

Low Temperature Synthesis and Optical Properties of ZnO Nanowires*

Chang Peng¹, Liu Su^{1,†}, Chen Rongbo¹, Tang Ying¹, and Han Genliang²

(1 School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China)

(2 Institute of Sensor Technology, Gansu Academy of Sciences, Lanzhou 730000, China)

Abstract: ZnO nanowire arrays are fabricated on anodized aluminum oxide templates with electric field-assisted electrochemical technology. Transmission electron microscopy results indicate that the nanowires are straight and uniform. X-ray diffraction patterns indicate that the nanowires are highly oriented. The result of selected area electron diffraction suggests that the nanowires are single crystals. The photoluminescence spectrum presents a broad-band luminescence in the region of 350~650nm. The effect of the assisted transverse electric field on the growth process of ZnO nanowires is also discussed.

Key words: ZnO; electrochemical; nanowires; PL spectrum

PACC: 8115L; 7855 **EEACC:** 2520D; 4220

CLC number: TQ153 **Document code:** A **Article ID:** 0253-4177(2007)10-1503-05

1 Introduction

Recently, zinc oxide (ZnO) has stimulated extensive research interest because of its excellent physical properties and numerous potential applications^[1]. As a II-VI compound semiconductor with a wide band gap (3.37eV), ZnO nanowires are emerging as candidates for nanoscale ultraviolet (UV) lasers, light-emitting diodes, photodetectors, and chemical sensors^[2]. Therefore, extensive research on the fabrication of ZnO nanostructures, such as nanowires, nanobelts, nanocables and nanotubes, has been carried out recently. The fabrication methods of one-dimensional ZnO nanostructures mainly focus on vapor transport processes at high temperatures ranging from 400 to 1150°C, including chemical vapor deposition (CVD)^[3], metal-organic vapor-phase epitaxy (MOVPE)^[4~5], and pulsed laser deposition (PLD)^[6]. Low temperature electrochemical deposition methods have been used to deposit ZnO^[7]. In those works, the template was used as a cathode. According to X-ray diffraction experiments, nearly all the single crystal products fabricated by the above methods have the same peak corresponding to ZnO (002) because they all grew perpendicularly to the substrates. In this report, anod-

ic aluminum oxide (AAO) template was utilized to fabricate single crystal ZnO nanowires via a simple electric field-assisted electrochemical deposition approach at low temperature (room temperature). All the obtained samples only have a sharp peak corresponding to ZnO (101).

2 Experiment

Briefly, a 99.999% pure Al foil was degreased and electropolished in a solution of perchloric acid, ethanol, and distilled water to produce a mirror-like surface^[8]. This film was then washed in distilled water, air dried, and anodized in 0.3M oxalic acid at room temperature using a constant anodizing voltage of 40V. The anodization was carried out for 0.5h to form a thick porous alumina film on the surface, which was then stripped off in hot chromic/phosphoric acid and the anodization was repeated again for 10h to form another porous alumina film with a thickness of a few microns. The two-step anodization process^[9] yielded an anodic alumina film with a well ordered array of about 80nm diameter pores. After the anodization, the remaining aluminum was etched by a saturated HgCl solution. Finally, the barrier layer was dissolved using 0.5M H₃PO₄ at 60°C for 50min. The AAO template to be used

* Project supported by the Natural Science Foundation of Gansu Province (No. 3ZS051-A25-034)

† Corresponding author. Email: liusu@lzu.edu.cn

Received 26 April 2007, revised manuscript received 18 June 2007

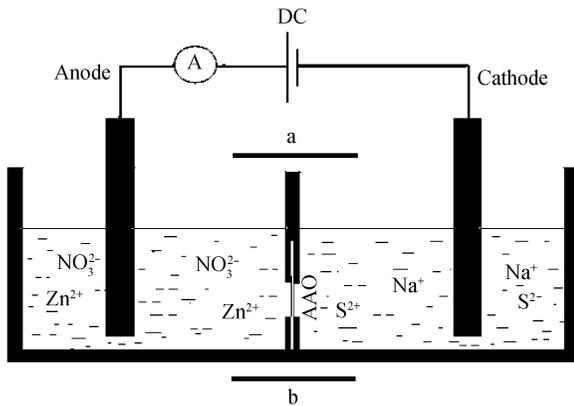


Fig.1 Device used to synthesize ZnO nanowires a and b are the half-sleeve form transverse electrodes.

in the following experiment was then obtained.

Figure 1 shows a schematic picture of the device that is used to synthesize the ZnO nanowires. The porous template is sealed in the middle of the device. Each side of the template has a graphite electrode (left and right). One is the cathode, which connects to the aqueous solution of Na_2S , and the other is the anode, which connects to the aqueous solution of $\text{Zn}(\text{NO}_3)_2$. A transverse electric field (between a and b) is applied with a voltage of 12.5V and a frequency of 50Hz to generate an infinitesimal disturbance in the formation process of the nanowires.

The Na_2S aqueous solution is prepared first at 0.0125M. The consistency of the $\text{Zn}(\text{NO}_3)_2$ aqueous solution calculated by Eq. (1) is 0.00166M.

$$N = \frac{CQ}{Mr^3} \quad (1)$$

where C is the consistency of the ions, Q is the electric charge of the same ions, M is the atomic weight, and r is the ionic radius.

Figure 2 shows the growth process of ZnO. If the transverse electric field (Figure 2(a)) is not applied, the nucleation occurs at random locations. Once ZnO is formed, the channel for the ions is blocked and the growth process stops. ZnO nanowires then cannot be synthesized. Figures 2 (b), (c) and (d) illustrate the growth process of ZnO nanowires in the transverse electric field. During the electrodeposition process, the major effect to control the growth orientation is the transverse electric field. Zn^{2+} and O^{2-} move in opposite directions in the transverse electrical field. When the electric field direction alternates,

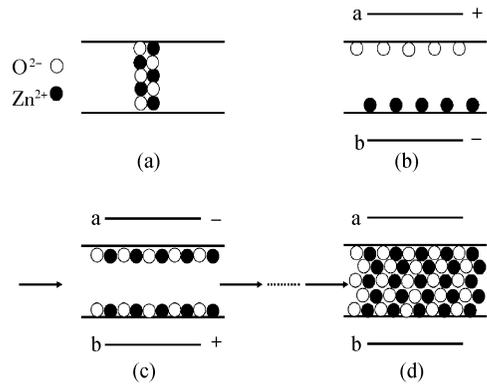


Fig.2 Growth process of ZnO (a) Without the transverse electric field; (b), (c), (d) With the transverse electric field

nucleation occurs on the walls of pores in the AAO template. ZnO nanotubes form and thicken radially gradually. Until the tubes are blocked, ZnO nanowires are synthesized.

In the experiment, the current density was about $10\text{mA}/\text{cm}^2$ at first, and then it decreased gradually to $10^{-3}\text{mA}/\text{cm}^2$ after 20min and maintained this constant current density.

Structural characterization was performed by means of X-ray diffraction (XRD) using a Rigaku/Max-2400 diffractometer with $\text{CuK}\alpha$ radiation (wavelength 0.154056nm). The bright field image of nanowires and selected area electron diffraction pattern (SAED) were taken by an EM-400T transmission electron microscope (TEM). The X-ray photoelectron spectrum (XPS) data were collected on a PHI-5702 X-ray photoelectron spectrometer using a monochromatic $\text{AlK}\alpha$ X-ray source. Photoluminescence (PL) spectra excited with 325nm UV light at 295K were collected with an FLS920T combined fluorescence lifetime and a steady state spectrophotometer.

3 Results and discussion

Figure 3 (a) shows a TEM image of dispersed nanowires with an average diameter of 60nm obtained by electrodeposition in the anodic aluminum oxide templates. The dispersed nanowires were obtained by dissolving AAO templates in 1M H_2SO_4 solution for 24h at 30°C . Enough templates (about ten pieces) have to be dissolved in 3mL H_2SO_4 solution to make sure that the nanowires

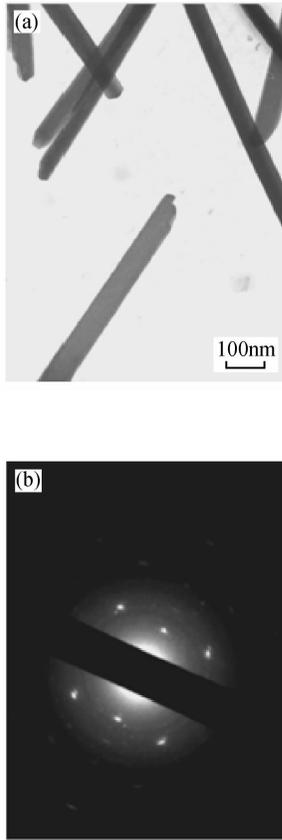


Fig.3 (a) TEM image of the ZnO nanowires; (b) SAED image of the as-grown products

are not dissolved entirely because ZnO is amphoteric oxide. In the corrosion process, the consistency of H^+ decreases gradually and then the nanowires can remain. The obtained nanowires were studied in detail by SAED. The SAED pattern shown in Fig.3 (b) suggests that the nanowire is a single crystal.

The XRD patterns of the nanowires in the AAO template deposited at 0.5, 1, 20 and 40V DC are shown in Fig. 4. Only one peak at $2\theta = 35.96^\circ$ is observed, which can be assigned to ZnO (101),

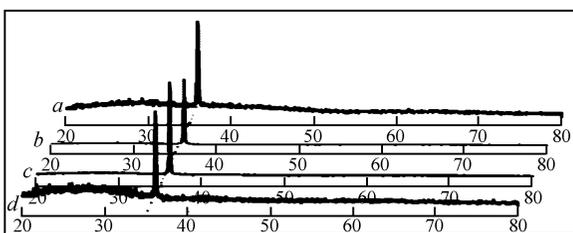


Fig.4 XRD patterns of ZnO nanowires in the AAO template at different voltages a: 0.5V; b: 1V; c: 20V; d: 40V

indicating that the ZnO nanowires are highly oriented hexagonally. This result is reproducible at different depositing DC voltages. No peaks for Zn or other impurities are found in the spectrum, which indicates that the as-grown sample is pure ZnO. The reason it is ZnO (101) but not (002) can be attributed to the special growth process. In other works, the ZnO grew perpendicularly to the substrates, but, in this work, the ZnO grew perpendicularly to the wall of the pores as discussed above.

The chemical composition of the ZnO nanowires deposited at 40V was obtained by XPS, and the results are shown in Fig. 5. Figure 5 (a) shows the full-range XPS spectrum, where only Zn, O, C, and Al peaks are present. Figures 5 (b) and (c) display the XPS spectra of the $Zn2p_{3/2}$ and O1s of ZnO nanowires. The binding energies in all the XPS spectra have been calibrated using C1s at 284.6eV, shown in Fig. 5 (d). The binding energies of O1s and $Zn2p_{3/2}$ provide a fairly complete picture of the samples. The $Zn2p_{3/2}$ XPS peak that appears near 1021eV coincides with the findings for ZnO. The O1s peak near 531eV is attributed to oxide ions in $ZnO^{[10]}$. These results indicate that pure ZnO nanowires have been obtained and they are in accordance with the results of XRD.

The room-temperature photoluminescence spectrum for the as-grown ZnO nanowires excited by a He-Cd laser operating at 325nm is shown as curve a in Fig. 6, which reveals a broad-band emission in the region of 350~650nm. The

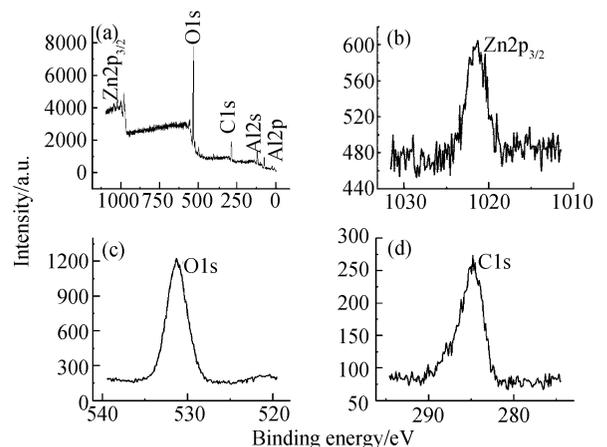


Fig.5 XPS spectra of ZnO nanowires deposited at 40V (a) Full range; (b) $Zn2p_{3/2}$; (c) O1s; (d) C1s

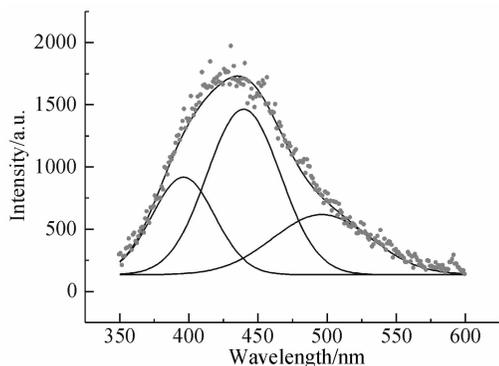


Fig. 6 PL emission spectra for the as-grown ZnO nanowires

emission peak at 380nm corresponds to the near-band-edge emission of ZnO attributed to the recombination of the free excitons. Obviously, there are visible emissions, including a violet emission at 446nm and a green emission at 510nm. They imply the presence of some defects. Previous studies on ZnO mostly reported green subgap luminescence (peak near 510nm), which has been attributed to defects associated with oxygen deficiency^[11]. The luminescence band at 446nm is caused by the transition from the level of the ionized oxygen vacancies to the valence band^[12].

4 Conclusions

In summary, single crystal ZnO nanowires were obtained at different voltages from 0.5 to 40V at room temperature. The morphologies, chemical compositions, and structures of the nanowires were characterized by TEM, SAED, XPS, and XRD, respectively. The as-grown products are single crystals with wurtzite structure and diameters of about 60nm. During the electrodeposition process, Zn^{2+} and O^{2-} move to the opposite direction in the transverse electrical field. When the electric field direction alternates, ZnO nano-

tubes are formatted and thickened along the radial gradually. Until the tubes are blocked, ZnO nanowires are synthesized. Broad-band luminescence in the region of 350~650nm is observed by PL spectra of the as-grown products due to the bound-exciton, vacancy-related transitions, and recombination between self-activated defect levels from (V_{Zn}, O_i) .

References

- [1] Pearton S J, Norton D P, Ip K, et al. Recent progress in processing and properties of ZnO. *Prog Mater Sci*, 2005, 50: 293
- [2] Yang P, Yan H, Mao S, et al. Controlled growth of ZnO nanowires and their optical properties. *Adv Funct Mater*, 2002, 12: 323
- [3] Wu J J, Liu S C. Low-temperature growth of well-aligned ZnO nanorods by chemical vapor deposition. *Adv Mater*, 2002, 14: 215
- [4] Park W I, Yi G C, Kim J W, et al. Schottky nanocontacts on ZnO nanorod arrays. *Appl Phys Lett*, 2003, 82: 4358
- [5] Ogata K, Maejima K, Fujita S, et al. Growth mode control of ZnO toward nanorod structures or high-quality layered structures by metal-organic vapor phase epitaxy. *J Cryst Growth*, 2003, 248: 25
- [6] Choi J H, Tabata H, Kawai T. Initial preferred growth in zinc oxide thin films on Si and amorphous substrates by a pulsed laser deposition. *J Cryst Growth*, 2001, 226: 493
- [7] Pauporté T, Lincot D. Heteroepitaxial electrodeposition of zinc oxide films on gallium nitride. *Appl Phys Lett*, 1999, 75: 3818
- [8] Bandyopadhyay S, Miller A E, Chang H C, et al. Electrochemically assembled quasi-periodic quantum dot arrays. *Nanotechnology*, 1996, 7: 360
- [9] Masuda H, Satoh M. Fabrication of gold nanodot arrays using anodic porous alumina as an evaporation mask. *Jpn J Appl Phys, Part 1*, 1996, 35: L126
- [10] Peng W Q, Cong G W, Qu S C, et al. Synthesis of shuttle-like ZnO nanostructures from precursor ZnS nanoparticles. *Nanotechnology*, 2005, 16: 1469
- [11] Vanheusden K, Warren W L, Seager C H, et al. Mechanisms behind green photoluminescence in ZnO phosphor powders. *J Appl Phys*, 1996, 79: 7983
- [12] Zhang D H, Wang Q P, Xue Z Y. Photoluminescence of ZnO films excited with light of different wavelength. *Appl Surf Sci*, 2003, 207: 20

ZnO 纳米线的低温生长及其发光特性*

常 鹏¹ 刘 肃^{1,†} 陈溶波¹ 唐 莹¹ 韩根亮²

(1 兰州大学物理科学与技术学院, 兰州 730000)

(2 甘肃省科学院传感技术研究所, 兰州 730000)

摘要: 采用电场辅助电化学沉积的方法在阳极氧化铝模板中沉积出 ZnO 纳米线阵列. 透射电子显微镜和 X 射线衍射测试结果表明, 制备的纳米线是单晶 ZnO 纳米线, 形貌均匀, 直径大约为 60nm, 并且择优于(101)晶面. 对生长过程中所加的辅助电场的作用给出了初步解释. 光致发光谱表明, 在 350~650nm 范围内存在一个很宽的发光峰.

关键词: ZnO; 电化学; 纳米线; PL 谱

PACC: 8115L; 7855 **EEACC:** 2520D; 4220

中图分类号: TQ153 **文献标识码:** A **文章编号:** 0253-4177(2007)10-1503-05

* 甘肃省自然科学基金资助项目(批准号:3ZS051-A25-034)

† 通信作者. Email: liusu@lzu.edu.cn

2007-04-26 收到, 2007-06-18 定稿