxidization. The microstructure properties and growth mechanism of SnO_2 nanowires embedded in AAM are discussed.

Experimental Section

The fabrication process involves three steps: (1) electrochemical generation of an alumina template with highly ordered hexagonal arrays of nanochannels; (2) electrodeposition of pure metal Sn in the alumina template; (3) oxidation of Sn nanowire array embedded in AAM in the air. The alumina membrane was formed by a two-step anodization process as described previously.[5,6] High-purity (99.999%) aluminum plate was annealed in a vacuum (673 K) and degreased in acetone. Aluminum plate was anodized in 0.3 M oxalic acid solution under constant voltages, 40 V for 4 h. After removal of the anodic oxide layer in a mixture of phosphoric acid (6 wt %) and chromic acid (1.5 wt %) solution at 60 °C for 6 h, the textured Al plate was anodized again for 8−12 h under the same conditions as for the first anodizing. Figure 1 shows an atomic force microscope (AFM) micrograph of an alumina membrane. The nanopores exhibit an almost perfect two-dimensional array with an hexagonal pattern. The nanohole diameter (40−90 nm) can be adjusted by the pore-widening treatment of immersing the substrates in 5 wt % phosphoric acid for different times. After coating a protecting layer on the surface of the porous alumina film, the remaining Al layer was removed in a saturated $HgCl_2$ solution. A subsequent etching treatment was performed in a 5 wt % phosphoric acid solution at 32 °C for 1−1.5 h to remove the barrier layer on the bottom side of the AAM. A layer of Au was sputtered onto one side of the membrane and used as the working electrode in a standard three-electrode electrochemical cell. Before mounting into the electrochemical cell, the AAM was immersed in deionized water under ultrasonic agitation for 2 min to clean the pollutant on the surface of the membrane and to expel the air bubbles from the pores. This step is very important for obtaining good nanowires and a homogeneous growth in the whole growing area. If there are gas bubbles in some pores, the growth of the nanowires cannot grow continuously and uniformly because of the embolism effects induced by the gas bubbles in the pores. The Sn nanowires were electrodeposited into the nanoholes by a three-electrode cell direct-current method in a solution containing 7 g/L $SnCl_2 \cdot 2H_2O$, and 25 g/L $Na_3C_6H_5O_7 \cdot 2H_2O$ solution at room temperature. The electrodeposition was performed at −0.8 V (vs saturated Ag/AgCl), with graphite serving as the counter electrode. After Sn nanowire array was electrodeposited into AAM, the assembly systems were annealed in the air at different temperatures to form an ordered SnO_2 nanowire array.

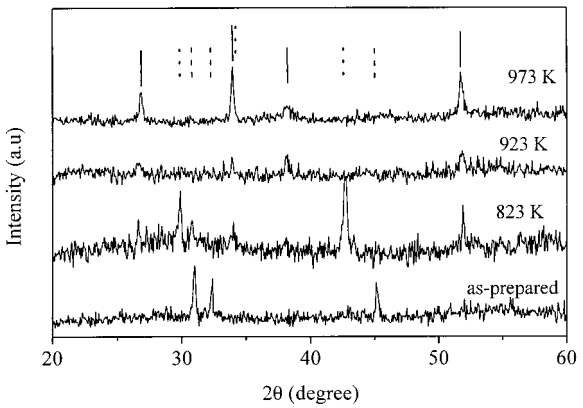

Figure 2. XRD patterns of the SnO_2/AAM assembly system annealed at different temperatures for 10 h. —, SnO_2; ..., SnO; - - -, Sn.

The X-ray diffraction (XRD) analyses were performed on a Philip·s PW1700 X-ray diffractometer with use of a Cu Kα X-ray source (λ = 0.15418 nm). The surface morphology and the structure of the SnO_2 nanowires were observed by a transmission electron microscopy (TEM) (JEOL: JEM-200CX). For TEM observation, the AAM was removed from the assembly system by dissolving the AAM in 0.5 M NaOH solution and washing several times with distilled water. Raman spectrum was performed at room temperature using a Raman spectrometry system of double monochromator (SPEX: SPEX-1403) and a 514.5-nm excitation source from an Ar^+ laser. The top image of the SnO_2 nanowire array grown in a template was observed by scanning electron microscopy (SEM) (JEOL: JSM-6300). For SEM observation, the SnO_2/AAM assembly system was cleaned in an ultrasonic bath for 1 min followed by a short etching of the alumina in aqueous NaOH. Before the SEM observation, metallic Pt was evaporated on the surface of the samples with the evaporation current of 7 mA for 45 min to form a conducting film to avoid electrostatic charging.

Results and Discussion

Figure 2 shows XRD patterns of the SnO_2/AAM assembly system oxidized at different temperatures for 10 h. It can be seen that the as-deposited nanowire array only consists of Sn, and after annealing at 823 K for 10 h, Sn transforms partially into SnO and SnO_2. The Sn and SnO diffraction peaks disappear when annealing temperature increases to 923 K. This indicates that a complete SnO_2 nanowire array embedded in AAM has formed and it is a polycrystalline cassiterite structure.

Figure 3 shows TEM micrograph of SnO_2 nanowires after the AAM was removed from the SnO_2/AAM assembly system. This figure shows that the diameter of SnO_2 nanowires is about 70 nm, which is basically equal to that of pores of the AAM used. Length of the nanowires is in the range of hundreds of nanometers to several microns. Longer nanowires might be obtained by using AAM with deep holes, and thermal oxidation at higher temperatures and longer times. Figure 3 also shows that the surface of the nanowires is rough and the diameter of individual SnO_2 nanowire is not uniform. The TEM diffraction pattern indicates that the

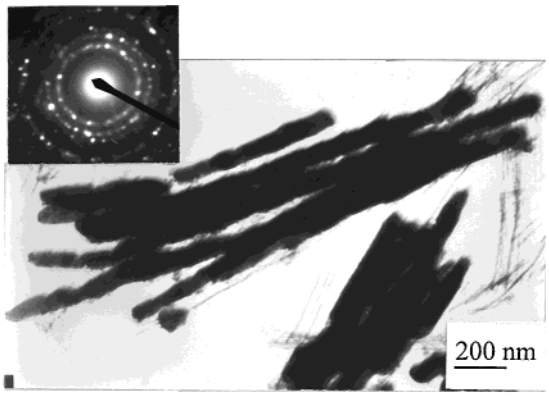

Figure 3. TEM micrograph of SnO_2 nanowires and corresponding electron diffraction pattern.

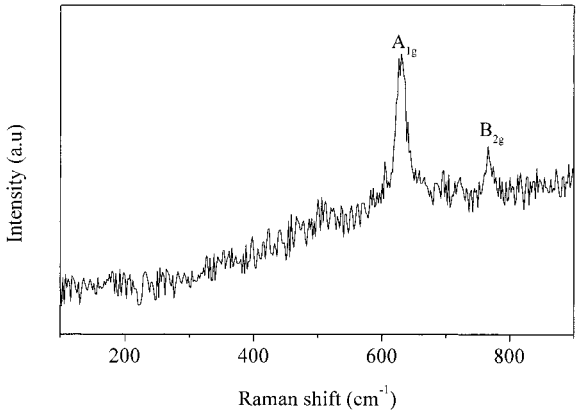

Figure 4. Raman spectrum of the SnO_2/AAM assembly system annealed at 923 K for 10 h.

SnO_2 nanowires in AAM pores were a polycrystalline structure, which is in agreement with XRD results. These results may imply that the SnO_2 nanowires growth is achieved by piling up small particles, not atom-by-atom growth of crystallites during thermal oxidation.

Figure 4 shows the Raman spectrum of SnO_2/AAM assembly system annealed at 923 K for 10 h. In this figure, only two broad Raman peaks denoted as A_{1g} and B_{2g} are present, which correspond to the Raman modes of polycrystalline cassiterite SnO_2.[17] This indicates that there is no SnO phase in the assembly system after the assembly system is annealed at 923 K, which is in agreement with XRD results. Since broadening of Raman peak is the signature of nanocrystals, this Raman spectrum further indicates that SnO_2 nanowires are made up with nanoparticles.

Figure 5 shows an SEM top image of a SnO_2 nanowire array grown in a template. The SnO_2 nanowires clearly are of a basically equal height and are uniformly embedded in AAM. The nanowires observed in Figure 5 are oriented in different directions, which could result from the mechanical forces during dissolution and drying.

The polycrystalline structure and surface roughness of SnO_2 nanowires may result from their special growth mechanism. The one-dimensional growth is unusual and

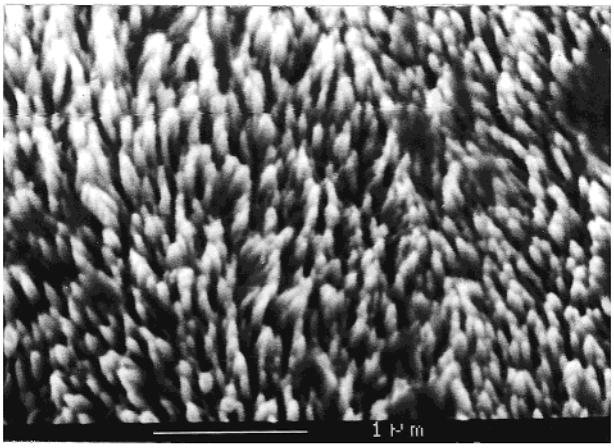

Figure 5. SEM top image of SnO_2 nanowire array embedded in AAM.

interesting for different preparation methods. It is expected that the capillary effect[3] of the anodic pores with large aspect ratio (depth/diameter) in alumina membrane is favorable for the nucleation and growth of nanowires in the pores. Although defects, such as microtwins, stacking faults, and low-angle grain boundaries, are also closely related to the nanowires growth, the defects in the wall of the pores may induce nonuniform orientation growth. This may be a source of surface roughness and polycrystalline structure of SnO_2 nanowires. On the other hand, the oxidation process of Sn to SnO_2 is complicated.[19] It can be deduced that oxidation begins at the surface of the Sn nanowires. At temperatures higher than 505.6 K, the Sn nanowires in AAM are liquid. Therefore, when the temperature is high enough to allow oxygen to diffuse into the Sn nanowires, Sn nanowires begin to be oxidized in random orientations (nuclei formation). As oxidation continues these nuclei grow further at different rates, because oxygen diffusion depends on the crystallographic orientation of the formed solid crystallites. The XRD results have indicated that oxidation does not occur directly from Sn to SnO_2, and the primary reactions taking place in AAM may be the conversion of Sn to SnO, Sn to SnO_2, and SnO to SnO_2. These reactions may be another source of the formation of the polycrystallinity and surface roughness of SnO_2 nanowires.

Large-scale uniform SnO_2 nanowire arrays have been fabricated based on the anodic alumina template by electrodeposition and thermal oxidation. This fabrication process could be used in synthesizing other low-melting-point metal oxide nanowire arrays. It is expected that the SnO_2/AAM assembly system could be used in fabricating functional nanodevices such as array solar cells and gas sensitive nanodevices.

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(19) Diéhuez, A.; Rdríguez, A. R.; Morante, J. R.; Nelli, P.; Sangaletti, L. Sberveglieri,G. *J. Electrochem. Soc.* **1999**, *146*, 3527.