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Physical properties of ZnO thin films deposited by spray pyrolysis technique

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Abstract

Thin films of ZnO have been prepared on glass substrates at different thicknesses by spray pyrolysis technique using 0.2 M aqueous solution of zinc acetate. X-ray diffraction reveals that the films are polycrystalline in nature having hexagonal wurtzite type crystal structure. The resistivity at room temperature is of the order 10^{-2} Ω cm and decreased as the temperature increased. Films are highly transparent in the visible region. The dependence of the refractive index, n, and extinction coefficient, k, on the wavelength for a sprayed film is also reported. Optical bandgap, E_g, has been reported for the films. A shift from $E_g = 3.21$ eV to 3.31 eV has been observed for deposited films.

Keywords: ZnO thin films; Spray pyrolysis; Structural; Electrical resistivity; Optical properties

1. Introduction

ZnO is a very interesting material for many different applications in both microelectronic and optoelectronic devices. It is a wide-bandgap oxide semiconductor with a direct energy gap of about 3.37 eV. As a consequence, ZnO absorbs UV radiation due to band-to-band transitions, while it can be used as transparent conductive oxide (TCO) thin films, mainly for applications such as solar cells, liquid crystal displays and heat mirrors [1–4]. Furthermore, ZnO is used as semiconducting multilayers, photothermal conversion system, gas sensors and optical position sensors [5]. From all the oxide materials studied, in the last years, zinc oxide (ZnO) has emerged as one of the most promising materials, due to its optical and electrical properties, high chemical and mechanical stability, together with its abundance in nature, which makes it a lower cost material when compared to the most currently used transparent conductive oxide materials (ITO and SnO_2). In order to improve the properties of the films, several techniques such as sputtering [6,7], thermal evaporation [8] and spray pyrolysis [9] have been applied for the production of ZnO. Spray pyrolysis technique is preferred among these techniques due to their cheaper, simpler and more versatile than the others, which allow the possibility of obtaining films with the required properties for different applications and also when large area of the films are needed.

In this work, thin films of ZnO are prepared by spray pyrolysis technique using a solution of zinc acetate with a concentration of 0.2 M dissolved in deionised water mixed with methanol in the ratio of 1:3. Structural, electrical and optical characterizations of the films have been carried out.

2. Experimental details

The spray pyrolysis is a cheap and simple technique based on chemical vapour deposition process (CVD). In this technique, the precursor of the material to be deposited is in solution and sprayed onto a heated substrate using air as carrier gas. The apparatus we used for our sprayed process is diagrammed in Fig. 1, and has been described in references [10,11]. The ZnO thin films were prepared by spraying a solution of zinc acetate (A.R. grade) with a concentration of 0.2 M dissolved in deionised water mixed with methanol in the ratio of 1:3 with spray rate of 5 ml/min. Slides of glass microscope ultrasonically cleaned were used as the substrates to support the ZnO films. The substrate temperature was kept over the heater at 420 °C and controlled by 871 digital Kethley thermometer connected to the heater.

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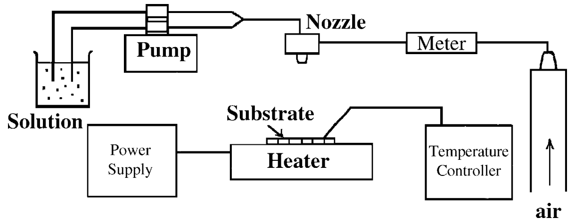

Fig. 1. Schematic diagram of the spraying system.

JEOL (model 60 PA) X-ray diffraction (XRD) system was used to determine the film structure. The analysis was made with Cu Kα radiation in the range of 30–70° with slow scanning speed (2°/min) and step width of 0.02°. The electrical resistivity of the prepared films was measured in the temperature range of 75–300 K by the Van der Pauw's method [12] in conjunction with the corresponding correction tables [13]. The conductivity type was identified by the hot point probe method. The optical characteristics of the ZnO films were measured with a Shimadzu spectrophotometer (model UV-3101PC) in the range from 200 nm to 1200 nm.

3. Results and discussion

3.1. Structural characteristics

ZnO films prepared without any doping show n-type structure. Possible reasons for this are donor formation by oxygen vacancies and interstitial zinc atoms [14]. XRD pattern of ZnO film prepared by spray pyrolysis at substrate temperature of 420 °C and spray rate at 5 ml/min is shown in Fig. 2. The peaks of the XRD were observed between 30° and 70°.

The presence of diffraction peaks indicates that the film is polycrystalline with a hexagonal wurtzite type crystal structure, and no amorphous phase is detected. It is revealed that the sprayed film has peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) directions of the hexagonal ZnO crystal structure.

Also, the XRD measurements revealed that all the sprayed films show a preferred growth orientation along *c*-axis, i.e. (1 0 0) plane, which is perpendicular to the substrate (Fig. 2). Lokhande and Uplane [1] obtained ZnO films prepared by similar technique (spray pyrolysis) with preferred orientation along (1 0 0) plane. While others [7,15,16] reported different orientation of the crystallites with (0 0 2), (1 0 3) and (1 0 1) reflections displaying the higher intensities when they used sputtering, pulsed laser deposition (PLD) and vapor condensation techniques for preparing ZnO thin films. On the other hand, Wang et al. [17] obtained polycrystalline ZnO films in hexagonal wirtzite structure without preferred orientation when they used thermal oxidation of Zn metallic films in air.

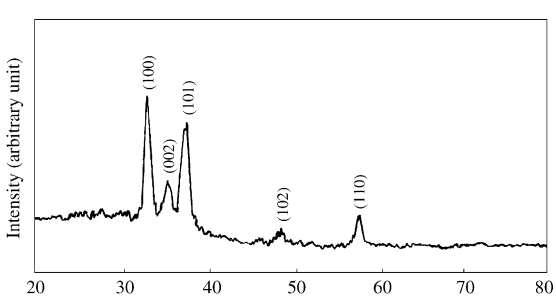

Fig. 2. X-ray diffractogram of sprayed ZnO thin film (t = 300 nm, T_S = 420 °C and R = 5 ml/min).

The d value, that is the interplanar spacing of (1 0 0) plane, of the film was evaluated from the position of (1 0 0) peak from the XRD data. The observed d value is 0.279 nm, which is in good agreement with the standard d value (0.2815 nm) taken from the Joint Committee of Powder Diffraction Standards (JCPDS) card file data [18]. The decrease in cell volume indicates disorder, which may be due to residual compression stresses in the film and/or substitution of elements of small size for elements of larger size [19,20]. Slow scan of XRD having step size 0.02° was used to calculate the grain size (D) using Scherrer's relation [21]:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where the constant k is the shape factor usually equal 1, λ the wavelength of the X-ray, θ the Bragg's angle and β is the width of half maxima. The grain size of the sprayed ZnO film is estimated to be around 20 nm. The XRD peak can be widened by internal stress and defects, so the mean grain size estimated by this method is normally smaller than the actual value.

3.2. Electrical behaviour

The resistivity of ZnO films depends on two parameters, the temperature and the solution flow rate. The resistivity of all the ZnO films sprayed under different conditions is ranging between $1.0 \times 10^{-2}\ \Omega$ cm and $2.6 \times 10^{-2}\ \Omega$ cm and this in agreement with other works [22,23]. The dependence of resistivity on substrate temperature and the spray rate of 5 ml/min is fixed is shown in Fig. 3. The minimum value of resistivity of about $1.35 \times 10^{-2}\ \Omega$ cm has been obtained at 420 °C substrate temperature. As shown from this figure, the electrical resistivity is influenced with the substrate temperature.

Fig. 4 shows the dependence of electrical resistivity on spray rate varying from 5 ml/min to 16 ml/min (the substrate temperature being kept constant at 420 °C). It is clear that the resistivity of ZnO films shows weak dependence on spray rate in the range investigated. At higher spray rate (above 5 ml/min), the films tend to be powdery in nature, for this we preferred to use lower flow rate (5 ml/min). The films of ZnO exhibited semiconducting behaviours with n-type and the resistivity was measured using aluminium contacts on the zinc oxide surface. Current–voltage curves show straight line characteristics and this indicate that the contacts are ohmic.

Fig. 5 shows the variation of the resistivity of ZnO films sprayed at 420 °C and spray rat at 5 ml/min as a function of