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Studies on the structural, electrical and optical properties of Al-doped ZnO thin films prepared by chemical spray deposition

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Abstract

Aluminium-doped zinc oxide films have been prepared by chemical spray pyrolysis technique. Variation of structural, morphological, electrical and optical properties with doping concentration is investigated in detail. The films were highly transparent to visible radiation and electrically conductive. XRD studies have shown that the films were polycrystalline in nature with (0 0 2) preferred orientation. SEM studies have revealed the smooth polycrystalline morphology of the films. Films deposited at optimum conditions have exhibited a resistivity of 2.45×10^{-4} Ωm with an optical transmittance of 97% at 550 nm.

Keywords: Zinc oxide films; Aluminium doping; Spray pyrolysis; Transparent conducting films

1. Introduction

Zinc oxide (ZnO) is a multifunctional material with a wide area of applications. ZnO films have attracted considerable attention because they can be made to possess high electrical conductivity, high infrared reflectance and high visible transmittance. Low resistive zinc oxide films have been achieved by doping with different Group III elements like aluminium, boron, indium, gallium or with Group VII elements like fluorine [1–8]. Many techniques including evaporation, chemical vapour deposition, spray pyrolysis, sputtering, etc., can be employed to deposit these films [9–14]. For thin film applications like solar cell fabrication, spray pyrolysis technique is found attractive as it can deposit layers on large areas and provides itself easy to automation. The properties of the deposited material can be varied and controlled by proper optimization of spraying conditions.

In spray pyrolysis technique, low resistive ZnO films are obtained either by post-deposition heat treatment in vacuum or by hydrogen atmosphere or by adding donor impurities, such as aluminium or indium. In the present study, aluminium-doped zinc oxide (AZO) films have been prepared by using spray pyrolysis technique. The effects of aluminium doping on the structural, electrical and optical properties of AZO films have been reported.

2. Experimental

Aluminium-doped zinc oxide films were deposited on glass substrates by spray pyrolysis technique. The deposition method involves the decomposition of an aqueous solution of zinc acetate (0.1 M). The dopant concentration (Al/Zn at.%) was varied from 0 to 1.5 at.%. The resulting solution was sprayed onto the heated substrates at a constant temperature of 450 ± 5 °C. The temperature of the substrate was monitored by a chromel–alumel thermocouple close to the substrates. Compressed air was used as the carrier gas. To enhance the conductivity as-deposited films were annealed at 300 ± 5 °C

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for 90 min under a vacuum of 10^{-5} mbar. Films from acetate solution having molarity 0.2 and 0.4 M were also deposited at the optimum impurity concentration keeping the process parameters constant. The apparatus and deposition details have already been reported [15,16].

Characterization of the films was carried out using a Philips PW 1710 X-ray diffractometer (XRD) and a JOEL 35C scanning electron microscope (SEM). Film thickness was measured by the Tolansky's interferometric method. The resistivity studies were carried out using a four-probe set-up and the transmission studies using a Shimadzu double beam spectrophotometer UV240.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the X-ray diffraction patterns of AZO films with different aluminium concentrations deposited at substrate temperature 450 ± 5 °C. All the peaks in the pattern correspond to the hexagonal structure of ZnO powder sample and are indexed according to the ASTM data card 5-664. No phase corresponding to aluminium/aluminium oxide or other aluminium compound was detected in the XRD patterns. The preferential orientation of all films is found to be along (0 0 2) crystal plane. The other peaks observed in the X-ray diffractograms were (1 0 0), (1 0 1), (1 0 2), (1 0 3) and (1 1 2). Undoped ZnO films have exhibited (0 0 2) crystal plane preferential orientation [14]. An analysis has been carried out for the preferred orientation planes of the investigated thin films. The results have revealed the existence of the preferred (0 0 2) orientation with the *c*-axis perpendicular to the substrate surface. Such preferred basal orientation is typically observed in aluminium-doped ZnO films [17–19]. The lattice constants calculated from the most prominent peaks and the ratio of relative intensities $I(0\,0\,2)/I(1\,0\,1)$ in the diffraction pattern of AZO films at 450 ± 5 °C for different dopant concentrations are given in Table 1. The lattice constants calculated are found to be in good agreement with ASTM data for ZnO powder. The texture coefficient is calculated to describe the preferential orientation using the expression [20]:

$$\mathrm{TC}(h\,k\,l) = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{N_r^{-1}\sum_{N_r} I(h\,k\,l)/I_0(h\,k\,l)} \quad (1)$$

where I is the measured intensity and I_0 is the measured standard intensity. The texture coefficient is calculated for the crystal planes (0 0 2) and (1 0 1). The value of the texture coefficient indicates the maximum preferred orientation of the films along the diffraction plane, meaning that the increase in preferred orientation is associated with increase in the number of grains along that plane. Fig. 2 represents the variation of TC(0 0 2) and TC(1 0 1) of ZnO films prepared at 450 ± 5 °C using 0.1 M zinc acetate solution for different aluminium concentrations.

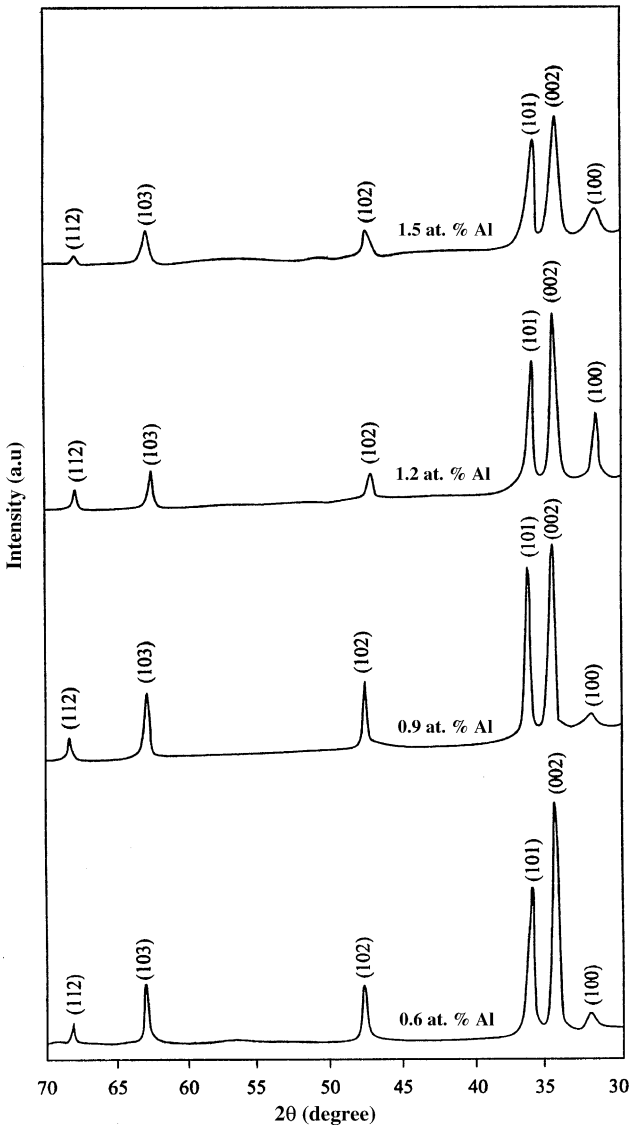

Fig. 1. XRD patterns of AZO films spray deposited at 450 ± 5 °C using 0.1 M zinc acetate solution with different aluminium concentrations.

Fig. 3 shows the X-ray diffractograms of AZO films deposited with different amounts of zinc acetate in the precursor solution. The preferential orientation of the AZO

Table 1
Lattice constants and $I(0\,0\,2)/I(1\,0\,1)$ ratios of zinc oxide films deposited at a substrate temperate 450±5 °C for different aluminium doping concentrations

Aluminium dopant concentration (at.%)	Lattice constants		Relative intensity $I(0\,0\,2)/I(1\,0\,1)$
	a_0 (nm)	c_0 (nm)	
0.6	0.3250	0.5198	1.628
0.9	0.3253	0.5202	1.098
1.2	0.3253	0.5208	1.311
1.5	0.3256	0.5200	1.167
ASTM	0.3249	0.5205	0.560