

DC electrochemical deposition of CdSe nanorods array using porous anodic aluminum oxide template

Cheng-min Shen, Xiao-gang Zhang, Hu-lin Li *

Department of chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

Received 31 July 2000; received in revised form 6 November 2000

Abstract

CdSe nanorods array were prepared using direct current potentiostatic deposition in porous anodic aluminum oxide template from aqueous CdSO₄ and H₂SeO₃ at room temperature (298 K). Electron microscope results show that these CdSe nanorods have a uniform length and diameter. X-ray energy dispersion analysis indicates that the atomic composition of Cd and Se is very close to a 1:1 stoichiometry. X-ray diffraction and electron diffraction pattern investigations demonstrate that CdSe nanorods are a uniform cubic CdSe crystal. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CdSe nanorods; DC electrodeposition; Semiconductor

1. Introduction

In recent, there has been intense interest surrounding the fabrication of nanosized materials obtained using templates, especially on the preparation of hollow nanowires of semiconductor and metal which are of great potential in testing and understanding fundamental concepts as well as their applications in the semiconductor industry and magnetic recording area [1–9]. There are many experimental approaches to fabricate nanowires by template techniques that involves electrochemical deposition of metal into nanometer-wide channels of anodic aluminum oxide (AAO) films, polycarbonate track etched membrane or nanochannel array glass [10–17]. Because the growth is controllable almost exclusively in the direction normal to the substrate surface, electrochemical synthesis in a template is taken as one of the most efficient methods in controlling the growth of nanowires and has been used to produce a variety of metal nanowires. However, studies on the preparation of semiconductor nanowires by direct current electrodeposition using templates are still scarce. Xu et al. reported preparation of CdSe

nanowire array by direct current (dc) electrodeposition in AAO template, but they deposited at high temperature (185°C) and using expensive organic reagent [17]. In this paper, we prepared CdSe nanorods in the aqueous solution containing CdSO₄–H₂SeO₃ at room temperature by dc potentiostatic deposition. The nanostructure and morphology as well as the atomic composition characterization of the nanorods were carried out using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray energy dispersion analysis (EDAX).

2. Experimental

An aluminum foil (99.999% in pure, size 0.10 × 10 × 20 mm³) was ultrasonically degreased for 10 min, etched in 1.0 mol l⁻¹ NaOH at room temperature for 3 min to remove the native oxide and washes thoroughly with distilled water, then electropolished in a mixed solution of HClO₄:CH₃CH₂OH = 1:4 for 20 s and promptly rinsed with doubly distilled water. Afterward, the aluminum foil was anodized at 160 V_{ac} for 2 h in 0.5 mol l⁻¹ phosphate acid solution. Each substrate was then exposed to a saturated HgCl₂ solution for 1 h, the oxide section separated from the aluminum substrate as the result of amalgamation of underlying

* Corresponding author. Tel.: +86-931-8912517; fax: +86-931-8912582.

E-mail address: lih1@lzu.edu.cn (H.-l. Li).

aluminum. Then the barrier layer was etched by immersing the films in 20 wt.% sulfuric acid for 1 h. The diameter and thickness of this film were about 200–250 nm and 30 μm . Finally, a gold film was deposited by vacuum evaporation onto a surface of the template membrane to provide a conductive contact [18].

A CHI660A Electrochemical Station (Cordova) was used for both the cyclic voltammetric measurement and the CdSe potentiostatic deposition in a three-electrode cell. The cell consists of AAO template as the working electrode, Pt gauze as the counter electrode and saturated calomel electrode (SCE) as the reference electrode, respectively. Cyclic voltammetry scans were recorded from -0.9 to 0.2 V at a scan rate of 10 mV s^{-1} , and potentiostatic deposited at -0.70 V versus SCE in the $\text{pH} = 2.5$ solution containing 0.25 mol l^{-1} CdSO_4 – 0.01 mol l^{-1} H_2SeO_3 – 0.25 mol l^{-1} Na_2SO_4 at room temperature.

For SEM image, the CdSe nanorods with AAO were removed by mounting the foil on n-type Si wafer using epoxy resin, and dissolving the AAO template in 1 M NaOH at 25°C for 1 h and washing several times with deionized water. Then, the above CdSe nanorods samples were sputter-coated with gold before the SEM

measurement in order to increase their conductivity. For TEM, the CdSe nanorods were detached from the substrate by 1 M NaOH for 1 h; then a small drop of the solution was placed on the Cu grids. SEM was carried out using a JEOL JSM-5600LV scanning electron microscope and equipped with a JEM-1200EX/S energy dispersive X-ray analysis (EDAX). A Hitachi 600 transmission electron microscope was used for the study of the morphology of the CdSe nanorods. XRD was carried out on a Rigaku D/MAX-2400 X-ray diffractometer using Cu– $\text{K}\alpha$ radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

3.1. Electrochemical behavior

Cyclic voltammetry was used to study the electrochemical reactions in the mixture solution of CdSO_4 , H_2SeO_3 and Na_2SO_4 , in order to find the suitable CdSe deposition potential. All voltammetry curves were recorded and scanned in the cathodic direction. pH value of the solution was adjusted by 0.5 M H_2SO_4 .

Cyclic voltammogram on AAO template in the $\text{pH} = 2.5$ solution containing 0.25 mol l^{-1} Na_2SO_4 was shown in Fig. 1a. In our selected potential window, substrate has no effect for deposition of CdSe films.

A cyclic voltammogram measured after adding 0.25 mol l^{-1} CdSO_4 + 0.25 mmol l^{-1} H_2SeO_3 + 0.25 mol l^{-1} Na_2SO_4 is shown in Fig. 1b. Deposition of CdSe starts at a potential about from -0.65 to -0.74 V versus SCE. In the reverse scanning the re-oxidation peak is observed at a potential -0.54 V versus SCE which is possible superimposition peak of compound CdSe and element cadmium because this peak is similar to a pure solution of CdSO_4 and no oxidation peak of CdSe is found [19]. The hysteresis between potential -0.75 and -0.72 V versus SCE indicates the reduction of CdSe occurs more easily on the CdSe formed dot than that on the AAO template hole, i.e. once the CdSe is formed in hole of template, deposition occurs already at the potential -0.72 V versus SCE. Altogether the above results confirm that CdSe film can be electrodeposited between potential of -0.65 and -0.75 V versus SCE.

The change of current density with time is shown in Fig. 2 during the dc potentiostatic electrodeposition at -0.70 V versus SCE for 120 min. It was observed that the cathodic current density decrease quickly at initial time and increase gradually. The sudden decrease in current density, then gradual increasing corresponded to the formation of CdSe nucleus and growth of CdSe nanorods in the AAO template, respectively. In our experiment, current density of dc electrodeposition is smaller so that the growth rate of CdSe nanorods is slower in the AAO template. The uniform of CdSe

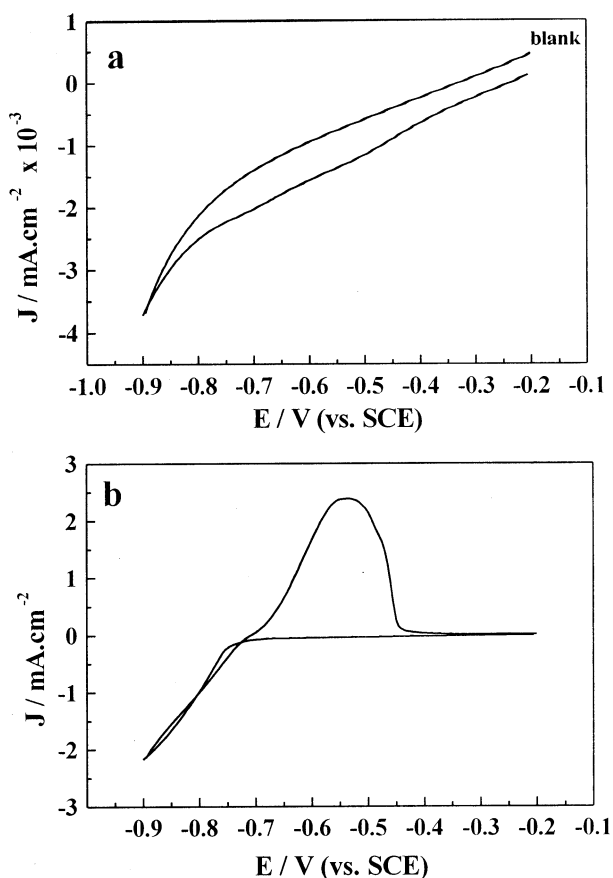


Fig. 1. Cyclic voltammogram on AAO substrate in the solution containing: (a) Blank; (b) 25 M CdSO_4 – 0.25 mM H_2SeO_3 – 0.25 M Na_2SO_4 ; $\text{pH} = 2.5$, Scan rate = 50 mV s^{-1} .

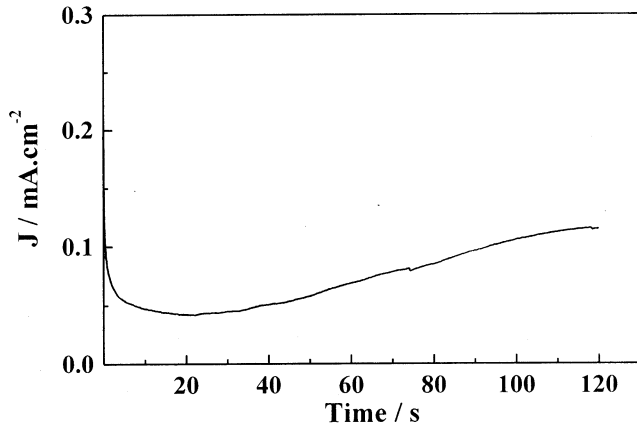


Fig. 2. Change in current density during potentiostatic electrodeposition at -0.70 V vs. SCE from solutions containing $0.25 \text{ mol l}^{-1} \text{ CdSO}_4$ – $0.25 \text{ mol l}^{-1} \text{ H}_2\text{SeO}_3$ – $0.25 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$.

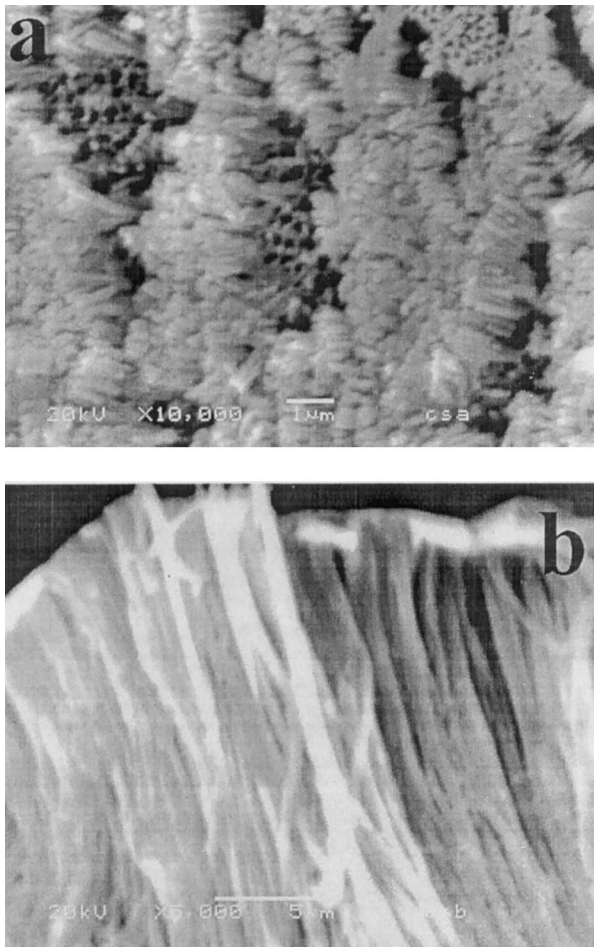


Fig. 3. SEM image of CdSe nanorods prepared by dc deposition: (a) plane figure; (b) section figure.

nanorods can be obtained in lower deposition current density.

3.2. SEM and TEM image

A typical morphology of the CdSe nanorods prepared by dc potentiostatic electrodeposition in AAO template is shown in the SEM image in Fig. 3. It is shown that CdSe nanorods have uniform diameters of about 200 nm, which corresponds closely to the pore diameters. The nanorods are about $25 \mu\text{m}$ in the length. We obtained that the nanorods can be found in the whole samples with as area of 0.8 cm^2 . This result indicates that the nanorods can be filled uniformly in the pore of the AAO template by dc potentiostatic electrodeposition.

Fig. 4a shows the TEM image of CdSe nanorods prepared in an AAO template. The as-produced nanorods are uniformly distributed and have a diame-

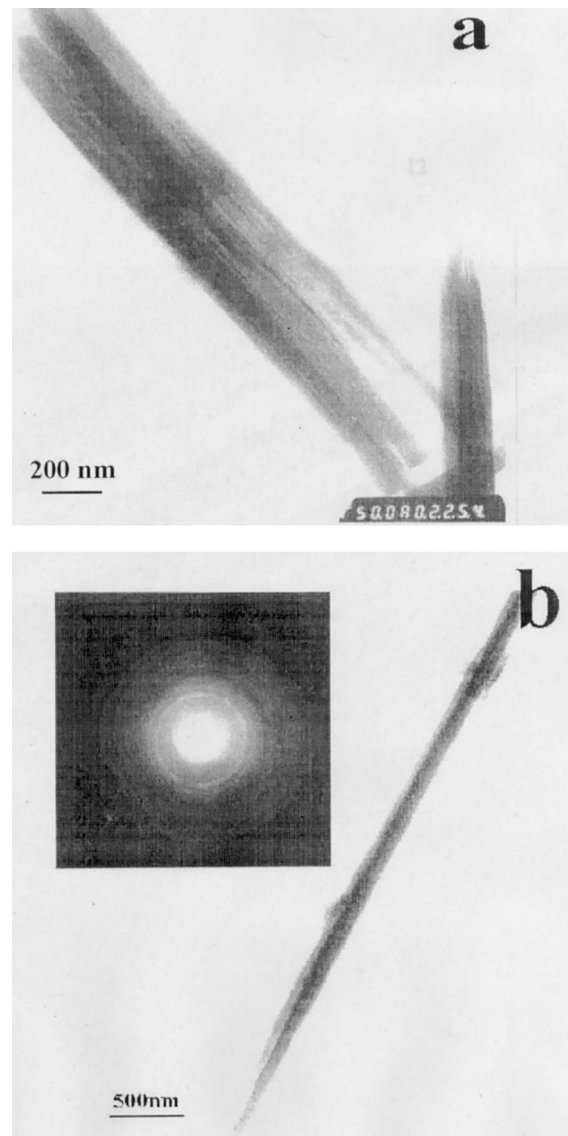


Fig. 4. TEM image of CdSe nanorods prepared by dc deposition: (a) nanorods array; (b) single nanorod of CdSe. The inset plot is the electron diffraction pattern taken from this nanorod.

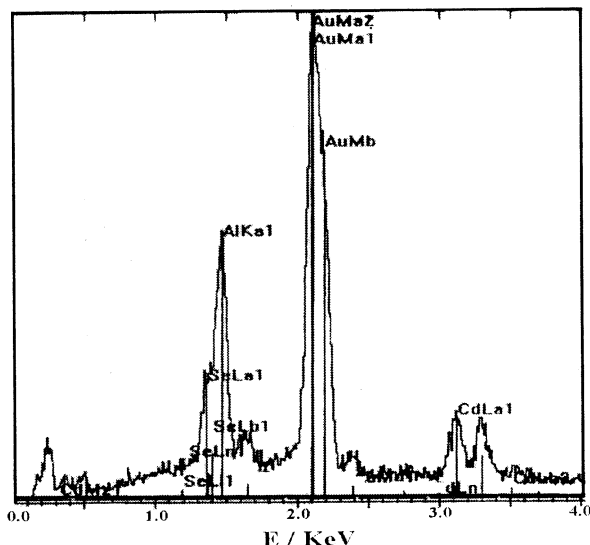


Fig. 5. EDAX spectrum of CdSe nanorods prepared by dc deposition.

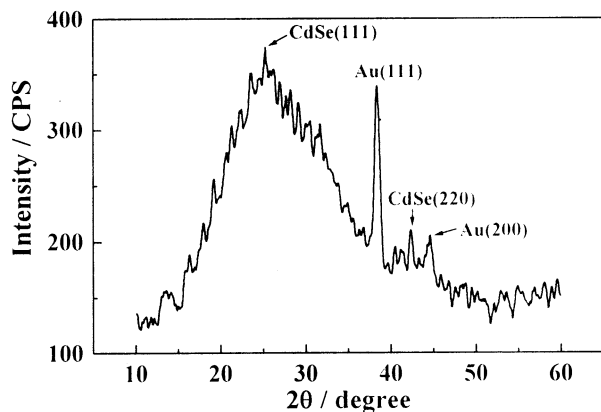


Fig. 6. XRD pattern of CdSe nanorods prepared by dc deposition.

ter of around 200 nm. The length and the diameter of these nanorods correspond exactly to that of the templates. The electron diffraction pattern taken from the CdSe nanorods is shown in the inset on the upper left of the micrograph. The diffraction spots correspond to the (111) and (220) diffraction planes a cubic CdSe crystalline.

The chemical composition of the CdSe nanorods was determined using EDAX. The EDAX analysis spectrum of CdSe nanorods is shown in Fig. 5. The peaks of element Cd and Se are found. Quantitative analysis results indicate an atomic composition of 51.3% Cd and 48.7% Se which is close to a 1:1 stoichiometry. In Fig. 5, peak of element Au was obtained because Au was sputter-covered on surface sample in ordered to provide conductivity of sample. This result also indicated that a few of Al_2O_3 were kept in the sample.

3.3. XRD spectrum

Fig. 6 shows X-ray diffraction (XRD) spectrum of the CdSe nanorods, where the diffraction peaks could be assigned to CdSe, Au and amorphous peak of AAO without element Cd and Se. These diffraction peaks of CdSe were observed closed to $2\theta = 25.3, 42.4^\circ$ corresponding to cubic (111) and (220) plane. The reason for weaker diffraction peaks of CdSe derived from a little of quantity CdSe in template and CdSe were not covered on the surface of template. EDAX results showed that surface on the template mainly were consisted of element Au and Al_2O_3 . In Fig. 6, a broader peak was observed at 2θ between 15 and 35° and it belonged to amorphous peak of AAO. This result was possible resulted in superimposition diffraction peaks of CdSe and AAO to peaks of CdSe became weak.

4. Conclusion

CdSe nanorods array were prepared using direct current potentiostatic deposition in porous anodic aluminum oxide template from aqueous containing CdSO_4 and H_2SeO_2 in $\text{pH} = 2.50$ at temperature 298 K. SEM, TEM and XRD results show that length and diameter of nanorods are uniform and CdSe nanorods are a cubic CdSe crystal. This work further proved that dc electrodeposition directly into the AAO template is a simple and efficient method of producing semiconductor nanorods arrays with well-controlled crystalline structure.

Acknowledgements

This work is supported by the National Science Foundation of China (No. 69871013).

References

- [1] V.M. Cepak, J.C. Hulteen, Che Guangli, et al., *J. Mater. Res.* 13 (1998) 3070.
- [2] S. Iijima, *Nature (London)* 354 (1991) 56.
- [3] P.R. Evans, G. Yi, W. Schwarzacher, *Appl. Phys. Lett.* 76 (2000) 481–71 (1999) 1957.
- [4] S.H. Yu, J. Yang, Z.H. Han, et al., *J. Solid State Chem.* 147 (1999) 637.
- [5] J.S. Suh, J.S. Lee, *Chem. Phys. Lett.* 281 (1997) 384.
- [6] Y.Q. Zhu, W.B. Hu, W.K. Hsu, et al., *J. Mater. Chem.* 9 (1999) 3173.
- [7] Y. Xie, P. Yan, J. Lu, Y.T. Qian, et al., *Chem. Comm.* 19 (1999) 1969.
- [8] D.P. Yu, Z.G. Bai, Y. Ding, et al., *Appl. Phys. Lett.* 72 (1998) 3485.
- [9] A. Colby Foss Jr., L. Gabor et al., *J. Phys. Chem.* 98 (1994) 2963.

- [10] T. Kyotani, B. Pradhan, A. Tomita, *Bull. Chem. Soc. Jpn.* 72 (1999) 1957.
- [11] M. Zhang, Y. Bando, K. Wada, *J. Mater. Chem.* 15 (2000) 387.
- [12] B.K. Pradhan, T. Kyotani, A. Tomita, *Chem. Comm.* 14 (1999) 1317.
- [13] J.A.M. Neto, L.C. Barbosa, C.L. Alves, *Appl. Phys. Lett.* 59 (1991) 2715.
- [14] J.D. Klein, R.D. Herrick, II, D. Palmer, et al., *Chem. Mater.* 5 (1993) 902.
- [15] N. Wang, Y.H. Tang, Y.F. Zhang, et al., *Chem. Phys. Lett.* 299 (1999) 237.
- [16] I. Serebrennikova, P. Vanysek, V.I. Birss, *Electrochem. Acta* 42 (1997) 145.
- [17] D.S. Xu, X.S. Shi, G.L. Lin, et al., *J. Phys. Chem. B* 104 (2000) 5061.
- [18] S.L. Pan, H.L. Zhang, Y. Peng, et al., *Chem. J. Chin. Univ.* 20 (1999) 1622.
- [19] C.M. Shen, X.G. Zhang, H.L. Lin, *Thin Solid Films* (submitted).