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Structural and Optical Properties of SnO_2 Thin Film by Nebulizer Spray Pyrolysis Technique

S.Palanichamy[1], L.Amalraj[1] J.Raj Mohamed[2] and P.S.Satheesh Kumar[3]

[1]P.G. and Research Department of Physics, Virudhunagar -626001, Virudhunagar, Tamilnadu, India
[2]P.G. and Research Department of Physics, H.H.The Rajah's College, Pudukkottai -622001, Tamilnadu, India
[3]Department of Physics, NPR College of Engineering & Technology, Natham, Dindigul-624 401, Tamilnadu, India

*Corresponding Author: S.Palanichamy[1], L.Amalraj[1]

E-mail: (e-mail: nanopalani@gmail.com)
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Abstract

Nano crystalline tin oxide (SnO_2) thin film was prepared at optimized substrate temperature 300 ^{0}C with 0.05M concentration using a simple and easy nebulizer spray pyrolysis technique. The film was characterized by X-ray diffraction analysis(XRD), optical transmittance study (UV-Vis-NIR double beam Spectrophotometer), scanning electron microscopy (SEM) and photoluminescence analysis(PL). The film was shiny, uniform and good adherent with polycrystalline nature. The X-ray diffraction pattern shows the tetragonal structured SnO_2 film with (110) preferred orientation. The average crystalline size was found to be 53.17 nm. SEM image exhibits that the film has no voids and cracks. The higher transmittance (91%) of photon energy was observed by transmittance spectra. The band gap energy of the as prepared SnO_2 thin film was obtained to be 3.78 eV.

Key word: absorption, band gap, Nebulizer spray pyrolysis, thin film
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1. Introduction

In recent years, the nano-structured metal oxides have been most widely studies materials owing to their many applications. Tin oxide (SnO_2) is the most important transparent conducting oxide (TCO) material among various TCO materials such as ZnO, CdO, In_2O_3 etc., due to their high transmittance, high reflectance, chemically inert, mechanically hard, not affected by atmospheric conditions. The SnO_2 film were used in various applications such as window materials in solar cell [1], gas sensors [2], transistor [3], optoelectronic devices [4], lithium batteries [5] , flat panel display etc., Its splendid physical and chemical properties makes it one of the top-quality material used for detection of distinct types of gases.

Different types of techniques have been used to prepare SnO_2 thin film such as electron beam evaporation

[6], sputtering [7], thermal evaporation [8], spray pyrolysis [9] and nebulizer spray pyrolysis [10]. The binary and ternary oxide thin film such as MgO [11], Cd doped SnO_2 [12], and Tin doped zinc oxide [13] have been deposited using Nebulizer spray pyrolysis technique. Among various techniques nebulizer spray pyrolysis is a simplified spray pyrolysis technique. This is cost effective, low volume of spray solution and time saving technique by which tiny droplets of particles can be deposited. The structural, optical, morphological and PL studies have been investigated and analyzed.

2. Experimental technique

Nebulizer spray pyrolysis technique consists of a nebulizer unit, temperature controller, a “well” shaped furnace and a compressor unit as shown in Fig.1. SnO_2 thin film was deposited on amorphous glass substrate by spraying an aqueous solution containing 0.05M tin tetra chloride (Sigma-Aldridge) with nebulizer spray pyrolysis technique. Well cleaned glass substrate of dimension 7.5 x 2.5 x0.25 cm^3 was kept on the preheated hot plate. The optimized substrate temperature was taken as 300 ^oC. The compressed air was used to carry the oxygen gas maintained at 2.5 Kg/cm^2 corresponding to average pressure solution rate of 5ml per 15 minutes. The distance between nozzle and substrate was kept at 3cm. It does not require high quality target and vacuum. The thickness of the film and rate of deposition can be easily controlled.

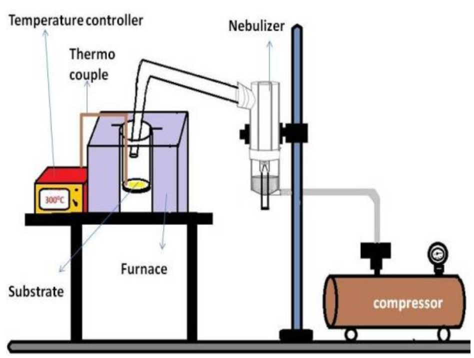

Fig.1 Schematic diagram of a Nebulizer spray pyrolysis technique

FILM CHARACTERIZATION

The chemical and structural phases of the SnO_2 thin film was determined by X-Pert Pro x-ray diffractometer (Cu- K_α, λ=1.5418 Å) over a 2θ range of 10-70^o. The optical properties using optical absorption spectrum was measured using UV-Vis-NIR double beam spectrophotometer (Hitachi U3410 model) over the wavelength range 300-1100 nm. Scanning electron microscope (SEM) was used to detect the dispersion of particles; rough morphology of the as deposited SnO_2 film was examined by scanning electron microscope (SEM, Genesis model). The thickness of the SnO_2 layers was found with a stylus profile meter (Mitutoyo SJ-301).

3. Results and Discussion

Structural analysis

Fig. 2 shows that the x-ray diffraction patterns for SnO_2 thin film deposited at optimized substrate temperature 300 ^oC. SnO_2 thin film exhibit four major diffraction peaks related to the diffraction angle 26.59^o (110), 33.82^o (101), 37.86^o (200) and 51.67^o (211) with a preferred orientation along (110) plane. The standard diffraction peak exhibited by SnO_2 thin film is matched with the JCPDS card No. 88-0287 corresponding to tetragonal structure. M.M.Abdullah et al [14] reported tetragonal structured SnO_2 thin film with (110) preferential orientations grown by thermal spray pyrolysis method. The lattice constants in the present case was a=b=4.715 and c= 3.167 Å whereas the reported values are a=b=4.738 and c=3.187Å.

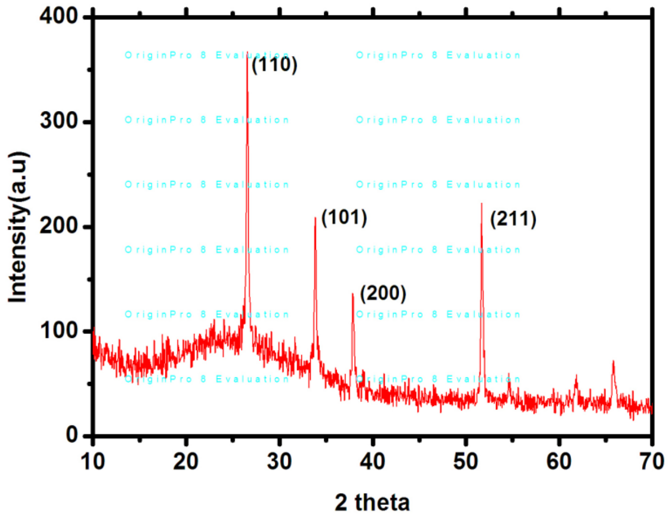

Fig. 2 X-ray diffraction pattern of SnO_2 thin film from 10^o to 70^o at room temperature.

The average crystalline size and strain for the as-deposited SnO_2 thin film for the substrate temperature at 300 ^oC can be studied by Williamson-Hall plot as shown in Fig. 2. In general, crystalline size and lattice strain influence the Bragg peaks in discrete ways such as instrumental factors, the existence of defects to the ideal lattice, differences in strain in different grains and the crystalline size. Both these two effects lift the peak width and intensity and shift the Bragg peak (2θ) position accordingly. It is much feasible to divide the effects of size and strain. The size broadening is independent of the length of the reciprocal lattice vector (q) and strain broadening increases with increasing q values. There will be both size and strain broadening come about in most of the cases.

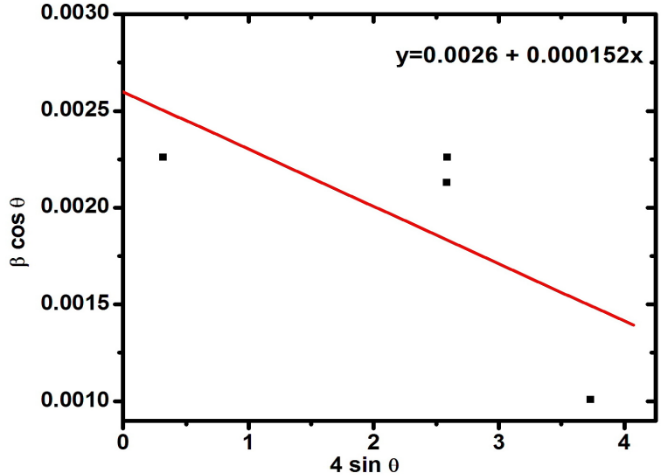

Fig. 3 depicts the Williamson-Hall analysis of SnO_2 thin film at optimized substrate temperatures assuming UDM. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

Williamson-Hall analysis is mainly used to divide these size and strain by combining the two equations.

$\beta_{hkl} = \beta s + \beta D$ ----------------------- (1)

$\beta_{hk} = (k\lambda/D\cos\theta) + (4\varepsilon \tan\theta)$ ------------------------ (2)

Rearranging the equation gives:

$\beta_{hkl}\cos\theta = (k\lambda/D) + (4\varepsilon \sin\theta)$ ---------------------- (3)

Equation (3) stands for the uniform deformation model (UDM), where the strain was assumed uniform in all crystallographic directions. The term ($\beta\cos\theta$) was plotted with respect to ($4\sin\theta$) for the peaks of SnO_2 with cubic phase. Therefore, the slope and y-intercept of the fitted time represent strain and grain size respectively. The results of the UDM analysis for the SnO_2 thin film are shown in Fig. 3.

The average grain size of SnO_2 thin film calculated by Debye-Scherrer formula [15]

$D=0.9\lambda/\beta\cos\theta$ ----------------------- (4)

Where,

λ – Wavelength of X-ray,(λ=1.5418Å)

β- FWHM (Full width Half Maximum)

θ- Angle of diffraction

The relation calculated the micro strain (ε) of SnO_2 thin film

$$\varepsilon = \beta \cos\theta/4 \quad \text{------------------------} \ (5)$$

The average grain size and micro strain of SnO_2 thin film deposited at substrate temperature 300 ^oC was found to be 53.17 nm and 1.7 x 10^{-4} whereas the average grain size and micro strain obtained by Williamson-Hall analysis was 50.34 nm and 1.0 x10^{-4}, which was closely matched with the Debye-Scherrer value.

Optical analysis

The substrate temperature influenced change in transmission and optical absorption spectra of SnO_2 film recorded in the wavelength range of 300-1100 nm are presented in Fig.4 and Fig. 5 respectively. Fig. 4 shows that the average transmittance of the film varies between 85 and 91%. It is noticed that large percentage of transmittance for the film grown at 300 ^oC substrate temperature due to the low in thickness of the film may be due to the decreased defect density and the decrease in the optical scattering of the film.

Fig. 5 depicts that the strong absorption edge in the ultraviolet region was incurred for SnO_2 thin film. This absorption edge in the ultraviolet region is owing to band-to-band transition to the conduction band have been involved. Moreover, the decrease in electron transition attributes the decrease in absorption.

The optical band gap of as deposited SnO_2 thin film is determined by applying the Tauc model [16]

$$(\alpha h\vartheta) = A\,(h\vartheta - E_g)^n \quad \text{--------------------------} \ (6)$$

Where E_g is the band gap, A is energy independent constant, ϑ is transition frequency and the exponent n characterizes the nature of the band transitions. For semiconductors, n=1/2, 2, 3/2, 3 values corresponding to the allowed direct, allowed indirect, forbidden direct, and forbidden indirect transition respectively. Since, n=1/2 and the absorption coefficient (not shown) is of the order of 10^4 cm^{-1} supports the direct band gap nature of SnO_2 semiconductor for allowed direct transition. Fig. 6 shows the plot for the variation of $(\alpha h\vartheta)^2$ against $h\vartheta$. The direct band gap energy values were obtained by extrapolating the linear portion to the energy basis at $\alpha = 0$.

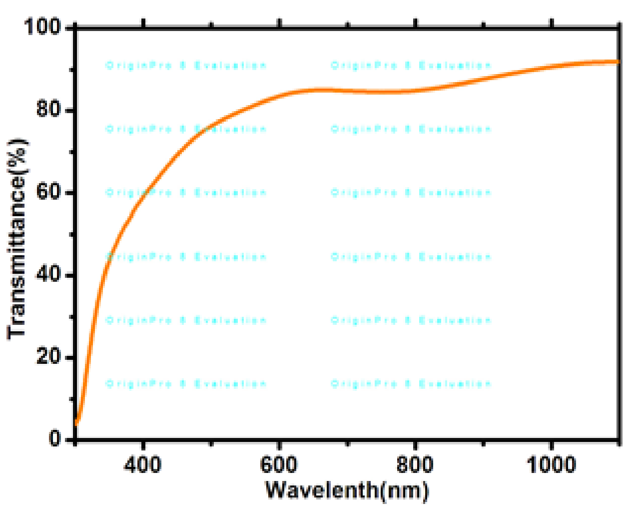

Fig. 4 Transmission spectra of SnO_2 thin film at 300 ^oC substrate temperature.

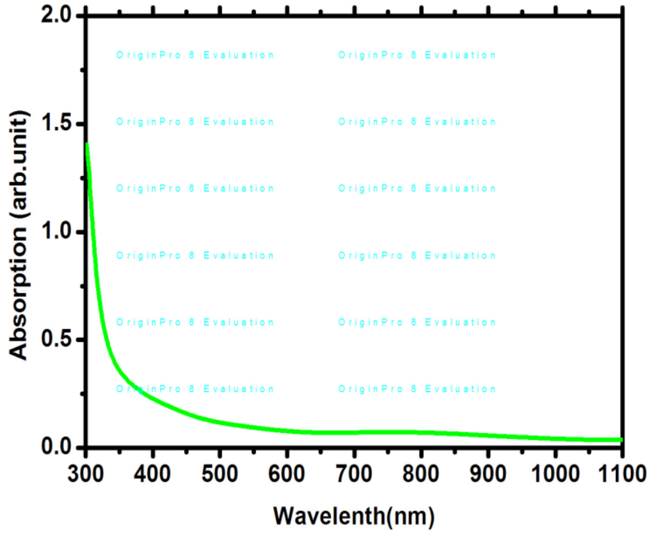

Fig. 5 Absorption spectra of SnO_2 thin film at 300 ^oC substrate temperature.

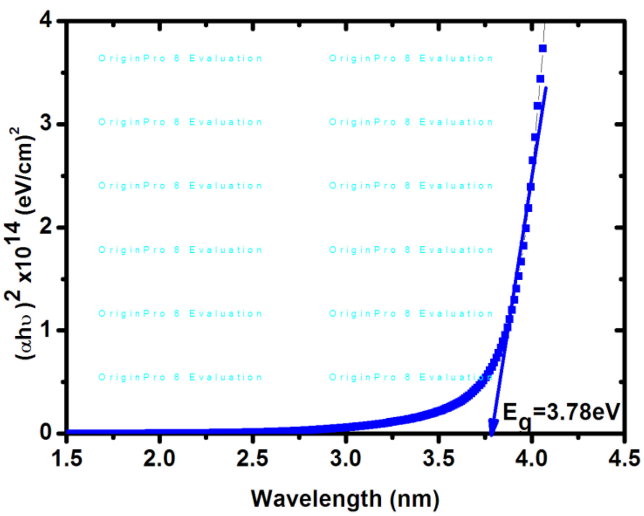

Fig. 6 The $(\alpha h\vartheta)^2$ versus hυ curves for the optical band gap determination of SnO_2 thin film.

It was observed that the obtained band gap energy is 3.78 eV. M.M.Abdullah et al [14] had reported a band gap value of 3.90 eV for the film prepared by the thermal spray pyrolysis technique at substrate temperature 450 ^oC of SnO_2 thin film on glass substrate. Moreover, the obtained band gap values are in good agreement with published band gap energy value (3.71eV) [17].

Morphological and elemental analysis

The scanning electron microscope is one of the versatile tool to study morphology of the surface of the film. The surface morphology of as prepared SnO_2 thin film was analyzed by SEM photograph shown in Fig.7. It is observed that SnO_2 film has poly- crystalline nature with in the nano scale range. Besides, the distributions of grains which are very smooth, homogeneous and very fine pores were observed on the entire surface of the film. The atomic percentage of tin and oxygen elements were observed as 60.3% and 39.7% respectively as shown in Fig.8.

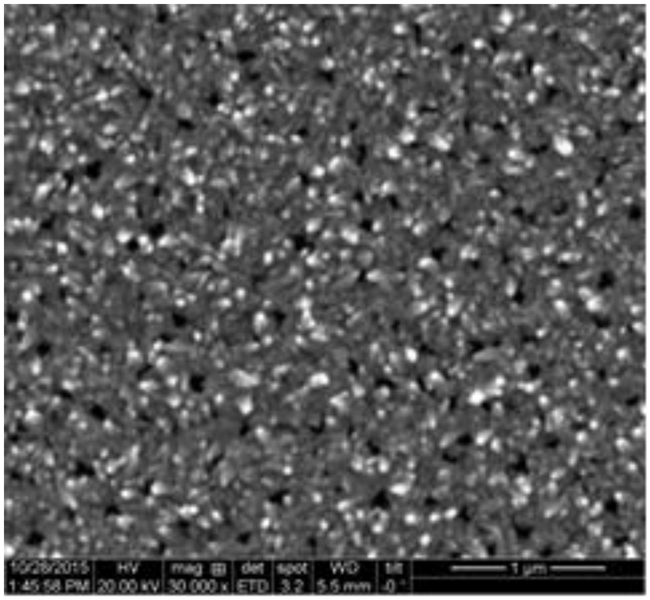

Fig. 7 Scanning electron microscope (SEM) image of SnO_2 thin film for the substrate temperature at 300 ^oC,

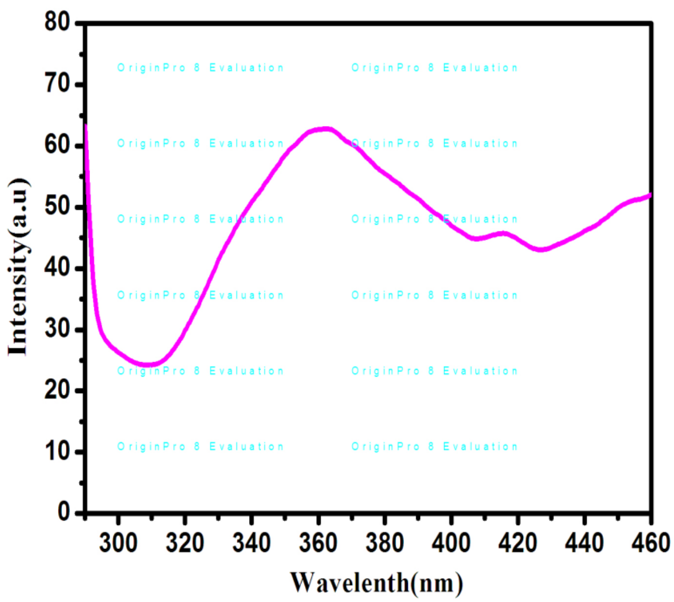

Fig.8. Photoluminescence spectrum of the SnO_2 thin film for the substrate temperature at 300 ^oC,

Photoluminescence analysis

Fig. 9 shows that Photoluminescence spectrum employed under the excitation wavelength of 270nm [18]. There are two emission peaks occurs. The broad emission peak observed at 360nm and another small peak observed at 415nm. Those two emission peaks typically occur at UV region and near UV region respectively. The deposited film cognate to defect levels within the band gap of SnO_2 colligated with various types of oxygen vacancies or Sn interstitials, which have formed during the synthesis process.

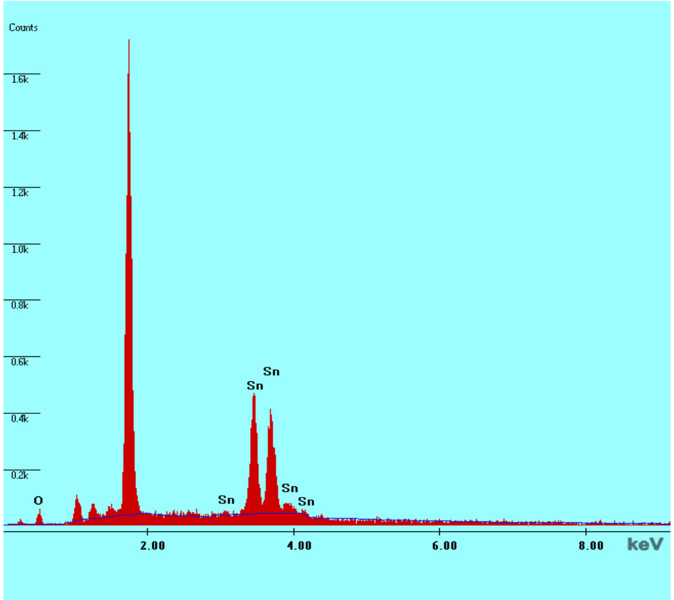

Fig. 9 Energy dispersive X-ray (EDX) pictures of SnO_2 thin film at substrate temperature 300 ^{o}C,

The interstitial position of Sn^{2+} ions originates in the near UV emission. It is explicated by the passage from prolonged Sn_i states, which are little below the Sn_i band and valence band. The excited electrons relax to prolonged Sn_i states and transit to the valence band with the emission in the near UV region. Sagal et al [19] described that the property of photoluminescence is sensible to the presence of defects and the quality of crystal structure.

IV Conclusion

Nano crystalline Tin oxide (SnO_2) thin film was prepared on micro glass substrate at 300 ^{o}C by Nebulizer spray pyrolysis technique. The x-ray diffraction pattern revealed that the as deposited film had tetragonal crystal structure with preferable orientation along (110) plane. The optical transparency increased up to 91 % in the visible region. The direct band gap value was found using transmittance curve by UV-VIS- spectrophotometer. The PL spectra consist of the broad emission peak located at UV region and small peak located at near UV region. The investigated results of the SnO_2 thin film deposited by nebulizer spray pyrolysis technique ensure the stability of the film and their employability in gas sensor applications.

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