



Preparation of ZnO Nanorods Films by Electrodeposition Method†

SHI-BIAO WU*, LING XU, HAI-YAN XU, FEI-FEI LI, YE-JUN GE, WEI YAO and PAN XU

School of Materials & Chemical Engineering, Anhui Jianzhu University, Hefei 230022, P.R. China

*Corresponding author: E-mail: wsbl@ahjzu.edu.cn

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Zinc oxide nanorods films were electrodeposited on indium tin oxide glass from aqueous solution by potentiostatic method. The XRD patterns indicate the films are polycrystalline with obvious (002) preferred crystal orientations. SEM morphology proves the ZnO nanorods' growth of c axis (002) preferred orientations. The optimal preparation conditions were followings: deposition time, temperature and deposition potential were 1 h, 80 °C and -1.0V (vs. SCE), respectively; Plating electrolyte contained 0.05 mol/L $Zn(NO_3)_2$, 0.1 mol/L hexamethylenetetramine and polyethylene glycol 400 (PEG 400); the volume ratio of PEG400 dosage and final plating electrolyte was 5 % in terms of percentage.

Keywords: Zinc oxide, Nanorods, Films, Electrodeposition method.

INTRODUCTION

Zinc oxide has been used in different areas, including solar cell¹, sensor², photoluminescence material³, together with photodegradation of organic pollutant^{4,5}. One-dimensional ZnO nanorods have been widely studied because the nanorods have various merits as an active layer such as a high mobility and a high surface/volume ratio⁶. The synthesis of high-quality ZnO nanorods films with controlled microstructure for optoelectronic and electronic devices is very important topic. Presently, various techniques for high-quality ZnO nanorods films growth have been studied⁷. Electrodeposition process is a novel fabrication method⁸. However, electrodeposition method for ZnO nanorods films preparation was relatively less reported. In this work, ZnO nanorod films on ITO conductive glass substrates has been fabricated *via* a low-temperature and environment-friendly soft chemical potentiostatic method.

EXPERIMENTAL

All reagents were of analytical grade and used without further purification. The ZnO nanorods films were electrodeposited on commercial ITO glass (HYSTN80, Huayi Conductive Glass Co. Ltd. Bengbu, Anhui, PRC) substrates in potentiostat mode. All electrodeposition experiments were carried out by three-electrode cell, using Zn foil (3 cm × 3 cm), indium

tin oxide glass substrate (1 cm × 1 cm) and saturated calomel electrode (SCE) as the counter electrode, working electrode and reference electrode, respectively. The cell was powered by a potentiostat (DJS-292, Shanghai REX Instrument Factory, Shanghai, PRC). Before deposition, the substrate was cleaned by ultrasonic treatment in toluene, acetone and ethanol in turn, rinsed by distilled water and washed with deionized water, then dried in air. Afterward, it was immersed in plating electrolyte containing 0.05 mol/L $Zn(NO_3)_2$, 0.1 mol/L hexamethylenetetramine (HMT) and polyethylene glycol 400 (PEG400). The volume ratio of PEG400 dosage and final plating electrolyte was from 3 to 9 % in terms of percentage. Deposition potential was -1.0V (vs. SCE). The electrodeposition was conducted at temperature arrangement of 65-90 °C and lasted for 0.5-2 h.

After deposition, the working electrode with ZnO nanorods films sample was taken from the cell and washed with deionized water, then dried in air at room temperature. The structure and overall crystallinity in the films was characterized through θ -2 θ scans operated on a X-ray diffractometer (Y-2000, Dandong radiative instrument group Co. Ltd. Liaoning, PRC) with CuK_{α} radiation. The films' surface morphology was investigated through scanning electron microscopy on a field-emission SEM (Sirion200, FEI Company, USA) operated at 10 kV voltage value.

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RESULTS AND DISCUSSION

Structure characterization and process conditions optimization

Effect of PEG400 dosage on the phase structure of ZnO nanorods films: Fig. 1 shows different X-ray diffraction (XRD) patterns of ZnO nanorods films samples obtained with the same electrodeposition temperature and time, *i.e.*, 80 °C and 1 h. Pattern 9 %, 8 %, 7 %, ..., 3 % are corresponding to the films obtained in the plating solutions which the volume ratio of PEG400 dosage and final plating electrolyte was 9 %, 8 %, 7 %, ..., 3 % in terms of percentage, respectively. Pattern on the bottom of the figure is standard XRD pattern of ZnO with Wurtzite structure.

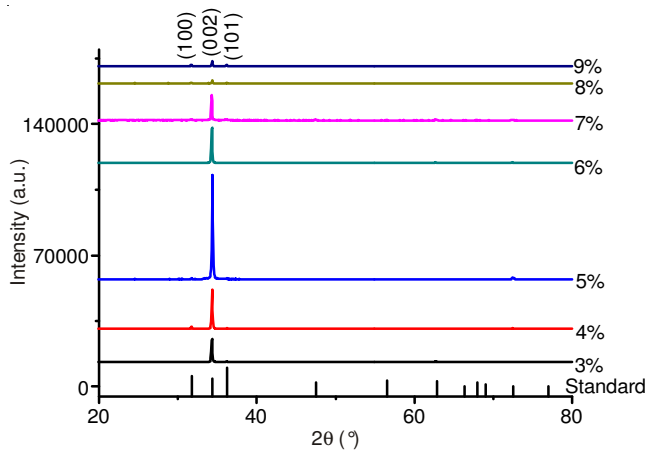


Fig. 1. Effect of PEG400 dosage on the phase structure of ZnO nanorods films

X-ray diffraction patterns are accurately accorded with the standard pattern. Strong reflections corresponding to (002) crystal plane are observed along with weaker reflections of (100), (101) and other planes of Wurtzite ZnO, indicating the films are polycrystalline with obvious (002) preferred crystal orientations. The preferred crystal orientations imply ZnO crystal grains are nanorods which longitudinal axis' direction are along with (002) orientations. Comparing XRD patterns' (002) peaks of samples in Fig. 1, it can also be observed that the film prepared with 5 % PEG400 dosage has the most strong (002) reflection peak than the others. Commonly, the strong reflection peaks imply the good degree of crystallinity⁸. According to the (002) peaks' intensity, the film deposited with 5 % PEG400 dosage has the best degree of crystallinity and optimal PEG400 dosage is 5 %.

Effect of deposition time on the phase structure of ZnO nanorods films: Fig. 2 shows different XRD patterns of ZnO nanorods films samples deposited at the same process conditions of the optimal sample in Fig. 1 except deposition time. Pattern 2.0, 1.5, 1.0 and 0.5 h are corresponding to the deposition time 2, 1.5h, 1 h and 0.5 h, respectively. On the whole, the films showed obvious growth of c axis (002) preferred orientations and good crystallinity. Comparing XRD patterns' (002) peaks in Fig. 2, it can also be observed that the film deposited for 1h has the most strong (002) reflection peak than the others. According to the (002) peaks' intensity, the

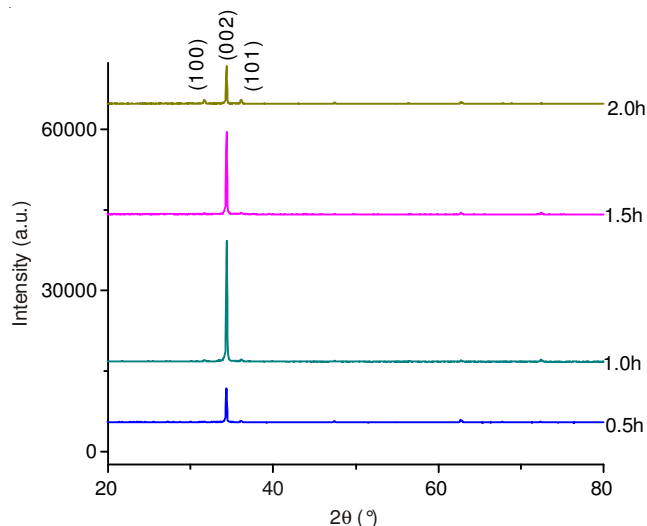


Fig. 2. Effect of deposition time on the phase structure of ZnO nanorods films

film deposited for 1 h has the best degree of crystallinity and optimal deposition time is 1 h.

Effect of deposition temperature on the phase structure of ZnO nanorods films: Fig. 3 shows different XRD patterns of ZnO nanorods films samples deposited at above process conditions except deposition temperature. From top to bottom, patterns are corresponding to the deposition temperature 90, 85, 80, 75, 70 and 65 °C, respectively. Comparing XRD patterns' (002) peaks in Fig. 3, it can be observed that the film deposited at 80 °C has the most strong (002) reflection peak than the others. According to the (002) peaks' intensity, the film deposited at 80 °C has the best degree of crystallinity and optimal deposition temperature is 80 °C.

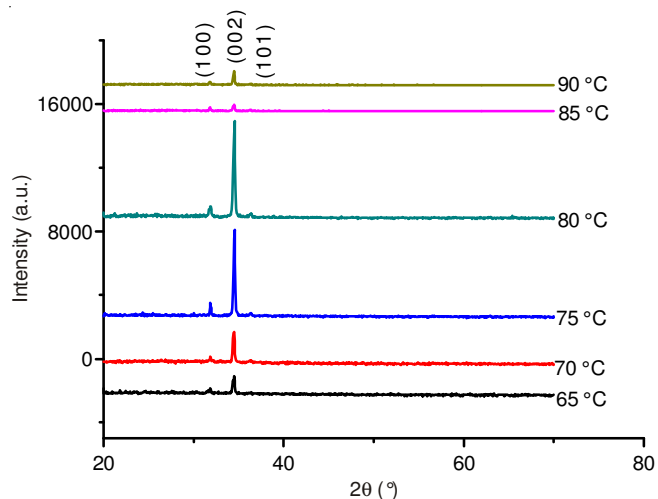


Fig. 3. Effect of deposition temperature on the phase structure of ZnO nanorods films

In a word, the optimal process conditions were as flowing: deposition time, temperature and deposition potential were 1 h, 80 °C and -1.0 V (*vs.* SCE), respectively. The plating electrolyte contained 0.05 mol/L Zn(NO₃)₂, 0.1 mol/L HMT and PEG400 which the volume ratio of PEG400 dosage and final plating electrolyte was 5 % in terms of percentage.

Morphology characterization and discussion: Fig. 4 shows the top-view SEM image of the ZnO film deposited on ITO substrate under the optimal process conditions as above. In the image, it can be seen that the uniform and dense film is constituted of nanorods which are right hexagonal prisms. These prisms have similar shape and size and the size is 1300 nm \times 130 nm in length and diameter. The slim prisms prove the ZnO nanorods' growth of c axis (002) preferred orientations. The ZnO film's XRD pattern is showed in Fig. 3 (80 °C). The most strong (002) reflection peak are accorded very well with the nanorods' growth of (002) preferred orientations.

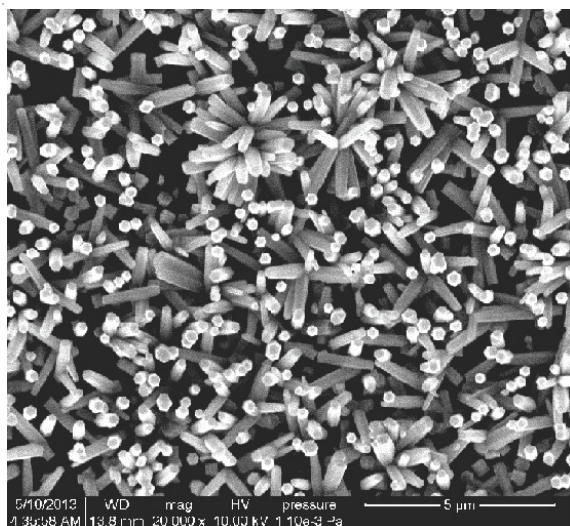


Fig. 4. SEM image of ZnO nanorods film deposited on ITO substrate under the optimal process conditions as above

Conclusion

In summary, a low-temperature and environment-friendly soft chemical electrodeposition technique has been success-

fully applied to fabricate ZnO nanorods films on ITO substrates. Because of conveniences, the potentiostatic mode is applied to deposition process. The optimal preparation conditions were followings: deposition time, temperature and deposition potential were 1 h, 80 °C and -1.0 V (*vs.* SCE), respectively; the plating electrolyte contained 0.05 mol/L Zn(NO₃)₂, 0.1 mol/L HMT and PEG400 which the volume ratio of PEG400 dosage and final plating electrolyte was 5 % in terms of percentage. The XRD patterns indicate the films are polycrystalline with obvious (002) preferred crystal orientations. SEM morphology characterization proves the ZnO nanorods' growth of c axis (002) preferred orientations.

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