A simple approach for the growth of highly ordered ZnO nanotube arrays

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ARTICLE INFO

Article history:

Received 7 May 2008

Received in revised form

23 September 2008

Accepted 27 September 2008

Available online 12 November 2008

Keywords:

ZnO nanotubes

Electrochemical deposition

Cathodoluminescence

ABSTRACT

A simple two-step approach to produce highly ordered ZnO nanotube arrays is introduced. In the first step, Zn nanotubes were prepared by the electrodeposition of Zn into the pores of anodic alumina membrane (AAM), and then they were oxidized in air and converted into ZnO nanotubes. This approach is very simple, molecular anchor free, and is capable of growing ZnO nanotubes at low temperature. The ZnO nanotubes synthesized by this method exhibit an intense and sharp cathodoluminescence at 378 nm and a weak defect emission at about 500 nm at room temperature, indicating good quality of the prepared samples. Our approach is very general, which provides an alternative method for preparing highly ordered metal oxide nanotube arrays with good quality at relatively low temperatures.

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1. Introduction

The fabrication of one-dimensional nanostructured materials is currently attracting considerable attention in view of their possible future applications in optical, electronic, magnetic and micromechanical devices [1–5]. Various procedures have been proposed and applied to the preparation of nanostructures, such as electron-beam lithography [6], chemical vapor deposition [7], and template method [8]. Among the methods reported, the template synthesis method pioneered by Martin has been widely adapted because of its many interesting and useful features [9]. Two types of templates were generally used, “track-etch” polymeric membrane and porous anodic alumina membrane (AAM). Nanoscopic cylinders can be embedded in templates by pressure injection, sol–gel chemistry, chemical deposition and vapor-phase technique [10–15]. A variety of nanowires and nanotubes has been prepared, including metals, semiconductors, polymers, carbon, and many other materials [16–20]. Electrochemical template synthesis is very suitable for fabricating metallic nanowires and nanotubes because of its flexibility to control the lengths of nanowires or nanotubes by varying the amount of metal deposited. However, most of the nanoscopic cylinders prepared by this method, to date, are not hollow nanotubes but solid nanowires. To obtain nanotubes, the pore walls of templates must be derivatized so that the electrodeposited metal preferentially deposits on the pore walls, that is, a molecular anchor

must be applied [9], which is quite a difficult task to be overcome. In addition, it may introduce excess impurities and deteriorate sample quality.

ZnO is recognized as a promising material for short-wavelength optoelectronic applications because of its superior optical properties of a wide direct band-gap of 3.37 eV and a large exciton binding energy of 60 meV [21,22]. Various kinds of methods have been introduced to prepare 1D ZnO nanostructures, such as nanowires, nanobelts, and nanotubes [23–25]. 1D ZnO nanostructures possess several intriguing properties, including high mechanical stability, negative electron affinity in various vacuum environments, and large piezoelectricity. They are promising excellent nanomaterials for field emission devices, light-emitting diodes, nanolasers, solar cells, and nanogenerators. [26]. Notably, there also exist some reports demonstrating the preparation of ZnO nanotubes by vapor-phase growth method [25]. However, this method generally requires high-temperature processes. In this paper, a simple and low-temperature electrochemical deposition procedure for fabricating highly ordered ZnO nanotube arrays is introduced. In the beginning, metallic Zn nanotubes were electrodeposited into the pores of AAM, and then they were oxidized and converted into ZnO nanotube arrays.

Several reports on the thermal oxidation of solid Zn nanowires embedded in AAM have been published [27,28]. In contrast, our previous work has demonstrated an electrodeposition method to fabricate hollow metal nanotubes [29]. The method applies the preferential plating of metal at the circular step edges of Au nanorings with hydrogen gas bubbling through the AAM pores. Here, we further extend the approach to the metal oxide system of ZnO.

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Fig. 1. XRD patterns of highly ordered Zn nanotube arrays: (a) without and (b) with thermal oxidation treatment at 300 °C.

The well-aligned arrays of ZnO nanotubes have been investigated by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) analysis, X-ray diffraction (XRD), as well as cathodoluminescence (CL) measurements.

2. Experimental

The anodic alumina membranes were formed by a two-step anodic anodization process, as described previously [30]. After the second anodization, the pore size of AAM was widened to about 100 nm by etching treatment in H_3PO_4 solution. In order to fabricate the Zn nanotube arrays, a layer of Au film (with a thickness of 200 nm) was deposited by sputtering as a working electrode on the bottom surface of the AAM at a rate of 0.7 nm s^{-1} . Zn nanotubes were grown from an electrolyte that contained $80 \text{ g l}^{-1} \text{ ZnSO}_4$ and $20 \text{ g l}^{-1} \text{ H}_3\text{BO}_3$ solutions, and were buffered to pH 2.5 with sulfuric acid. The electrodepositions were carried out at a constant current density of 5 mA cm^{-2} , with pure Pt wire as the anode at room temperature for 2 h. After the electrodeposition of Zn nanotubes, the Zn/AAM assembly system was annealed in the atmosphere at $300 \pm 2^\circ\text{C}$ for 35 h to transform the Zn nanotubes into ZnO nanotubes.

The morphology of AAM, Zn, and ZnO nanotube arrays was determined by field emission SEM (FE-SEM, JSM-6500F) equipped with EDX spectrometer. XRD patterns were obtained on a PANalytical X'Pert Pro diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 40 mA. The CL spectra were carried out using a temperature-controllable cathodoluminescence detector (Mono CL, Gatan) installed in a FE-SEM, which was performed at an accelerating voltage of 10 kV. The CL detector enables measurements of the CL spectra between 200 and 850 nm. For SEM observation, the AAM was partly dissolved with 1 M NaOH solution, and then carefully rinsed with deionized water several times.

3. Results and discussion

Typical XRD patterns of the as-synthesized and annealed samples are shown in Fig. 1. The XRD patterns clearly show that the common polycrystalline structure. In Fig. 1a, all the diffraction peaks can be attributed to a hexagonal close-packed structured Zn phase (JCPDS File 04-0831). No peak associated with ZnO was found for the electrodeposited Zn nanotubes in the nanochannels of AAM (Fig. 1a). Even for 1-week exposure in the air at room temperature, there is no ZnO peak observed from the XRD pattern. This result shows a stable nature of the as-synthesized metal nanotubes. After AAM with Zn nanotubes deposited in its pores heated at 300°C for 35 h, all of the Zn peaks disappeared. It implies that the metal nanotubes in the pores of AAM have been oxidized thoroughly. In Fig. 1b, the peak positions and their relative intensities are consistent with those of the standard powder diffraction patterns of ZnO (JCPDS File 36-1451), which proves that uniform polycrystalline structure of the ZnO nanotubes. The broadening of the ZnO peaks is due to the effect of small particle size. These

results indicate that the well-aligned arrays of ZnO nanotubes with regular hexagonal shape can be achieved by the simple thermal oxidation. Note that the diffraction peak at 44.4° came from Au substrate.

Fig. 2a shows the tilt-view SEM image of Zn nanotube arrays on the Au substrate. The SEM images reveal that the as-grown sample is composed of well-aligned Zn nanotube arrays. The length of

Fig. 2. Scanning electron microscope images of as-prepared Zn nanotube arrays. (a) tilt-view of aligned Zn nanotubes. (b) high-magnification SEM image of the bottom of the Zn nanotube arrays. A top view of zinc nucleation is shown in the inset high-magnification SEM image.

Fig. 3. Schematic of the growth mechanism of Zn nanotubes via the template-based electrochemical deposition method (solid circles represent Zn and open circles represent hydrogen bubbles).

the Zn nanotubes is about several tens of micrometers. It can be seen that the nanotubes have open ends on top and are arranged in parallel and well-ordered way. The outer diameter of the Zn nanotubes is in the range of 90–110 nm, which corresponds to the pore diameter of the AAM. The inner diameter of the Zn nanotubes is in the range of 40–60 nm. The compactness of the Zn nanotubes is quite high, about $1 \times 10^9 \text{ cm}^{-2}$, corresponding to the pore density of the AAM. The bottom of the Zn nanotube arrays shown in Fig. 2b confirmed that the roots at the bottom of Zn nanotube arrays were open. Besides, it is shown that an ordered Au nanoring arrays were obtained by using the bottom surface of the AAM as a mold [31]. The inset of Fig. 2b reveals a high-magnification SEM image of the zinc nucleation which was preferentially electroplated at the circular step edges of Au nanorings [32].

The growth procedure of Zn nanotube arrays is schematically shown in Fig. 3. To interpret this growth mechanism of Zn nanotube arrays, we propose the hypothesis that circular step edges of the Au nanorings serve as preferential sites for the deposition of metal ions (Fig. 3b). It can be attributed to the fact that circular step edges have the ability to catalyze electron transfer to metal ions in solution [33]. However, it cannot explain why the tubes do not deposit radially to create wires. It was suspected that the hydrogen gas evolution plays a significant role in the formation of the nanotubes (Fig. 3c) [34]. During the electrochemical deposition of Zn nanotube arrays within AAM, hydrogen gas evolution ordinarily accompanies metal Zn electrochemical deposition because the reductive potential of hydrogen gas is higher than metal Zn. Hence, hydrogen gas continuously evaporates from the cathode through the central region of nanopores, the Zn elements are therefore preferentially attached to the pore wall. Subsequently, Zn nanotube arrays were formed (Fig. 3d). We stress here that the formation of Au nanorings is a key step for the Zn nanotube growth, because in the AAM template a nanoring arrays serve as circular step edges for fabricating Zn nanotubes.

It is worth noting that using AAM as templates most Zn nanowires have been synthesized previously [27,28,35]. Instead, we have successfully synthesized hollow Zn nanotubes by using AAM as templates. According to the report given by Zhao et al. [31], the formation of metal nanoring is strongly dependent on the deposition rate of metal. If the rate of deposition is low, the pore is closed early, and the hole in the nanoring is very small and a nanocone is obtained instead. From above SEM images, it is clear to see that the Au film only consists of many nanorings

with holes in their centers. Therefore, we believe that the deposition rate of gold in our case ($\sim 0.7 \text{ nm s}^{-1}$) is high enough to form Au nanorings, while the deposition rate used by previous reports ($< 0.3 \text{ nm s}^{-1}$) [27,28] is low and the pore is closed. This explains why nanowires were grown by previous reports [27,28] instead of nanotubes obtained here, even the used method is identical.

Fig. 4 shows SEM images and EDX spectrum of ZnO nanotubes by thermal oxidation of Zn nanotubes. In Fig. 4a, we display a low-magnification SEM image of aligned ZnO nanotubes after partly removing AAM. The surface layer was not completely removed, which made the ZnO nanotubes stick together. The length of the nanotubes is up to several tens of micrometers. From Fig. 4b, it can be seen that the nanotubes have open ends and are arranged in parallel and well-ordered way. The outer diameter and the compactness of the ZnO nanotube arrays are similar to those of the Zn nanotube arrays described above, which were pre-determined by the characteristic of the AAM. The EDX spectroscopies of nanotubes shown in Fig. 4c confirmed that the nanotubes were composed of zinc and oxygen. Quantitative analysis reveals that the atomic ratio of Zn to O is very close to 1:1 stoichiometry. Note that the Au peak in Fig. 4c originates from the Au substrate.

To further investigate the optical properties of the highly ordered ZnO nanotube arrays, the CL measurement was conducted at an acceleration voltage of 10 kV. Fig. 5 shows the CL spectrum of ZnO nanotubes, which is similar to the photoluminescence spectra of ZnO nanowires [36]. The CL spectrum is composed of two peaks around 378 and 500 nm, respectively. The sharp UV band at 378 nm can be attributed to near band-gap transition of ZnO [37]. The green band emission around 500 nm results from the radiative recombination that arises from the singly ionized oxygen vacancy [38]. The strong and sharp band edge emission indicates that the grown ZnO nanotube arrays are indeed composed of good quality of ZnO material.

Finally, let us compare our result shown here with published reports for one-dimensional ZnO nanostructures based on the templation of AAM [27,28,39,40]. In addition to the different growth mechanism, a distinct feature can be noted that the optical spectra always accompany a large defect emission in previous works, which implies the materials have more defects than ours. We therefore believe that the good quality ZnO nanotube arrays synthesized here can find several potential applications in optoelectronics, such as field effect emitters and light-emitting devices.

Fig. 4. Scanning electron microscope images and energy dispersive spectrum of as-prepared ZnO nanotubes. (a) low-magnification of aligned ZnO nanotubes. (b) tilted-view of ZnO nanotube arrays. (c) energy dispersive spectrum of the nanotubes.

Fig. 5. Cathodoluminescence spectrum (300–700 nm) of highly ordered ZnO nanotube arrays.

4. Conclusions

In summary, we have demonstrated that the process based on template-based electrodeposition synthesis and thermal oxidation is an efficient method for the fabrication of highly ordered ZnO nanotube arrays with good quality. Notably, this method does not require chemical modification of the inner surface of the template pores, and enables the growth of ZnO nanotubes at low temperature. This simple method should be able to serve as a general approach for the growth of other metal oxide nanotube arrays, which have great potential in the application of optoelectronic devices.

Acknowledgements

This work was supported by the Ministry of Education and National Science Council of the Republic of China. We thank Dr. R.S. Chen for XRD characterization.

References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] H. Dai, E.W. Wong, Y.Z. Lu, S. Fan, C.M. Lieber, *Nature* 375 (1995) 769.
- [3] A.P. Alivisatos, *Science* 271 (1996) 933.
- [4] A.M. Morales, C.M. Lieber, *Science* 279 (1998) 208.
- [5] S. Fan, M.G. Chapline, N.M. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, *Science* 283 (1999) 512.
- [6] A. Chen, S.J. Chua, P.X. Chen, Y. Chen, L.K. Jian, *Nanotechnology* 17 (2006) 3903.
- [7] H.Y. Lin, C.L. Cheng, Y.Y. Chou, L.L. Huang, Y.F. Chen, K.T. Tsen, *Opt. Express* 14 (2006) 2372.
- [8] Y.L. Chen, C.C. Chen, J.C. Jeng, Y.F. Chen, *Appl. Phys. Lett.* 85 (2004) 1259.
- [9] C.R. Martin, *Science* 266 (1994) 1961.
- [10] I.E. Huber, *J. Mater. Res.* 15 (2000) 1816.
- [11] Y. Zhou, C. Shen, H. Li, *Solid State Ionics* 146 (2002) 81.
- [12] P. Forrer, F. Schlotting, H. Siegenthaler, M. Textor, *J. Appl. Electrochem.* 30 (2000) 533.
- [13] X.Y. Zhang, L.D. Zhang, Y. Lei, L.X. Zhao, Y.Q. Mao, *J. Mater. Chem.* 11 (2001) 1732.
- [14] Z.B. Zhang, X.Z. Sun, M.S. Dresselhaus, J.Y. Ying, J.P. Heremans, *Appl. Phys. Lett.* 73 (1998) 1589.
- [15] Y.G. Guo, L.J. Wan, J.R. Gong, C.L. Bai, *Phys. Chem. Chem. Phys.* 4 (2002) 3422.
- [16] S. Valizadeh, J.M. George, P. Leisner, L. Hultman, *Electrochim. Acta* 47 (2001) 865.
- [17] Y.G. Guo, C.J. Li, L.J. Wan, D.M. Chen, C.R. Wang, C.L. Bai, Y.G. Wang, *Adv. Funct. Mater.* 13 (2003) 626.
- [18] D. Routkevitch, T. Bigioni, M. Moskovits, J.M. Xu, *J. Phys. Chem.* 100 (1996) 14037.
- [19] R. Parthasarathy, C.R. Martin, *Nature* 369 (1994) 298.
- [20] T. Kyotani, L. Tsai, A. Tomita, *Chem. Mater.* 8 (1996) 2109.
- [21] K. Hummer, *Phys. Stat. Sol. (b)* 56 (1973) 249.
- [22] A. Mang, K. Reimann, St. Ruhenacke, *Solid State Commun.* 94 (1995) 251.
- [23] S.W. Kim, Sz. Fujita, Sg. Fujitha, *Appl. Phys. Lett.* 86 (2005) 153119.
- [24] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 291 (2001) 1947.
- [25] J.J. Wu, S.C. Liu, C.T. Wu, K.H. Chen, L.C. Chen, *Appl. Phys. Lett.* 81 (2002) 1312.

- [26] L. Schmidt-Mende, J.L. MacManus-Driscoll, *Mater. Today* 10 (2007) 40.
- [27] Y. Li, G.W. Meng, L.D. Zhang, *Appl. Phys. Lett.* 76 (2000) 2011.
- [28] Y. Li, G.S. Cheng, L.D. Zhang, *J. Mater. Res.* 15 (2000) 2305.
- [29] C.L. Cheng, J.S. Lin, Y.F. Chen, *Mater. Lett.* 62 (2008) 1666.
- [30] H. Masuda, K. Fukuda, *Science* 268 (1995) 1466.
- [31] S. Zhao, H. Roberge, A. Yelon, T. Veres, *J. Am. Chem. Soc.* 128 (2006) 12352.
- [32] E.C. Walter, B.J. Murray, F. Favier, G. Kaltenpoth, M. Grunze, R.M. Penner, *J. Phys. Chem. B* 106 (2002) 11407.
- [33] R.J. Bowling, R.T. Packard, R.L. McCreery, *J. Am. Chem. Soc.* 111 (1989) 1217.
- [34] D.M. Davis, E.J. Podlaha, *Electrochem. Solid-State Lett.* 9 (2006) C62.
- [35] J.G. Wang, M.L. Tian, N. Kumar, T.E. Mallouk, *Nano Lett.* 5 (2005) 1247.
- [36] N.E. Hsu, W.K. Hung, Y.F. Chen, *J. Appl. Phys.* 96 (2004) 4671.
- [37] Y.C. Kong, D.P. Yu, B. Zhang, W. Fang, S.Q. Feng, *Appl. Phys. Lett.* 78 (2001) 407.
- [38] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983.
- [39] L. Li, S. Pan, X. Dou, Y. Zhu, X. Huang, Y. Yang, G. Li, L. Zhang, *J. Phys. Chem. C* 111 (2007) 7288.
- [40] A.B.F. Martinson, J.W. Elam, J.T. Hupp, M.J. Pellin, *Nano Lett.* 7 (2007) 2183.