Molar concentration Effects on the Optical and Structural Properties of nanostructural SnO₂ Thin Films

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Abstract Thin films of nanostructured SnO₂ with different molarities were prepared by chemical spray pyrolysis technique. XRD analysis reveals that all the films were tetragonal polycrystalline with a preferred orientation along (110) plane. AFM measurements indicate that the value of the grain size for 0.05 M, 0.1 M and 0.15 M were 111nm, 78 nm and 58 nm respectively. SEM micrograph proved the existence of small cracks on the film surface, EDS confirmed the composition percentage ratio of Sn and O₂ and no trace of impurities could be detected. PL spectra gives the indication about optical energy gap and the effect of concentration on it which appeared as a blue shift. The transmittance was studied for the deposited thin films, identifying that the transmittance decreases by the increase in molarity. The value of the optical energy gap of the deposited thin films was increased upon increasing molar concentration due to quantum confinement effect. The Urbach energy was also studied, their values decrease as the molar concentration increase.

Introduction

Stannic oxide had a considerable attention due to its amazing properties like, eminent chemical stability, high transparency, low resistivity, SnO₂ is insulator in its bulk condition, while it shows a semiconductor behavior when prepared as a thin film due to the deviation from stoichiometry result as n-type semiconductor, top most infrared reflectivity, SnO₂ possesses high electron mobility and wide band gap together with non toxicity and redundancy in nature[1-4]. For these reasons SnO₂ was spotlighted in many numerous applications such as potential anode in lithium ion batteries[5], solar cells [6], gas sensors[7,8], varistors[9] and photocatalysis[10].

Various experimental techniques were adopted to fabricate SnO₂ thin films depending on kind of application such as, rf sputtering[11], sol-gel[12], pulsed laser deposition[13], successive ionic layer adsorption and reaction SILAR[14], electron beam evaporation technique[15], chemical vapor deposition[16] and spray pyrolysis[17,18]. Spray pyrolysis technique was used in this work to deposit SnO₂ thin films onto quartz substrates with different concentrations and study the effect of molarity on the structural, morphological and optical properties of nanostructure SnO₂ thin films.

Experimental details

Thin films of SnO₂ have been prepared by chemical spray pyrolysis technique. Aqueous solution of SnCl₄.5H₂O with different molarities (0.05, 0.1, 0.15M) was used as a source of Sn, Quartz substrates were used to deposit SnO₂. After many trials, the following conditions were chosen in order to obtain homogenous films, pinhole free, well adherent to substrates. These conditions arrived at the following: substrate temperature was 500 °C and was kept constant during the deposition process, distance between substrate and nozzle was 28 cm, spraying time was 10 s lasted by 90 s to obviate immoderate cooling, deposition rate was 4 ml/min. nitrogen was used as a gas carrier.

The thickness of the film was measured by gravimetric method and was in the range of 300 nm. Structural properties were carried out using X-Ray Diffraction Technique (Shimadzu - XRD6000, Shimadzu company /Japan). Morphological properties were accomplished by Jeol JSM-6335F scanning electron microscope equipped with (EDAX). Topographical was achieved by atomic force

microscopy (AFM) Nasoscope III and Dimension 3100. Photoluminescence and the transition energy of the samples were measured using the (ELICO, SL174, spectrofluorometer, Xe Lamp Power Supply). Transmittance and absorbance were measured by using a double beam spectrophotometer (Schimadzu 1650 UV probe Japan) in the wavelength range (350-1100)nm. All the measurements were achieved at room temperature .

Results and discussion

The XRD Patterns recorded for molar concentration of SnO_2 thin films are shown in Fig. (1). Utilizing the JCPDS data card no. 41-1445 , these films were found to be of cassiterite type with a tetragonal structure. The main diffraction peaks attributed to (110) ,(101), (200), and (211) of SnO_2 these peaks indicate the polycrystallinity of these films, have a preferred orientation along (110) which remains prevalent irrespective of the molar concentration .Small peaks were shown in 0.05 M and 0.1 M and vanish when we reached 0.15 M. The lattice constant values for a_0 and c_0 were tabulated in Table 1, these values were in good agreement with the data obtained by JCPDS data card no. (41-1445). The average crystallite size was calculated using Scherrer formula for different molarities and was found to decrease as the molar concentration increase as can be seen from Table 1. Texture coefficient[19] was calculated for the deposited thin film , their values were shown in Table 1 indicating unequivocally that the preferred orientation is along(110). The number of crystallite per unit area and the dislocation density[20] were obtained also. Their values were listed in Table 1 showing increase as the concentration increased.

Fig. 1 XRD patterns for different molarities of SnO_2 thin films

Table 1 Dstructural parameters for different molarties of SnO₂ thin films

molarity	a _o (Å)	c _o (Å)	Strain	D _{av} (nm)	T _C	No of crystallites /unit area (m ⁻²) x 10 ¹⁸	Dislocation density /(m ⁻²) x 10 ¹⁶
0.05	4.741	3.190	-0.094	21	1.32	0.0378	0.226
0.1	4.767	3.182	0.156	6	1.71	1.6200	2.700
0.15	4.769	3.225	-1.192	4	1.51	5.4600	6.250

Fig. 2 depicts the AFM images (0.125 x 0.125) μm with Granularity Cumulation Distribution Report of SnO₂ with a different morality grown on quartz substrate this measurement was performed near the center region of the deposited thin films . It can be seen that by increasing the molarity the grain size decrease. wo mechanisms control the kinetic grain growth these are ripening and coalescence , ripening responsible for the reduction of surface to bulk ratio , while coalescence deals with the combination of two small grains with the same size to merge into larger grain[21]. AFM measurements indicated that the surface roughnes and RMS roughness were smooth, the film with 0.1 M was smoother than the 0.05 M and 0.15 M . The values of roughness average , RMS roughness and grain size were listed in Table 2.

Table 2 AFM Parameters (roughness average , RMS roughness and grain size)

Molarity	Roughness average (nm)	RMS roughness (nm)	Grain size (nm)
0.05	1.810	2.110	111
0.1	0.485	0.565	78
0.15	1.400	1.300	58

Fig. 3 represent the SEM micrograph of SnO₂ thin films with different molarity concentrarion prepared by spray pyrolysis . no evidence of well crystalline can be observed, these results were in good agreement with Patil *et al.* [22], but it can be seen that better crystallinity in comparsion between the variation of molarity was presented in Fig.1-a and Fig 1-b ,while Fig 1-c show small cracks on the film surface which might be due to the variation of expansion and intrinsic stress [23]. Table 3 shows the composition percentage of Oxygen and Tin , no other contribution of impurities was detected. EDS were secure to get information concerning the film composition[24].EDS analysis disclose the oxygen/tin atomic ratio , their values were 2.597 ,1.4271 and 0.792 for 0.05 M, 0.1M , 0.15M respectively.

Fig. 4 shows the PL spectra which were measured at room temperature of SnO₂ prepared with different concentrations . The peak of (0.05M) was around 320 nm is very broad and was shifted toward lower wavelength (blue shift) as the molar concentration increase due to quantum confinement effects.

Fig. 2 AFM Topograph and Granularity Cumulation Distribution of SnO_2 with different molarties

(a)

(b)

(c)

Fig. 3 SEM photograph of different molarity for SnO_2 thin films (a) 0.05 M (b) 0.1M (c) 0.15M

Table 3 EDS contribution of SnO_2 with different molar concentration

molarity	Oxygen %	Tin %
0.05	66.93	25.77
0.10	58.80	41.20
0.15	44.19	55.81

Fig. 4 PL spectra of SnO_2 with different molar concentration at room temperature.

The optical transmittance spectra of SnO_2 prepared with different molar concentration were shown in Fig 5 . From this figure, it can be recognized that the increase in molar concentration has scored in a decrease in transmittance . A decrease in the transmittance of SnO_2 thin film might be due to an increase in light scattering by defect on the surface of the film , the surface of the thin film creates a defect state with oxygen deficiencies which reduce the crystal size[24,25]. The average transmittance at 550 nm was 66.77, 62.89,49.18 for 0.05 M ,0.1 M and 0.15 M respectively

Fig. 5 Transmittance versus wavelength of the as deposited SnO_2 thin films

Fig. 6 depicts the relation between the absorbance and wavelength, it can be seen that there is a shift in the absorption edge toward shorter wavelengths (blue shift) this blue shift can be attributed to the quantum confinement [26,27]. It has been believed that the absorbance is molarity dependence. The value of the optical energy gap can be estimated by Tauc formula [28] according to the following relation

$$(\alpha h\nu) = A (h\nu - E_g)^r \quad (1)$$

Where α represents the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical energy gap, while A is a constant which depends on reduced mass, refractive index and speed of light [29]. As we observe that SnO_2 thin film exists in tetragonal structure only and because of the sharpness of the absorption edge which shows linearity against energy for the as-deposited films [30]. The extrapolation of the linear part can be useful in determining the optical energy gap as shown in Fig. 7, the value of the optical energy gap was estimated to be increased as the concentration increases because of the quantum confinement effect. This behavior is in good agreement with Varnamkhasti *et al.* [31].

Fig. 6 Absorbance versus wavelength for the as deposited thin films

Fig, 7 $(\alpha h\nu)^2$ versus photon energy for the as deposited thin films with different concentration

The value of Urbach tail of the SnO_2 thin films can be estimated from the known relation [32]:

$$\alpha = \alpha_o \exp \left(\frac{E}{E_U} \right) \quad (2)$$

Where E_U represents the width of the exponential absorption edge, E is the photon energy, and α_o is constant. Fig 8 shows the relation between $\ln(\alpha)$ as a function of photon energy so, the Urbach energy was calculated from the inverse of the slope, it can be seen from the results that E_U decrease with increase of concentration, showing an inverse relation with the optical energy gap. These results were in good agreement with Rahal *et al.* [33].

Fig. 8 $\ln(\alpha)$ versus photon energy for the as deposited thin films with different concentrations

Conclusions

The effect of different molar concentration was studied successfully. XRD analyses show that all the deposited thin films were polycrystalline. The average crystallite size obtained by Scherrer formula gave an indication about the location of nanostructure. AFM micrograph confirms the existence of nanostructure with a value that decreases as the molar concentration increases. The optical energy gap was estimated, showing an increase in its value as the molar concentration increases, and this is because of the quantum confinement effect.

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