



Structural and Optical Properties of Zn₂SnO₄ Thin Films prepared by Spray Pyrolysis

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Abstract

Zn₂SnO₄ thin films were prepared using spray pyrolysis technique over cleaned glass substrate with zinc chloride and tin (IV) chloride as precursors. The preparative parameters such as substrate temperature, solution concentration, distance from spray-nozzle to substrate, pressure of carrier air, etc., were optimized to obtain large area, uniform, thin films. The substrate temperature during deposition is varied between 350°C to 500°C to study the influence of temperature over the structural properties of Zinc Stannate (Zn₂SnO₄) thin films. The structural analysis of Zn₂SnO₄ thin films were carried out using X-ray Diffraction (XRD) technique and it is observed that the films are highly crystalline. Various diffraction peaks of Zn₂SnO₄ powder were observed in the XRD pattern. The surface morphology of the films were studied by using Scanning Electron Microscope (SEM). The EDAX analysis shows the percentage of doping. Optical transmittance measurements indicate that the Zn₂SnO₄ films have a direct band gap of the films varies from 3.1 to 3.4 eV which is then confirm the formation of well-crystallized Zn₂SnO₄ films. PL spectra in the green region, which means Zn₂SnO₄ film, may have application as green light emitter.

Keywords: Spray pyrolysis; Zinc Stannate; Thin films Doping.

1. INTRODUCTION

One-dimensional semiconducting oxides have attracted great attention in recent years due to their unique properties. Among them, binary oxides such as ZnO and SnO₂ have been focused on mostly, but ternary oxides, which may show better properties, are still less studied.

Zinc Stannate (E_g =3.6eV) is an excellent functional material with high electron mobility, high electrical conductivity and low visible absorptions (Kumaravel et al. 2012). These specific properties lead to several applications in pioneer technologies including photo-voltaic devices (Ghosh et al. 2004), flat-panel displays, thin film solar cells and gas sensors. Various processing routes of synthesizing Zn₂SnO₄ were reported such as hydrothermal method (Foletto et al. 2013), thermal evaporation (Du et al, 2010), high temperature calcination, electron beam evaporation, rf magnetron sputtering (Sato et al. 2009), chemical vapor deposition (Nikolić et al, 2001)

and spray pyrolysis (Kumaravel et al. 2010). In this study, formation and properties of Zn₂SnO₄ synthesized via spray pyrolysis were investigated. Effect of calcination temperature on the formation of different phases of Zn₂SnO₄ was completely studied. Spray pyrolysis is a versatile deposition method because it allows the use of inexpensive precursor materials, good control of layer stoichiometry, and most importantly large area coatings can be obtained by using low cost equipment's, in low energy consuming conditions. In spray pyrolysis the deposition rate, thickness and uniformity of the films are the consequence of nucleation and crystal growth processes which are mainly influenced by the deposition temperature and precursor solution concentration. In this paper, Zinc Stannate (Zn₂SnO₄) thin films have been deposited by spray pyrolysis using zinc chloride and tin (IV) chloride as precursors. The effect of deposition parameters on properties such as structural, surface morphology and Optical properties were investigated by X-ray diffraction,

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Scanning Electron Microscope, Optical transmittance measurements and PL spectra.

2. EXPERIMENTAL DETAILS

Film Deposition

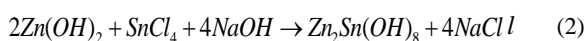
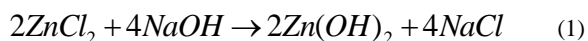
0.1 M Zinc chloride was dissolved in 25 ml of de-ionized water and stirred for 10 minutes using magnetic stirrer. NaOH solution was added slowly from a burette

with Zinc chloride solution until the pH value reached 7. Similarly 0.1 M tin (IV) chloride solution was prepared. Tin (IV) chloride solution was added with zinc chloride solution slowly under gentle stirring condition. Then NaOH solution was again added till the pH value reaches 7. The prepared solution was sprayed onto ITO glass substrates using spray pyrolysis technique. The optimized preparative parameters for Zn₂SnO₄ thin films deposition are listed in Table.1.

Zn₂SnO₄ thin films were synthesized through solid-state chemical reaction between the metal salts and alkali medium at room temperature. The reaction process can be described by Equation (1), (2) and (3).

Table 1. Optimized preparative parameters for Zn₂SnO₄ thin films

Deposition spray rate	0.5 ml/minutes
Substrate temperature	450°C
pH of the solution	7
Deposition time	10 minutes
Nozzle to substrate distance	5 cm
Carrier gas pressure	30 psi



CHARACTERIZATION TECHNIQUE

X-ray diffraction data of the nebulizer sprayed Zn₂SnO₄ films were recorded with the help of Philips Model PW 1710 diffractometer with Cu K α radiation ($\lambda=0.1542$ nm). Surface morphological studies and compositional analysis were carried out using a scanning electron microscope and energy dispersive X-ray analysis setup (EDAX) which is attached with SEM (Philips Model XL 30), respectively. The electrical resistivity of the films was studied using a four-point probe method. Optical absorption spectrum was recorded using a JASCO-V-570 spectrophotometer. The room temperature photoluminescence spectrum was performed on a spectrofluorimeter (fluorolog model FL3-11).

3. RESULTS AND DISCUSSION

XRD Analysis

The Zn₂SnO₄ thin films were analysed by X-ray diffraction to study structural identification and changes in the crystallinity. Figure-1 shows XRD pattern for the Zn₂SnO₄ films annealed at 350°C – 500°C. The observed 'd' values are in good agreement with standard 'd' values of JCPDS [1]. The diffractograms shows well-defined peaks corresponding to (2 2 0), (3 1 1), (2 2 2), (4 0 0), (5 3 3) and (6 2 2) planes of the material polycrystalline in nature have cubic structure. Moreover, the intensity of the (3 1 1) plane increases with the increase in substrate temperature (450°C), thereafter slightly decreased. The crystallite size (D) of Zn₂SnO₄ thin films were evaluated using Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4)$$

Where, D is the mean crystallite size, β is the full width in radiation at half maximum of the diffraction peak, θ is Bragg's angle of the XRD peak, and λ is the wavelength of the X-radiation (1.5406Å°).

The calculation of crystallite size from XRD is a quantitative approach which is widely accepted and used in scientific community. The average crystallite size is increased with increasing annealing temperature revealing a fine crystalline structure.

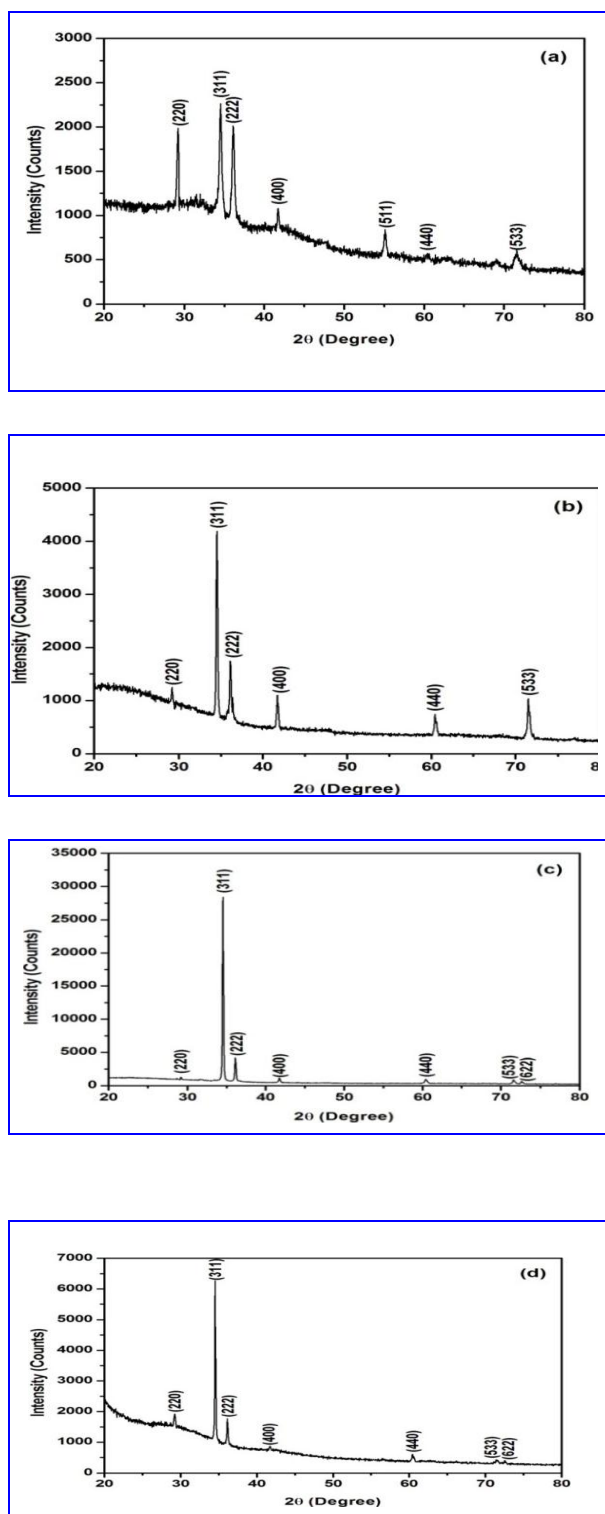


Fig. 1: XRD patterns of Zn_2SnO_4 thin films deposited at different temperatures a) 350°C b) 400°C c) 450°C and d) 500°C.

SEM : The high magnification surface morphologies of Zn_2SnO_4 thin films annealed at 350°C - 500°C were carried out using SEM images are shown in Fig. 2. The growth of the films was observed to be uniform and well covered over the substrate. As seen in Fig. 2a-d, the surface morphologies of the films change with the increase in substrate temperature. It is observed that in Fig.

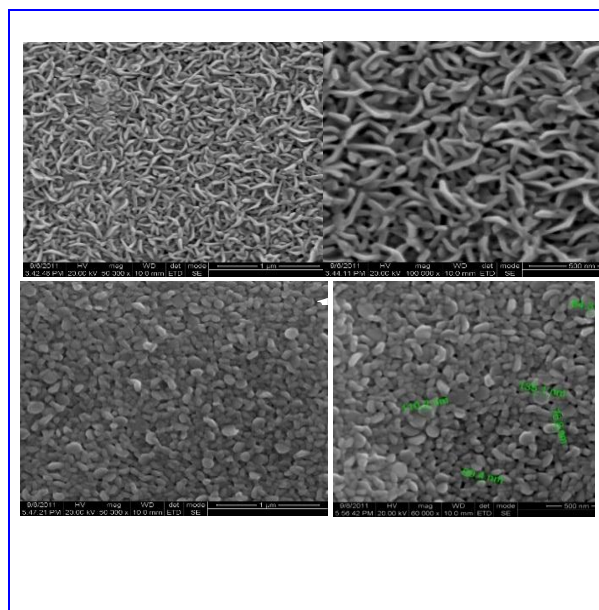


Fig. 2: SEM images of Zn_2SnO_4 thin films deposited at different temperatures: a) 350°C b) 400°C c) 450°C and d) 500°C.

2a- a1, the surface morphology of deposited film show micro rods, smooth, dense, without pinholes with uniform distributed grains. The grain size is observed to be uniformly distributed with an average diameter ~ 75 nm. From Fig. 2d-d1, the images indicate that the films are having affected grains due to the increase of substrate temperature (500°C) with an average diameter of the order of 112-120 nm.

Fig 3 a and b shows, the EDAX spectrum of Zn_2SnO_4 thin films deposited at substrate temperature from 350°C– 500°C. A typical EDAX spectrum is recorded in the binding energy region of 0–10 keV. EDAX analysis shows the presence of Sn, Zn and O elements of the starting solution in the solid films, and the amount of Sn element slightly increases with the decrease of Zn content. The peak at 1.75 keV is due to the glass component.

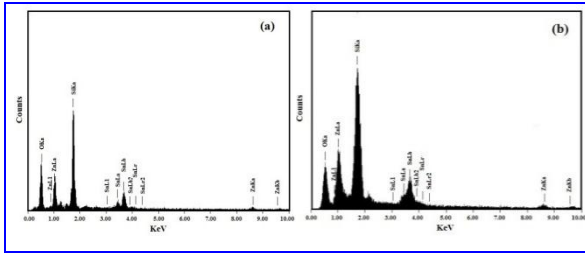


Fig. 3: EDAX spectra of Zn₂SnO₄ films deposited at different temperatures: a) 350°C and b) 400°C

4. OPTICAL PROPERTIES

Optical studies were performed for the prepared films by measuring the transmittance in the wavelength region 300-1100 nm using a JASCO-V-570 spectrophotometer. Fig.4a-d shows the wavelength (λ) dependence of the transmittance of Zn₂SnO₄ films prepared at different substrate temperatures. Nature of transmittance spectra shows (Fig. 4a-d) a series of transmittance maxima

at two wavelength regions 450 nm and 750 nm and the shift towards longer wavelength side. The films also show a sharp decrease of transmittance in the ultra-violet region and this may be caused by the fundamental absorption of light. At an identical withdrawal speed, it is also noticed that the absorption edge of the transmittance shifts towards longer wavelength side in the ultra-violet region as the substrate temperatures decrease for the Zn₂SnO₄ films. The higher-energy electronic transitions from valence to conduction bands confirm the direct type of semiconducting nature of the material. We further interpolate the optical absorption data to the semiconductor absorption function corresponding to the direct band-to-band transitions. The absorption coefficient (α), energy gap (E_g) and photon energy ($h\nu$) are related as:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (5)$$

where, A is a constant and n assume values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

For allowed direct type of transitions

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (6)$$

A plot of $(\alpha h\nu)^2$ versus $h\nu$ is a straight line whose intercept on energy axis gives the energy gap ' E_g ' as shown in Fig. 5a-d for different temperatures. The straight line nature of the plots over a wide range of photon energy indicates the direct type transition. The optical gaps have been then determined by the extrapolation of the linear regions on energy axis.

After increasing substrate temperature to 500°C, the direct band gap energy increases to 3.4eV.

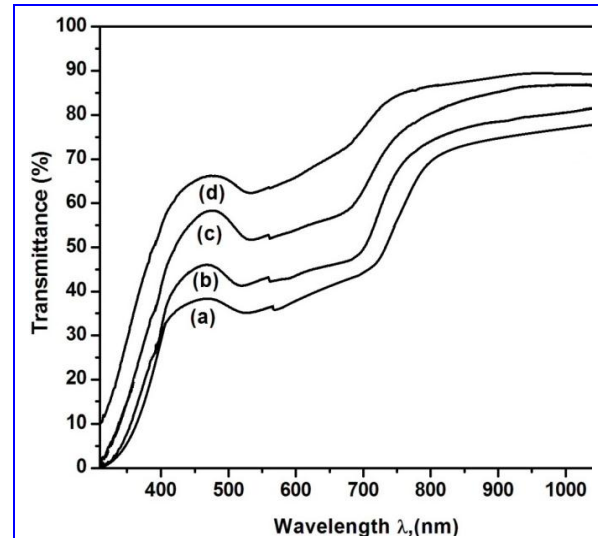


Fig.4: Transmittance spectra of Zn₂SnO₄ thin films deposited at different temperatures a) 350°C b) 400°C c) 450°C and d) 500°C

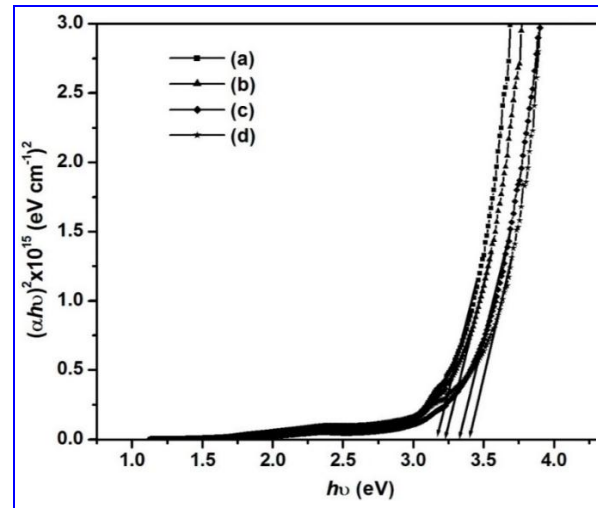


Fig. 5: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the Zn₂SnO₄ thin films deposited at different temperatures: a) 350°C b) 400°C c) 450°C and d) 500°C.

5. PHOTOLUMINESCENCE SPECTRA

PL spectra of Zn_2SnO_4 thin films under 375 nm UV ray excitation with different substrate temperatures 400°C, 450°C and 500°C is shown in Fig. 6. It can be seen from Fig. 6, there are two emission bands in the spectra: a sharp blue emission peak around 488 nm and a sharp visible deep-level broad green emission centered at 550 nm for the Zn_2SnO_4 films. Substrate temperature increases up to 500°C as peak intensity increased. The reduction in PL intensity lower substrate temperature 400°C may be attributed to the filling of oxygen vacancies, which results in lower concentrations of oxygen vacancies. The oxygen vacancies will induce defect levels within the band gap that generate the green emission of the Zn_2SnO_4 thin films.

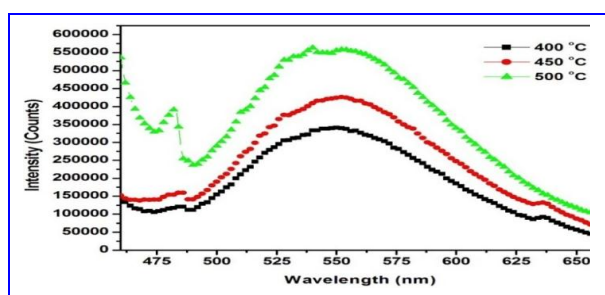


Fig. 6: PL spectra of Zn_2SnO_4 thin films deposited at different temperatures.

6. CONCLUSION

Thin films of Zn_2SnO_4 films were deposited on glass substrates at different substrate temperatures 350°C, 400°C, 450°C and 500°C using nebulizer spray pyrolysis technique. X-ray diffraction analysis confirmed that the Zn_2SnO_4 films are polycrystalline with cubic structure. Zn_2SnO_4 films prepared at substrate temperatures 450°C have better crystallinity levels as compared to other substrate temperatures. SEM studies reveal that the Zn_2SnO_4 films have uniformly distributed grains over the entire surface of the substrate. The presence of elemental constituents was confirmed from EDAX analysis. PL spectra in the green region, which means Zn_2SnO_4 film, may have application as green light emitter. Optical transmittance measurements indicate that the Zn_2SnO_4 films have a direct band gap of the films various from 3.1 to 3.4 eV which in then confirm the formation of well-crystallized Zn_2SnO_4 films.

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