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Influence of Substrate Temperature on Zno Thin Film Deposition by Spray Pyrolysis Technique

Physics

KEYWORDS : ZnO thin film, Spray pyrolysis, Substrate Temperature, XRD, Energy band gap.

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ABSTRACT

Zinc oxide (ZnO) thin films were fabricated on glass substrate by Spray Pyrolysis technique for the typical solution concentration of 0.05M of Zinc acetate along with Isopropyl alcohol and de-ionized water. The effect of temperatures on the quality of thin film have been studied for the fixed substrate temperatures (Ts) of 300°C,400°C and 500°C. The surface morphology of the prepared thin films were analyzed by Scanning Electron Microscopy (SEM). The structural determination was done by X-ray diffraction (XRD). It is observed that the fabricated ZnO thin films were of polycrystalline in nature with a hexagonal Wurtzite structure. Using UV-Visible spectrophotometer the optical absorption characteristics of the samples were studied. The Energy band gap (Eg) were estimated for all the fabricated thin films and were found to have a variation from 3.16eV to 3.31eV, as the substrate temperature was increased . An estimated band gap minimum of 3.16 eV was noticed for the film fabricated for the specific Ts of 300o C.

Introduction

Zinc oxide is a II-VI compound of n-type semiconductor. It is a promising material for the applications in both optoelectronic and microelectronic devices. It has widespread applications such as antireflection coatings in solar cells, liquid crystal displays [1], gas sensors[2] ultrasonic transducers [3], blue light emitting diodes (LED) [4]. Zinc oxide is one of transparent conducting oxide (TCO) materials. Due to its exciton binding energy of about 60 meV they can be used as transparent electrodes in displays [5]. Thin films of ZnO have high optical transparency in visible and near-infrared region [6], high chemical and mechanical stability in hydrogen atmosphere [7]. Due to these properties ZnO plays vital role in the fabrication of electronic and optoelectronic applications. The properties of thin films which are the basis for their application in technological devices. ZnO can be prepared by Magnetron sputtering, Thermal evaporation and Chemical vapor deposition, Pulsed laser deposition, Sol-gel and Spray Pyrolysis deposition. Of all the above methods spray pyrolysis is a simple, safe and cost effective method. The spray pyrolysis technique allows the coating of large surface area and the solution is sprayed directly onto the substrate. The advantage of this method is the deposition of thin film possible without any high vacuum system [8].

In this study ZnO thin films were deposited by the spray pyrolysis setup and the effect of substrate temperature on the growth of ZnO films were studied.. The substrate temperatures [T_S] were varied from 300°C to 500° C. From the X-Ray diffraction studies polycrystalline Zinc oxide structure could be observed. SEM images of these films were reported. The variation of substrate temperature affects the adhesivity, surface smoothness and hence the crystallinity [9].The substrate temperature is the critical parameter that influences the crystallinity and hence the crystallite size and band gap of the deposited films.

Experimental Details

ZnO thin films were deposited by the Spray Pyrolysis setup. The substrates were precleaned with chromic acid for 30 minutes and de-ionized water. The Precursor solution was 0.05M of Zinc acetate dihydrate $Zn(CH_3COO)_2 . 2H_20$, Isopropyl alcohol and de-ionized water (volume ratio 3:1) were used as a solvent. The prepared solution was kept in a magnetic stirrer for 30 minutes and then heated to 80° C in a magnetic stirrer to get a homogenous mixture.

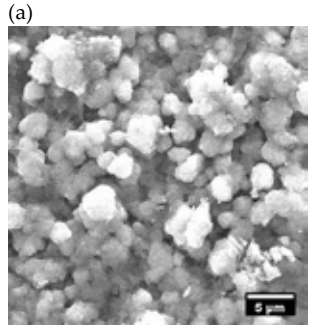
Indigenously developed spray pyrolysis unit has been utilized in the preparation of thin films. It consists of a glass nozzle, substrate heater (hot plate) with a temperature (P.I.D) controller and a compressor for gas (air). The carrier gas and the prepared solution are fed into the glass nozzle at a flow rate of 7ml/min. The substrate to nozzle distance was kept at 25cm. The pressure of the carrier gas was kept at 25kg/cm^2.

Spray pyrolysis involves many processes that take place simultaneously. The most important of these are aerosol generation and transport, solvent evaporation, droplet impact with consecutive spreading, and precursor deposition [9]. Many parameters were found to affect the film preparation namely substrate temperature, substrate nature, spraying rate, solution molarity [9], distance between the substrate and the spray nozzle. Among these substrate temperature is found to be the most critical parameter [9]. The effect of the substrate temperature Ts, on the characteristics of ZnO thin films was studied by fixing the other parameters. Optimum information on temperature which gives highly semiconducting properties of undoped ZnO for future work is reported.

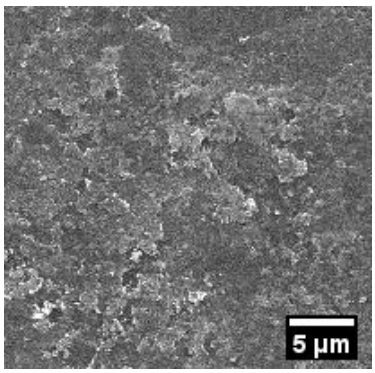
Results and Discussion

SEM images of ZnO thin films deposited at (a) 300°C (b) 400°C were shown in Figure.(1). For three different substrate temperatures the corresponding morphologies were shown. When the substrate temperature (T_S) is 300°C the granular structure with some hexagonal plates could be observed. As the substrate temperature (T_S) increases to 400°C with granular structure, the surface becomes smooth and uniform. At (T_S) 500°C still there was no grain formation and the surface yields rough, non adherent films.

(a)



(b)



(c)

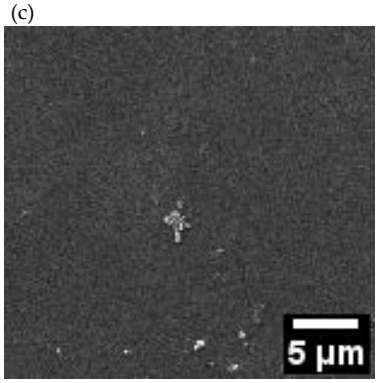


Figure 1. SEM Images of ZnO thin films synthesized at different substrate temperatures (T_S) (a) 300 ^{0}C (b) 400^0 C (c) 500^0 C.

This is because the precursor precipitates on the surface of the droplet, when the surface concentration exceeds the solubility limit. Precipitation occurs due to rapid solvent evaporation and slow solute diffusion. According to Dainius Perednis et.al at high substrate temperature (above 450˚C) powdery films were produced due to vaporization and decomposition of the precursor before reaching the substrate [9]. This results in the rough film at the substrate temperature 500˚C.

Figure.2 XRD pattern of ZnO thin films at substrate temperatures (T_S) 300˚C,400˚Cand 500˚C

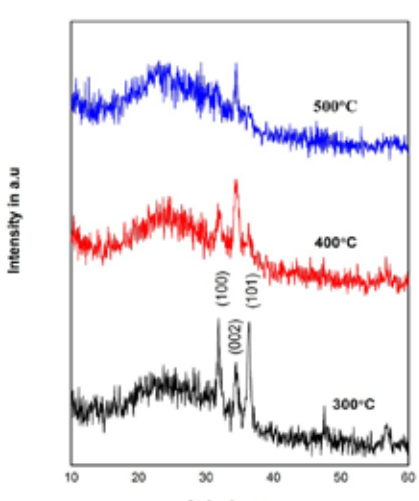


Figure .2 shows the X-ray diffraction pattern of ZnO thin film at three different substrate temperatures (T_S) 300˚C, 400˚C, and 500˚C.The structural studies of the films have been carried out using X'PertPRO X-ray diffractometer. The diffraction pattern was obtained with 2θ from 10˚ to 80˚. The XRD pattern of ZnO thin film shows that the films are polycrystalline with hexagonal Wurtzite structure. The result is in agreement with the literature (JCPDS card no: 36-1451). There are three strong peaks and three small peaks observed at 300˚C. The strong peaks observed at 2θ =31.86˚, 34.41˚, 36.42˚ can be attributed to (100), (002), and (101) planes correspond to the formation of hexagonal Wurtzite structure, indicating preferential orientation along C-axis [5]. When T_S increases to 400˚C the intensity of (100) and (101) peak decreases but for (002) plane the intensity increases. . The growth along (002) plane is enhanced. At 500˚C the (100), (101) peaks disappears and relatively a sharp peak for (002) plane with more amorphous phase could be observed. According to Lado Filipovic et.al at high temperature the chemical reaction subsequently occurs in vapour phase, this homogenous reaction leads to the condensation of molecules into crystallites in the form of a powder. This explains the amorphous phase of the film at 500˚C[10].The decrease in peak intensities at 400˚C and above may be attributed to some sort of atomic disorder in the crystal lattice.[11] The substrate temperature 300˚C points to optimum temperature. Above this, the peaks intensity decrease, revealing reduced crystallinity.

The lattice constants a and c of the Wurtzite structure of ZnO were calculated using relations(1) & (2) given below (C.Suryanarayana and M.Grant Norton,1998) [12]:

$$a = \sqrt{\frac{1}{3}} \times \frac{\lambda}{\sin\theta} \qquad (1)$$

$$c = \frac{\lambda}{\sin\theta}\ , \qquad (2)$$

θ is the Bragg diffraction angle and λ is the wavelength of the X-ray incident CuKα radiation (1.54060A˚). For (002) plane, the calculated lattice constant values are a = 3.11 A˚ and c = 5.24 A ˚ which agrees with JCPDS card data.

These diffraction peaks shows that ZnO thin films with more crystallinity could be observed between substrate temperature (T_S) 300˚C and 400˚C. The average crystalline sizes D for the films were estimated based on Scherrer's formula [5]

$$D = \frac{0.94\lambda}{\beta\cos\theta} \qquad (3)$$

Where θ is the Bragg diffraction angle, λ is the wavelength of the X-ray incident CuKα radiation (1.54060A˚), and β is FWHM of the diffraction peak. The thickness measurements are done with XRD. The optical characterization of ZnO thin films were done by UV-VIS spectrometer in the optical range 200-1100nm. The optical band gaps of the films are determined from UV absorption data by applying the Tauc's model, in the high absorbance region [4]:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \qquad (4)$$

where hν is the photon energy, E_g is the optical band gap, and C is a constant .Fig.3 represents the relationship between $(\alpha h\nu)^2$ and hν which is useful in estimating the E_g values of the prepared thin films.. The E_g value could be obtained by extrapolating the linear portion of the curves to αhν = 0. The estimated optical band gap values of the prepared thin films are listed in table.1

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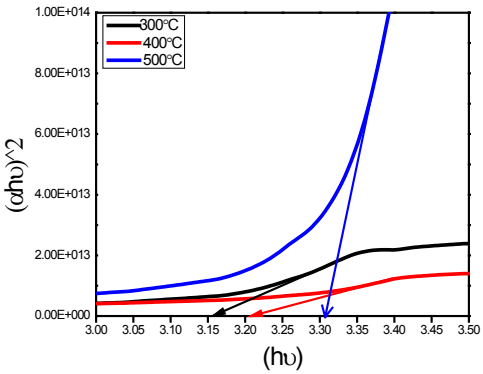

Figure 3: The plot of $(\alpha hv)^2$ vs. photon energy for ZnO films at different substrate temperatures.

It is seen from Figure (3) that optical band gaps (E_g) are 3.16eV, 3.21eV, 3.31eV for substrate temperatures (T_S) 300°C, 400°C, and 500°C respectively. As observed by Subhash Chander,S. Choudhary, A.et.al, the band gap is decreased with increase in film thickness. Thickness of the developed films for the substrate temperatures (T_S) 300°C, 400°C, and 500°C decreases from 1.46 μm to 0.67μm. During the deposition of films at room temperature, the structure defects are created in films owing to the allowed states in the forbidden region which revealed the reduction of the optical energy band gap with thickness [13]. In the film forming process it is possible that some dislocations are involved. The dislocation density of thin films is given by the Williamson and Holman relation [4]:

$$\delta = n / D^2 \qquad (5)$$

where 'n' is a factor which is unity. During film formation it is likely that some micro strain could be developed in the film. The micro strain (ε) developed in the film has been calculated using the relation

$$\varepsilon = \beta \cot \theta / 4 \qquad (6)$$

The crystal size, optical band gap values, thickness, micro strain and dislocation densities for the three substrate temperatures (T_S) are summarized in the Table1.

Table 1: Changes in average crystallite size, band gap, micro strain and dislocation density with the increase in substrate temperature of the deposited ZnO films.

Substrate temperature (Ts) °C	Thickness (t) μm	Crystallite size (D)nm	Optical band gap (E_g) eV	Dislocation density (δ) $x10^{14}$[m]$^{-2}$	Micro strain(ε) $x10^{-3}$
300	1.46	32.38	3.16	9.537	1.298
400	1.42	14.58	3.21	47.562	4.019
500	0.67	21.16	3.31	20.93	3.919

As the substrate temperature (T_S) increases from 300°C to 500°C, the thickness decreases but the crystallite size decreases from 32.38nm to 14.58 nm. It could be observed that a minimum band gap of 3.16eV is achieved for a substrate temperature 300°C which is very close to the value reported by R. Ashok Kumar et.al [8]. At 500°C (T_S) though the crystallite size increases compared to 400°C, the optical band gap value increases. The estimated band gap value, the micro strain and the dislocation densities are found to be minimum for the substrate temperature (T_S) 300°C, when compared to the values reported for higher temperatures.

Conclusion

In the present work the influence of substrate temperature on the growth of ZnO thin films by spray pyrolysis technique has been studied. Zinc oxide thin films were successfully prepared on glass substrate for the substrate temperatures (T_S) of 300°C, 400°C and 500°C. The film growth is achieved along the c-axis of the hexagonal structure normal to the surface of the glass substrate. The film morphology was found to be shifted from a crystalline nature to amorphous nature while increasing the deposition temperature. The X-ray diffraction results revealed that ZnO films were polycrystalline in nature with a hexagonal Wurtzite structure and were in nano crystalline range [14]. According to T. Prasada Rao et.al the crystallite size increases with the thickness of the deposited films [15]. When the substrate temperature (Ts) increases from 300°C to 500°C, optical band gap of films increase from 3.16eV to 3.31eV. The band gap is less for the substrate temperature 300°C and crystallite size is about 38.38 nm. Further the micro strain and dislocation densities are low for the same substrate temperature. Hence the substrate temperature (Ts) 300°C is optimized for solar cell applications in future.

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