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Annealing induced reorientation of crystallites in Sn doped ZnO films

K. Ravichandran *, M. Vasanthi, K. Thirumurugan, B. Sakthivel, K. Karthika

Post Graduate & Research Department of Physics, AVVM Sri Pushpam College (Autonomous), Poondi, Thanjavur 613 503, Tamil Nadu, India

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ABSTRACT

Tin doped ZnO thin films were prepared by employing a simplified spray pyrolysis technique using a perfume atomizer and subsequently annealed under different temperatures from 350 °C to 500 °C in steps of 50 °C. The structural, optical, electrical, photoluminescence and surface morphological properties of the as-deposited films were studied and compared with that of the annealed films. The X-ray diffraction studies showed that as-deposited film exhibits preferential orientation along the (002) plane and it changes in favour of (100) plane after annealing. The increase in crystallite size due to annealing is explained on the basis of Ostwald ripening effect. It is found that the optical transmittance and band gap increases with increase in annealing temperature. A slight decrease in resistivity caused by annealing is discussed in correlation with annealing induced defect modifications and surface morphology.

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1. Introduction

Nowadays, researches on the fabrication of transparent conducting oxide (TCO) thin films have been increased much [1,2]. Among the TCOs, ZnO is gaining much attention due to its wide band gap ($E_g \sim 3.3$ eV), high exciton binding energy (60 meV), possession of high optical transmittance and lower electrical resistivity at room temperature along with low cost, non-toxicity and abundance in nature [3,4]. These films find applications in several devices like conductive gas sensor [5], solar cells [6,7], light emitting diodes (LEDs) [8,9], thin film transistors (TFTs) [10,11], optical communication systems [12,13], heat mirrors [14,15], cathodoluminescence devices [16], flat panel displays [17], photocatalysts [18,19] and non-linear optical devices [20,21].

Undoped and doped ZnO films can be fabricated using various methods, such as, thermal evaporation [22], sol–gel [23], Successive Ionic Layer Adsorption and Reaction (SILAR) [24], Chemical Bath Deposition (CBD) [25], RF sputtering [26] and spray pyrolysis technique [27]. Of these, spray pyrolysis is a simple and inexpensive technique for large area coatings [28].

Hence, it is necessary to investigate the growth orientation and recrystallization of ZnO structures for the development of ZnO based devices suitable for various technological applications. Nanocrystalline ZnO films with (100) preferential orientation find applications in non linear optics [29]. Similarly, ZnO films grown along (002) plane found to be suitable for piezoelectric applications [30].

In this work, Sn doped ZnO films with (100) orientation have been fabricated using a simplified spray pyrolysis technique and the annealing induced variations in their properties have been analysed and reported. To the best of our knowledge, reports on Sn doped ZnO films with (100) preferential orientation is seldom available in the literature.

2. Experimental details

2.1. Preparation of ZnO:Sn films

Tin doped ZnO thin films have been deposited onto glass substrates using a simplified spray technique by employing a perfume atomizer, generally used for cosmetics. The precursor solution was prepared by dissolving 0.2 M of zinc acetate dihydrate $Zn(CH_3COO)_2{\cdot}2H_2O$ and 6 at.% of tin (II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$) in a mixture of de-ionized water and ethanol in the ratio of 3:2. A few drops of acetic acid were added to get a clear solution. The starting solution was stirred thoroughly using a magnetic stirrer, for one hour and the solution was sprayed onto the hot glass substrates maintained at a temperature of 330 ± 5 °C using a chromel–alumel thermocouple. The nozzle to substrate distance was kept as 30 cm. The other process conditions adopted in this work are presented in Table 1.

* Corresponding author. Tel.: +91 04362 278602, mobile: +91 9443524180; fax: +91 4374 239328.
E-mail addresses: kkr1365@yahoo.com, kkravi1365@gmail.com (K. Ravichandran).

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Table 1
Deposition parameters employed in this study.

Solvents	De-ionized water + ethanol (3:2) and a few drops of acetic acid
Annealing temperatures	350, 400, 450 and 500 °C
Nozzle to substrate distance	30 cm
Spray angle with respect to the plane of the substrate	45°
Spray interval	5 s
Spray time	1 s
Spray rate	0.15 mL/spray

2.2. Characterization of ZnO:Sn films

The structural properties of ZnO:Sn thin films were studied using X-ray diffraction technique (PANalytical-PW 340/60 X'pert PRO) with Cu Kα (λ = 1.5406 Å). The thickness of the films was estimated using surface profilometer (Profilometer: Surftest SJ 301) and weight gain method and the average thickness was found about 500 nm with probable error which is ⩽5%. Optical transmittance spectra were recorded using UV–Vis–NIR spectrophotometer (Perkin Elmer Lambda 35). The electrical measurements were carried out using both four probe apparatus (van der Paw configuration) and Hall probe apparatus (ECOPIA HMS-3000). The Photoluminescence spectra were taken using spectro fluorometer (450 W, Jobin Yvon-FLUOROLOG-FL3-11). The surface morphology of the films is observed using atomic force microscope (AFM) (Veeco-di CPII). The experiments were repeated four times by maintaining the same optimum process conditions in order to confirm the reproducibility and repeatability. The deviations in the values are within the acceptable limit of ⩽5%.

3. Results and discussion

3.1. Structural studies

In order to use ZnO films efficiently in many devices, it is necessary to understand the structural, optical and electrical properties of ZnO films [31]. The structural properties of ZnO films were investigated using the X-ray diffractometry. The X-ray diffraction patterns of the as-deposited and annealed ZnO:Sn (6 at.%) films are shown in Fig. 1. The films exhibit diffraction peaks at 31.62°, 34.37° and 36.12° correspond to the planes (100), (002) and (101), respectively. The XRD profile shows that all the films have hexagonal wurtzite structure according to the JCPDS card No.: 36–1451. Of the observed peaks, the predominance is found to be in favour of (002) plane for the as-deposited film as seen from Fig. 1. Eventhough, the intensity of (002) peak is predominant over that of (100) and (101) peaks, the broadened nature of (002) diffraction line compared to the other two peaks indicates that the crystallites associated with (002) plane are very much smaller in size than that related to the other two. But, during the annealing treatment at 400 °C, this (002) peak begins to lose its predominance, and at the same time, the (100) peak grows remarkably at the cost of the other two peaks. This trend continues with a higher pace when the annealing temperature is increased to a higher value *viz.* 450 and 500 °C. This phenomenon can be explained on the basis of Ostwald ripening effect [32]. According to this effect, in a system like a crystalline solid comprising of smaller and larger crystallites, the smaller ones tend to diffuse into the larger ones on acquiring sufficient thermal energy. Here, the annealing temperature provides the necessary thermal energy for this effect to take place and in the present study, this critical recrystallization is found to start at 400 °C and above this annealing temperature, this effect continues to occur in a higher degree.

The quantitative variations in the preferential orientation of the films are estimated through the texture coefficient calculations using the formula [33]

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{o(hkl)}}{(1/N)\sum_{N=1}^{N} I_{(hkl)}/I_{o(hkl)}} \tag{3.1}$$

The calculated texture coefficient values of the peaks (100), (002) and (101) are plotted as a function of annealing temperature in Fig. 2. It is obvious from the plot that the texture coefficient of (100) plane increased nearly eight times when the annealing temperature is increased from 350 °C to 500 °C indicating a strong reorientation of crystallites during the annealing process.

It is noteworthy to mention here that ZnO films with (100) plane as the preferential orientation offer a specific advantage in non-linear optical applications [29].

The lattice parameters are estimated from the relation [34]

$$1/d^2 = (4/3)((h^2 + hk + l^2)/a^2) + (l^2/c^2) \tag{3.2}$$

where d is d-spacing and a and c are lattice constants. The calculated a and c values are given in the Table 2. The crystallite sizes of the films are calculated using the Scherrer's formula [35].

$$D = 0.9\lambda/\beta\cos\theta \tag{3.3}$$

where λ is the wavelength of the X-ray (Cu Kα – 1.5406 Å); β is the full-width at half-maximum (FWHM) of the peak and θ is the Bragg's angle. The crystallite size calculated from the FWHM of the (100) plane increases with the increase in the annealing temperature as can be seen from Fig. 3. Moreover, it is also found that the intensity of the other two peaks (002) and (101) decreases gradually as the annealing temperature increases indicating the decrease in the number of crystallites oriented along these two planes. These two results confirm that the above discussed Ostwald ripening effect was very much taken place during the annealing process.

3.2. Optical studies

The transmission spectra of as-deposited and annealed ZnO:Sn films are shown in Fig. 4. All the films show good optical transmittance in the visible range. The transmittance of the films increases from 70% to 90% as the annealing temperature increases which may be due to the enhancement in the grain size as observed from the AFM images (Fig. 8). It is well known that as the grain size increases, the grain boundary decreases resulting in a reduction in the grain boundary scattering and a consequent enhancement in the transmittance.

The optical band gap (E_g) values are estimated using the plot drawn for the first derivative of transmittance with respect to wavelength against the average wavelength (Fig. 5). The E_g value is found to increase from 3.36 eV to 3.45 eV as the temperature increases from 350 °C to 500 °C (Table 2). This increase in band gap may be due to the Moss–Burstein effect.

3.3. Electrical studies

The variations in the values of resistivity (ρ), carrier concentration (n) and mobility (μ) as a function of annealing temperature are shown in Fig. 6. All the films exhibit n-type conductivity as observed from the sign of the Hall voltage. The mobility (μ) and carrier concentration (n) of the films are found from the Hall measurements using the relation [33]

$$\mu = 1/n\rho q \tag{3.4}$$

where q is the charge of an electron.

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