EFFECT OF OXYGEN FLOW RATE ON STRUCTURAL AND OPTICAL PROPERTIES OF SnO_2 THIN FILMS PREPARED BY APCVD TECHNIQUE

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Thin films of tin oxide were deposited on glass substrates at temperature 400°C under various flow rates of oxygen using atmospheric pressure chemical vapor deposition method (APCVD). The synthesized thin films were characterized by X-Ray Diffraction (XRD), UV-VIS spectrophotometer and Field Emission Scanning Electron Microscopy (FE-SEM) to study the structural and optical properties. The results of X-ray diffraction showed that the crystallite size in these thin films were varied as a result of varying deposition conditions, and the average crystalline size was found using Scherrer equation which showed decreasing with decreasing the flow rate within (4-8 NL/h). FE-SEM images of the films showed that the particle size for two samples were 24.2 and 32.3 nm which corresponding to flow rates 4 and 5 NL/h respectively. The optical band gaps of the films were in the rang (3.72-4.1 eV).

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1. Introduction

Among various semiconducting oxides, SnO_2 has been the most popular for different applications such as gas sensors [1], photovoltaic cells [2] transistors [3], lithium batteries [4], solar cells [5] , heat reflection Coatings [6] etc. Tin oxide SnO_2 is a one of the semiconducting oxides that has unique optical, electrical, transparent, conductive properties [7]. Tin oxide (SnO_2) is wide band gap an n-type semiconductor of tetragonal structure and can resist high temperature[8]. However it can be made using different techniques, such as sputtering [9],evaporating tin grains in air [10], Atmospheric pressure chemical vapor deposition [11], thermal evaporation of oxide powders [12], rapid oxidation of elemental tin [13], the sol–gel method [14] ion beam assisted deposition [15], and spray pyrolysis [16]. In this work we study the optimization of oxygen gas flow rate on substrate at temperature 400℃ and their impacts on the structural and optical properties of SnO_2 thin films. The aim of this paper is to reporting the grain growth behavior of tin oxide where prepared using (APCVD) method to optimization the condition of synthesized the SnO_2 thin film, because the Atmospheric pressure chemical vapor deposition method is inexpensive method and easy synthase of Goode quality thin films and its effective techniques to prepare films due to its ability for deposit large uniform area with low fabrication cost, simplicity and low deposition temperature.

2. Experimental details

The SnO_2 films were deposited on glass substrates by Atmospheric pressure chemical vapor deposition (APCVD) method in an open tube system. The SnO_2 films were grown by evaporating $SnCl_2$, supplied according to the chemical relation.

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$$SnCl_2 + O_2 \rightarrow SnO_2 + Cl_2 \quad (1)$$

The vapor was allowed to react with the oxygen inside the oven (High Temperature Furnace (Microprocessor Controlled Furnace) –HTI CORPORATION model GSL-1600X – Germany).

SnO_2 thin films were deposited on the cleaned glass as a substrates were the glass substrate was first cleaned via ultrasonically with acetone, ethanol, and deionized water, in a consecutive manner, for 20 min.

Grown condition involved a gas mixture of argon and O_2, Which ran through the two separate gas flow meter to controlling their flows, also we take the optimizations for distance between the boat which consist of $SnCl_2$ materials and glass substrate in a range 5, 7, 10 cm, subsequently we found the optimum time deposition of oxygen flow rate is about 30 min, and then controlled the prepared samples gas flow rate by taken different percentage of oxygen rate 4,5,6, and 8 NL/h, where (NL/h means normal litter per hour). It was found that the properties of the films varied with the variation of temperature inside the oven and flow rate of the oxygen.

For good quality of thin SnO_2 films the periodic time it should be at 30 min of deposition time with distance between the boat which consist of $SnCl_2$ material and glass substrata 7 cm with flow rate of the oxygen must be within the range of 4 normal liter per hour. The thicknesses of the films were in the range between 450 to 550 nm. By analysis XRD, and FE-SEM for studied chemical compositions, structural surface morphology of the films. The optical transmittance and absorbance spectra were recorded using a double beam UV- visible spectroscopy 2600 Shimadzu Co. Japan. Spectrophotometer in the wavelength range 200 to 1100 nm, which can be measure the energy band gap, of the samples.

3. Results and discussion

Structural properties

X – Ray Diffraction (XRD) for SnO_2thin films

Structural characterization of SnO_2 thin film were performed by Day Petronic Company-Iran with a diffract meter (XRD) model: Analytical Philips (XPERT-PRO) equipped with CuKα (λ= 1:54178Å) using a generator voltage of 40 kV and a current of 40 mA, the scans were run over the range (5.0°-79.97°), using step size [0:039°]. X-ray diffraction (XRD) of SnO_2 thin film prepared by Atmospheric pressure chemical vapor deposition technique at substrate temperatures of (400℃) with different oxygen flow rate (4, 5, 6, and 8) NL/hour. The peaks of the XRD were observed in the range from 2θ (20°-70°) the diffraction peak shows that the film is have tetragonal structure at 400℃ which is corresponding to (110), (101) and (211). The x-ray analysis shows the intensity of the peak will be change with changing the gas flow rate. The crystallite size of SnO_2 thin films of different gas flow rate was estimated from Scherrer equations [17, 18] , using the full width at half maximum (FWHM) for above three peaks.

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (2)$$

where D is the crystallite size, λ the X-ray wavelength, θ the Bragg diffraction angle and β the full width at half maximum (FWHM). The x-ray analysis data have been listed in Table 1. The results shows the smallest crystallite size is (24.4 nm) for A4 (4NL/h), and this value will be change with changing the oxygen flow rate, this indicates that the crystallite size increases with increasing the amount of oxygen flow rate as shown in Fig. 1.

Table 1. The x-ray data of SnO_2 thin films at various substrate Gas flow rate (2θ (deg), full width at half maximum (FWHM) and Crystallite size).

Gas(NL/h)	*h*	*k*	*l*	*Pos.[°2Th.]*	*FWHM [2θ]*	*D(nm)*	*Average*	*S.*
8	1	1	0	26.564	0.172	47.457		
	1	0	1	33.881	0.134	61.975	51.26196	A1
	2	1	1	51.668	0.199	44.354		
6	1	1	0	26.543	0.29	28.146		
	1	0	1	33.8654	0.141	58.896	43.29773	A2
	2	1	1	51.696	0.206	42.852		
5	1	1	0	26.579	0.29	28.148		
	1	0	1	33.907	0.14	59.323	43.04062	A3
	2	1	1	51.7648	0.212	41.651		
4	1	1	0	26.564	0.39	20.930		
	1	0	1	33.881	0.38	21.854	24.40667	A4
	2	1	1	51.668	0.29	30.436		

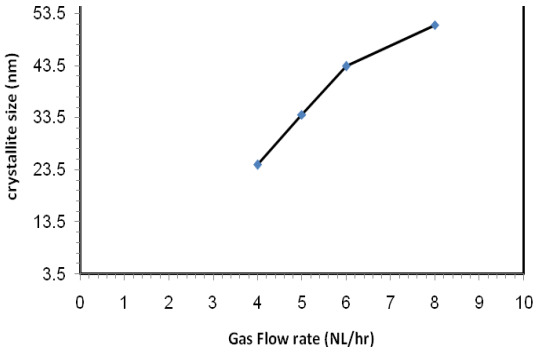

Fig. 1. Crystallite size as a function of the oxygen gas flow rate.

Fig. 2 shows the XRD patterns of SnO_2 films for substrates temperature at 400℃ with different gas flow rate.

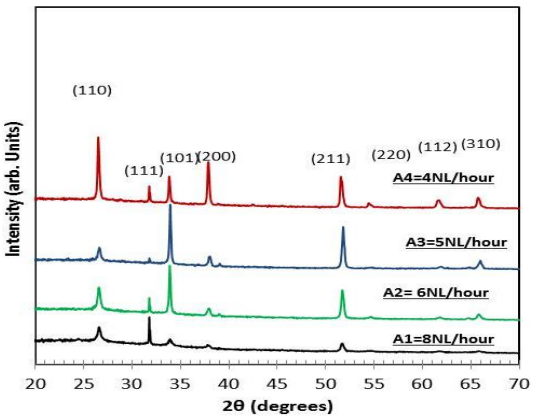

Fig. 2. XRD patterns of SnO2 films for substrates temperature 400℃ with different gas flow rate (A1=8NL/hr, A2=6NL/hr, A3=5NL/hr, A4=4NL/hr).

FE-SEM study

The surface morphology of the SnO_2 thin films deposited on a glass substrate for different gas flow rate between (4and5NL/hr) by Atmospheric pressure chemical vapor deposition tested by Field Emission Scanning Electron Microscope (FE-SEM) are shown in Fig.3 (a-b) . From the morphology image one can be seen from the SnO_2 thin films at different substrate for oxygen flow rate are quite similar except for a small decreasing in particle size, besides that, there are some crystal shapes structures, agglomeration of grains. Clearly, we found that the films deposited with gas flow rate of 4 NL/h at substrate temperature 400 Ĉ have the crystallite size less of the films deposited compared to the other Sample of different gas flow rate. From the (FE-SEM) images the crystallite size values of the SnO_2 thin films are found to be in the range of (24.2-32.3) nm corresponding to the value of oxygen flow rate between (4 ,5 NL/h) respectively.

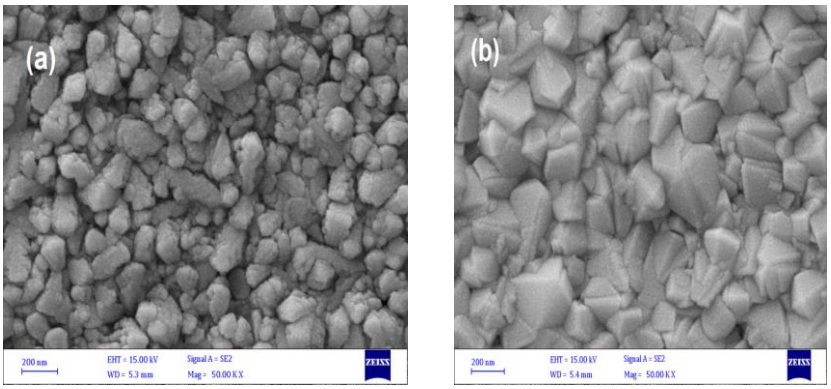

Fig. 3. FE-SEM micrographs of SnO_2 prepared by APCVD thin film (a) 4 Nl/h, (b) 5 NL/h.

Optical properties

The room temperature optical band gap energy have been investigated in the range 200-1100nm by double beam UV- visible spectroscopy 2600 from Shimadzu Co. Japan.

The optical band gap energy of the synthesized SnO_2 thin films is shown in Fig. 4(A1-A4). The band gap energy can be calculated from the fundamental absorption, which is corresponding to electron excitation from the valence band to the conduction band.

The optical band gap of the system has been estimated from these absorption spectra. According to the Tauc relation, the absorption coefficient, α, is given by [19].

$$\alpha h\nu = A(h\nu - Eg)^n \tag{3}$$

Where, Eg- band gap energy, A- proportionality constant, $h\nu$ is the energy of photon and n is an index which takes four values 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition (n = 1/2 for the direct gap). The plot between $(\alpha h\nu)^2$ and hv produces a straight line, and the extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the band gap of the sample.

The band gap energy values of SnO_2 thin films are found to be3.86 ,3.82 ,4.1, and 3.72 eV for gas flow rate4, 5, 6, and 8 NL/h respectively, which is much similar to the values reported by K. Lagha etc [20]The results shows that the band gap energy influenced by the amount of gas flow rate, these values are in the range of previously published experimental and theoretical results since it is well known that SnO_2 family is an n-type wide-band-gap semiconductor material (Eg = 3.6 eV at 300 K). Where inherent oxygen vacancies play a role as an n-type dopant [21, 22].

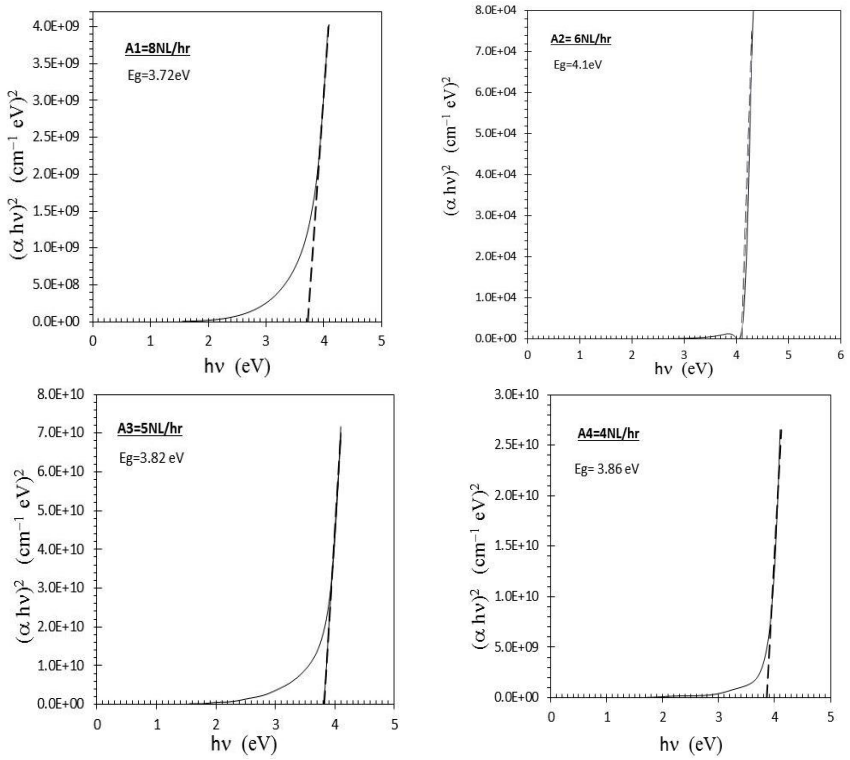

Fig. 4. Plot of (αhm)2 versus photon energy (hυ) for SnO_2 thin films (a) prepared at different substrate oxygen flow rate: (A1) =8NL/hr, (A2)=6NL/hr, (A3)= 5NL/hr and (A4) =4NL/hr at substrate temperature 400 °C.

The obvious explanation of this effect is the absorption of the photons by the generated defects in the crystal.

4. Conclusions

The pure tin oxide SnO_2 thin films were prepared on glass substrates by APCVD technique. To obtain SnO_2 thin films, the $SnCl_2$ employed with oxygen gas for this purpose. Different value of gas flow rate (4, 5, 6, and 8NL/h) are used as a function of fixed temperature (400°C). This preparation technique gives a good quality for SnO_2 films deposition. The XRD analysis revealed that SnO_2 deposited at 400°C and 8 NL/h flow rate give the largest crystallite size, compared with smallest crystallite size that obtained at 4NL/h. The effect of gas flow rate on crystallite size was investigated as well. FESEM images showed that with 8 NL/h flow rate, the crystallite size of the sample will be largest. This result is a good agreement with the result that obtained from XRD analysis. The films also showed semiconducting behavior with band gap energy of 3.86 eV at 4 NL/h.

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