RESEARCH ARTICLE

Production of Transparent Conducting ZnO Thin Films with Preheated Temperature by Sol-Gel Spin Coating Technique

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ABSTRACT: To date, thin film deposition with low cost technique and desired process parameters has been intensively studied. The cost effective sol-gel spin coating has been widely used for the deposition of different types of elements in thin film form. ZnO thin films can also deposit with the application of this technique. The prepared solution led to deposit high crystalline ZnO thin films without annealing at elevated temperature. The crystal structure of deposited films was characterized by X-ray diffraction technique. Narrowed and high intensity diffraction peak at 34.4° clearly indicated that the films exhibit hexagonal wrutzite structure of ZnO. The optical properties of these films were typically studied using UV-vis NIR double beam spectrophometer, the optical transmittance in the visible region was more than 90% and showed sharp absorption edge. SEM images showed earth warm like wrinkle surface. The four probe method revealed electrical resistivity of 1. 4 Ω cm.

KEYWORDS: Sol-gel deposition, ZnO film, structural, optical, electrical properties.

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1. INTRODUCTION

In recent past, ZnO thin films have been received increasing attention for arrays of applications in opto-electronics device such as transparent electrode for solar cell [1], light emitting diodes [2], flat panel displays [3]. ZnO has wide band gap (3.37 eV) with high excitonic binding energy (60 meV) and n-type conductivity [4, 5]; these peculiar properties exhibit high transmittance in visible region and high electrical conductivity. Besides, ZnO is a low-cost, non-toxic, high chemical and thermal stability [6-9]. Several methods have been employed for deposition of ZnO thin films such as sputtering, spray pyrolysis, pulsed laser deposition (PLD) and sol-gel processing. Of these methods, sol-gel has attracted interest for depositing thin films because of its significant advantages: simplicity, inexpensive, large area coating and ease dope.

In sol-gel deposition, most of the researchers are found amorphous ZnO films before post annealing treatment. To get high quality ZnO films after as-prepared, the films were annealed at high temperatures. Kumar et al. [10] reported the sol-gel deposited films are in amorphous state, which are transformed into crystalline state during the annealing process. Bu et al. [11] reported that the coated films were sintered in two step process. Initially, the film was sintered at 250 °C to evaporate the solvent and then annealed at 550 °C to crystallite the film. There are no studies on ZnO film properties in literature for as-prepared film, because of the poor in crystalline nature of films before annealing. In the present work, therefore, we concentrated to deposit high crystalline quality ZnO thin films with good optical transmittance without the post annealing treatment. The films deposited at preheated temperature of 200 °C were studied their structural, optical and surface morphology properties and reported.

2. EXPERIMENTAL

2.1 Deposition of thin films

Un-doped ZnO and F doped ZnO thin films were deposited by a sol-gel technique. The host and dopant materials were zinc acetate dehydrate ($C_4H_{10}O_6Zn$) and ammonium fluoride (NH_4 F), respectively. Ethanol was used as solvent and monoethanol amine (MEA) was used as stabilizer. For the preparation of starting precursor, 0.1 M of zinc acetate dihydrate and 0.1 M of ammonium fluoride (5 at. %) were dissolved in combining of 19 mL ethanol and 1 mL of monoethylene amine. This solution was stirred at 60 °C for 2h to get clear and homogeneous solution, while solution container was wrapped tightly with aluminum foil to avoid the evaporation of solvent, which maintaining the appropriate viscous of solution. Then the solutions were aged for 24 h at room temperature. The glass substrates were immersed in the diluted HCl for 2 h to etch dust particle if any on surface to be coated and then subjected to the ultrasonic waves and then thoroughly cleaned with acetone. The precursor solution was dropped on to the glass substrate, which was rotate at the speed of 5000 rpm for 60 s by a spin coater. After the coating, the film was preheated at 200 °C for 10 min to evaporate the solvent and organic residuals as well as for

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the crystallization of ZnO. The coating procedures have been repeated for 10 cycles to get a quality film. The flow chart of ZnO thin film preparation by sol-gel technique is shown in Figure 1.

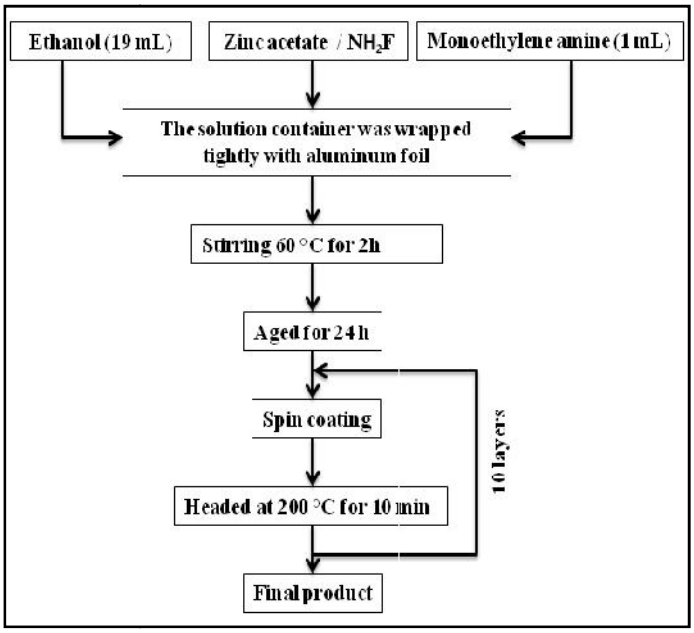

Figure 1 Flow chart of preparation of ZnO films by sol-gel technique

3. CHARACTERIZATION TECHNIQUES

The structural properties of the deposited films were analyzed with the help of XRD profiles obtained using X-ray diffractometer (PANalytical PW 340/60 X'pert PRO). The optical studies were carried out using UV-vis-NIR double beam spectrophotometer (Perkin Elmer-Lambda 35 model). The surface morphological and electrical studies were carried out using scanning electron microscope (HITACHI S-3000 H) and four probe technique, respectively.

4. RESULTS AND DISCUSSION

4.1 Chemistry of precursor solution

The zinc acetate is added with ethanol solvent and it dispersed as Zn^{2+} ions and acetate. The low ionized nature of both OH^- ions from the ethanol and Zn^{2+} ions from zinc acetate easily forms $Zn(OH)_2$ in the stock solution. MEA acts as a stabilizer, the presence of amine increases the pH value which can encourage the formation of $Zn(OH)_2$. During the deposition, each thin layer of $Zn(OH)_2$ heated at 200 °C for 10 min, which can give the sufficient thermal energy for covert from $Zn(OH)_2$ to ZnO. The clear mechanism of ZnO formation is given below:

$$C_2H_5OH + C_4H_{10}O_6Zn \longrightarrow Zn(OH)_2 + C_2H_5 + CH_3COO^-$$

$$Zn(OH)_2 \xrightarrow{200\,^\circ C} ZnO + H_2O\ (vapour)$$

4.2 Structural studies

The sol-gel deposited film was confirmed as ZnO by the obtained XRD pattern compared with the standard JCPDS profile.

Figure 2 shows the XRD patterns of un-doped ZnO and F doped ZnO thin films. Several researchers reported that the sol-gel deposited films were in amorphous nature or power crystallinity before annealing at high temperatures [12]. Kumar et al. reported that the XRD pattern of the as-prepared thin film exhibits amorphous nature, while the same films annealed at 700 °C have a hexagonal wurtzite structure and the increase in annealing time improved the crystal quality of the films [13]. But, in the present study, good crystalline ZnO films were obtained only at the preheat temperature of 200 °C. In the case of un-doped ZnO film, the diffraction peak only at 34° was observed. A strong diffraction peak at 34.4° and two weaker peaks at 31.7° and 36.2° were observed for F doped film, indicting the reorientation of crystallite. Besides, no peaks associated to fluorine compounds were observed. The diffraction peaks at 31.7°, 34. 4° and 36.2° in the XRD patters could be indexed as (100), (002) and (101) plane of ZnO, according to the JCPDS card no. 36-1451 [14]. For all films, the peak at 34.4° shows the highest relative intensity, which indicated that the ZnO film has a preferred oriented along (0 0 2) plane. The mean crystallite size was calculated using Scherrer's formula

$$D = \frac{0.9^a}{\cos^-}$$

Where, λ is the wavelength of used X-ray (1.5406 Å), β is full width at half maximum (FWHM) and θ is Bragg's angle. The crystallite size of ZnO film is 21 nm and increased for F doped film. The calculated other structural parameter 'c' values are well fitted with the standard value (5.20661 Å) (Table 1).

4.3 Optical studies

The optical transmittance spectra of un-doped and F doped ZnO thin films were recorded as a function of wavelength in the range of 300-1100 nm, as shown in Figure 3. Un-doped ZnO film exhibits the average transmittance around 93% in the visible region, where as the transmittance slightly decreases for the F doped films (91 %). The decrease in transmittance of doped films may be ascribed to scattering of photons at the grain boundaries and absorption of photon by defects in the films. The introduction of F atoms into the ZnO matrix remarkably deforms the crystal structure and forms more defects *viz.* oxygen vacancies and zinc interstitials. These intrinsic defects can generate more number of free electrons, which can decrease the transmittance by means of absorption of photons by the free electrons. The interference pattern of transmittance spectra is clearly indicating the smooth and uniform surface of the films. The characteristic absorption of ZnO shifts to higher energy as the F doping, indicating the widening of band gap value of the doped films. Optical band gap value of the films was calculated by Tauc's plot (inset Figure 3). The calculated band gap values are given in Table 1.

The band gap value of un-doped ZnO film is found to be 3.22 eV, this value is matched with reported literatures [15, 16]. The obtained result shows the value of band gap increases for F doping. The increase in band gap value may be attributed to Moss Burstein effect caused by generation number of free electrons [17]. These films are more appropriate for the shorter wavelength applications in opto-electronic devices.

4.4 Morphological studies

The surface morphology of the films was carried out using SEM. SEM images of un-doped ZnO and F doped ZnO thin films are shown in Figure 4. It is observed that the surface morphology of the films is almost identical. The SEM images show the wrinkle surface; there is no remarkable variation in grains after F doping. Besides, the images consist of worm like network; each worm is interlinked by tiny threads.

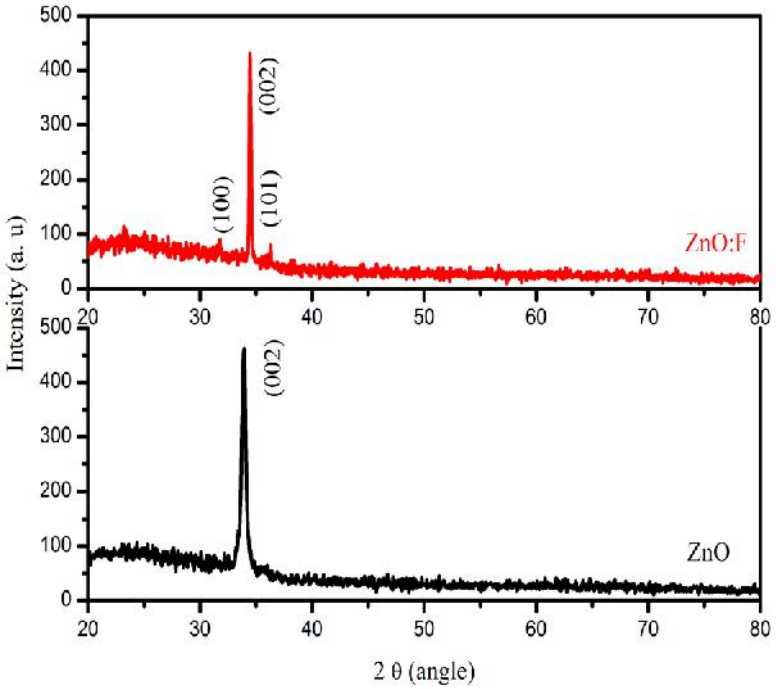

Figure 2 XRD pattern of ZnO and F doped ZnO thin films

Table 1 Structural parameters and band gap of ZnO and F doped ZnO thin films

Sample	'c' (Å)	Crystallite size (nm)	Band gap (eV)
ZnO	5.20801	21.8	3.23
ZnO:F	5.20749	24.6	3.24

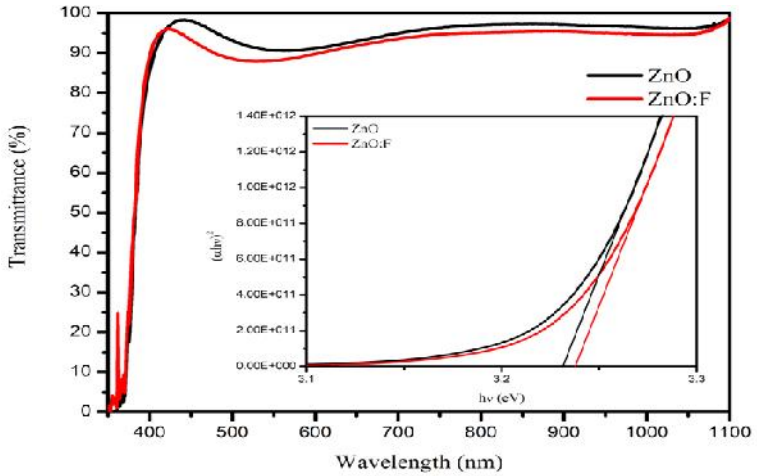

Figure 3 Transmittance spectra of ZnO and F doped ZnO thin films

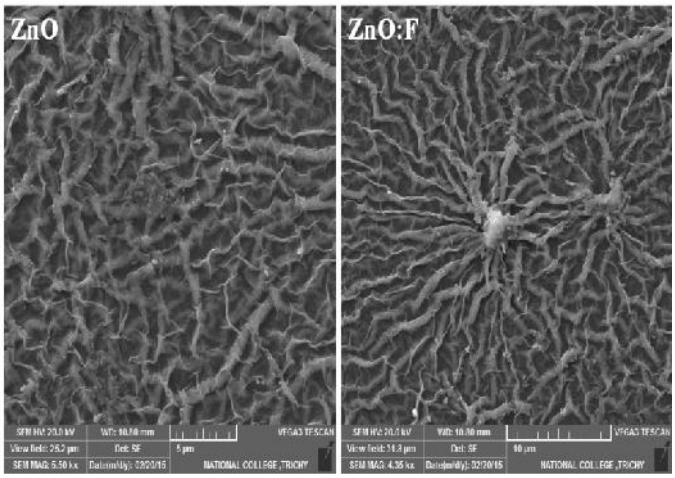

Figure 4 SEM images of ZnO and F doped ZnO thin films

4.5 Electrical studies

The electrical properties of un-doped and F doped ZnO films were measured using four probe technique. In the case of un-doped ZnO films, the electrical conductivity can be ascribed to point defects such as zinc interstitials and oxygen vacancies. Both defects generate number of free electrons into the ZnO lattice. The resistivity of un-doped ZnO film is 4.2 Ω cm. The introduction of F^- ions into the precursor solution reduces the resistivity to 1.4 Ω cm which can be due to generation of free electrons resulted by the incorporation F^- ions into the O^{2-} sites.

5. CONCLUSION

Un-doped ZnO and F doped ZnO thin films were successfully deposited on to the glass substrates; only at preheat temperature of 200 °C by a sol-gel technique. The XRD studies clearly indicated that the ZnO films possess a hexagonal wurtzite crystal structure and the crystallite size decreased to 20 nm for F doped ZnO film. The optical transmittance spectra showed more than 90 % transmittance in the visible region. The band gap energy value of the films increased from 3.23 to 3.24 eV after F doping. Earth warms like wrinkle surface of the films was observed from the SEM images. The F doped (5 at. %) ZnO film exhibits electrical resistivity 1.4 Ω cm.

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