

J. Nano- Electron. Phys.
3 (2011) No1, P.146-150

© 2011 SumDU
(Sumy State University)

PACS numbers: 81.15.Pq, 61.46.Km

TEMPLATE ASSISTED GROWTH OF ZINC OXIDE-BASED NANOWIRES BY ELECTROCHEMICAL DEPOSITION

T. Singh, D.K. Pandya, R. Singh

Thin Film Laboratory, Department of Physics,
Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India
E-mail: triloks.iitd@gmail.com

Ordered ZnO and Zn_{1-x}Cd_xO nanowire/nanorod arrays were fabricated by cathodic electrodeposition based on anodic alumina (AAO) membrane and polycarbonate membrane (PCM) from an aqueous solution containing zinc nitrate precursor at different bath temperatures. The electrodeposition process involves the electroreduction of nitrate ions to alter the local pH within the pores and precipitation of the metal oxide within the pores. X-Ray diffraction measurements showed that the nanowires/nanorods were of wurtzite crystallographic structures and the average length and diameter of nanorods were measured by SEM and TEM. HRTEM measurements confirm the crystallinity and elemental composition of grown nanowires on PCM/AAO templates.

Keywords: ZnO, NANOWIRES, ELECTRODEPOSITION, TEM.

(Received 04 February 2011, in final form 18 March 2011)

1. INTRODUCTION

Template-assisted synthesis has been employed widely to prepare solids of defined dimension [1]. Several techniques of forming materials in templates have been developed, including chemical vapor deposition (CVD) [2], sol-gel deposition [3], in situ polymerization [4] and electrodeposition [5]. Nanostructured materials have attracted great interest due to their unique chemical and physical properties, which can be influenced not only by the preparation procedure but also by their shape and size [6, 7]. The morphology of the nanostructures plays a key role especially on the optoelectronic properties of the materials, which determine the performance of semiconductors to be used in solar cells, as photo transistors and diodes, transparent electrodes, and so on. Among group II – VI semiconductor materials, ZnO is one of the most attractive functional semiconductor material for the fabrication of optoelectronic devices operating in the blue and ultraviolet region because of a direct wide band-gap of 3.37 eV and an exciton binding energy of 60 meV [8, 9]. It is well known that the realization of bandgap engineering to create barrier layers and quantum wells in device heterostructure is an important step for the design of ZnO-based devices. CdO is an *n*-type semiconductor with a direct band-gap of 2.3 eV and an indirect band-gap of 1.36 eV [10]. The ternary Zn_{1-x}Cd_xO alloy can allow the bandgap tuning from 3.37 eV (band-gap of ZnO) to a narrower band-gap, i.e., into the visible spectral range, and their preparation have been reported [11]. The control over morphology and size of semiconductor materials represents a great challenge in realizing the

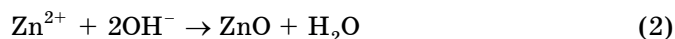
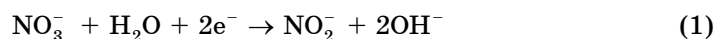
design of novel functional devices. In this paper, we investigated an electrodeposition method for the growth of ZnO-based nanowires/nanorods by applying a negative potential to the substrate. Electrochemical deposition allows mixing of the chemicals at atomic level thus reducing the possibility of undetectable impurity phases, [12] and it is a good candidate to solve the problem of the small thermodynamic solubility of CdO in ZnO [13]. Furthermore, the electrochemical deposition presents a simple, quick and economical method for the preparation of $Zn_{1-x}Cd_xO$ nanorods.

2. EXPERIMENTAL

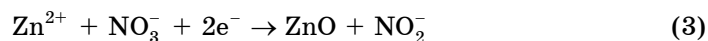
ZnO and ZnCdO nanowires/nanorods were synthesized by electrodeposition into nuclear track etch polycarbonate membrane (PCM) and anodic alumina membrane (AAO) (Whatman). The rated membrane thickness, nominal pore size, and pore density of PCM and AAO membranes were 6 μm , 100 nm, 6×10^8 pores/ cm^2 and 60 μm , 100 nm, 8×10^8 (pores/ cm^2) respectively. One side of the membrane was first coated with a 100 nm thick layer of gold, to serve as working electrode. The electrical contact was made to the membrane working electrode using gold coated silicon substrate. A platinum sheet $2 \times 3 \text{ cm}^2$ was used as counter electrode and saturated calomel electrode was used as reference electrode. Electrosynthesis was performed under potentiostatic control using a Perkin Elmer 260 A instrument. The electrolyte (bath) temperature was varied from 70 to 90 $^\circ\text{C}$. Electrosynthesis of ZnO was in an electrolyte containing zinc nitrate precursor solution. For the growth of ternary compound nanowires/nanorods the precursor solutions were obtained by varying the zinc nitrate and cadmium nitrate concentrations in de-ionized water. The cadmium concentration for the growth of nanostructures was varied from 4 to 16 atomic percent. The electrochemical deposition of ternary ZnCdO compounds were carried out at the deposition potential of -1.0 V (vs. SCE) 20 - 40 min. After the deposition the sample was removed from electrolyte and rinsed in de-ionized water. For the structural studies, X-ray diffractometer (Philips Xpert Pro) using CuK_α ($\lambda = 1.5405 \text{ \AA}$) radiation in 2θ range 20 - 800 was used. Scanning electron microscopy images were obtained using EVO-50. Energy dispersive X-ray spectroscopy analysis was obtained from Bruker-ASX (QuanTax 200).

3. RESULTS AND DISCUSSION

The electrodeposition process of ZnO nanowires/nanorods mainly includes two parts: first, an increase of pH, in this case due to the reduction of nitrate ions, and second the precipitation of zinc oxide. On reduction of nitrate in the presence of zinc ions the following two reactions occurs:



The total reaction may be written as,



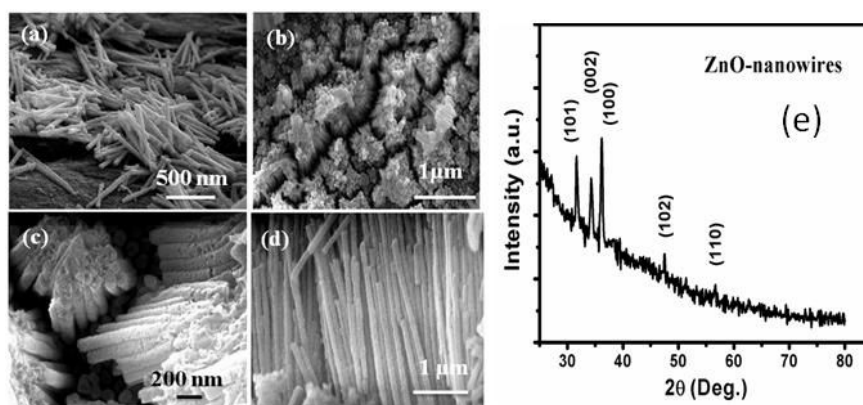


Fig. 1 – SEM image of ZnO nanowires grown (a) at 70 °C in PCM, (b) and (c) at 80 °C in AAO membrane and (d) cross-sectional view of ZnO nanowires and (e) X-ray diffraction pattern of ZnO nanowires

The SEM image of ZnO nanowires/nanorods synthesized at 70 - 90 °C in PCM and AAO membrane is shown in Fig. 1a-d. Fig. 1a shows SEM image of ZnO nanorods grown at 70 °C in PCM template and completely dissolve in dichloromethane. Fig. 1b and c shows the top view of the ZnO nanowires with the AAO template partly dissolve in 1 M NaOH solution. The arrays of nanowires in the image are vertically standing. The cross-sectional image of ZnO nanowires arrays deposited for 30 minute is shown in Fig. 1d. The nanowires are oriented in same direction and some nanowires are broken off due to the mechanical forces during etching of template. The majority of nanowires are approximately 20 μm in length (deposition rate approximately ~ 0.6 μm), which can be modulated by varying the deposition time. In order to obtain high filling of uniform nanowires arrays the membrane is ultrasonicated in an ethanol for 5 min and then dipped in electrolyte for 10 min. The Cd concentration was varied from 0 - 16 at%. X-ray diffraction patterns of ZnO nanowires arrays embedded in AAO template is shown in Fig. 1 e. Strong reflections corresponding to (100), (002) and (101) planes are observed along with the weaker reflections of (102) and (110) planes of wurtzite ZnO, indicating ZnO nanowires are polycrystalline. We have observed from the X-Ray Diffraction patterns that there is no phase separation up to 16 at% of Cd. Fig. 2 shows the ZnCdO nanorods with the average diameter of 100 - 120 nm and average length up 3 - 4 μm. In the primary solution the Cadmium concentration was varied from 0 - 16 at%. No substantial change were observed up to 16 at% in the dominant peak reflections but there is a peak shift towards low-angle side when compared with the pure ZnO. This shift in peak implies that there is a compressive stress in the *c*-axis orientation.

The lattice expansion indicates that the substitution of Zn atom by larger Cd atom. TEM images are shown in Fig. 3. Energy dispersive spectrum confirms the presence of Zn and oxygen in the arrays of nanowires shown in Fig. 3 a. ZnO nanowires grown in AAO/PCM templates are tapered along the

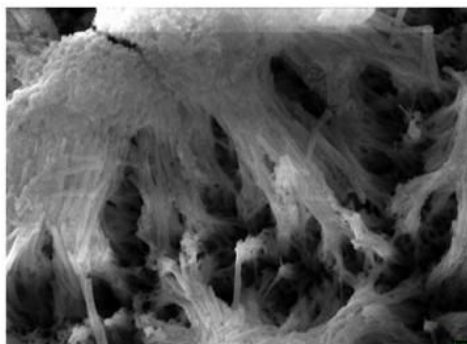


Fig. 2 – SEM of $Zn_{0.96}Cd_{0.04}O$ Nanorods grown in AAO template at 80 °C

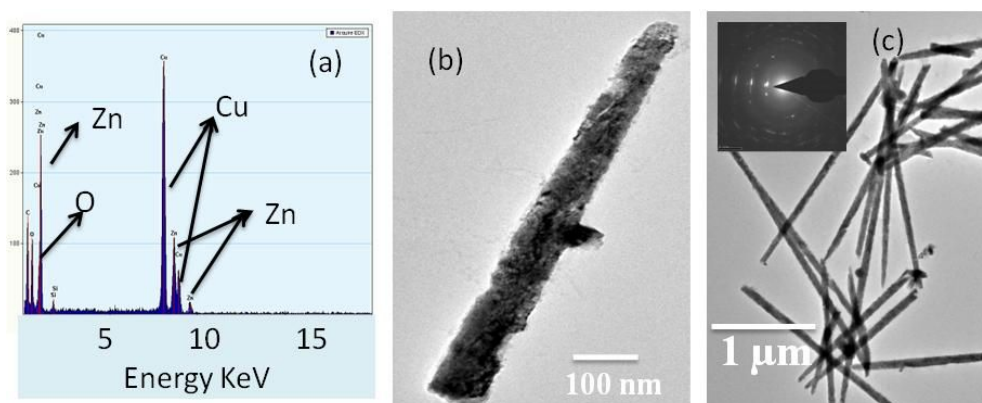


Fig. 3 – EDS spectrum of ZnO nanowires (a), TEM image of ZnO nanowires at 70 °C in PCM (b) and at 90 °C (c) (in inset SAED pattern of ZnO nanowires)

growth direction and shown in Fig. 3 b and c. The nanowires grown by electrochemical method are of polycrystalline nature and selected area electron diffraction pattern is shown in Fig. 3 c.

4. CONCLUSIONS

We have shown that the electrodeposition is an effective technique to synthesize ZnO and ternary ZnCdO nanowires/nanorods in the porous polycarbonate and anodic alumina membrane. The nanowires were grown at a constant potential – 1.0 V and deposition temperature was varied from 70 - 90 °C. XRD analysis showed the ZnCdO nanorods were of pure ZnO wurtzite structures. It was also observed that there was compressive stress in the c-axis orientation. TEM measurements showed the nanowires/nanorods were of good crystalline quality.

REFERENCES

1. M. Lai, D.J. Riley, *Chem. Mater.* **18**, 2233 (2006).
2. L. Huang, J.S. Wind, P.S. Obrien, *Nano Lett.* **3**, 299 (2003).
3. B.B. Lakshmi, K.P. Dorhout, R.C. Matrin, *Chem. Mater.* **9**, 857 (1997).

4. R.C. Matrin, S.L. Van Dyke, H.Z. Cai, B.W. Liang, *J. Am. Chem. Soc.* **112**, 8976 (1990).
5. S. Park, H.J. Lim, W.S. Chung, A.C. Mirkin, *Science* **303**, 348 (2004).
6. A.P. Alivisatos, *Science* **271**, 933 (1996).
7. C.M. Lieber, *Solid State Commun.* **107**, 607 (1998).
8. V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxides*, (Cambridge University Press: Cambridge: 1994).
9. H. Cao, J.Y. Xu, D.Z. Zhang, S.H. Chang, S.T. Ho, E.W. Seelig, X. Liu, R.P.H. Chang, *Phys. Rev. Lett.* **84**, 5584 (2000).
10. I.D. Makuta, S.K. Poznyak, A.I. Kulak, E.A. Streltsov, *Phys. Status Solidi A* **111**, 193 (1989).
11. C.X. Shan, Z. Liu, Z.Z. Zhang, D.Z. Shen, S.K. Hark, *J. Phys. Chem. B* **110**, 11176 (2006).
12. Y.J. Li, C.Y. Wang, M.Y. Lu, K.M. Li, L.J. Chen, *Cryst. Growth Des.* **8**, 2598 (2008).
13. F. Bertram, S. Giemsch, D. Forster, J. Christen, R. Kling, C. Kirchner, A. Waag, *Appl. Phys. Lett.* **88**, 061915 (2006).