Influence of Substrate Temperature on Structural, Electrical and Optical Properties of Nanostructured SnO$_2$ thin Films Deposited by Spray Pyrolysis Technique

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Abstract—SnO$_2$ nanostructured thin films were deposited on ultrasonically cleaned glass substrates at different substrate temperatures using the spray pyrolysis technique. The influence of substrate temperature on structural, morphological, electrical and optical properties of thin films have been investigated by X-ray diffraction (XRD), scanning electron microscopy(SEM), energy dispersive spectroscopy (EDAX), two probe method and UV-Vis spectroscopy respectively. It was found that the deposited thin films were showing a tetragonal structure with a preferred orientation along (200) direction. Scanning electron microscopy results have shown that the substrate temperature influenced the growth mechanism of the SnO$_2$ thin films. Optical properties of thin films were analyzed by UV-Vis spectrophotometer. Optical band gap values were determined using Tauc extrapolation at different substrate temperatures. As the substrate temperature increased from 350°C to 450°C, optical band gap was found to increase from 3.14 eV to 3.67 eV. The figure of merit has been calculated from transmission spectra and the electrical properties are analysed and discussed.

Keywords—SnO$_2$, Spraypyrolysis, XRD, Opticalproperties

I. INTRODUCTION

Transparent and conducting oxide materials (TCOs) have been showing the promising material for transparent electrodes for the recent past. TCOs have large electrical conductivity and high optical transmittance with direct band gap energy [1,2]. They have been widely used in the fields of electronics, optoelectronics and photovoltaic applications [3, 4]. The majority of these TCO materials research have been focused over the past few decades on the three main n-type materials such as In$_2$O$_3$, SnO$_2$, and ZnO. Most of them are a concern with empirical studies to improve the performance of these semiconducting metal oxides and meet ever-increasing industrial requirements. Among these materials, Tin oxide (SnO$_2$) is grabbing much attention of researchers due to its naturally non-stoichiometric prototypical nature, an n-type semiconductor with a wide band gap of 3.6eV, plasma frequency in the infrared region, transparency for visible light, and low electrical sheet resistance. Due to these features, SnO$_2$ is widely using in solar cell applications [5], gas sensor [6] electrochromic devices and flat panel displays [7]. Thin films as a 2D system are of great importance to many real time applications. Their material costs are very low and also execute better performance when it comes to surface processes.

In practice, prepared tin oxide thin films contain a good number of oxygen vacancies, making electrons available for conduction which makes thin films are very usefull in various applications. Various techniques have been employed to deposit tin oxide thin films such as chemical vapour deposition (CVD) [8], sol–gel technique [9], spray pyrolysis [10], RF sputtering [11] and pulsed laser deposition [12]. Among all these techniques, spray pyrolysis is a flexible technique for preparation of transparent conducting oxides. It has proved to be reproducible, simple and inexpensive, as well as an appropriate method for large area applications. Apart from the simple experimental setup, fast growth rate and huge production capability for large area coatings make them useful for a solar cell as well as industrial applications. In addition to the afore said, spray pyrolysis opens up the feasibility to control the thin film morphology and grain size in the nanometer range.

II. RELATED WORK

In this paper we focussed to present investigation, the spray pyrolysis technique is used to deposit nanostructured SnO$_2$ thin films at different substrate temperatures by keeping the concentration of precursor and rate of flow as constant. Furthermore, the effects of substrate temperature on the
structural, optical and electrical properties of the SnO₂ thin films are investigated.

III. METHODOLOGY

The required amount of tin (II) dichloride dehydrate (SnCl₂·2H₂O) (99.8%, Sigma-Aldrich) is dissolved in deionised water and stirred continuously for 30 min. A few drops of hydrochloric acid were added to obtain a clear solution. All the glass substrates (Blue star, India) are ultrasonically cleaned for 10 minutes in a soap solution, distilled water and finally rinsed with ethanol. Then after dried in a hot air oven for fifteen minutes at 100°C. The precursor solution is sprayed using PC interfaced chemical spray pyrolysis equipment (Holmarc Model no: HO-TH-04BT) at different substrate temperatures in the ranging of 350 to 450°C, and other optimised deposition conditions are tabulated in table 1.

![Image](image.png)

Table 1 Optimized deposition conditions

| Condition       | Description                |
|-----------------|----------------------------|
| Solvent         | Di-ionized water           |
| Precursor       | SnCl₂·2H₂O                 |
| Concentration   | 0.1M                       |
| Solution flow rate | 1 ml/min          |
| Carrier gas     | Dry air                    |
| Carrier gas pressure | 0.8 bar             |
| Substrate pressures | 350 °C – 450 °C          |
| Substrate       | Glass                      |
| Deposition time | 15 minutes                 |

The structural characteristics of the films were studied using X-ray diffraction (Rigaku Ultima IV X-ray diffractometer, Tokyo, Japan). The morphology of the thin films was observed using scanning electron microscope (Carl ZEISS EVO 18, Germany). The optical transmittance spectra were recorded by using a double beam shimadzu UV-3100 spectrophotometer in the wavelength range of 200-900 nm at room temperature. The electrical properties were studied by using two probe measurement techniques and connecting an electrometer (Keithely 6517B) was used to monitor the sheet resistances.

IV. RESULTS AND DISCUSSION

A. Structural studies

i) X-ray diffraction studies

Fig. 1. Depicts the X-ray diffraction (XRD) data of tin oxide thin films deposited at various substrate temperatures. The X-ray diffraction reveals that the SnO₂ thin films are casseriterite tetragonal structure with rutile phase and it is good in agreement with JCPDS card No. 41-1445. Hence it is confirming that the material deposited is SnO₂. It is found that all the films are polycrystalline nature with dominant peaks correspond to (200), (211), (110), (101), (310) and (301) orientations, similar results have been reported [13] At low substrate temperature the intensity of the (110) is high while increasing the substrate temperature intensity is decreased and also the intensity of (200) reflection is increased, it is attributed due to the recrystallization process at higher substrate temperature and also manifests that better crystalline thin films deposited at higher substrate temperature. The crystallite size is determined using Debye Scherrer’s formula [14].

\[
Crystallite\ size\ (d) = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)
\]

Where \(\lambda\) is the wavelength of Cu Kα radiation (1.5406 Å), \(\beta\) is the full width at half maximum (FWHM) corresponding to the diffraction angle \(2\theta\). Calculated crystallite size values are tabulated in table 2. It is noticed that crystallite size increased with increasing substrate temperature. This may be caused by the fact that the smaller crystallites have sharper surfaces convexity. Hence it provides a larger area of associate between adjacent crystallite, making possible coalescence process to from larger crystallites.

In fact, the deposition process involving dislocation is a matter of importance. Dislocations are imperfect in a crystal associated with a mismatch of the lattice in one part of the crystal with respect to another part. Unlike, interstitials atoms and vacancies, dislocations are not equilibrium imperfections i.e., the thermodynamic discussion is insufficient to explain their existence in the noticed dislocation densities. The crystallization levels of the thin films are good because of their low number of defects in the thin film. Dislocation density and strain were determined from equations (2) & (3) [15-17]. With increasing the substrate temperature dislocation density (\(d\)) found to be decreased. This may be attributed due to an increase in the grain size and decrease in the internal micro-strain within the thin films. The decrease in dislocation density shows the formation of good quality thin films. It is due to the non-homogeneous strain component near grain boundaries. The variation of strain and dislocation density with substrate temperature is tabulated in table-2.
Strain ($\varepsilon$) = $\frac{3\cos\theta}{4}$ -------------(2)
Dislocation density ($\delta$) = $\frac{1}{d^2}$ -------------(3)

The preferred orientation of the different crystalline planes can be calculated by Harris’s analysis, by calculating texture coefficient and it is determined by using equation (4) [18]. the texture coefficient of (200) plane increases remarkably with a concomitant decrease in (110) with increasing substrate temperature during the deposition process which results in reduced planar density on (110) plane up to 450°C. Variation of texture coefficient for all miller planes concerning the substrate temperatures is shown in fig.2

Texture coefficient (TC) = $\frac{I(hkl)/I_0(hkl)}{\sum I(hkl)/I_0(hkl)}$ -------------(4)

Where $I(h k l)$ and $I_0(h k l)$ are the integrated intensity ratios of the thin films and bulk randomly oriented SnO$_2$ powder respectively in X-ray diffraction pattern for a given peak and n is the number of diffraction peaks considered for calculation.

![Figure 2](image1.png)

Fig.2. variation of texture coefficient of SnO$_2$ thin films

The (200) plane is considered as preferred orientation in all thin films with different substrate temperature. This analysis confirms that huge vacancies lie on (200) plane in the case of the thin film which is deposited at higher substrate temperature. Effects of these changes on electrical properties have been discussed at the end of this paper. The structural parameters such as lattice constants and interplanar spacing for the tetragonal structure is determined by the following relation [19,20].

$$\frac{1}{d^2} = \left(\frac{h^2+k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right)$$ -------------(5)

Where a, c are lattice constants d is the interplanar spacing and (hkl) are miller indices of the corresponding plane. Calculated lattice constants are tabulated in table2. The lattice constant ‘a’ is decreasing with increasing the substrate temperature.

### Table 2 Structural properties of SnO$_2$ thin films at different substrate temperatures

| Substrate temp. (°C) | Crystallite size from XRD (nm) | Dislocation density (10$^{15}$ lines/meter$^2$) | Strain | Lattice parameters |
|----------------------|-------------------------------|-----------------------------------------------|--------|-------------------|
| 350                  | 18                            | 2.67                                         | 1.8 X 10$^{5}$ | a = 0.47, c = 0.317 |
| 400                  | 23                            | 1.77                                         | 1.5 X 10$^{5}$ | a = 0.46, c = 0.315 |
| 450                  | 24                            | 1.69                                         | 1.4 X 10$^{5}$ | a = 0.45, c = 0.316 |

### ii) Scanning electron microscopy and Elemental analysis.

The surface features of SnO$_2$ thin film sprayed at various substrate temperatures have shown in Fig. 3. It is apparent that a notable morphology variation is observed while the substrate temperature is increased. At lower substrate temperature (350°C) particles were formed in small size with low density. As substrate temperature increases in the range of 400-450°C, particles were formed in to lager size and high density due to the amount of greater heat provided to the system assisting the enhancement in crystallization. However, energy dispersive spectra indicate that well defined peaks corresponding to Sn and O which confirms that the final thin film stoichiometry is SnO$_2$.

![Figure 3](image2.png)

Fig. 3. SEM images and EDX spectra of SnO$_2$ thin films

### iii) Optical properties

The transmission spectra of tin oxide thin films deposited at different substrate temperatures as a function of wavelength from 300-900nm are shown in fig.4. The average transmission percentage in the visible region has been found to vary from 62% to 82% depending upon the substrate temperature for all the samples. As the increase in transmission percentage is increased with increasing substrate temperature. At lower substrate temperatures, i.e. at 350°C, relatively lower transmission percentage is due to the development of milky films and that is due to partial decomposition of sprayed droplets. In general in the visible region of the spectrum, the transmission is very high. It is
due to the fact that the reflectivity is less and there is low absorption due to movement of free electrons from valance band to conduction band due to optical interference effects. It is possible to maximise the transmission percentage of the tin oxide thin films at a particular region of wavelengths. Relatively higher transmittance of about 82% at 890nm for the films deposited at 450°C has been observed. In order to determine the thickness of the thin films (t) can be calculated by using the wavelengths corresponded to two successive peaks in transmittance spectra (λ₁ and λ₂) and following relation [21].

\[
\text{Thickness (t)} = \frac{\lambda_1 \lambda_2}{2(n_1 \lambda_2 - n_2 \lambda_1)} \quad \text{(6)}
\]

Where \(n_1\) and \(n_2\) are the corresponding refractive indices and can be approximated by \(n_1 \approx n_2 \approx 2\) as follows

\[
t \approx \frac{\lambda_1 \lambda_2}{4(\lambda_2 - \lambda_1)}
\]

The results of the optical and structural measurements for SnO₂ films at different substrate temperatures are 541nm, 510nm and 470nm.

The optical band gap (\(E_g\)) of the thin films is determined from the extrapolation of the linear part of the \((ahv)^2\) against \((hv)\) plot using the following formula [22]

\[
ahv = A (hv - E_g)^\frac{1}{2} \quad \text{(7)}
\]

Absorption coefficient (\(\alpha\)) is calculated by using the following equation

\[
\alpha = \frac{1}{T} \ln T
\]

Where \(T\) is the transmittance and ‘t’ is the thickness of the film.

The variation of \((ahv)^2\) with the energy of a photon of SnO₂ thin films prepared at various substrate temperatures have depicted in Fig. 5. The optical band gap of the thin film is increased from 3.18 eV to 3.67 eV as substrate temperature increased from 350°C to 450°C. This increase in band gap is attributed to increase in carrier concentration of the thin films. This shift of the band gap with change in carrier concentration can be explained by the Burstein–Moss effect [23].

iv) Electrical studies

Electrical properties of the thin films depend on structural properties and deposition parameters such as substrate temperature, thickness and concentration of the solvent etc. In SnO₂ thin films, we have investigated the effect of the substrate temperature on the electrical properties by using two probe measurement technique using formula [24]. The prepared samples have been placed inside air tight enclosed test chamber where an arrangement of heating the substrate to optimum operating temperature. All the three samples are tested to analyze the resistance variation with change in substrate temperature. The decrease in resistance with an increase in substrate temperature can be also explained by the fact that the crystallite size increases notably with increasing the substrate temperature, thus reducing the grain boundary scattering and increasing conductivity. This decrease in resistance is also associated with the observed increase in carrier mobility.

In transparent conductor applications, electrical and optical parameters play a key role. Both conductivity and transmittance should be as high as possible for solar cell applications. The figure of merit (\(\Omega\)) of a transparent conducting film was calculated by using the formula [25,26]

\[
\text{Figure of merit (\(\Omega\))} = \frac{T^{10}}{R_s} \quad \text{(8)}
\]
thin film prepared at optimised deposition parameters. Hence the obtained thin films with high uniformity, low resistivity and high transmittance in the visible region can be further employed to prepare high transparent opto electronic devices.

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REFERENCES

[1] C.Kilic.A.Zunger,” Oligins of Coexistence of Conductivity and Transparency in SnO2,” Phys.Rev.Lett.88 – 095501-2002.
[2] Minoru Oshima, Yoshino Kenji “Characteristic of Low Resistivity Fluorine-Doped SnO2 Thin Films Grown by Spray Pyrolysis “ Jpn J Appl Phy:50 05FB15-1-2 -2011.
[3] Outezmabet R, Bouras N. ThinSolid Films”Microstructure and physical properties of nanofaceted antimony doped tin oxide thin films deposited by chemical vapor deposition on different substrates”- 515:6518-20-2007
[4] Wang Jain Tao. Shi Xiang Lei, Zhong Xin Hua, Wang Jain Nong, Sanderson Kevin D “Morphology control of fluorine-doped tin oxide thin films for enhanced light trapping”etal. Sol Energy Mater Sol cells;132:578-88-2015.
[5] J.R. Brown, P.W. Haycock, L.M. Smith, A.C. Jones, E.W. Williams,”Response behaviour of tin oxide thin film gas sensors grown by MOCVD”, Sens. Act. B 63, 109, 2000.
[6] J. Lontchi, B. Khalfallah, M. Abaab, “Thermal Evaporated Undoped and Na-doped CuSnS2 with Copper Contact for Photovoltaic Applications”, International Journal of renewable energy Research, Vol. 6 (2), pp.520-526, 2016.
[7] O.K . Varghese, L.K. Malhotra., “Studies of ambient dependent electrical behavior of nanocrystalline SnO2 thin films using impedance spectroscopy”, Journal of Applied Physics 87, 7457, 2000.
[8] Sheel D.W. and Gaskell J.M., “Deposition of fluorine doped indium oxide by atmospheric pressure chemical vapour deposition”. Thin Solid Films, 520, 1242–124, 2011
[9] Cachet, H. “Films and powders of fluorine-doped tin dioxide. In Fluorinated Materials forEnergy Conversion” Tsuyoshi, N., Henri, G., Eds.; Elsevier Science: Amsterdam, The Netherlands, 513–534, 2005
[10] A.A. Yadav, E.U. Masumdar, "Photoelectrochemical investigations of cadmium sulphide (CdS) thin film electrodes prepared by spray pyrolysis", J. Alloy. Compd., Vol. 509, Issue 17, pp. 5394-5399, 2011.
[11] K. Ellmer, J. Hinze, J. Klae.r, “Copper indium disulfide solar cell absorbers prepared in a one step process by reactive magnetron sputtering from copper and indium targets”, Thin Solid Films, Vol. 413, pp.92-97, 2002..
[12] Tailong Gui Long Hao, Jianmin Wang Lipeng Yuan Wei, Jia Dong Xiaoli, Chin Opt Lett “Structure and features of SnO2 thin films prepared by RF reactive sputtering” 8:134-6: 2010.

[13] V. Vasu, A. Subrahmanyan, “Physical properties of sprayed SnO2 films” Thin Solid Films, 202: 283-1991.

[14] P. Nagaraju, Y. Vijayakumar, GLN Reddy, M. V. Ramanreddy, “Preparation and characterization of nanostructured Gd doped cerium oxide thin films by pulsed laser deposition for acetone sensor application” Materials Science and Engineering B 226-99-106 December 2017.

[15] A. Sraf M. Akter S M J. Khan A.F. Ali Z and Qayyum “Synthesis, characterization and dielectric properties of SnO2 thin films”, A. J. Alloys Compd. 509 2414-2001.

[16] Ravichandran K. Muruganathan G and Sakhivel B’ Highly conducting and crystalline doubly doped tin oxide films fabricated using a low-cost and simplified spray technique”, Physica B 404 4299- B 2009.

[17] M. Dhanam, R. Balsudharprabhu, S. Jayakumar, P. Gopalkrishnan, M. D. Kannan, Phys “Preparation and Study of Structural and Optical Properties of Chemical Bath Deposited Copper Indium Diselenide Thin Films” Stat. Sol. (a) 19(1) 149-2002.

[18] S. Valanarasu, V. Dhanasekaran, M. Karunakaran, R. Chandramohan, T. Mahalingam “Role of Solution pH on the Microstructural Properties of Spin Coated Cobalt Oxide Thin Films” J. Nanosci. Nanotechnol. 14, 4286-2014.

[19] Reddy, A.S., Figueiredo, N.M., Cavaleiro, A; Pulsed direct current magnetron sputtered nanocrystalline tin oxide films. Appl. Surf. Sci. 258, 8902-8907, 2012.

[20] Demet Tatar Guven Turgut, Duzgun Bahattin “Fluorine highly doped nanocrystalline SnO2 thin films prepared by SPD technique” Rom J Phys 25(20): 4080-7: 2013.

[21] D. Vikraman, H.J. Park, S.I Kim, M. Thaiyan, “Magnetic, structural and optical behavior of cupric oxide layers for solar cells” J. Alloys Compd. 686, 616-2016.

[22] P. Nagaraju, Y. Vijayakumar, M. V. Ramana reddy “Room-temperature BTEx sensing characterization of nanostructured ZnO thin films” J.Asian ceramic societies, vol5,4,402, 2017

[23] H. Kim C. M. Gilmore “Electrical, optical, and structural properties of indium–tin–oxide thin films for organic light-emitting devices” volume 86, J. Appl.Phys, 6451, 1999.

[24] Allag Abdellkrım, Saad Rahnane, Quahab Abdelouahab, Attouche Hafida, and Kouidri Nabila “Optoelectronic properties of SnO2 thin films sprayed at different deposition times” Vol. 25, No. 4:2016.

[25] Babar A R, Shinde S S, Moholkar A V, Bhosale C H, Kim J H and Rajpure K Y “Structural and optoelectronic properties of antimony incorporated tin oxide thin films” J.Alloys Compd. 505 416-2010.

[26] S.A. Knickerbocker, A.K. Kulkarni, J. Vac.”Calculation of the figure of merit for indium tin oxide films based on basic theory” Sci. Technol. A 13-108-1995.

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