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

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Abstract. Since transparent conducting oxides can be as a buttom 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 different modified surfaces of the substrate- ITO/ glass, FTO/ glass and ZnO(DMSO)/ITO/ 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 ZnCl2 and 100 mM KCl as supporting electrolyte and dissolved oxygen at 90 ^{0}C 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 of one substrate- ZnO(DMSO)/ITO/ glass used is ZnO film made by dimethylsulfoxide (DMSO) electrodepositing on ITO (indium tin oxide)/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-2Θ configuration with a copper anticathode (CuKα, 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

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.

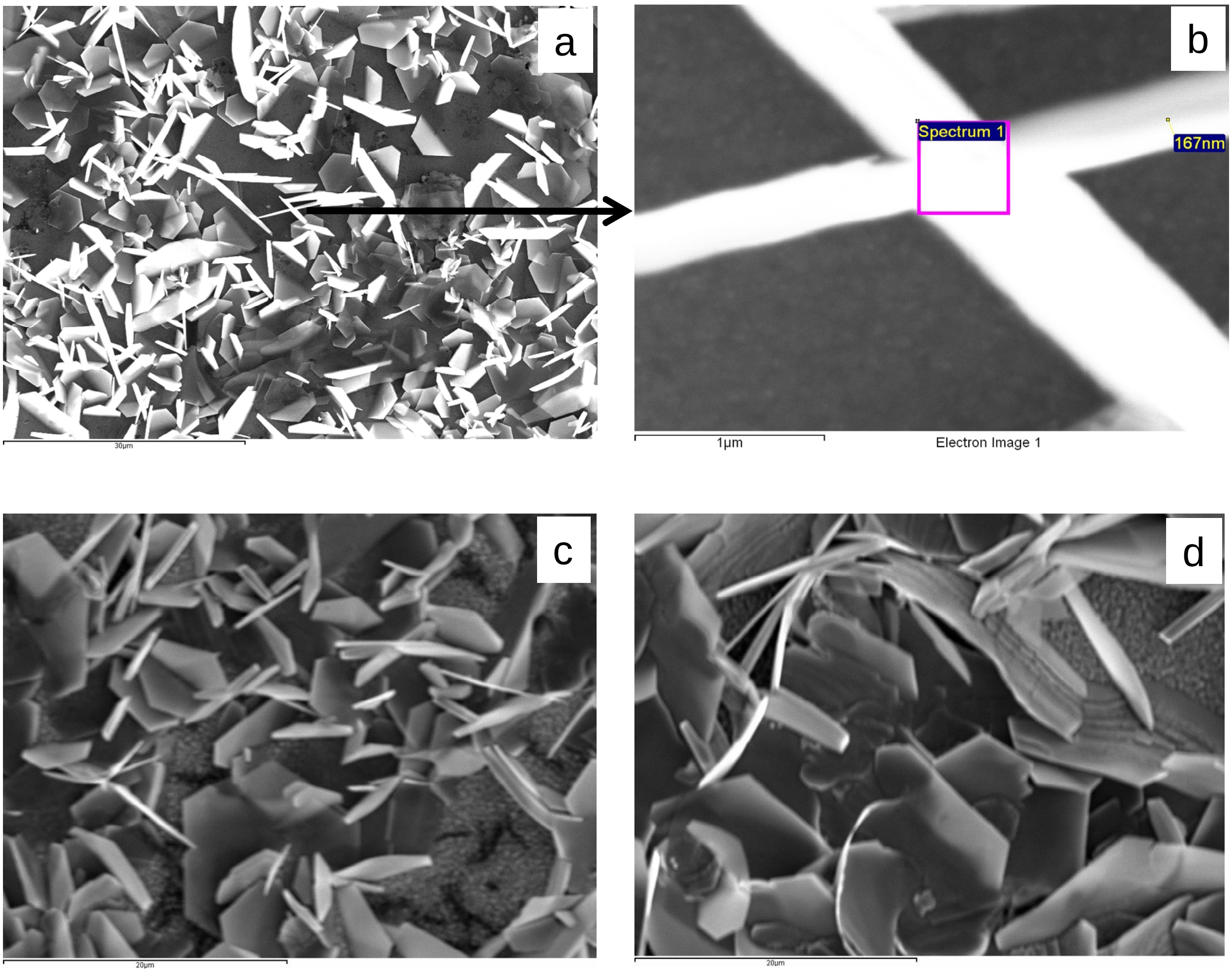

Fig.1 SEM images of ZnO films prepared on the different surfaces of substrates. (a) ITO/glass, SEM: × 4000, scale : 30 micrometers ; (b) further zoom of photo (a) and a selected red square position for EDS analysis, SEM: × 40000, scale : 10 micrometers ; (c) FTO/glass, SEM: × 3000 , scale : 20 micrometers; (d) ZnO(DMSO)/ITO/glass, SEM: × 3000 , scale : 20 micrometers.

Fig.1 shows some SEM images of these kinds of ZnO films on ITO/ glass, FTO/ glass, ZnO(DMSO) ITO/glass substrates. SEM reveals an aggregation of flat pentagonal flake which looks like ZnO quasi-3D structures consisted of quasi-nanowalls in Fig 1(a), and curve pentagonal flake in Fig 1 (c) , (d). 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 ITO layer do not exhibit ordered pattern and build up the quasi-3D structure. The thickness of the flakes or walls is approximately 160 nm in Fig 1(b) and one edge size of a pentagonal flake is about 3.16 μm in Fig 1(a).

EDS analysis was selected in the photo of SEM and its spectrum is shown in Fig.3. In its spectrum atomic percentage of O and Zn is 76.72% and 23.28% respectively. It indicates that there is larger intrinsic – Zinc vacancy (Vzn, 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 Zn $(OH)_2$. This is why finally the zinc oxide film with Vzn forms and grows.

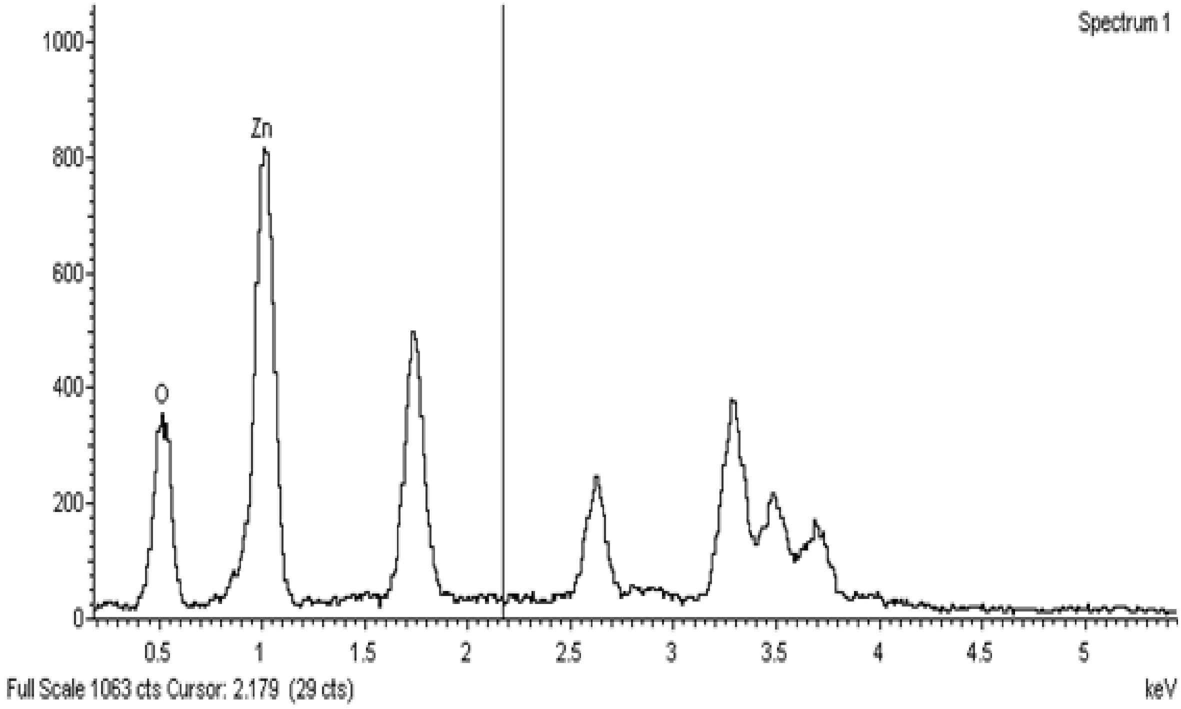

Fig.2 Energy Dispersive X-ray Spectroscopy (EDX) and the quantitative elemental analysis of ZnO thin films for a selected red square position in SEM image of Fig. 1(b). All analyzed elements are normalized.

Generally it is realized that micro structure of ZnO film is of more functional and PL may gives much information about relation of the structure. There are various models being proposed to explain the complex PL band of ZnO materials. A strong PL emission peak at 370 nm is the intrinsic PL emission of ZnO crystallites due to the near band-edge emission (NBE) . It had mostly been attributed to the radiative transition between electron (in conduction band) and hole (in valence band) recombination process, of course it corresponds to the bound exciton (BE). PL spectra of the ZnO thin films from the temperature of 6 k to 300 k were measured. Two broadening PL emissions at 350-440 nm and 471-770 nm, which belong to broader NBE and deep level emission (DLE) respectively, are observed. Comparing previous results of PL band of ZnO, it is deduced that the broad NBE band shows two components—one band centred around 370 nm (3.351 eV) and another one centred around 420 nm in the range.

Conclusion

The ZnO on modified surfaces of substrates such as ZnO/ITO/polymer-PEN and ZnO doped Ga/ITO/polymer-PEN 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 controlled aggregation structure of flat and curve pentagonal flake of ZnO is obtained by us.

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