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Sensing Properties of SnO_2 Thin Films Prepared by Ultrasonic Nebulizer Method

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Abstract: (SnO_2) thin films have been deposited on glass substrate by using ultrasonic nebulizer method at different substrate temperature (200, 300, 400 and 500°C). The effects of substrate temperature on the structural, surface morphological, optical and ethanol gas sensing properties of films have been investigated. X-ray diffraction patterns indicated that the films are single phase SnO_2 with polycrystalline tetragonal structure and preferred orientation in the (110) direction and crystallite size increases as the substrate temperature increases up to 400°C but then decrease at 500°C. The surface roughness is slightly increase with the increase of substrate temperature up to 400°C and then decrease at 500°C which has been investigated by Atomic Force Microscopy (AFM). The optical properties of the films have been studied over a wavelength (250-850) nm. A high optical energy-gap of 3.65 eV was achieved at temperature 400°C. The effect of substrate temperature and operating temperature on performance of the sensor material has been investigated to choice optimum substrate temperature and optimum operating temperature for ethanol gas. The results showed high response to ethanol C_2H_5OH gas at operating temperature 225°C for the SnO_2 film prepared at 400°C substrate temperature.

Key words: SnO_2, thin films, gas sensors, substrate temperatures, optimum substrate, investigated

INTRODUCTION

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 (Fukuda and Ichimura, 2013), gas sensors (Vaezi and Zameni, 2012), transistor (Boratto *et al.*, 2014), optoelectronic devices (Nehru *et al.*, 2012), lithium batteries (Feng *et al.*, 2015), etc. Its splendid physical and chemical properties make it one of the top-quality materials used for detection of distinct types of gases. Thin films of SnO_2 have been fabricated using a variety of methods including spray pyrolysis (Patil *et al.*, 2012), ultrasonic spray pyrolysis (Palanichamy *et al.*, 2016), chemical vapour deposition (Ohgaki *et al.*, 2010), activated reactive evaporation (Bari and Patil, 2014), ion-beam assisted deposition (Chung *et al.*, 1999), sputtering (Georgieva *et al.*, 2014) and sol-gel methods (Ramesh *et al.*, 2014). Among these, we will focus more particularly in this study on thespray ultrasonic technique that is a low-cost method suitable for large-scale production.

It has several advantages in producing highly transparent thin films such as a relatively homogeneous composition, simple deposition on glass substrates because of the low substrate temperatures involved, easy control of film thickness and a fine and porous microstructure.

In the present study, we have investigated the effect of substrate temperature on the structural optical and sensing properties of SnO_2 thin films deposited by ultrasonic nebulizer method.

MATERIALS AND METHODS

Experimental details: SnO_2 thin films were deposited onto preheated glass slides at different substrates temperature (200, 300, 400 and 500°C) by Ultrasonic Nebulizer Deposition (UND) technique which transforms the liquid to a stream. In order to get good quality films and complete combustion all the deposition parameters such as the distance between the substrate and the nozzle, gas flow rate must be optimized. Film thickness (t) measured by weight difference method.

The structural properties of the films were characterized by X-Ray Diffraction (XRD) using Philips diffractometer with Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA in the range (20-80°) with a scan speed of (8°/min). Surface studies of the samples were done with the help of Atomic Force Microscopy (AFM). Optical transmission and absorption spectra of the films were recorded in the wavelength range of

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250-850 nm using UV-VIS-NIR spectrophotometer. The gas sensing properties were evaluated at various operating temperatures, from 25-400°C by measuring the changes of resistance of the sensor in air and in the 20 ppm ethanol gas.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the films deposited at different substrate temperature (200, 300, 400 and 500°C) are shown in Fig. 1. The films could not be prepared at temperatures higher than 500°C because glass substrates have been used for depositing the films and the glass bends beyond 525°C (Chu *et al*., 2012).

The most intense peak was observed in XRD at (110) plane and additional peaks along (101), (200), (211), (002), (310) and (202) planes were observed. All the samples were found to be SnO_2 polycrystalline with tetragonal structure. The values of lattice constants a and c are calculated using Eq. 1 (Hazaa, 2015):

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Where:

d = The interplanar spacing
h, k, l = Are the miller indices

It is seen from Table 1, that the calculated values of a and c are in good agreement with the standard values for SnO_2 tetragonal structure. The texture coefficient $T_{c(hkl)}$ for the (hkl) orientations were estimated from the following relation (Eq. 2) (Hazaa, 2015):

$$T_{c(hkl} = \frac{\frac{I_{(hkl)}}{I_{o(hkl)}}}{\frac{1}{N}\sum N\frac{I_{(hkl)}}{I_{o(hkl)}}} \quad (2)$$

Where:

$I_{(hkl)}$ = The measured intensities
$I_{o(hkl)}$ = Corresponding to recorded intensities accor ding to the JCPDS
N = The number of diffraction peaks

A sample with randomly oriented crystallite yields $T_{c(hkl)} = 1$ while the larger this value, the larger abundance of crystallites oriented at the (hkl) direction. The calculated texture coefficients $T_{c(hkl)}$ are presented in

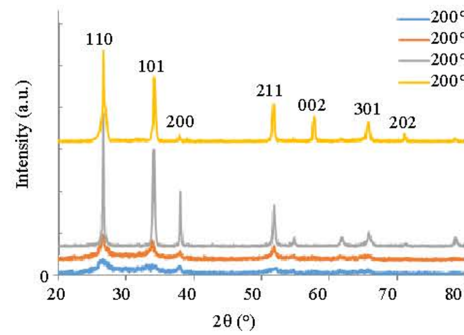

Fig. 1: The XRD pattern of SnO_2 prepared at different substrate temperature (200, 300, 400, 500°C)

Table 1: The grain size, texture coefficient and lattice constant for the SnO_2 thin films

x	hkl	FWHM (XRD)	G.S (nm)	Tc	a (Å)	c (Å)	a ASTM (Å)	c ASTM (Å)
	(110)	0.7300	11.6	1.5821				
	(101)	0.6400	13.5	0.6543				
	(200)	0.5400	16.2	0.5475				
	(211)	0.6200	14.8	0.3426				
	(110)	0.6200	13.7	1.9212				
	(101)	0.5200	16.6	1.1653				
	(200)	0.4800	18.2	0.5424				
	(211)	0.5100	18.0	0.8364				
	(110)	0.2643	32.2	2.9538				
	(101)	0.1779	48.7	1.6545				
	(200)	0.1928	45.5	0.9608				
	(211)	0.2199	41.9	0.7875				
	(110)	0.3479	24.5	1.9421				
	(101)	0.1988	43.6	1.1873				
	(200)	0.2030	43.2	0.1667				
	(211)	0.2782	33.1	0.7435				

Table 2: AFM characteristics of SnO_2 thin films

Substrate temperature (°C)	RMS (nm)	Roughness (nm)	Average grain size (nm)
200	5.04	4.15	24.6
300	7.30	6.50	43.7
400	15.60	14.02	76.3
500	9.30	8.50	59.1

Table 2. From the texture coefficient calculations, it was found that the preferential orientation of deposited films with different temperature was along (110) plane.

Also, it was observed that the preferred orientation of the (110) direction peak became more intense and sharper with increasing substrate temperature up to 400°C then slightly decrease at 500°C. This indicates that the crystallinity was improved and the grain size became larger with the increase in the substrate temperature.

The X-ray diffraction patterns have also been used to estimate the crystallite size (it could be smaller or equal to the grain size) of SnO_2 thin films by using Scherrer's Eq. 3 (Hazaa *et al*., 2016):

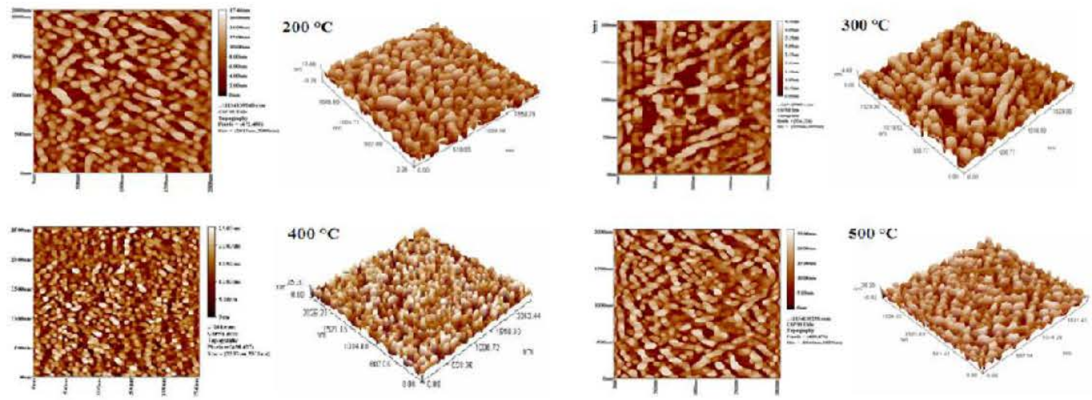

Fig. 2: AFM image of SnO_2 thin films

$$D = \frac{k'\lambda}{\beta \cos \theta} \qquad (3)$$

Where:

- D = The mean size of the crystallite
- k' = A dimensionless factor around 0.9
- λ = The X-ray wavelength
- β = The line broadening at half the maximum intensity (FWHM) in radians
- θ = The Bragg angle

The variations of the crystallite size for different plane are reported in Table 2, it was found that the crystallite size increased with increasing substrate temperature from 200-400°C and then it decreased for the deposition temperature of 500°C. The results reveal that the crystalline quality improvement in other words, the maximum crystallinity occurs in the film at 400°C.

Surface morphology: AFM pictures (2D and 3D view) of SnO_2 thin films grown at various substrate temperatures Ts are shown in Fig. 2. The average grain size, RMS and Roughness value of surface roughness were found to increase with increase in the substrate temperature and then it decreased for the deposition temperature of 500°C as listed in Table 2 and average particle size is slightly larger than that obtained from the XRD results and lies in the range of nm. Availability of thermal energy at higher T_s is responsible for increased grain size (Hegde *et al.*, 2011). The variation of grain size and surface roughness with T_s is listed in Table 2.

Optical properties: The optical transmittance T spectrum of SnO_2 films as function of substrate temperatures in the wavelength range (250-850 nm) is shown in Fig. 3. It is seen that the optical transmittance of the films increased from 37-90% (λ = 650 nm)with increasing of the substrate

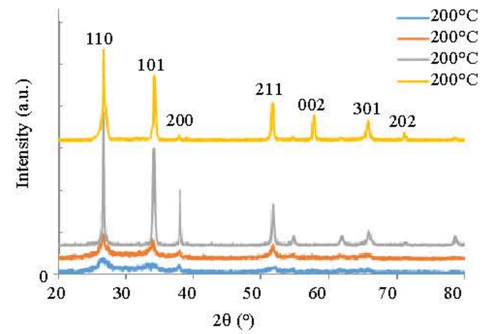

Fig. 3: Transmittance spectra of SnO_2 thin films

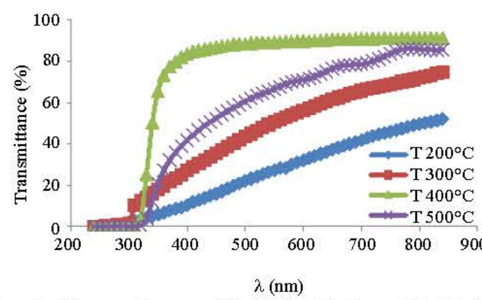

Fig. 4: Absorption coefficient with hυ of SnO_2 thin films

temperatures from 200 to 400°C then decreased to 76% at 500°C. The absorption coefficient (α) was calculated using the following relation (Eq. 4) (Hazaa, 2015):

$$\alpha = (1/t)\ \ln(I/T) \qquad (4)$$

where, t is the thickness of the film. It is clear from Fig. 4 that the films have a high absorption coefficient (α>105 cm^{-1}) which gives an indicate that all films have direct band gap. The di rect optical band gap (E_g), estimated from the $(\alpha hv)^2$ versus photon energy (hv) plot as in Fig. 5 and listed in Table 3.

Films grown at 200°C have shown lower optical band gap value of 2.2 eV, this lower band gap value may be due to poor crystallinity of the films. Optical band gap

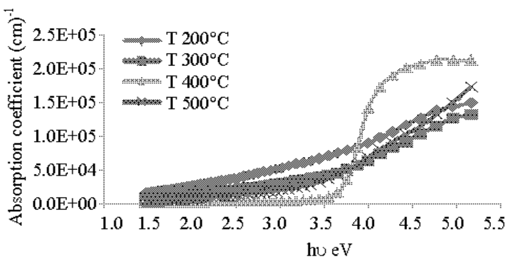

Fig. 5: Plots ($\alpha h\upsilon$) 2 with $h\upsilon$ of SnO_2 thin films

Table 3: The estimated values of energy gap of SnO_2 thin films

Substrate temperature (°C)	E_g (eV)
200	2.40
300	2.90
400	3.65
500	3.30

increased with increase in T_s and reached 3.65 eV for the film deposited at 400°C, this value of band gap is comparable with the reported value for SnO_2 thin films (Hazaa, 2015; Hazaa *et al.*, 2017).

Gas sensor: In order to investigate the sensor characteristics of SnO_2 films, the resistance of the films deposited at different substrate temperature was measured in air and in the presence of ethanol gas and different operating temperature 25-400°C. Usually, Sensitivity (S) can be defined as R_a/R_g for reducing gases or Rg/Ra for oxidizing gases where R_a and R_g are the resistance of the sensor in the presence of air and target gas, respectively (Hazaa *et al.*, 2016; El-Sayed and Yakout, 2016).

From Fig. 6, it is clearly seen that the resistance of all films decrease as operating temperature increase before and after exposed to the ethanol vapor. This behavior in sensor response was reported in various metal oxides (Korotcenkov *et al.*, 2013; Patil *et al.*, 2011). It is clear that, the resistance decrease as substrate temperatures increasing up to 400°C but when the substrate temperatures is above 400°C, the resistance of the films increased which is attributed to crystallinity of films (mobility carriers). Also, it is clear from Fig. 7, that the resistance decrease after exposed to the 20 ppm ethanol gas because ethanol is reducing gas, it removes adsorbed O^- species from the surface and reinjects the electron back in to the material, thereby reducing the resistance.

Figure 8 shows the variation of sensitivity of the SnO_2 sensor with operating temperature in the range 25-400°C. It is found that sensitivity of SnO_2 films increases with increase in operating temperature and shows maximum peak values at optimal temperature and then the sensitivity decreases with further increase in temperature. At the optimal temperature, the activation energy may be enough to complete the chemical reaction. The optimum working temperature was determined at

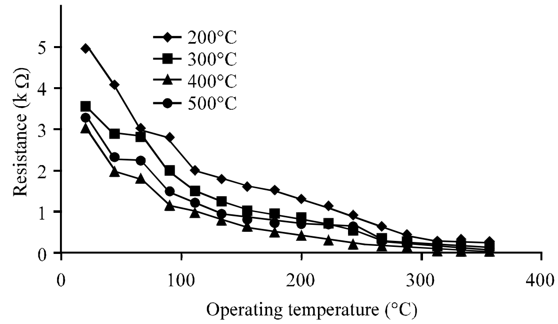

Fig. 6: Resistance with operating temperature of SnO_2 thin films without gas

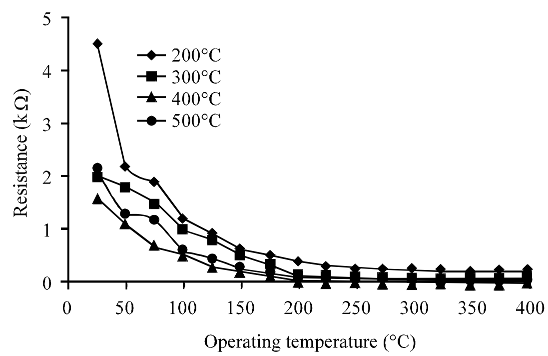

Fig. 7: Resistance with operating temperatue of SnO_2 thin films with 30 ppm ethanol gas

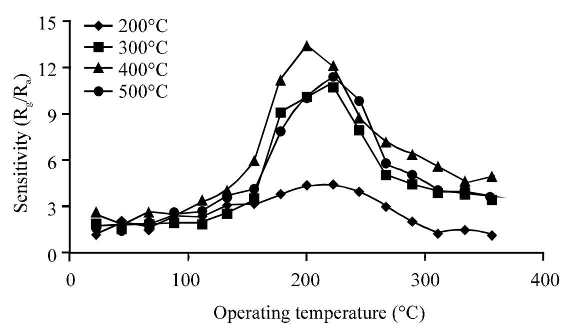

Fig. 8: Sensitivity with operating temperature of SnO_2 thin films

250°C for all sensors, except the films prepared at substrate temperature 400°C one which exhibits a maximum response at 225°C which is attributed to decrease of defect of films which leads to increase in mobility carriers. A better improvement in the sensitivity and operating temperature is seen in our case than the earlier reports (Mishrai *et al.*, 2009; Abdullah *et al.*, 2012).

CONCLUSION

Tin Oxide (SnO_2) thin films have been successfully deposited using the ultrasonic nebulizer method. XRD pattern of thin films showed polycrystalline SnO_2 tetragonal structure with the best crystallinity obtained at 400°C. It was observed that the prepared films have wide direct energy gap makes these films good material for optoelectronic applications. From the gas sensor characterization studies, it is clear that the SnO_2 can be used as an ethanol sensor effectively. The maximum sensitivity and lowest optimized operating temperature 225°C obtained for the SnO_2 film prepared at substrate temperature 400°C.

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