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Effects of bath temperature on the morphology of ZnO nano-rods and its optical properties

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ABSTRACT

ZnO nano-rod arrays with different morphologies were vertically grown on indium-tin oxide (ITO) glass substrates using the electrochemical deposition (ECD) method processing in a two-electrode cell. The bath temperature plays a key role in the growth process. The effect of growth bath temperature was studied with respect to the morphological, structural, and photoluminescence properties of the ZnO nano-rod arrays. The ZnO nano-rod arrays fabricated at 85 °C bath temperature had the best morphology, structural and optical qualities. The clear lattice fringes in the image of high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) showed that a single-crystal structure of ZnO nano-rods with the growth direction along the [002] direction. The top-sectional field emission scanning electron microscopy (SEM) images results revealed that the bath temperature played a key role in the morphology evolvement of the ZnO nano-rods. A sharp peak in the UV region and a weak broad peak in the visible region between 400 and 500 nm were shown in the room temperature photoluminescence (PL) spectra of the samples, suggesting that the ZnO nano-rod arrays with high-quality crystals were obtained. This synthesis method provided a low cost and easy route for the preparation of 1D ZnO nanostructures.

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1. Introduction

ZnO is a well-known semiconductor material with wide and direct band gap (3.37 eV) at room temperature. ZnO nanostructures have received broad attention due to their promising applications in the fields of sensors, solar cells, thin film transistors and light emitting diodes [1–6]. The photo-electronic properties of the ZnO devices depend on the ZnO nano-structural characteristics (size, morphology, orientation, surface-to-volume, crystalline density, ductility, corrosion resistance, and diffusion permeability) [1–6,14]. The morphology plays a crucial role in the nonlinear optical properties of the ZnO low-dimension structures [7] and the substrate plays here a crucial role. In recent years, a large variety of growth methods of one dimensional (1D) ZnO nano-rods/nanowires have been prepared [6–9]. However, the condition of vacuum, high temperature or high pressure and some complicate instruments are necessary for these synthesis methods. In addition, ZnO morphology and growth direction were not easy to control. Since direct ECD of ZnO films was reported firstly in 1996 [10], a lot of research group prepared 1D ZnO nanorods/nanowires successfully by simple ECD on various substrates [11,12]. However 1D ZnO nanostructures should be grown in three-electrode cell in which the anode electrode was made of a Pt material in ECD, and hence the cost is higher. So we used low cost silver sheet material as the anode electrode and control the morphology during ZnO growth by changing water bath temperature.

In this paper, ZnO nano-rod arrays were grown vertically on ITO glass substrates by a simple ECD method in a two-electrode cell, without the other supporting electrolyte and the reference electrode, and the anode electrode was of a silver sheet material. The ZnO morphology directly affects photoelectric properties of the devices, so we control the morphology during ZnO growth by changing water bath temperature. This experiment is aimed to discuss how water bath temperature affects the morphology of the ZnO, so we must keep the other growth parameters (such as concentration, current intensity, and growth time) constant, such as 0.003 M/L concentration of zinc nitrate, 0.2 mA/cm^2 current intensity and 30 min deposition times. The only parameter of water bath temperature was changed in the experiment, such as 50 °C, 60 °C, 70 °C, 80 °C, 85 °C and 90 °C. In addition, room temperature PL of as-prepared ZnO nano-rod arrays was also investigated.

2. Experimental

All chemicals in the experiment were of analytical reagent grade. The ECD of ZnO nanostructures was performed in a self-made two-electrode glass cell. The ECD cell was put into a water bath at 50 °C, 60 °C, 70 °C, 80 °C, 85 °C and 90 °C, respectively during whole ECD. A pure silver sheet with an area of 1.0 × 2.0 cm^2

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was used as the anode electrode, ITO substrates ($1.0 \times 2.0\ cm^2$) with ZnO seed layer were used as the cathode, and electrolyte solution was 0.003 M/L zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) aqueous solution without any supporting electrolyte. The deposition was performed at a constant current density of 0.2 mA/cm^2. The deposition times were 30 min. Finally, the as-prepared ZnO nanorod arrays were washed with deionized water, annealed at 260 °C for 2 h.

The structures of as-prepared samples were characterized by a Rigaku-TTRIII X-ray powder diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). Field emission scanning electron microscopy (FESEM) images were obtained using a JEOL JSM-7500F microscope with an acceleration voltage of 15 kV. Transmission electron microscopic (TEM), and HRTEM images were obtained on a JEOL JEM-2200FS transmission electron microscope with an acceleration voltage of 200 kV. The PL spectra were recorded on SHIMADAZU RF-5301PC spectrophotometer.

3. Results and discussion

ZnO nano-rod arrays were electrodeposited on ITO glass substrate. Field emission scanning electron microscopy (FESEM) images were obtained using a JEOL JSM-7500F microscope with an acceleration voltage of 15 kV. Fig. 1 shows top view SEM images of as-synthesized ZnO samples ECD in 0.003 M/L zinc nitrate ($Zn\ (NO_3)_2 \cdot 6H_2O$) aqueous solution of 30 mL for 30 min at 50 °C, 60 °C, 70 °C, 80 °C, 85 °C and 90 °C. The flower bud-like ZnO nanorods with stripes on their surface were formed when the water bath temperatures at 50 °C and 60 °C. For the ZnO samples prepared at higher temperatures, such as 70–90 °C, the ZnO nanorods with hexagonal shapes were clearly observed. But the ZnO nanorods with nano-particles on their surface were formed when the water bath temperature reached 70 °C. And when the samples were deposited at 90 °C, the ZnO nano-rods were disorderly. Corresponding to these SEM pictures, it is clear that the morphology of ZnO nanorods is better, when the deposition temperature is 80 °C and 85 °C, respectively. And the diameter of the ZnO nano-rods decreased with the increase of deposition water bath temperatures.

In addition to the morphological parameters, the crystal parameters are also indispensable criteria for selecting high quality ZnO nano-rods. Fig. 2 shows the XRD pattern of the as-prepared ZnO samples at various temperatures. All peaks of the samples could be indexed to the ITO and hexagonal wurtzite ZnO. From Fig. 2, we can see that the intensity of three main diffraction peaks such as (100), (002) and (101) obviously changed with the increase of deposition water bath temperatures. At the deposition temperature of 50 °C, the

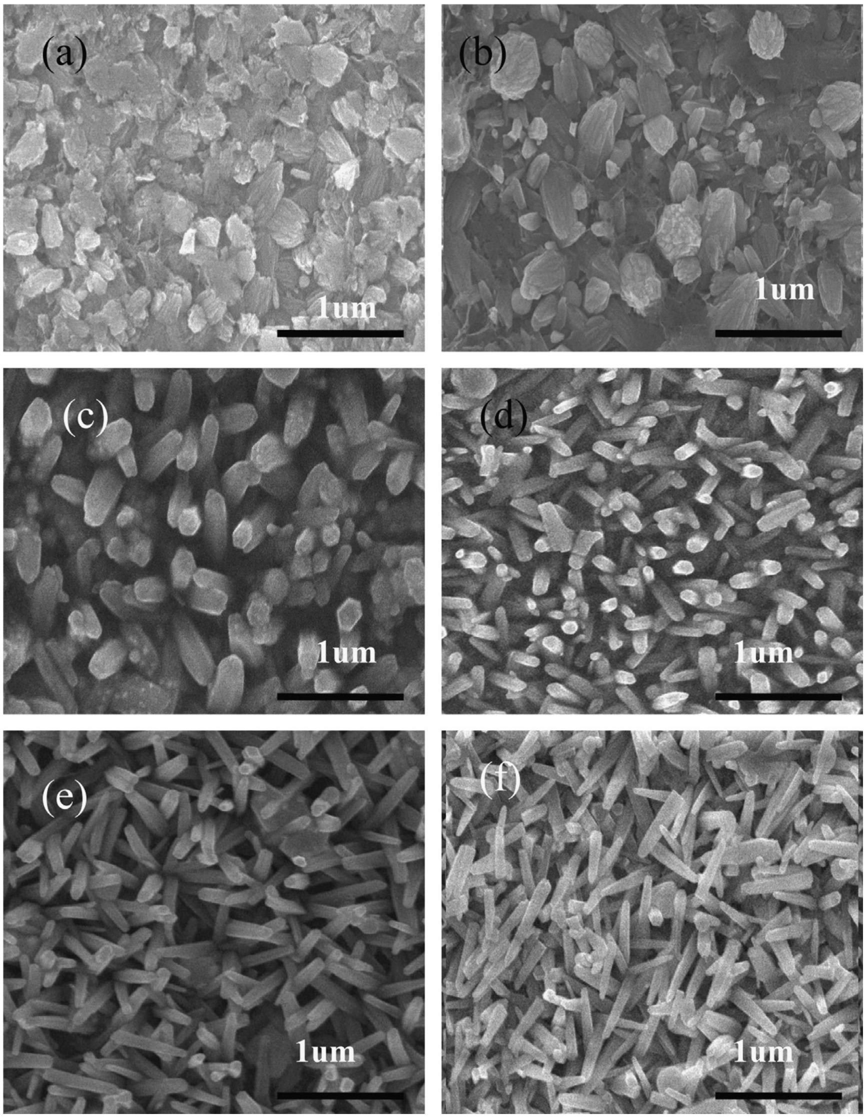

Fig. 1. SEM images of ZnO nano-rod arrays grown at different water bath temperatures: (a) 50 °C, (b) 60 °C, (c) 70 °C, (d)80 °C, (e) 85 °C, (f) 90 °C. Scale bar: 1 μm.

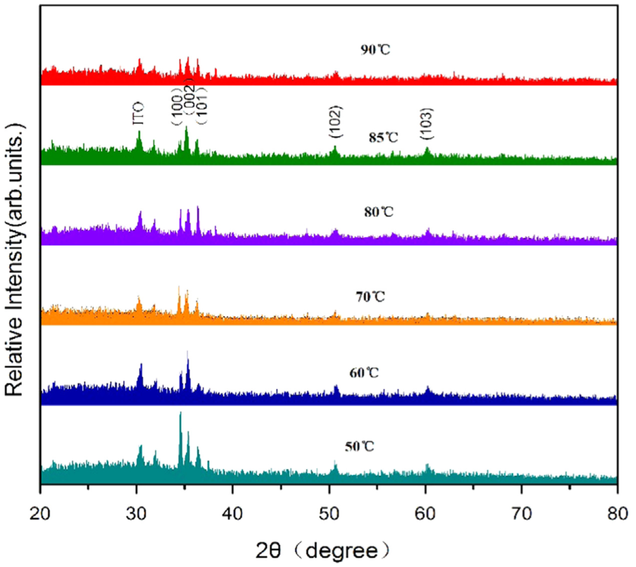

Fig. 2. XRD pattern of ZnO nano-rod arrays grown at different water bath temperatures: 50 °C, 60 °C, 70 °C, 80 °C, 85 °C and 90 °C.

flower bud-like ZnO nano-rods with preferred (100) orientation grow. The samples with preferred (002) orientation grow when the deposition temperature reaches 60 °C. The ZnO nano-rods with preferred (002) orientation grow when the deposition temperature reaches 85 °C. The higher intensity of the [002] diffraction peaks indicates that the nano-rod arrays are oriented in the *c*-axis direction and perpendicular to the ITO glass substrate at 85 °C. Corresponding to the XRD picture, it is clear that the morphology of ZnO nano-rods is the best, when the deposition temperature is at 85 °C.

To further confirm the epitaxial growth of the single crystalline ZnO nano-rod, TEM was used to characterize the ZnO nano-rod arrays grown at a bath temperature of 85 °C for 30 min using a current of 0.2 mA. (According to the SEM, XRD and room temperature PL results of the ZnO samples, we think that ZnO grown in the water bath temperature of 85 °C has the best morphology, so we selected it.). The HR-TEM image (Fig. 3) confirms that the ZnO nanorod is a single crystal structure and the spacing between two lattice planes was 0.26 nm, which is consistent with the *d* spacing of the (002) crystal planes of wurtzite ZnO.

The PL spectra were recorded on SHIMADAZU RF-5301PC spectrophotometer. Spectral resolution is 1 nm. Fig. 4 shows the PL spectra of the ZnO nanorods under different water bath temperature that were measured at room temperature by using a 350 nm excitation. The PL spectra of all samples show a sharp UV emission accompanied by a broad and weak blue green emission. The UV emission is contributed from the near band edge emission. The UV emission peaks have not shifted with increased of the deposition water bath temperatures. The UV emission peak's intensity increased with increase of the deposition water bath temperatures. But the UV emission peak's intensity instead decreased when the deposition water bath temperatures increased to 90 °C. It attributed to the morphology and growth direction of the ZnO nano-rod arrays. The broad and weak blue green emission accompanied by a blue shoulder at 480 nm, which could be ascribed to the oxygen vacancy or oxygen dangling bonds associated with the zinc vacancies [13] or intrinsic defect states. It was the deep-level emission. The deep-level emission intensity was gradual and weakly increased with the increase of the water bath temperature. It also indicates that the as-synthesized ZnO samples were of high-quality crystals from room temperature PL spectra of the samples.

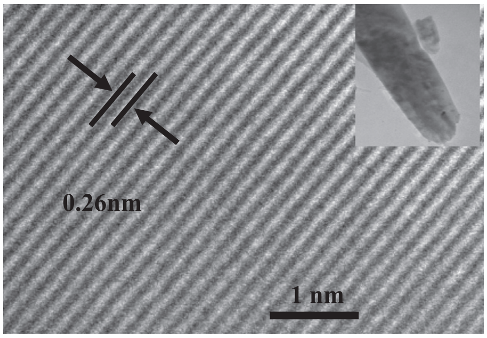

Fig. 3. HR-TEM image of the ZnO nano-rods grown at a bath temperature of 85 °C

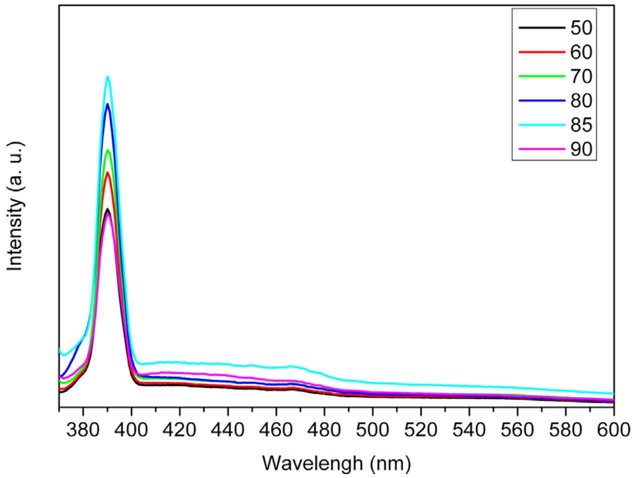

Fig. 4. PL spectrum of ZnO nano-rod arrays grown at different water bath temperatures: 50 °C, 60 °C, 70 °C, 80 °C, 85 °C and 90 °C.

According to the results and discussions above, we think that ZnO grown in the water bath temperature at 85 °C has the best morphology. And the reproducibility of the compound fabrication was very good.

4. Conclusions

In this paper, we reported the growth of vertically aligned ZnO nano-rod arrays on ITO glass substrates by a simple ECD method in a two-electrode cell without any other supporting electrolyte and the reference electrode. The bath temperature played a key role in the growth process. The results of SEM TEM and XRD pattern indicated that the ZnO nano-rod arrays grown in the water bath temperature at 85 °C has the best morphology. The samples were room temperature PL of the ZnO nano-rod arrays suggesting that the ZnO nano-rod arrays with high-quality crystals were obtained. The vertically aligned nano-rod arrays will provide an important reference for further photo-electronic devices.

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References

[1] Shi YH, Wang MQ, Can H, Yang Z, Deng JP, Song XH, et al. Sens Actuators B 2013;177:1027–34.

[2] Liu ZK, Li JH, Sun ZH, Tai GA, Lau S, Yan F. Nano 2012;6:810–8.
[3] Song B, Li CS, Li YN, Wu YL, Loutfy R. J Am Chem Soc 2007;129:2750–1.
[4] Zhang XM, Lu MY, Zhang Y, Chen L, Wang ZL. Adv Mater 2009;21:2767–70.
[5] Chen WJ, Liu WL, Hsieh SH, Tsai TK. Appl Surf Sci 2007;253:6749–53.
[6] Xiang B, Wang PW, Zhang XZ, Dayeh SA, Aplin DPR, Soci C, et al. Nano Lett 2007;7:323–8.
[7] Ebothe J, Kityk IV, Benet S, Claudet B, Plucinski KJ, Ozga K. Opt Commun 2006;268:269–72.
[8] Li ZK, Huang XT, Liu JP, Li YY, Li GY. Mater Lett 2008;62:1503–6.
[9] Cai YX, Li XW, Sun P, Wang B, Liu FM, Cheng PF, et al. Mater Lett 2013;112:36–8.
[10] Penton S, Lincot D. Adv Mater 1996;8:166–70.
[11] Lee SJ, Park SK, Park CR, Lee JY, Park J, Do YR. J Phys Chem C 2007;111:11793–801.
[12] Pauporte T, Bataille G, Joulaud L, Vermersch FJ. J Phys Chem C 2010;114:194–202.
[13] Vanheusden K, Warren WL, Seager CH, Tallant DK, Voigt JA, Gnade BE. J Appl Phys 1996;79:7983.
[14] Straumal BB, Mazilkin AA, Protasova SG, Straumal PB, Myatiev AA, Schütz G, et al. Ferromagnetism of nanostructured zinc oxide films. Phys Met Metall 2012;113(13):1244–56.