ROLE OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CHEMICALLY SPRAYED SnO₂ THIN FILMS

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 SnO_2 thin films of (400±10) nm thickness have been deposited by chemical spray pyrolysis method (CSP) on glass substrates at different substrate temperatures (200, 300 and 400) °C using tin chloride pentahydrate (SnCl₄.5H₂O) solution. The structural properties and morphology of the films have been studied using XRD and AFM respectively. XRD analyses showed that these films are polycrystalline in nature with tetragonal rutile structure with preferred orientation of (110). The crystallite size in this direction was estimated by Williamson-Hall and Scherrer methods and it was found to be 46.48 and 27.9 nm respectively. The grain size, average roughness and root mean square (RMS) values of all films were estimated by AFM and found to be increased as the substrate temperature increases. The effect of substrate temperature change on the optical properties in the range of (300-900) nm for all prepared films was investigated by recording the transmittance and absorbance spectra. The results showed that the transmittance increases with increasing the substrate temperature. The optical energy gap for allowed direct electronic transition was calculated and it was found that it increases with increasing the substrate temperature from 2.82 to 3.79 eV, while the Urbach energy decreases from 945 to 711 meV with increasing the substrate temperature.

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1. Introduction

Tin dioxide (SnO₂), is an important n-type semiconductor with tetragonal Rutile structure having lattice parameters a = b = 4.737 Å and c = 3.826 Å. The unit cell contains two tin and four oxygen atoms. Each tin atom is bounded to six oxygen atoms at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms. Tin oxide has been extensively investigated for gas sensors, optical-conductive coatings for solar cells and electro catalytic anodes [1,2], glass coatings for furnace windows as well as transparent electrodes for liquid crystal displays [3]. Tin dioxide (SnO₂) has a density of (6.95 g/cm³) and molecular weight of (150.69 g/mol). Its melting point is (2643 K) [4].

2. Experimental

Chemical spray pyrolysis technique was used to deposit (SnO₂) films on glass substrates at different substrate temperature of (200, 300, 400 °C). The spray solution was prepared by mixing (0.1M) aqueous solution of tin chloride pentahydrate (SnCl₄.5H₂O). Other deposition conditions such as spray nozzle to 9substrate distance (30 ± 1 cm), spray time (10 s), spray interval (3 min) and pressure of the carrier gas (1.5 bar) were kept constant during the deposition process as mentioned elsewhere [5]. The X ray diffraction patterns for the prepared films were obtained by (Ultima IV X-ray diffractometer) goniometer using copper target (Cu, 1.5416 Å) and Atomic Force Microscope (AFM) micrographs were recorded by using scanning probe microscope type (SPM-AA3000), contact mode, supplied by Angstrom Advanced Inc. Optical properties in the

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wavelength range of (300 - 900) nm were investigated by using UV-VIS-NIR spectroscopy (Shimadzu, UV-1800).

3. Results and discustion

The X-ray diffraction patterns of SnO_2 deposited at different substrate (200, 300 and 400) °C are shown in Figure (1). The highest four diffraction peaks are (110), (101), (200) and (211), which is in agreement with the International Centre for Diffraction Data (ICDD) card number (41-1445) with a tetragonal unit cell showing a preferred orientation along (110).

The average crystallite size along with the microstrain of the films can be determined using Williamson-Hall (W-H) formula shown below [6]:

$$\beta_{hkl}\cos\theta = \frac{\kappa\lambda}{D} + 4S\sin\theta \tag{1}$$

where β_{hkl} is full width of half maximum, *D* is the average crystallite size, *K* is constant and was assumed to be equal to 0.9, λ is wavelength for Cu target for XRD instrument, θ is Bragg's angle for all peaks, and S is the microstrain in the film.

If $\beta \cos \theta$ is plotted with respect to $4\sin \theta$ for all peaks, strain and crystallite size can be calculated from the slope and y-intercept of the fitted line respectively. The crystallite size for all films is also calculated for (110) direction by Scherrer's formula by using the relation [7]:

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \tag{2}$$

It is observed that the crystallite size of tin oxide thin films from the (110) peaks increases with increasing substrate temperature. Structural parameters of tin oxide thin films are shown in Table 1.



Fig. 1. X-ray diffraction patterns of SnO_2 prepared at different substrate temperatures.

Sample		T = 200 °C	T = 300 °C	T = 400 °C	ICDD
(hkl)		(110)	(110)	(110)	(110)
2θ (deg)		26.63511	26.62955	26.61247	26.611
d_{hkl} (Å)		3.34399	3.34467	3.34678	3.3492
FWHM (deg)		3.9699	2.2554	0.2927	-
D	Scherrer	2.057	3.621	27.90	-
(nm)	W-H	5.12	7.59	46.84	-
$T_{c(hkl)}$		1.666	1.7241	1.8072	-
Microstrain S		0.01293	0.00963	0.00151	-
Lattice constant (a _o) Å		4.7514	4.8062	4.7379	4.738
Lattice constant (c _o) Å		3.1864	3.2036	3.1841	3.187

Table 1. Structural parameters of SnO₂ thin films.

The texture coefficient (*Tc*) represents the texture of a particular plane, in which greater than unity values imply that there are numerous of grains in that particular direction. The texture coefficients Tc(hkl) for all samples have been calculated from the X-ray data using the well-known formula [8]:

$$T_c(hkl) = \frac{I(hkl)/I_o(hkl)}{N^{-1} \sum I(hkl)/I_o(hkl)}$$
(3)

where I(hkl) is the measured intensity, $I_o(hkl)$ is intensity of the ICDD standard data, N is the number of peaks and (hkl) are Miller indices.

The texture coefficient is calculated for crystal plane (110) of the SnO_2 films. All values of texture coefficient were greater than 1 which indicates the abundance of grains in the (110) direction. These results are in agreement with the results obtained by Saleh et al. for SnO2 thin films deposited by APCVD technique using various oxygen flow rates [9].

The 3D AFM micrographs of the SnO_2 thin films are shown in Fig. 2. The size of the scanned area was (2×2) μ m². AFM results show homogenous and smooth thin films. The average grain size, average roughness and root mean square (RMS) roughness for all samples estimated from AFM are given in Table 2. The average grain size, average roughness and RMS roughness of the film increase with increasing substrate temperature for all samples. The results of grain size obtained from AFM investigation are qualitatively in agreement with those obtained from XRD analysis shown in Table 1.

Table 2. The grain size, average roughness and root mean square roughness of SnO₂ thin films.

Sample	Surface Roughness (nm)	RMS (nm)	Grain size (nm)
SnO ₂ (200 °C)	0.882	1.02	102.79
SnO ₂ (300 °C)	1.13	1.37	108.80
SnO ₂ (400 °C)	1.56	1.82	112.12



Fig. 2. 3D AFM images of SnO₂ thin films. a) 200°C; b) 300°C; c) 400°C

The transmittance (T) spectra of the SnO₂ films at different substrate temperatures are shown in Fig. 3. It can be seen that the transmittance of the films increases with increasing the substrate temperatures.



Fig. 3. Transmittance spectra of SnO₂ films at different substrate temperatures.

The absorbance (A) spectra of the SnO_2 films with different substrate temperatures are shown in Fig. 4. It is clear that the absorbance decreases with increasing the wavelength for all films; also we noted that the absorbance decreases with increasing the substrate temperature.



Fig. 4. Absorbance spectra of the SnO₂ films at different substrate temperatures.

The following relation can be used for calculating the reflectance (R) [10]:

R + A + T = 1 (4) Fig. 5 shows the reflectance as a function of the photon energy of the SnO₂films with different substrate temperatures.



Fig. 5. Reflectance spectra of the SnO_2 films at different substrate temperatures.

The following relation can be used for calculating the absorption coefficient (α) [11]:

$$\alpha = \frac{2.303 A}{t} \tag{5}$$

where *t* is the film thickness.

From Fig. 6 it can be observed that the absorption coefficient of the SnO_2 films decreases with increasing substrate temperature. It is clear also that at high photon energies, absorption coefficient has high values which may lead to the conclusion that direct transition of electrons occurs [12].



Fig. 6. Absorption coefficient of the SnO_2 films at different substrate temperatures.

The optical energy gap (E_g) is given by the classical relation [13]:

$$\alpha h \nu = B (h \nu - E_a)^r \tag{6}$$

where B is a constant, hv is the incident photon energy and r is equal to (1/2) for the allowed direct electronic transition.

The optical energy gap can be estimated by plotting $(\alpha h\nu)^2$ versus $(h\nu)$, then extrapolating the straight line from the straight part of the plot to the photon energy axis at the value $(\alpha h\nu)^2 = 0$ gives the optical energy gap for the film [14].

The variation of optical energy gap as a function of substrate temperatures of SnO_2 films is shown in Fig. 7. The optical energy gap of the films decreases with increasing substrate temperatures. The values of optical energy gap are listed in Table 3.



Fig. 7. Optical energy gap of SnO₂ films at different substrate temperatures.

Table 3. Values of optical energy gap of SnO_2 films at different substrate temperatures.

Substrate temperature (°C)	E _g (eV)
200	2.82
300	3.71
400	3.79

The refractive index (n_0) can be determined from the reflectance (R) by using the relation [15]:

$$\mathbf{n}_{o} = \left[\left(\frac{1+R}{1-R} \right)^{2} - \left(\mathbf{K}_{o}^{2} + 1 \right) \right]^{1/2} + \frac{1+R}{1-R}$$
(8)

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Fig. 8 shows the variation of the refractive index with the photon energy of the SnO_2 films with different substrate temperatures. It is clear from this figure that the refractive index of these films slightly decreases with increasing the substrate temperature.



Fig. 8. Refractive index of SnO₂ films at different substrate temperatures.

The extinction coefficient (k_o) can be determined by using the relation [16]:

$$K_o = \frac{\alpha \lambda}{4 \pi} \tag{9}$$

Fig. 9 shows the variation in extinction coefficient as a function of the photon energy of the SnO_2 films with different substrate temperatures. It can be noticed that the extinction coefficient decreases as the substrate temperatures increasing. This is attributed to the decreases in absorption coefficient as the substrate temperatures increasing.



Fig. 9. Extinction coefficient of SnO_2 films at different substrate temperatures.

The variation of the real (ε_1) and imaginary (ε_2) parts of dielectric constant values versus photon energy of SnO₂ films with different substrate temperatures are shown in Figs. 10 and 11 respectively. The behavior of real part of dielectric constant is similar to that of refractive index because of the smaller value of (K_o^2) compared with (n_o^2) [17]:

$$\varepsilon_1 = n_o^2 - K_o^2 \tag{10}$$

However, the imaginary part of dielectric constant is mainly depends on the extinction coefficient, which is related to the variation of absorption coefficient [17]:

$$\varepsilon_2 = n_o^2 \, K_o^2 \tag{11}$$

It is found that the real and imaginary parts of dielectric constant decreases with increasing of substrate temperatures.



Fig. 10. Real part of the dielectric constant of SnO₂ films at different substrate temperatures.



Fig. 11. Imaginary part of the dielectric constant of SnO₂ films at different substrate temperatures.

4. Conclusions

Thin films of SnO_2 have been successfully synthesized by chemical spray pyrolysis technique. The structural, morphological and optical properties of these films were investigated. The XRD results showed that all films are polycrystalline in nature with tetragonal structure and preferred orientation along (110) plane. The intensity of peaks, the crystallite size increased with increasing substrate temperature, while dislocation density, number of crystal decreased with increasing substrate temperature. AFM results showed that the average grain size, average roughness and root mean square (RMS) increased with increasing substrate temperature. These results were qualitatively in agreement with the results of crystallite size obtained by XRD results.

The transmittance spectra of the SnO_2 films increase with increasing the substrate temperature. The results showed that the optical energy gap for allowed direct electronic transition increases with increasing substrate temperatures and varies from 2.82 to 3.79 eV, and the detailed study of the effect of substrate temperature on the optical properties has shown that all the optical parameters such as absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant have been affected by increasing the substrate temperature.

References

[1] S. C. Ray, M. K. Karanjai, D. Dasgupta, Surface and Coatings Technology 102(1), 73 (1989).
[2] M. Batzill, U. Diebold, Progress in Surface Science 79, 147 (2005).

- [3] A. J. Freeman, K. R. Poeppelmeier, T. O. Mason, R. P. H. Chang, T. J. Marks, MRS Bul 25, 45 (2000).
- [4] J. E. House, K. A. House, Descriptive Inorganic Chemistry, Illinois Wesleyan University, Bloomington, Illinois, (2010).
- [5] N. A. Bakr, S. A. Salman, M. N. Ali, Advances in Materials 5(4), 23 (2016).
- [6] Y. T. Prabhu, K. V. Rao, V. S. Kum, B. S. Kumari, World Journal of Nano Science and Engineering 4, 2 (2014).
- [7] R. H. Bari, S. B. Patil, International Letters of Chemistry, Physics and Astronomy 17(2), 125 (2014).
- [8] M. Caglar, S. Ilcan, Y. Caglar, Trakya Univ. J. Sci. 7(2), 153 (2006).
- [9] A. M. Saleh, N. A. Bakr, Z. T. Khodair, Digest Journal of Nanomaterials and Biostructures 13(3), 603 (2018).
- [10] K. L. Chopra. S. Major, D. K. Pandya, Thin solid film 102, 1 (1983).
- [11] Z. H. Khan, N. Salah, S. Habib, A. A. Al-Hamid, S. A. Khan, Optics & Laser Technology 44, 6 (2012).
- [12] M. Take, International Journal of Application or Innovation in Engineering & Management 2, 413 (2013).
- [13] J. Tauc, "Amorphous and Liquid Semiconductors", Plenum, London, (1974).
- [14] S. Ilican, M. Caglar, Y. Caglar, F. Yakuphanoglu, Optoelectron. Adv. Mat. 3(2), 135 (2009).
- [15] B. A. Ezekoye, C. E. Okeke, Pacific Journal of Science and Technology 7(2), 108 (2006).
- [16] S. W. Xue, X. T. Zu, W. L. Zhou, H. X. Deng, X. Xiang, H. Deng, Journal of Alloys and Compounds 448, 21 (2008).
- [17] A. K. Baker, P. E. Dyer, Applied Physics A: Materials Science & Processing 57, 543 (1993).