International Journal of Scientific Research in Physics and Applied Sciences **Research Paper**
Vol.7, Issue.2, pp.01-06, April (2019) **E-ISSN:** 2348-3423
DOI: https://doi.org/10.26438/ijsrpas/v7i2.16

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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Available online at: www.isroset.org

Received: 15/Feb/2019, Accepted: 12/Mar/2019, Online: 30/Apr/2019

***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^{o}C to 450^{o}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, Opticalpraperties*

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_2O_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] electro chromic 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 SnO_2 thin films are investigated.

III. METHODOLOGY

The required amount of tin (II) dichloride dehydrate ($SnCl_2.2H_2O$) (99.8%,Sigma-Aldrich) is dissolved in deionised water and stirred continuously for 30min. 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.

Table 1 Optimized deposition conditions

Condition	Description
Solvent	Di-ionized water
Precursor	$SnCl_2.2H_2O$
Concentration	0.1M
Solution flow rate	1 ml/min
Carrier gas	Dry air
Carrier gas pressure	0.8 bar
Substrate temperatures	350 °C – 450 °C
Substrate	Glass
Deposition time	15minutes

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 200-900nm 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 SnO_2 thin films are cassiterite 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 SnO_2. 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].

$$\text{Crystallite size (d)} = \frac{0{\cdot}9\lambda}{\beta \cos\theta} \quad \text{--------- (1)}$$

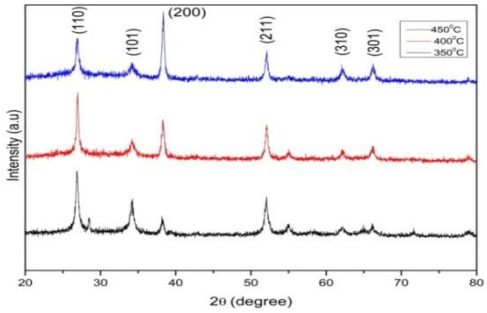

Fig.1. X-ray diffraction data of SnO_2 thin films deposited at various substrate temperatures

Where λ is the wavelength of Cu Kα radiation (1.5406A°), β is the full width at half maximum (FWHM) corresponding to the diffraction angle 2θ. 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 lower micro strain (ε) values which show the 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 (δ), 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 (ε) = $\frac{\beta\cos\theta}{4}$ ----------(2)

Dislocation density (δ) = $\frac{1}{d^2}$ ----------(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

$$\text{Texture coefficient (TC)} = \frac{I(hkl)/I0(hkl)}{1/n \sum_1^n I(hkl)/I0\ (hkl)} \text{ ----------(4)}$$

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.

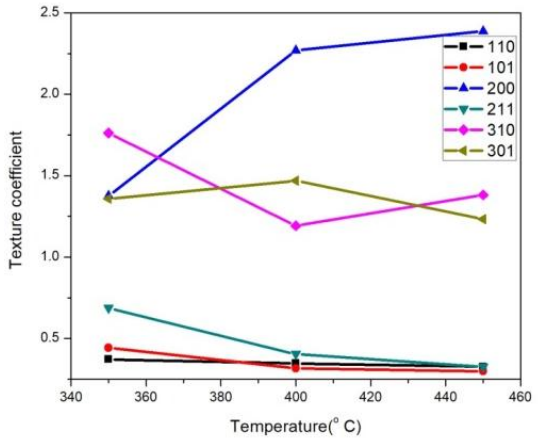

Fig.2. variation of texture coefficient of SnO_2 thin films

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].

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

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	
				a (nm)	c (nm)
350	18	2.67	1.8 X 10^{-3}	0.47	0.317
400	23	1.77	1.5 X 10^{-3}	0.46	0.315
450	24	1.69	1.4 X 10^{-3}	0.45	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^{0}C) particles were formed in small size with low density. As substrate temperature increases in the range of 400-450^{0}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.

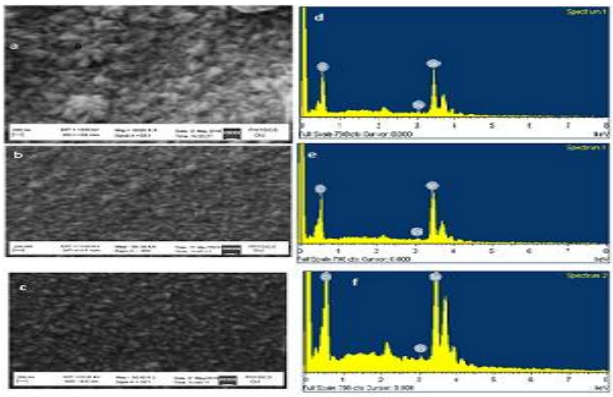

Fig. 3. SEM images and EDX spectra of SnO_2 thin films

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 ℃, 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 sthe pectrum, 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^{o} 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 (λ_1 and λ_2) 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 SnO_2 films at different substrate temperatures are 541nm, 510nm and 470nm.

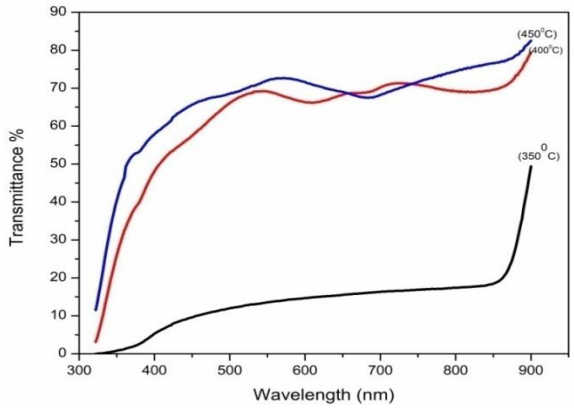

Fig. 4.The Transmittance spectra of SnO_2 thin films

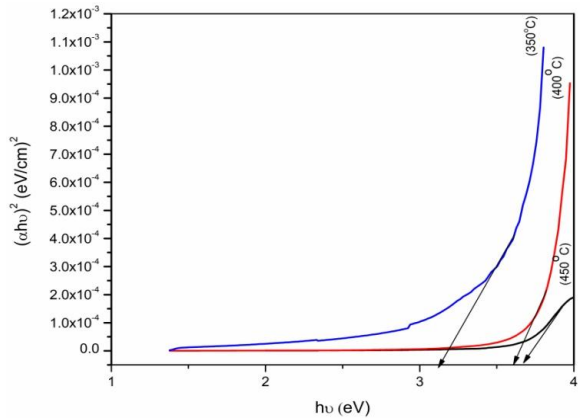

Fig.5. Tauc plot of SnO_2 thin films deposited at various substrate temperatures

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

$$\alpha h\nu = A\,(h\nu - E_g)^x \quad \text{----------(7)}$$

Absorption coefficient (α) is calculated by using the following equation

$$\alpha = \left(\frac{1}{t}\right) \ln T$$

Where T is the transmittance and 't' is the thickness of the film.

The variation of $(\alpha h\nu)^2$ with the energy of a photon of SnO_2 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 ℃ to 450 ℃ . This increase in band gap is attributed to increase in carrier concentration of the thin films. This shift of the band gap with cha ange 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 SnO_2 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 (Ø) of a transparent conducting film was calculated by using the formula [25,26]

$$\text{Figure of merit } (Ø) = \frac{T^{10}}{R_s} \quad \text{-------(8)}$$

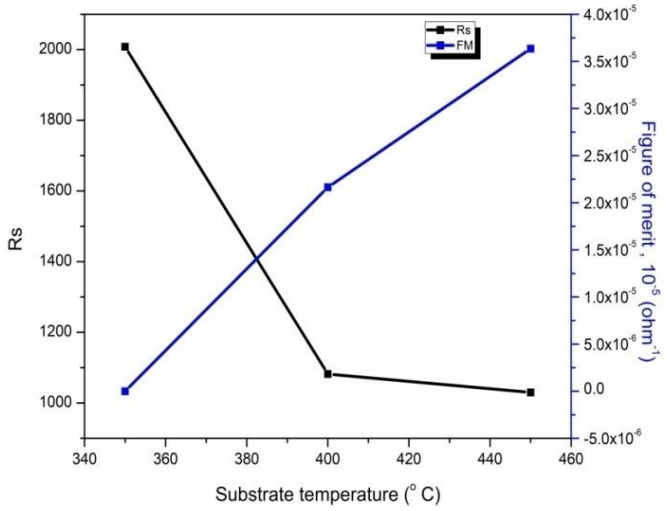

Fig.6.Variation of figure of merit and substrate temperature

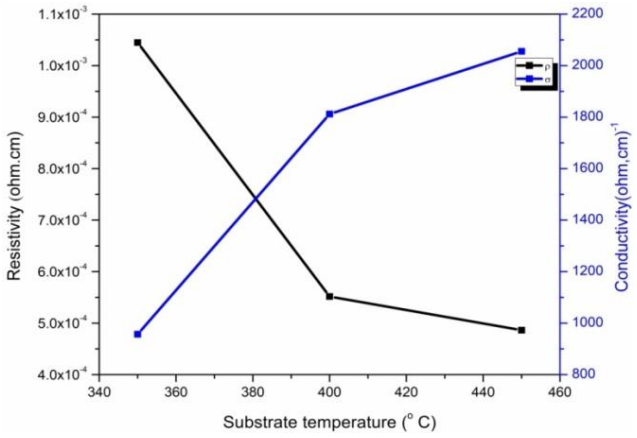

Fig. 7.Variation of conductivity and resistivity with sheet resistance as a function of substrate temperature

Where T is the transmittance at a particular wavelength 550nm and R_s is the sheet resistance. Transmittance is a function of wavelength and it is used to calculate Ø in this study. The figure of merit of 3.63X 10^{-5} Ω^{-1} was observed for the substrate prepared at 450°C. This is possible due to the formation of the good-quality film in the senses of conductivity and transmittance.

V. Conclusion and Future Scope

SnO_2 thin films can be deposited by using simple and low-cost spray pyrolysis technique. The prepared thin films are polycrystalline nature with tetragonal structure. It is found that the crystallite size is increased with increasing substrate temperature. In addition lattice constant 'a', micro strain and dislocation densities tend to decrease with increase in the substrate temperature. Low sheet resistance with the high-visible transmission (~82%) is obtained at higher substrate temperature. The resistivity is low as 4.86X$10^{-4}\Omega$ cm and figure of merit value is 3.6×10^{-5} Ω^{-1} is observed for the SnO_2 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.

Acknowledgments

Authors express their thanks to Sri. Ch. Gopal Reddy, Chairman, Dr. A. Raji Reddy, Director, CMR Technical Campus for their constant encouragement during present work and to DST-SERB, India for providing financial assistance in the form of a project(ECR/2016/000534) for establishing nanosensor lab in the department..

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