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Effect of acetic acid on ZnO:In transparent conductive oxide prepared by ultrasonic spray pyrolysis

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ABSTRACT

Undoped and indium doped zinc oxide (ZnO) transparent conductive oxide were prepared by a low-cost Ultrasonic Spray Pyrolysis. The influence of acetic acid on properties of the ZnO thin films was investigated. The complex formed by [CH_3COO^-] and [Zn^{2+}] in precursor solution was better for the growth of ZnO film. The acetic acid added in precursor solution can supply [CH_3COO^-] for both [Zn^{2+}] and [In^{3+}] to form complexes. That made the [Zn^{2+}] and [In^{3+}] have similar statement, which can promote the indium doping in the ZnO films. The surface morphology, structural and electrical properties of the ZnO thin films were influenced by the acetic acid adding. The total transmittance of the ZnO thin films is above 80% in the wide wavelength region from 400 nm to 2000 nm.

1. Introduction

The most prominent advantage of ZnO is that it is a II–VI semiconductor with a wide and direct band gap of about 3.37 eV at room temperature and a high exciton binding energy of 60 meV. ZnO films have been extensively investigated either as a transparent conductive oxide or as a semiconductor for solar cells and electronic applications [1,2] due to its features such as high electrical conductivity, optical transparency, easy preparation, and high stability in hydrogen plasma. Metal organic chemical vapor deposition (MOCVD) [3,4] and sputtering [5,6] are commonly utilized to prepare ZnO thin films. However, the cost is relativity high. Ultrasonic spray pyrolysis (USP) has received extra attentions because of its simplicity, suitability for product industrialization, and low-cost. Utilizing USP to prepare ZnO-TCO has more potential than it is commonly recognized. Doping with indium can improve the electrical properties of sprayed ZnO thin films [7–11]. In addition, substrate temperature [12], annealing [13,14] and the pH of precursor solution [15] have important influences on electrical, structural and optical properties of ZnO thin films. The acetic acid was commonly utilized to avoid the precipitation of Zn–OH species [16] and change the pH of precursor solution [15]. But lack detailed studies concerning the effect of acetic acid on the undoped and indium doped ZnO thin films by USP. Therefore, the research on the effect of acetic acid can help us further understand the USP method for preparing the ZnO thin film.

In this paper, in order to study the effect of acetic acid on sprayed-ZnO thin films, the undoped and indium doped ZnO films with different acetic acid adding in the precursor solution are prepared by USP. The effects of acetic acid on the pH value of the precursor solution and the properties of the undoped ZnO thin films are investigated. Moreover, the influence of acetic acid on the electrical and structural properties of the indium doped ZnO thin films is investigated too. The optical properties of the ZnO films are reported.

2. Experimental details

The films were deposited by USP on corning eagle 2000 glass substrates. A 0.2 mol/L solution of zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] diluted in ethanol and deionized water (3:1) was used for the films preparation. For the undoped ZnO thin films, the acetic acid was added in the zinc acetate solution in the volume proportion, which was increased from 0 to 10 vol.% by the step of 1 vol.%. For the indium doped ZnO (ZnO:In) thin films, indium acetate [$In(CH_3COO)_3$] was added in the precursor solution after the acetic acid was added. The doping ratios [In]/[Zn] were 1 and 2 at.%. For the 1 at.% indium doped ZnO thin films, the acetic acid content in the total precursor solution was 4, 6, 7, 9 and 11 vol.%. For the 2 at.% indium doped films, the acetic acid was added at 14, 15, 17, 18 and 19 vol.%. The total volume of the precursor solution increased slightly with the acetic acid adding because the volume of zinc acetate solution was fixed.

After the corning eagle 2000 substrate was heated to 750 K, the aerosol of the precursor solution was nebulized by an ultrasonic agitation with 1.7 MHz, and transported into the growth chamber by air at a flow rate of 11 L/min. The growth time of all the thin films was 60 min.

The surface morphology of thin films was observed by a field emission scanning electron microscope (FE-SEM, JSM-6700F). The [In]/[Zn] ratios in the ZnO:In thin films were determined by Energy

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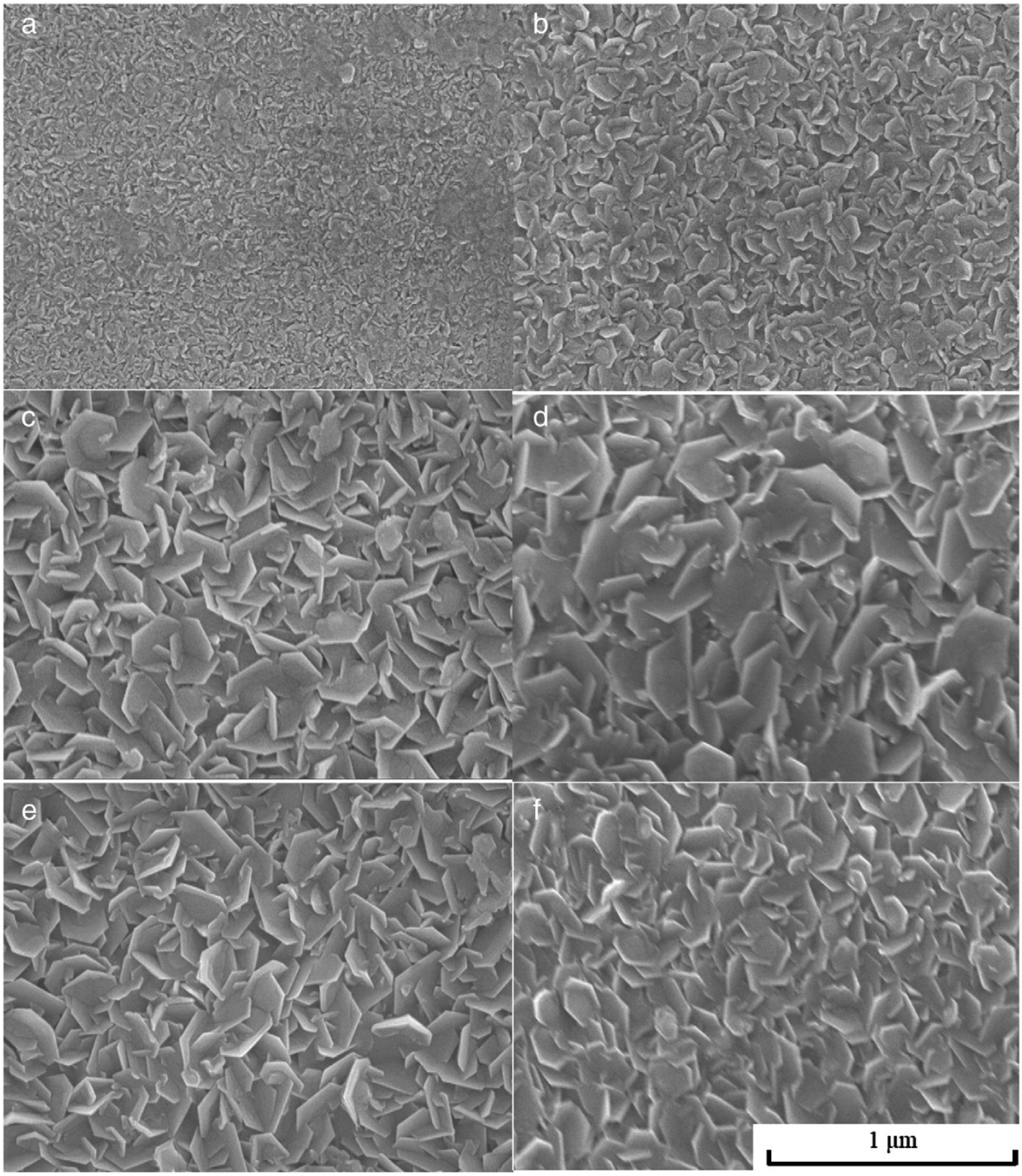

Fig. 1. SEM images of the undoped ZnO with different acetic acid added in the precursor solution. (a) 0 vol.%, (b) 2 vol.%, (c) 4 vol.%, (d) 5 vol.%, (e) 6 vol.%, and (f) 8 vol.%.

dispersive X-ray spectroscopy (EDS). The electrical properties were obtained by Hall-effect measurements using van der Pauw method (Accent HL5500 PC). X-ray diffraction (XRD, X'Derpro Co. $\lambda_{Cu} = 1.542$ Å) analysis was performed to investigate the crystallographic structure of the ZnO:In thin films. The optical transmittance of these films was evaluated by UV–visible–NIR spectrometer (Cary 5000 UV–VIS produced by Varian Company). All the structural, electrical and optical measurements were executed at room temperature.

Table 1
Grain size of the undoped ZnO and ZnO:In with different acetic acid added.

Undoped ZnO		1 at.% In doped ZnO thin films		2 at.% In doped ZnO thin films	
Acetic acid adding (vol.%)	Grain size (nm)	Acetic acid adding (vol.%)	Grain size (nm)	Acetic acid adding (vol.%)	Grain size (nm)
0	23.69	4	25.20	14	31.65
2	31.58	6	31.65	15	31.65
4	37.90	7	41.79	17	48.31
5	53.01	9	32.60	18	31.66
6	38.25	11	31.65		
8	37.89				