

Preparation of ZnO Thin Films by Galvanostatic Method†

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Zinc oxide films were electrodeposited on ITO glass from aqueous solution containing 0.2 mol/L zinc nitrate using galvanostatic method. The morphology was characterized by scanning electron microscopy. The structure of the films was investigated with XRD method. The electrodeposition process conditions are followings: electric cell temperature is 60 °C; current density is 5-10 mA/cm².

Key Words: ZnO, Electrodeposition, Galvanostatic method.

INTRODUCTION

Zinc oxide, as one of most popular *n*-type semiconductor oxides, is a versatile material with a wide band gap of *ca.* 3.37 eV and having a Wurtzite structure. It is a proper semiconductor for solar cell fabrication due to its suitable optical properties¹. It is an attractive solar cell window layer material since it is transparent. Therefore, the synthesis of high-quality ZnO thin film material with controlled microstructure for optoelectronic and electronic devices is very important topic. Presently, various techniques for high-quality ZnO thin film growth have been studied²⁻⁵. Electrodeposition process is a novel fabrication method^{6,7}. There were quite a few process carried out in potentiostatic mode. However, galvanostatic mode was relatively less reported. In this work, well defined nanostructured ZnO films with unique morphologies on ITO conductive glass substrates have been fabricated simply by using aqueous solution containing zinc nitrate instead of any toxic and expensive reagents *via* a low-temperature and environment-friendly soft chemical galvanostatic method.

EXPERIMENTAL

All reagents were of analytical grade and used without further purification. The thin films were electrodeposited on commercial ITO glass (HYSTN80, Huayi Conductive Glass Co. Ltd. Bengbu, Anhui, PRC) substrates in galvanostatic mode. 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 the plating electrolyte which contained 0.2 mol/L Zn(NO₃)₂. The electrodeposition

was conducted at 60 °C and 5 or 10 mA/cm² in a two-electrode arrangement using a Zn foil as the counter electrode and the substrate as working electrode. The counter and working electrodes areas were 3 cm × 3 cm and 1 cm × 1 cm, respectively. The two-electrode cell was powered by a manostat (WYJ. 5A 30V) which was selected for experimental simplicity as the electrolyte was conductive sufficiently that its iR loss was not a concern. The distance between the working and counter electrode was maintained at 5 cm and the plating operation lasted for 20 min. Subsequently, the working electrode with film 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 film was characterized through θ -2 θ scans operated on a Y-2000 X-ray diffractometer (XRD) with CuK α radiation. Surface morphology was investigated through scanning electron microscopy (SEM) on a Sirion 200 field-emission SEM operated at 5 kV voltage value.

RESULTS AND DISCUSSION

Current density is the key parameter to control the thin film electrodeposition during the processing, since it plays important role of deposition speed as well as adjusting working electrode's potential value. A series of experiments with various value of current density has been investigated. The results show that white ZnO thin films have been obtained as the current density arranging from 5-10 mA/cm² at 60 °C for 10 min with the electrolyte which contained 0.2 mol/L Zn(NO₃)₂. The thin films were all uniform, crack-free and pore-free. Fig. 1 shows the top-view SEM images of the films obtained.

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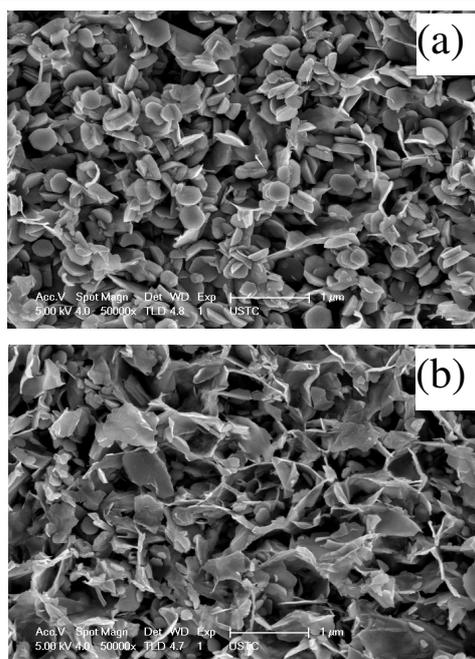


Fig. 1. SEM images of the films obtained with current density of (a) 5, (b) 10 mA/cm²

In image (a), it can be seen that the uniform and dense film is constituted of crystalline grains which are like hexagonal plates. These plates have similar shape and thickness and its size is about 300 nm × 200 nm in diameter and height. The plates stack up tightly resulting in an uncertain orientation. The morphology of sample (b) is obviously different from the sample (a). In image (b), it can be seen that film is constituted of crystalline grains like amorphous sheets without simple and regular shape. Comparing SEM images of (a) and (b) samples in Fig. 1, it can be observed that variation of current density in the deposition system has notably effect on determination of micro-morphology of the deposited ZnO thin films. Because the higher current density results in more irreversible electro-deposition process, the film prepared with 10 mA/cm² is more amorphous than with 5 mA/cm².

Fig. 2 shows different XRD patterns of the obtained thin film samples with different current density. Pattern (a) and (b) are corresponding to two films obtained with current density of (a) 5, (b) 10 mA/cm², respectively. Pattern (c) is standard XRD pattern of ZnO with wurtzite structure.

Peaks on the XRD patterns (a) are accurately accorded with the standard pattern. Strong reflections corresponding to (100), (002) and (101) planes are observed along with weaker reflections of (102), (110), (103) and (112) planes of Wurtzite ZnO, indicating the films are polycrystalline without obvious preferred orientation. On the XRD patterns (b), there are very weak peaks which are not like the patterns (a) at all, indicating the films are amorphous. Comparing XRD patterns of (a) and (b) samples in Fig. 1, it can also be observed that the film prepared with 10 mA/cm² is more amorphous than with 5 mA/cm².

Conclusion

In summary, a low-temperature and environment-friendly soft chemical deposition technique has been successfully applied to fabricate ZnO thin films. Because of simplicity, the

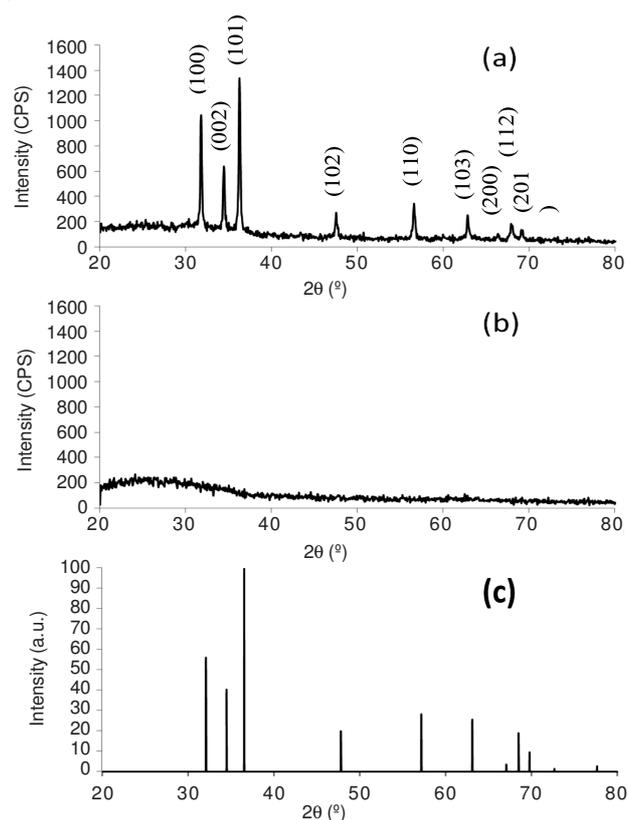


Fig. 2. XRD patterns of the films obtained with current density of (a) 5, (b) 10 mA/cm²

galvanostatic mode is applied to deposition process. The results show that ZnO thin films can be electrodeposited as current density arranging from 5-10 mA/cm² at 60 °C for 10 min with the electrolyte which contained 0.2 mol/L Zn(NO₃)₂. Current density is the key parameter to the film deposition. Hexagonal plate-like morphology can be obtained at 5 mA/cm², while amorphous sheet-like morphology has been obtained at 10 mA/cm². The ZnO thin films *via* a simple galvanostatic method may have potential applications such as optical-electric functional materials and thin films catalysis, *etc.*

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