

The aggregation structure of flat pentagonal flake ZnO films by electrodeposition method

Chunyu Liu¹, Yongjian Chen¹, Haining Cui^{1, a*}, B. Marí², Rong Wang^{1, b,*}

¹ Department of Optical Information Science and Technology, College of Physics, College of Zhaoqing (526061), Jilin University, Changchun(130012), P. R. China

² Departament de Física Aplicada-IDF. Universitat Politècnica de València, Camí de Vera s/n, 46022 València, Spain

^acuihaining2009@126.com, ^bWangr@jlu.edu.cn

Keywords: electrodeposition; ZnO films; pentagonal flake structure; column structure; Energy Dispersive X-ray Spectroscopy (EDX).

Abstract. Since transparent conducting oxides can be as a bottom layer of complex film electrodes, electrodeposition technique may produce ZnO films depending on variety conditions and modified surface layers of substrates in electrochemical procedures. Here we invested the structure and morphologies of ZnO films by using modified surfaces of the substrate-ZnO:Ga(sputtered) / glass.

Introduction

Zinc oxide (ZnO) is one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region, owing to a direct wide band gap and a large exciton binding energy. It has been shown that ZnO thin films can be deposited electrochemically and that the films produced are of high structural quality [1]. ZnO layer made by electrodeposition method is for potential application of grade material and semiconductor junction devices. As we know, control of morphology and structures of oxides are of great importance for above applications and their implementation on technological devices. Zinc oxides had be obtained in different structures such as Pentagonal ZnO nanorods, hexagonal ZnO collunms, sheet nano-zinc oxide crystals with a hexagonal, pentagonal, rectangular or an irregular form etc.[2]. Different temperatures, solute and post-annealing for fabrication and characterations of ZnO films were systematically investigated by authors. In this paper, We will focus the structure of ZnO films, especially pentagonal flake structure, relation of morphologies and the surface of substrates.

Experimental Details

In the electrodeposition procedure of ZnO films a three electrode electrochemical cell is need. It contains a aqueous solution with 25 mM (or 5 mM) ZnCl₂ and 100 mM KCl as supporting electrolyte and dissolved oxygen at 90 0C temperature[3]. The conducting substrate was set up as a working electrode and was located near the referential cathode at approximately 1cm. A potentio/galvanostat was used to keep a constant potential (-0.70 V) during the deposition. During the electrodeposition process four main growth variables- molarity ratios of solution, concentration of the solution, potential and modified surface of substrates have been controlled at a fixed time and temperature. The modified surface layer ZnO:Ga of one substrate- ZnO:Ga /glass used is ZnO layer made by reactive magnetron sputtering on glass.

Scanning electron microscopy (SEM) images and quantitative elemental analysis were obtained by using a JSM 6300. The content ratio of elements in the film was obtained by means of Energy Dispersive X-ray Spectroscopy (EDX). For structural characterization it has been measured by an high-resolution X-ray diffraction (XRD) in the Θ -2 Θ configuration with a copper anticathode (CuK α , 1.54 Å). Optical properties were monitored by transmittance using a Xe lamp and in association with a 500 mm Yvon-Jobin HR460 spectrophotometer using back-thinned CCD detector optimized for the UV-VIS range. Photoluminescences (PL) measurements were carried out at 6k-300k temperature using a He-Cd Laser as a light source at an excitation wavelength of 325 nm.

Results and Discussion

Morphology and structures of ZnO films. Generally electrochemical procedures permit the synthesis of ZnO films on different morphologies depending on the solute, concentrations of the solutions, temperature, PH value, and electrical potential ,etc. Until now , these have been systematically investigated. In order to know that the variant morphologies of synthesised ZnO films depending on the surface of substrate, here the different modified surfaces of substrates has been used in the electrochemical method. We found a regularity of the film growth about the effect of the substrate mainly.

The sample A were prepared at aqueous solvent with 25 mM ZnCl_2 , 100 mM KCl , -0.7 V potential and 90 °C temperature for Fig.1, and the sample B with 5 mM ZnCl_2 ,etc. for Fig.2 . Fig.1 shows some SEM images of these kinds of ZnO films on ZnO:Ga / glass substrates with a grow process in different deposition time (690s, 950s and 2800s) or charge accumulation from 0.1C to 1.0 C . SEM reveals an aggregation of flat pentagonal flake which looks like ZnO quasi-3D structures consisted of quasi-nanowalls in Fig 1. These quasi-nanowalls are half tilted to and half predominantly normal to the substrate. These pentagonal flakes that grew up on the surface of the first basic layer do not exhibit ordered pattern and build up the quasi-3D structure. Fig.2 reveals that there are no an aggregation of flat pentagonal flake structure in SEM images of these kinds of ZnO films (sample B) on ZnO:Ga / glass substrates, and only some scatter particles.

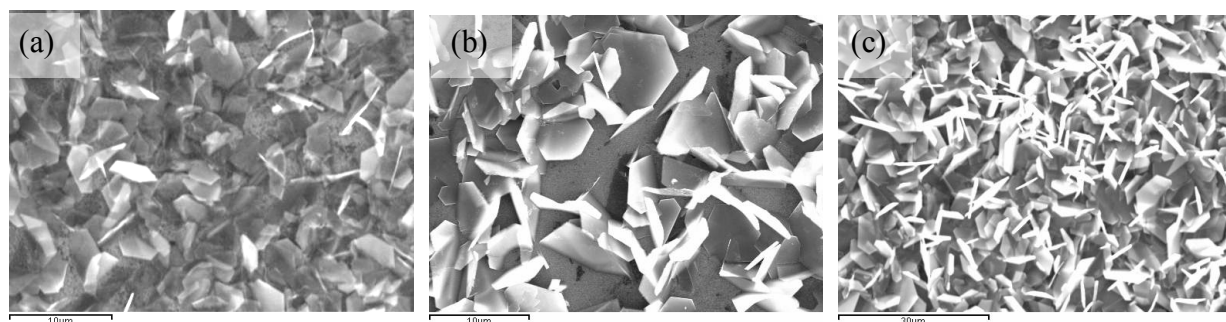


Fig.1.SEM images of ZnO films (sample A) grown in different deposition time on ZnO:Ga (sputtered)/glass substrate. (a) 690s, SEM: $\times 40000$, scale : 10 micrometers; (b) 950 s, SEM: $\times 40000$, scale : 10 micrometers; (c) 2800 s, SEM: $\times 15000$, scale : 30 micrometers.

EDS analysis was selected in the suitable position of SEM photo image. The EDS spectra of ZnO grow process about Fig.1 are measured and their representative spectrum for Fig. 1(b) is shown in Fig.3. They show us different atomic percentage of O and Zn in ZnO grow process in different time 690s, 950s and 2800s for (a)- (c) respectively. The atomic percentage of O and Zn is 59.77% and 23.32% for deposition time from of 690s. The atomic percentage of O and Zn is 65.99% and 29.72% for deposition time from of 950s. The atomic percentage of O and Zn is 74.88% and 21.64% for deposition time from of 2800s. All data indicates that there is larger intrinsic – Zinc vacancy (V_{Zn} , Acceptors). The reason is possibly due to possibly the initial formation of an hydroxides in the solution, which would slowly dehydrates. In fact zinc hydroxide forms at room temperature by precipitation of Zn^{2+} by OH^- addition [4] , and it means and suggests that the film is $\text{Zn}(\text{OH})_2$. This is why finally the zinc oxide film with V_{Zn} forms and grows. From above it can be deduced that atomic percentage of O and Zn in ZnO grow process is varied. At the beginning, Zinc vacancy is dominant ; in the middle of deposition time the dominant Zinc vacancy decreases ; later Zinc vacancy becomes dominant once again. These can be proved by PL study, the 440nm PL peak comes from V_{Zn} will decrease for the increasing deposition time from 690s-950s.

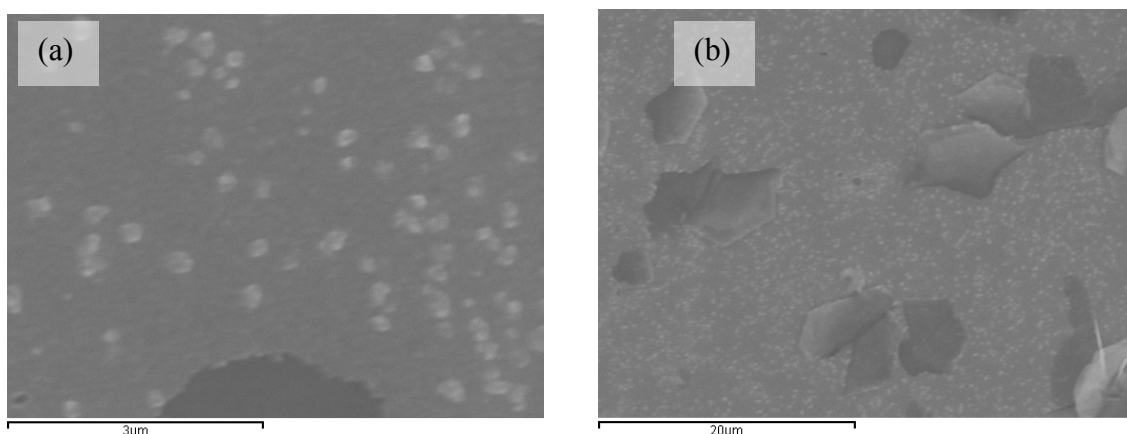


Fig.2. SEM images of ZnO films (sample B) grown on ZnO:Ga (sputtered)/glass substrate for $Q=-0.3$ C. (a) SEM: $\times 20000$, scale : 3 micrometers; (b) SEM: $\times 3000$, scale : 20 micrometers.

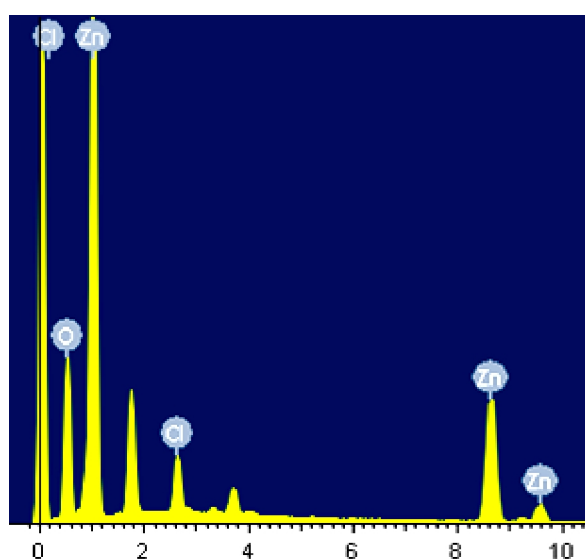


Fig.3 Energy Dispersive X-ray Spectroscopy (EDX) and the quantitative elemental analysis of ZnO thin films (sample A) grown in 950 s. All elements are analyzed (normalised).

Conclusion

The ZnO on modified surfaces of substrates such as ZnO:Ga(sputtered) /glass were prepared by the electrochemical method. We carried out the experiments by adjusting concentration of the solution, potential, substrate and deposition time. The combination of the effect of solution and potential on the growth of the film, the aggregation structure of flat pentagonal flake ZnO films is obtained . EDS analysis and its spectrum show us that atomic percentage of O and Zn in ZnO grow process is varied and there is larger intrinsic – Zinc vacancy (V_{Zn} , Acceptors) state in the deposited ZnO films.

Acknowledgements

We acknowledge partial financial supports from Jointly Funded Project (No. 61179055) of Chinese Civil Aviation Authority and National Natural Science Foundation of China, Talent Grant (2013-ZQXY-05) of Educational Commission of Guangdong Province, China.

References

- [1] T. Pauport'e, R. Cort'es, M. Froment, B. Beaumont, D. Lincot, *Chem. Mater.* 14 (2002) 4702.
- [2] Zhifeng Liu, Zhengguo Jin, Jijun Qiu, Xiaoxin Liu, Weibing Wu and Wei Li , Preparation and characteristics of ordered porous ZnO films by a electrodeposition method using PS array templates, *Semicond. Sci. Technol.* 21 No 1 (January 2006) 60-66.
- [3] M. Tortosa, M. Mollar, B. Marí, *Journal of Crystal Growth* 304, 97 (2007) 97-102.
- [4] G.Deroubaix, P.Marcus, *Surf.Interf.Anal.*18(1992)39.