Research Article

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Structural, Compositional and Optical Properties of Nebulizer Sprayed Tin Oxide (SnO_2) Thin Films at Different Temperatures

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ABSTRACT

SnO_2 thin films are prepared by employing nebulizer spray pyrolysis (NSP) technique with various substrate temperatures as 300 ºC, 350 ºC, 400 ºC and 450 ºC. The morphological and optical properties of the materials are determined. The micro structural parameters like grain size, dislocation density, strain and crystallite size under different deposition temperatures are calculated. The X-ray diffraction pattern shows that the films are highly crystalline in nature. The grains of the thin films are found to grow with increased temperature. The grain growth and smoothness of the surface are observed from the scanning electron microscopy (SEM) analysis. The stoichiometric analysis is done by energy dispersive x-ray (EDX) analysis. From the UV-VIS spectrum it is observed that the percentage of transmission is enhanced with the increase of the substrate temperature. The photoluminescence (PL) spectra show the very sharp peaks indicating the interstitial oxygen vacancies.

Keywords: Nebuliser sprayed pyrolysis; SnO_2 thin films; Tin oxide.

1. INTRODUCTION

Metal oxide semiconductor thin films are the most promising devices among solid-state chemical sensors, due to their small dimensions, low cost, low power consumption, online operation and high compatibility with micro electronic processing. Tin oxide is an n-type, wide band gap semiconductor (Eg = 3.7eV) with the tetragonal rutile structure (Ravichandran *et al.* 2009; Moholkar *et al.* 2009; Sahni *et al.* 2007; Kenji Murakami *et al.* 2007; Rozati, 2006). Tin oxide serves as an important base material in a variety of conductance type gas-sensing devices (Patil *et al.* 2011; Nath and Nath, 2009; Kim *et al.* 2001; Manal Madhat Abdullah *et al.* 2012). Transparent, crack-free and adherent layers were obtained on different types of substrates (Si, SiO_2/Si). Various methods have been employed to prepare SnO_2 thin films including sputtering (Chatelon *et al.* 1994), spray pyrolysis (Gordillo *et al.* 1994; Nath and Nath; 2009; Yadav *et al.* 2008), dip coating, spin-coating sol–gel process (Mishra *et al.* 2002; Bose *et al.* 2002; Kilic and Zunger, 2002), chemical vapor deposition (Kilic and Zunger, 2002; Yadav *et al.* 2008), physical vapor deposition (Paraguay *et al.* 1999) and photochemical deposition (Daisuker and Masaya, 2006). Tin dioxide based thin films *n*-type semiconductors are attractive from the scientific and technological point of view (Paraguay *et al.* 1999). In the present work, SnO_2 thin films are synthesized by NSP method.

In a perfect tin oxide lattice, all the charge carrying valence electrons are tightly bound to the tin and oxygen atoms. Since activation energy of 3.7 eV is required to lift the valence electrons up to the conduction band, the probability of spontaneously elevating one electron at room temperature is a negligibly small value of 3.85×10^{-64} cm^{-3}. The deposited SnO_2 thin films were characterized for their structural, surface morphological, compositional and optical properties. X-ray diffraction was used for studying the structural properties of the films. Scanning electron microscopy was used to identify the surface morphology of the prepared films. The energy dispersive analysis by X-rays (EDX) was used to identify the elemental content in the films. The optical parameters were analyzed from the transmittance spectra obtained using UV-Vis-NIR spectrophotometer. The scope for material applications in the fabrication of gas sensor (Kim, *et al.* 2001; Abdullah *et al.* 2012), solar cells (Albery and Archer, 1977), light emitting diodes, photo diodes, photo detectors, and many other optoelectronic devices[Kim, *et al.* 2001; Albery and Archer, 1977; Ferrere *et al.* 1997) etc., can be known from the results obtained.

2. EXPERIMENTAL TECHNIQUES

Analytical grade tin (IV) chloride and sodium hydroxide pellet were used for the film preparation. Schematic diagram of the NSP setup is shown in fig. 1.

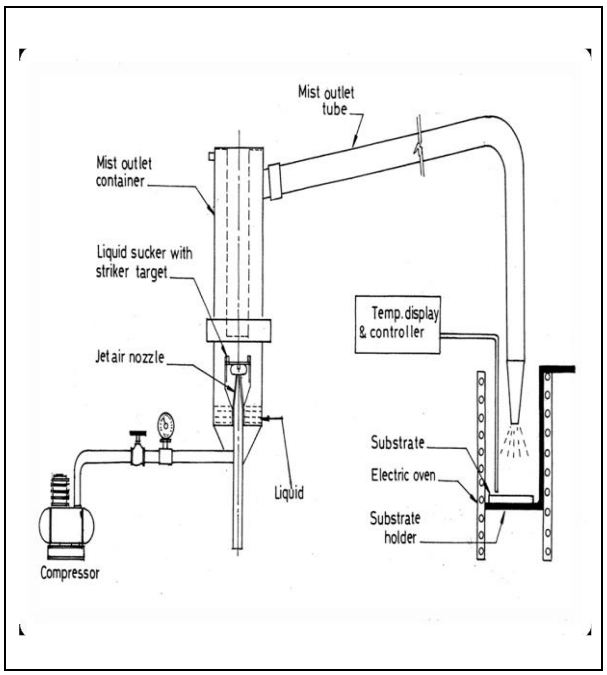

Fig. 1: Experimental setup of nebulizer spray pyrolysis

The spray solution was prepared by dissolving 0.1 M tin (IV) chloride in 50 ml of de-ionized water. This solution was then stirred for 10 minutes using magnetic stirrer. Few drops of concentrated hydrochloric acid were added to the solution for increasing the solubility of the solute. The mixed solutions were stirred well and heated for 3 hr at 60 °C. This solution was sprayed onto glass substrates heated at temperatures 300 °C, 350 °C, 400 °C and 450 °C in air. The substrate temperature was varied from 300 °C to 450 °C and controlled within ±5 °C using a Iron-Constantan thermocouple kept on the metallic hot plate surface. The deposition rate was fixed as 0.5 ml/minute. The distance of the nozzle to the substrate was set as 10 cm. The carrier gas pressure inside the apparatus was taken as 30 Pa. The pH of the bath was measured using digital pH meter (HANNA instruments). The pH of the solution was maintained as 5 and the deposition time taken was 10 min.

3. INSTRUMENTATION

X-ray diffraction data of the nebulizer sprayed SnO_2 samples were recorded with the help of X-ray diffractometer (Bruker D6 advanced diffractometer) with CuKα radiation (λ=0.1540 nm).The surface morphological studies were carried out using a high resolution scanning electron microscope (FEI Quanta FEG 200).The room temperature photoluminescence (PL) spectrum was performed on a spectrophotometer (Fluorolog Model FL3-11). Optical absorption spectrum was recorded using an UV-VIS-NIR spectrophotometer (Model JASCO-V-570).The composition of SnO_2 thin films was analyzed by the EDX micro analytic unit attached with scanning electron microscope (FEI Quanta FEG 200). Thickness of the deposited films was estimated using stylus profilometer (Miltutoyo SJ-301).

4. RESULTS & DISCUSSIONS

4.1 Structural Properties

4.1.1 X-ray Diffraction of SnO_2 Films

The crystalline material structure, including atomic arrangement, crystallite size and imperfections, were investigated. Fig.2 illustrates the XRD patterns of SnO_2 thin films at various temperatures. From the pattern, it was seen that all the diffraction peaks were positioned at (2 0 0) which revealed that the films were highly crystalline in nature with preferential orientation along the (2 0 0) plane. The peak also showed the phase purity that is no other secondary phases of the sample. The particle size t, dislocation density ρ and strain η of SnO_2 films were calculated using the following formulae.

$$\text{Particle size } t = \frac{0.9\lambda}{\beta cos\theta} \text{nm},$$

$$\text{Dislocation density } \rho = \frac{1}{D^2} \text{ lines/m}^2$$

$$\text{Strain } \varepsilon = \frac{\lambda}{Dsin\theta} - \frac{\beta}{tan\theta}$$

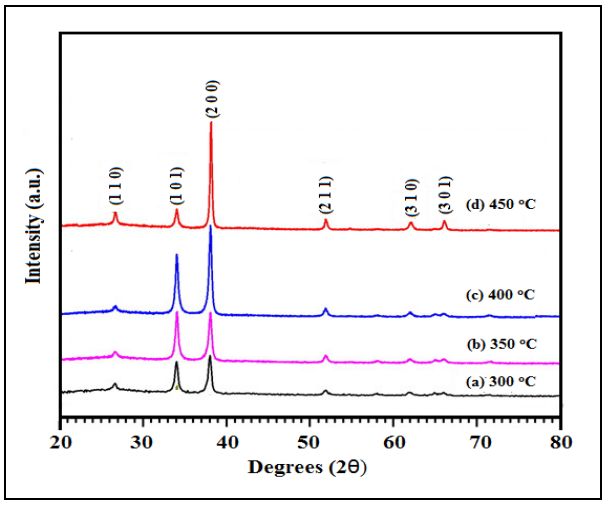

Fig. 2: XRD pattern of SnO_2 thin films

4.1.2 SEM Analysis of SnO_2 Thin Films

A uniform surface and tiny grains were observed from fig. 3(a) with average grain size of 250 nm at 300 °C. Grains were found to grow with increased temperature. The grain growth and smoothness of the surface were improved at the temperatures of 350 °C, 400 °C and 450 °C as shown in fig. 3(b), 3(c) and 3(d). Uniform surface morphology with larger grains was

observed on the surface of SnO_2 films at 450 ºC. No cracks or pinholes were observed. The scanned surfaces were uniformly covered with inter connected grains showing very limited grain boundary area. The crystallite size varied in the range from 33 nm to 66 nm as the temperature of SnO_2 film deposition increased from 300 ºC to 450 ºC.

4.2 Energy Dispersive Analysis by X-ray Spectroscopy (EDX)

The EDX spectrum demonstrates the stoichiometry analysis of the elements present in the SnO_2 thin films. Fig.4 shows the EDX pattern of the SnO_2 films deposited under the optimized conditions from temperature 300 ºC to 450 ºC. It was observed from the EDX spectrum that the prepared SnO_2 has the nearly stoichiometric ratio of Sn and O but with oxygen deficiency. The ratio of Sn:O was found to be 52.98 : 47.02. This is clearly evident that this oxygen deficiency gives lower resistivity to SnO_2 films heated at 450 ºC in the present study.

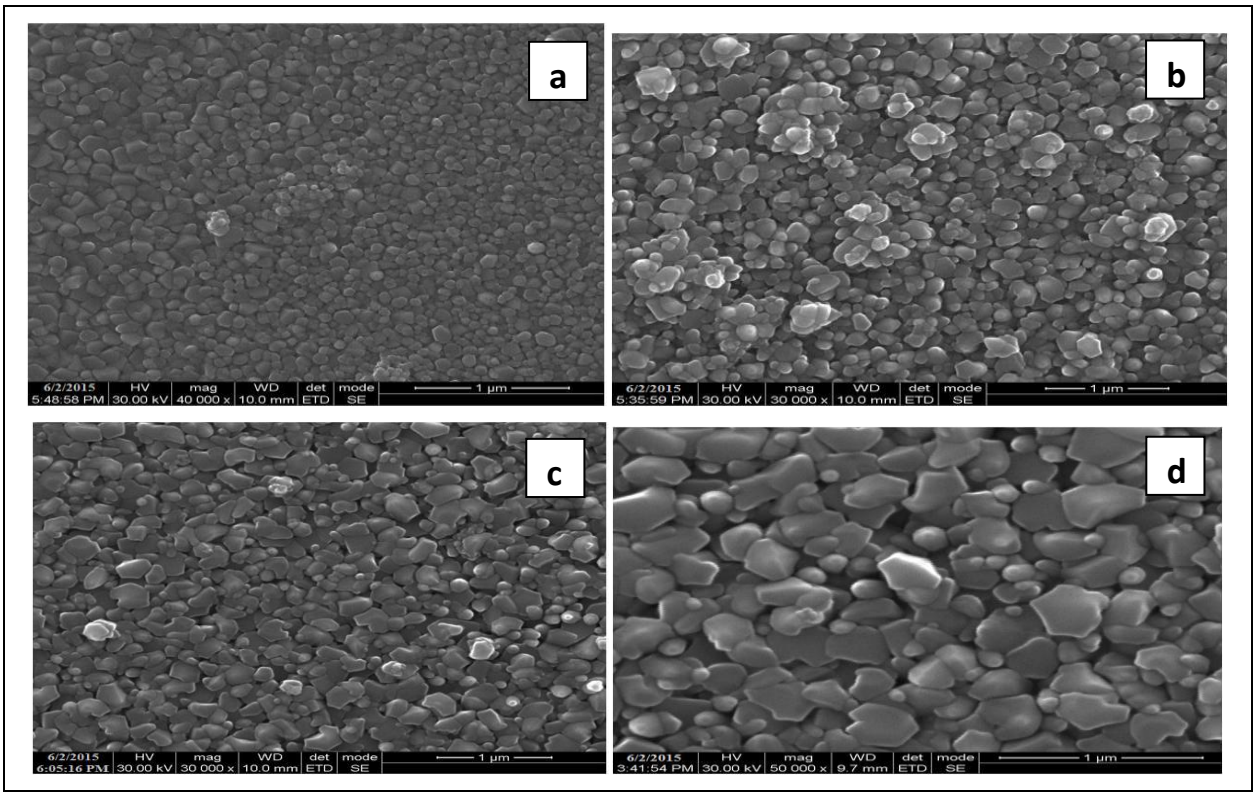

Fig. 3: SEM analysis of SnO_2 thin films (a) 300 ºC (b)350 ºC (c) 400 ºC (d) 450 ºC

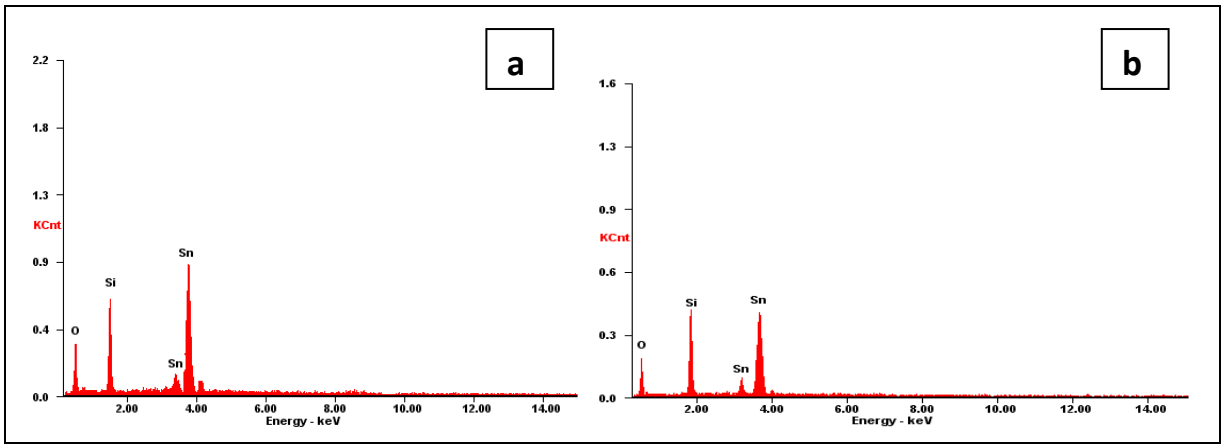

Fig. 4 (a & b): EDX patterns of SnO_2 thin films (a) 300 ºC (b) 350 ºC

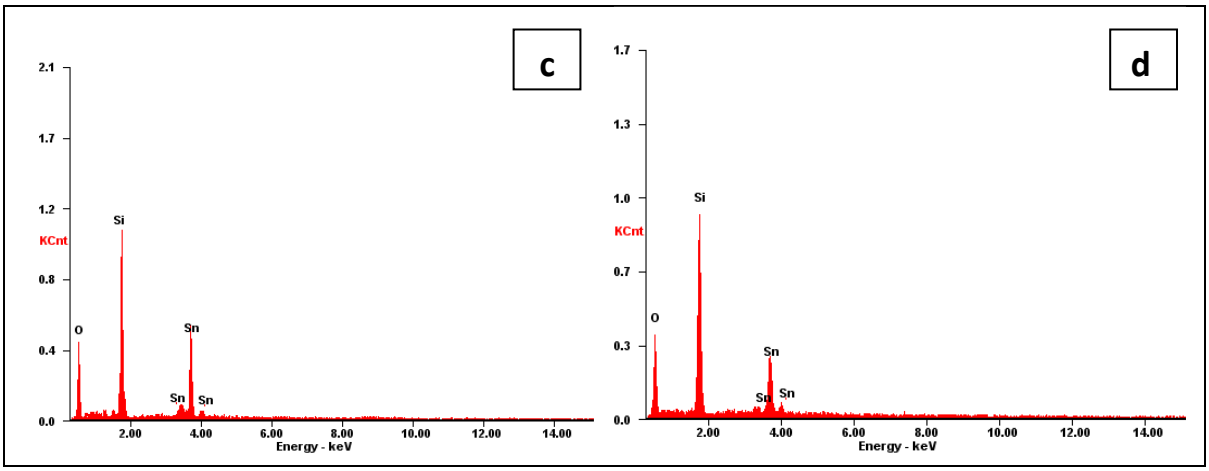

Fig. 4 (c & d): EDX patterns of SnO_2 thin films (c) 400 °C (d) 450 °C

4.3 Thickness Measurement

Thickness is one of the physical properties which differentiate a thin film from the bulk. In all the thickness measurement technique, it is generally assumed that the films are homogenous and more or less uniformly deposited on the substrate, so that the film will have a mean thickness. In the present study, the thickness of the substrates was measured using "stylus profilometer" at various points on the substrate and their average was taken as the film thickness. The SnO_2 films deposited under the optimized conditions from temperature 300 °C to 450 °C measured the film thicknesses as 222 nm, 227 nm, 232 nm and 239 nm respectively.

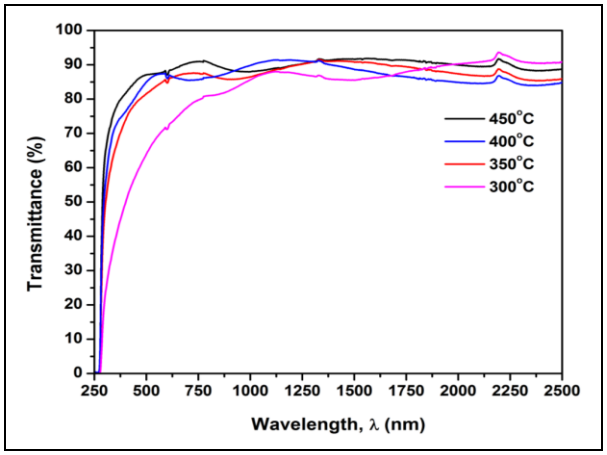

Fig. 5: Transmittance spectrum of SnO_2 thin films

5. OPTICAL PROPERTIES

5.1 Ultra Violet-Visible (UV-Vis) Spectroscopy

Fig. 5 shows the transmission spectra in the wavelength region of 200-2500 nm for the SnO_2 films deposited at different heating temperatures 300 °C, 350 °C, 400 °C and 450 °C. The transmittance at 450 nm for each spectrum was observed as about 82, 86, 87 and 89% respectively.

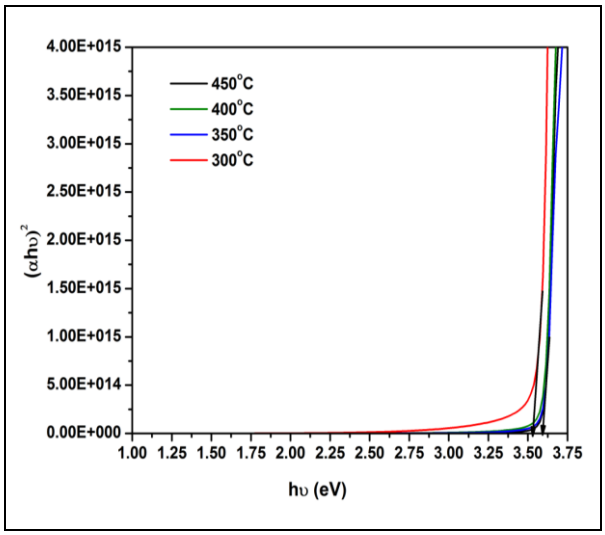

Fig. 6: Plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for the SnO_2 films

It was observed that as the percentage of transmission enhanced with increase in heating temperature. Maximum percentage transmission was recorded for the SnO_2 film deposited at a temperature of 450 °C were shown in fig. 5. It was reported that SnO_2 semiconductor oxide film is a degenerate semiconductor material with band gap values (Eg) varying in the range of 3.45 to 4.58 eV (Sahni *et al.* 2007; Kenji Murakami *et al.* 2007).

The variation of $(\alpha h\nu)^2$ versus $(h\nu)$ for the SnO_2 films deposited at different temperatures was shown in fig.6. The straight line portion indicates that the optical transition was direct in nature. The direct gap value had been determined by extrapolating the vertical straight

line portion of the plot to the energy axis. The values of band gap energy from 3.52 to 3.65 nm were given by the intercept on energy axis for the SnO_2 films heated from 300 ºC to 450 ºC. These values are higher than the value of Eg = 3.57 eV reported for single crystal SnO_2.

5.2 Photoluminescence (PL) Spectra

The room temperature photoluminescence (PL) spectra are shown in fig.7. It was observed from fig. 7, that there were two emission bands in the spectra: a sharp ultra-violet (UV) near-band emission peak centered around 392 nm (3.11 eV) and a sharp visible deep-level green emission centered around 462 nm (2.65 eV) for the SnO_2 films.

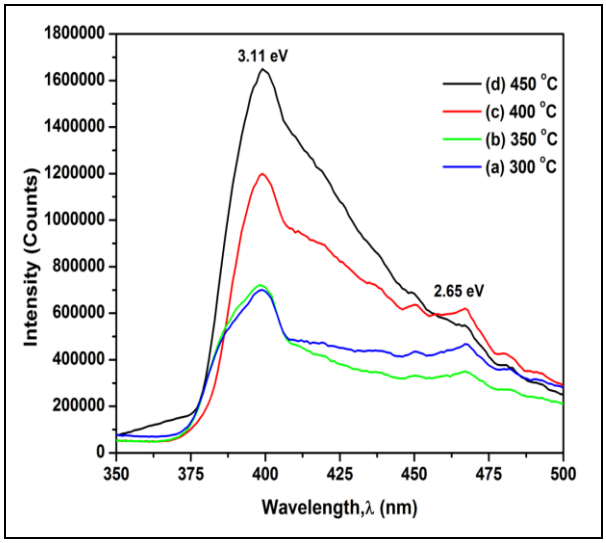

Fig. 7: Plots of PL spectrum of SnO_2 thin films

This ultra-violet peaks can be attributed to the oxygen vacancies in SnO_2. Fig.7 shows the PL spectra of all films with a very sharp peak below 462 nm due to the presence of interstitial oxygen vacancies. The origin of the blue-green emission is due to transition from conduction band to the acceptor level corresponding to the anti-site of oxygen.

6. CONCLUSION

This study investigated the effect of the substrate temperature on the structural, optical, compositional and morphological properties of undoped SnO_2 films prepared by nebulizer spray pyrolysis deposition method. The films were deposited at various substrate temperatures ranging from 300 °C-450 °C in steps of 50 °C and characterized by different optical and structural techniques. X-ray diffraction studies showed that the crystallite size and preferential growth directions of the films were dependent on the substrate temperature. These studies also indicated that the films were amorphous at 300 °C and polycrystalline at the other substrate temperatures used. UV and visible spectroscopic studies revealed that a strong vibration band, characteristic of the SnO_2 stretching mode, was present around 630 cm^{-1} and that the optical transmittance in the visible region varied over the range 75–95% with substrate temperature, respectively. The films deposited at 400 °C exhibited the best results of the characterizations used.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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