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Physical properties of Ga-doped ZnO thin films by spray pyrolysis

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ABSTRACT

Gallium doped zinc oxide (GZO) thin films were prepared using the simple, flexible and cost-effective spray pyrolysis technique. The physical properties of the films were studied as a function of increasing gallium dopant concentration from 1 to 9 at.%. The films were characterized by various methods to understand their structural, morphological, optical and electrical properties. The X-ray diffraction analysis revealed that the films were polycrystalline in nature having a hexagonal wurtzite type crystal structure with a preferred grain orientation in the (0 0 2) direction. Scanning electron microscopy (SEM) measurements reveal that the surface morphology of the films changes continuously with a decrease in the grain size due to Ga doping. All the films showed nearly 90% of transparency in the entire visible region. A blue shift of the optical band gap was observed with an increase in Ga doping. Room temperature photoluminescence (PL) measurement of the deposited films indicates incorporation of Ga in ZnO lattice. At 3 at.% Ga doping, the film has lowest resistivity of 6.8×10^{-3} cm while the carrier concentration is highest.

1. Introduction

Zinc oxide (ZnO) is the subject of increasing interest in the last few years owing to its potential applications in ultraviolet (UV) optoelectronic devices [1,2], transparent conducting oxide (TCO) thin films [3,4] and spintronics [5]. For the design and realization of ZnO-based devices, one of the most relevant issues is doping. This issue is especially important for the applications of ZnO as TCO, which necessarily involves the heavy doping with trivalent elements from the group III. By means of doping, large conductivities combined with large ranges of transparency in the visible (VIS) and near UV range are obtained [6,7]. Much effort has been devoted to the development of an alternative to indium based transparent electrodes because of the scarcity of its principal component, indium. Tin doped indium oxide (ITO) is indeed the most widely used TCO for flat panel display (FPD) or solar cell applications. However, indium is a very expensive material and ITO is less stable in hydrogen plasma. Therefore, impurity doped zinc oxide (ZnO), such as Al or Ga-doped ZnO, has recently gained much attention [8–12] as an alternative material to ITO. Ga-doped ZnO (GZO) is more stable with respect to oxidation due to gallium's greater electronegativity in comparison with aluminium [13]. It has also been reported that heavily Ga-doped ZnO is more stable when subjected to moisture than Al-doped ZnO [14]. Moreover, recent studies have reported the use of ZnO as an air stable anode in an OLED, providing additional evidence of GZO as a promising TCO for organic device applications [15]. It is believed that the introduction of Ga can increase free electron density by replacing the host atoms (Zn) [16]. The substitution of Ga is possible due to the smaller radius of Ga (0.062 nm) compared with Zn (0.083 nm). Several approaches have been proposed and developed for the preparation of Ga-doped ZnO thin films such as magnetron sputtering [17], spray pyrolysis [18], metal-organic chemical vapour deposition (MOCVD) [19], pulsed laser deposition (PLD) [20], arc plasma evaporation [21], dip-coating [22] and ion plating [23]. Among these, spray pyrolysis is one of the most used methods. Spray pyrolysis has been developed as a powerful tool to prepare various kinds of thin films such as metal oxides, superconducting materials, and nanophase materials. In comparison with other chemical deposition techniques, spray pyrolysis has several advantages such as high purity, excellent control of chemical uniformity, and stoichiometry in multi-component system. Other advantages of the spray pyrolysis method are that it can be adapted easily for production of large-area films, and to get varying band gap materials during the deposition process.

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In this work, we report the structural, optical and electrical properties of the transparent conducting GZO thin films prepared by spray pyrolysis method. We sought optimum deposition conditions yielding GZO films with desired physical properties, specifically good crystalline quality microstructure, low resistivity and high transparency.

2. Experimental details

Spray pyrolysis is an effective method for the deposition of thin films of metallic oxides, as is the case with the GZO material. The precursor solution for spray pyrolysis was prepared by dissolving an appropriate amount of zinc acetate dihydrate and gallium nitrate in the mixture of deionized water and ethanol at room temperature. In this mixture, ethanol concentration was 10 ml in 100 ml solution. A few drops of acetic acid were added to aqueous solutions to prevent the formation of hydroxides. The concentration of gallium was varied from 1 to 9 at.%. The total concentration of the solution was maintained at 0.1 mol l^{-1}. The glass substrates were cleaned thoroughly with acetone, isopropanol and finally with deionized water with the help of an ultrasonic bath. The nozzle was at a distance of 20 cm from the substrate during deposition. The solution flow rate was held constant at 3 ml/min. Air was used as the carrier gas, at the pressure of 2 bar. When aerosol droplets close to the substrates, a pyrolytic process occurs and highly adherent GZO films were produced. The GZO thin films were deposited at substrate temperature at 623 K with 200 nm thickness.

The thickness was measured using Stylus profile meter. The structural properties were studied by X-ray diffraction measurements (XRD) using Rigaku D/Max ULTIMA III diffractometer with CuK_α radiation ($\lambda = 1.5406$ Å). The average dimensions of crystallites were determined by the Scherrer method from the broadening of the diffraction peaks. The optical measurements of the ZnO thin films were carried out at room temperature using shimadzu UV-1700 Spectrophotometer in the wavelength range 300–1100 nm. PL measurements were performed using the 325 nm line from a Xenon pulse lamp as the excitation source and a UV–vis photomultiplier tube were used to detect the PL signals. JEOL JSM 35 electron microscope was used to record SEM micrographs. Electrical properties, namely resistivity, Hall mobility, and carrier concentration were measured at room temperature using a standard Hall measurement system (Ecopia, Model: HMS-3000) in van der Pauw configuration.

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the XRD patterns of the as-prepared ZnO thin films doped with different Ga concentrations. All the films show the existence of a very strong peak corresponding to (0 0 2) and weak peaks corresponding to (1 0 0), (1 0 1) reflections of the wurtzite phase of ZnO. Apart from ZnO characteristic peaks, no peaks that correspond to either gallium, zinc or their complex oxides could be detected. This observation suggests that the films do not have any phase segregation or secondary phase formation. It is also observed that the full width at half maximum (FWHM) of the peak corresponding to the (0 0 2) reflection increases with Ga incorporation in the films. The FWHM value increases from 0.1333° to 0.1759° as Ga doping concentration increases from 1 to 9 at.%. These results indicate that increasing Ga doping concentration could degrade the crystallinity of the GZO films due to small crystallites in the films. The crystallite size '*P*' is calculated using Scherrer's formula [24,25]:

$$P = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

where β is the broadening of the diffraction line (FWHM) and λ is the X-ray wavelength. The instrumental broadening effect has been removed by using the XRD pattern of a standard silicon sample. It is seen that as doping increases the crystallite size decreases up to 9 at.% as shown in Table 1. The preferential or random growth of polycrystalline thin films can be understood from calculating the texture coefficient TC (*h k l*) for all planes. The texture coefficient is calculated using the following equation [25]:

$$TC(hkl) = \left(\frac{I_{(hkl)}/I_{r(hkl)}}{\left[1/n \sum I_{(hkl)}/I_{r(hkl)}\right]} \right) \tag{2}$$

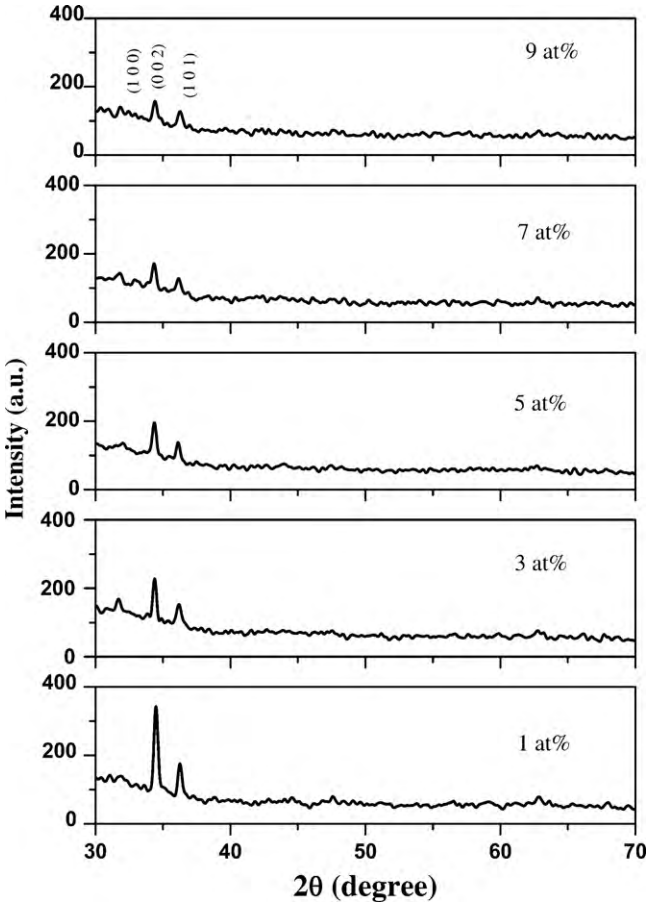

Fig. 1. XRD patterns of GZO thin films with various Ga concentrations.

where $I_{(hkl)}$ indicate the X-ray diffraction intensities obtained from the films, and n is the number of reflections observed in the XRD pattern. $I_{r(hkl)}$ is the intensity of the reference diffraction pattern(JCPDS card 75-0576). It is clear from the definition that the deviation of texture coefficient from unity implies the film growth in preferred orientation. Table 1 shows the variation of the texture coefficient with variation of Ga doping concentration for the (0 0 2) plane. The texture coefficient for all the films has a relatively (>1) higher value along the (0 0 2) plane. It can be concluded that the crystallites are preferentially oriented along the (0 0 2) plane. Moreover, the intensity of the (0 0 2) peak gradually decreases with the increase in the Ga content in the films. This behaviour indicates that the increase in the doping concentration deteriorates the crystallinity of the films, which may be attributed to the influence of stresses arising from the difference in the ionic radii of zinc and gallium [26]. Assuming that the broadening of the diffraction peak ($W_{2\theta}$) is due to both crystallite size and strain, the variance of 2θ values can be written as

$$W_{2\theta} = \left[\frac{\lambda\sigma}{2\Pi^2 P \cos\theta}\right] + 4\tan^2\theta \left\langle \varepsilon^2 \right\rangle \tag{3}$$

where σ is the angular range over which the intensity is appreciable and $\langle\varepsilon^2\rangle$ is the mean squared strain. Dislocation density 'ρ' is defined as the length of the dislocation lines per unit volume of the crystal [27]. Williamson and Smallman [28] suggested a method of calculating the dislocation density using the expression:

$$\rho = \left[\frac{\sqrt{12}\left\langle \varepsilon^2 \right\rangle^{1/2}}{Pd}\right] \tag{4}$$