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Studying Effect of Mg Doping on the Structural Properties of Tin Oxide Thin Films Deposited by the Spray Pyrolysis Technique

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Abstract
Mg doped tin oxide transparent conducting thin films were deposited at a substrate temperature of 450°C by spray pyrolysis method. Structural properties of the films were investigated as a function of various Mg-doping levels from 0 to 9wt% while all other deposition parameters such as substrate temperature, spray rate, carrier gas pressure and distance between spray nozzle to substrate were kept constant. The results of x-ray diffraction have shown that the deposited films are polycrystalline structure in tetragonal phase with preferential orientations along the (101), (301), and (211) planes. The relative intensities, distance between crystalline planes (d), crystallite size (D), dislocation density ( ) and lattice parameters (a), (c) were determined. The variations of the surface morphology have been studied by Scanning Electron Microscope (SEM).
Keywords: Thin films, Magnesium doped Tin Oxide, Spray pyrolysis, Structural properties, Scanning electron microscope.

1. Introduction

Transparent conducting oxides (TCO_s) are semiconductors that are produced from a combination of metal and oxygen such as: ZnO, In_2O_3, SnO_2 .The studying of TCO_s thin films is very important because of their special properties that is used in technology applications [1].

Tin oxide (SnO_2) is considered as one of the most important member of the TCO_s for its unique electrical and optical properties because it has low electrical resistivity, high optical transparency in visible region, high optical reflectance in infrared region and chemical inertness. So, SnO_2 is used in solar cells, sensor gas, display devices and in other important applications [2].

SnO_2 is an n-type semiconductor with wide band gap energy (E_g = 3.5-4 eV) [3]. SnO_2 has tetragonal structure belonging to the P42/mnm space group. The lattice parameters are a = b = 4.7382 and c = 3.1871 Å [4]. Its unit cell contains two tin and four oxygen atoms as is shown in figure 1. The tin atom is at the center of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle [5,6].

So nowadays we notice the importance of thin films in our practical life and from this point many techniques in depositing thin films have appeared with high Accurate qualities such as: thermal vacuum evaporation, sputtering, pulsed laser ablation, chemical vapor deposition, chemical bath, dip coating, spin coating and spray pyrolysis. The spray pyrolysis is the simplest, cheapest alternative method to manufacture thin films that is used in industrial applications [7]. There are many characteristics of this method such as : it is suitable for preparing doped and pure thin films because of their simple experimental manufacturing, we can prepare films from high melting temperature materials that we can't prepare in other methods, economic technique because the used devices don't need vacuum or complicated devices, we can add several dopants that are different in concentration, we can change deposition factors (type of used substrates – temperature of substrate – composition of solution – flow rate solution – distance between the spray nozzle and substrate) to get films that have special electrical and optical properties [8].

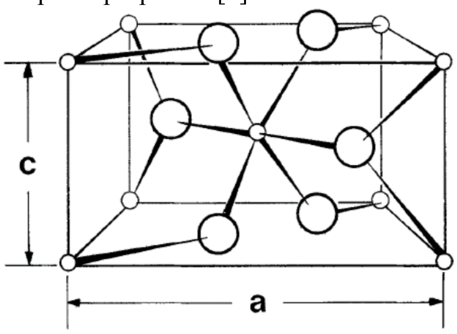


Fig. 1: Unit cell of the crystal structure of SnO_2. Large circles indicate oxygen atoms and the small circles indicate tin atoms.

2. Experimental details

The undoped and Mg doped SnO_2 thin films were deposited by using a homemade spray pyrolysis apparatus in Albaath University. Starting solution of SnO_2 was prepared by dissolving 1M Stannous chloride ($SnCl_4$, 99%, Merck, Germany) in 25 ml of ethanol (C_2H_6O, 99.8%, Sigma-Aldrich, Germany) and distilled water with ratio 7/3 (7 for distilled water and 3 for ethanol) and with adding few drops of HCl in this solution. For Mg doping, magnesium chloride ($MgCl_2$, 98%, Riedel-de haen, Germany) was dissolved in solution as dopant material source. In order to grow undoped and Mg doped SnO_2 films varied from 1 wt% to 9 wt% by weight percentage (with 2 wt% step), the necessary amounts of these solution were prepared. All spray solutions were stirred to obtain homogenous solutions. The resultant solutions were sprayed on glass substrates (Citoglas, 7.5cm * 2.5cm * 0.1cm). The glass substrates were rinsed with HCl and then cleaned with ethanol. Finally, they were cleaned with distilled water by using an ultrasonic cleaner (Trans sonic 700/H) and then dried with air compressor. Fig. 2 shows the schematic diagram of the spray pyrolysis apparatus. The substrate temperature was fixed as 450 °C on hot metallic plate and controlled with temperature control unit. The nozzle to substrate distance was 25 cm and the time for the film deposition was about 15 min. after the deposition operation, the substrates was kept cooled at room temperature. All experiments were done under approximately similar conditions. The chemical reaction of thin film formation of SnO_2 is as follows [9]:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl \quad (1)$$

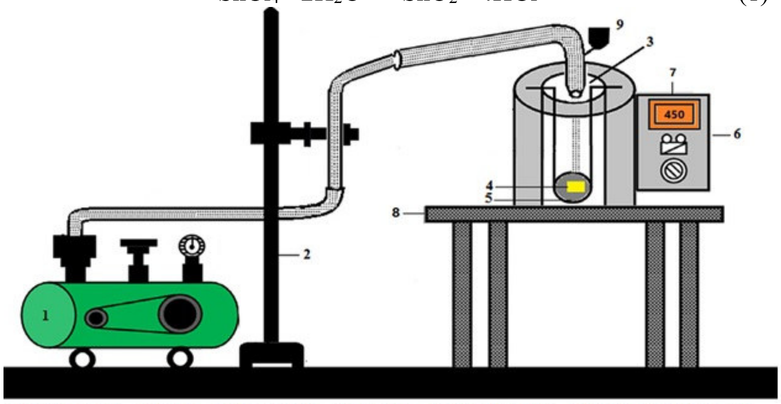


Fig. 2. Schematic diagram of the spray pyrolysis apparatus.

The undoped and Mg doped SnO_2 thin films were studied by X-ray diffractometer (Philips PW 1840) with operation values as following: Voltage 40KV, Current 30 mA, 2θ° values between 20° to 80°, wavelength $\lambda_{\alpha 1}$=1.54056 Å, anode Cu. Surface morphology of the thin films were studied with scanning electron microscope (QUANTA 200).

3. Results and discussions

3.1 Structural properties

The X-ray diffraction patterns of undoped and Mg doped SnO_2 thin films prepared at substrate temperature 450 °C with various Mg concentration 0 wt%, 1 wt%, 3 wt%, 5 wt%, 7 wt% and 9 wt% are shown in Fig. 3a, b, c, d, e, f respectively. The XRD reveals that all films are having polycrystalline nature with tetragonal structure and peaks correspond to (110), (101), (200), (211) and (301) planes. The preferred orientation is (101) for undoped film. The preferred orientation with increasing the Mg dopant concentration changed to (301) plane at 1 wt% and 3 wt% doping levels then it changed again to (211) plane at 5 wt%, 7 wt%, 9 wt% doping levels.

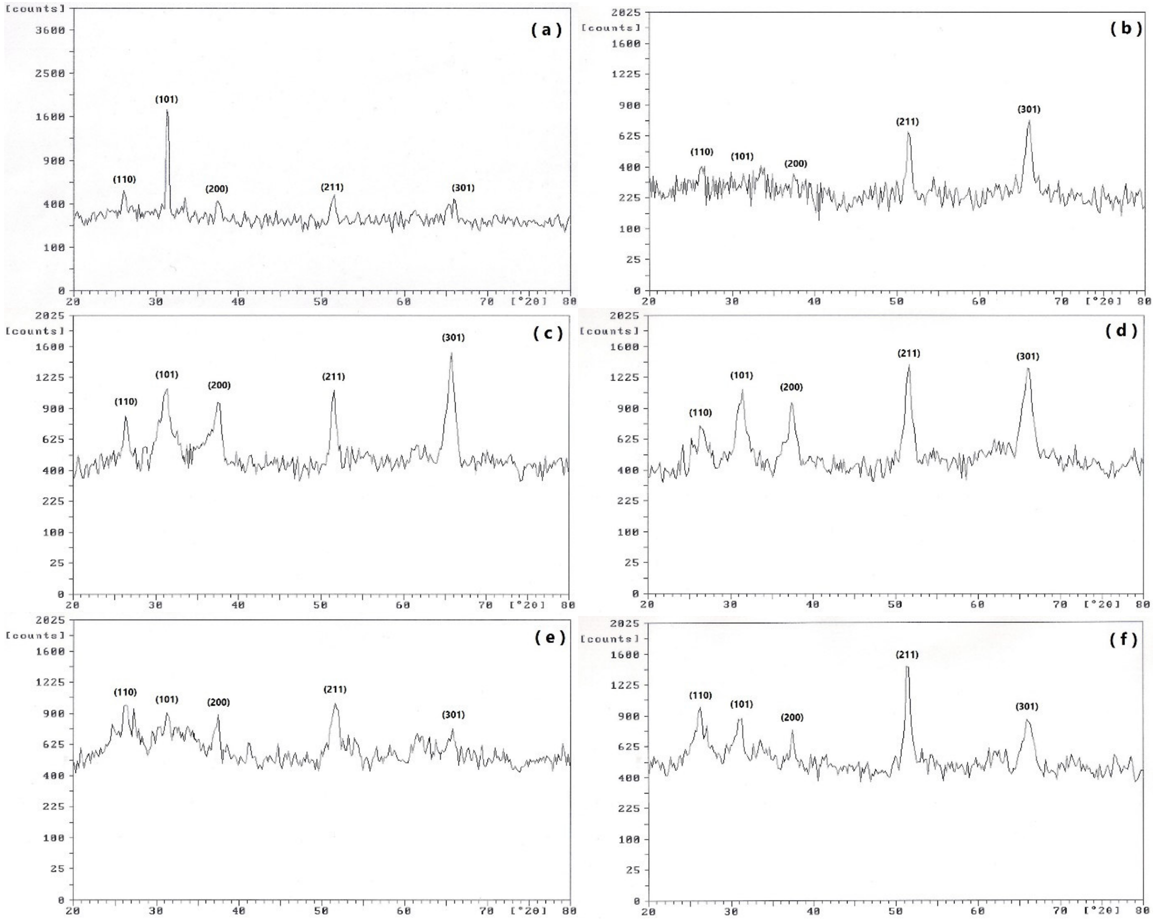


Fig. 3: XRD results of (a) pure SnO_2, (b) 1 wt% Mg doped SnO_2, (c) 3 wt% Mg doped SnO_2, (d) 5 wt% Mg doped SnO_2, (e) 7 wt% Mg doped SnO_2, (f) 9 wt% Mg doped SnO_2.

Table (1) shows results of structural values of undoped and Mg doped SnO_2 thin films.

Table (1)

Samples	2θ (deg)	(hkl)	d (Å)	Rel. int. [%]	β (deg)	D (nm)	Average D(nm)	δ (10^{15} lin/m^2)	Lattice const.	
									a(Å)	c(Å)
SnO_2 pure	26.01	(110)	3.42	25.6	0.424	20	18.48	2.5	4.80	3.13
	31.23	(101)	2.86	100	0.375	22.9		1.9		
	37.40	(200)	2.40	16.4	0.731	12		6.9		
	51.36	(211)	1.77	22	0.671	13.7		5.3		
	65.96	(301)	1.41	16.4	0.415	23.8		1.8		
SnO_2:Mg (1 wt%)	26.22	(110)	3.39	40.4	0.685	12.4	20.10	6.5	4.80	3.18
	31.23	(101)	2.86	30.9	0.210	41		5.9		
	37.40	(200)	2.40	30.9	0.421	20.8		2.3		
	51.30	(211)	1.78	84.9	0.632	14.6		4.7		
	65.96	(301)	1.41	100	0.843	11.7		7.3		
(3 wt%)	26.22	(110)	3.39	43.2	0.474	18	11.88	3.1	4.80	3.18
	31.23	(101)	2.86	65.5	1.001	8.6		13.5		
	37.40	(200)	2.40	55.7	0.896	9.8		10.4		
	51.36	(211)	1.78	66.1	0.633	14.5		4.8		
	65.90	(301)	1.42	100	1.16	8.5		13.8		
(5 wt%)	26.22	(110)	3.39	38.4	0.79	10.8	9.48	8.6	4.80	3.18
	31.23	(101)	2.86	79.9	1.159	7.4		18.3		
	37.39	(200)	2.40	62.3	0.79	11.1		8.1		
	51.36	(211)	1.78	100	0.896	10.3		9.4		
	65.90	(301)	1.42	96.8	1.264	7.8		16.4		
(7 wt%)	26.20	(110)	3.40	96.7	0.632	13.5	22.42	5.5	4.80	3.18
	31.23	(101)	2.86	83.5	0.527	16.3		3.8		
	37.40	(200)	2.40	79.1	0.843	10.4		9.2		
	51.36	(211)	1.78	100	0.949	9.7		10.6		
	65.90	(301)	1.42	54.9	0.159	62.2		0.26		
(9 wt%)	26.20	(110)	3.40	60.9	0.474	18	14.36	3.1	4.80	3.18
	31.23	(101)	2.86	50.3	0.738	11.7		7.3		
	37.40	(200)	2.40	39	0.421	20.8		2.3		
	51.30	(211)	1.78	100	0.632	14.6		4.7		
	65.90	(301)	1.42	48.5	1.475	6.7		22.3		

The relative intensities of undoped and Mg doped SnO_2 thin films are calculated. The distance between crystalline planes values (d) are calculated by using following relation:

$$2d.\sin\theta = n\lambda \quad (2)$$

Where d is distance between crystalline planes (Å), θ is the bragg angle, λ is the wavelength of X-rays (λ=1.54056 Å).

The crystallite size is calculated from Scherrer's equation [10]:

$$D = \frac{0.94\lambda}{\beta.\cos\theta} \quad (3)$$

Where, D is the crystallite size, λ is the wavelength of X-ray, ß is full width at half maximum (FWHM) intensity in radians and θ is braggs's angle.

The dislocation density is defined as the length of dislocation lines per unit volume and calculated by following equation [2]:

$$\delta = \frac{1}{D^2} \quad (4)$$

The lattice constants a and c for tetragonal phase structure are determined by the relation [11]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (5)$$

Where d and (hkl) are distance between crystalline planes and Miller indices, respectively.

The calculated lattice constants a, c values are given in table 1. It was seen that a, c and c/a match well with JCPDS data (a=b= 4.737 Å and c= 3.185 Å).

The change in peak intensities is basically due to the replacement of Sn^{4+} ions with Mg^{2+} ions in the lattice of the SnO_2. This process leads to the movement of Sn^{4+} ions in interstitial sites.

Figure 4 represents variation of the average grain size with different concentrations of Mg doped SnO_2 films. We observed from table 1 that 1 wt% Mg doped SnO_2 is the closest value to undoped film.

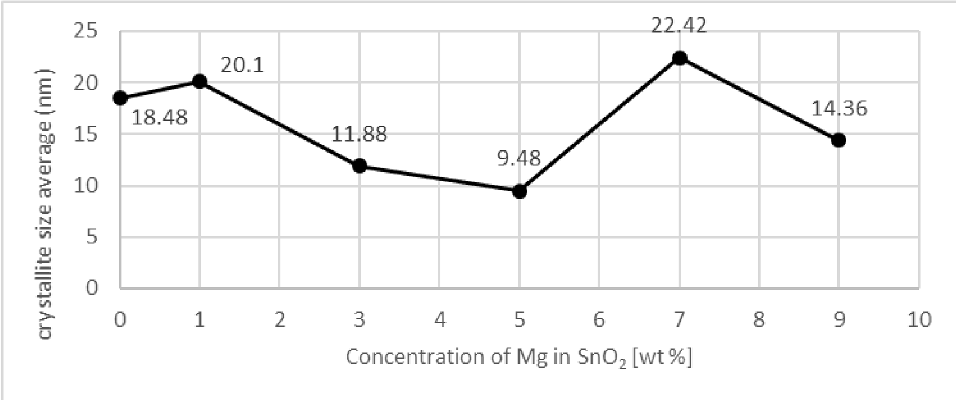
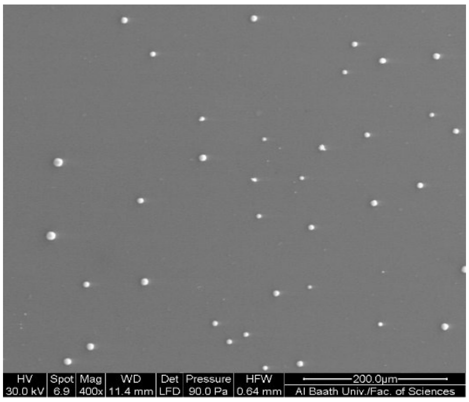


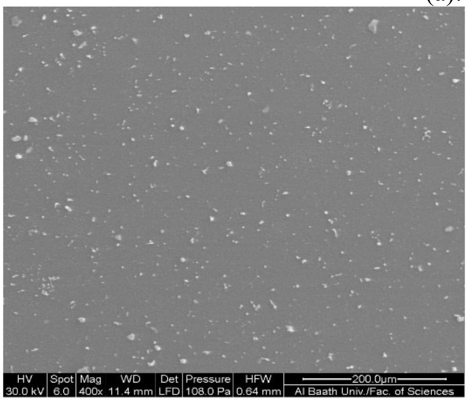
Fig. 4: variation of the average crystallite size with different concentrations of Mg doped SnO_2 films

3.2 SEM analysis

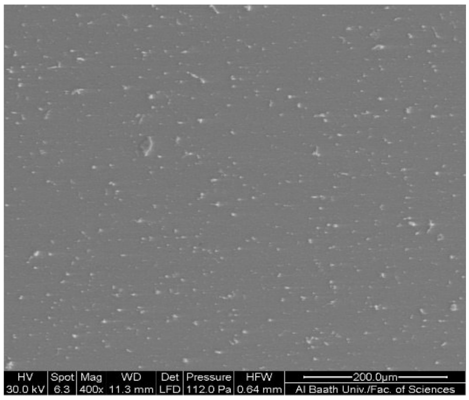
The undoped and Mg doped SnO_2 thin films were studied by scanning electron microscope (Quanta 200) with magnification 400x. SEM micrographs of undoped and Mg doped SnO_2 thin films are shown in Fig. 5.



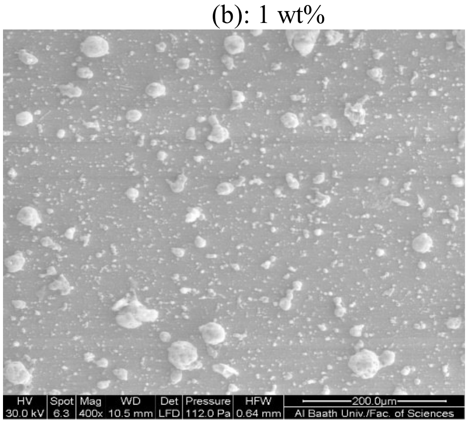
(a): Pure



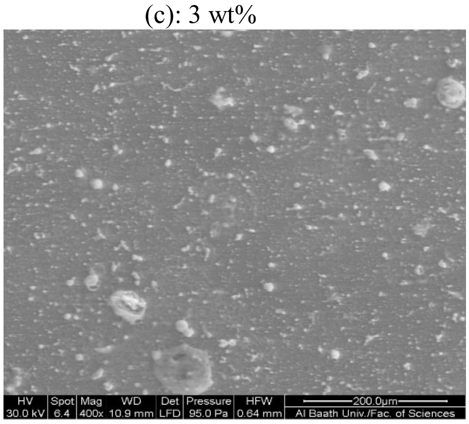
(b): 1 wt%



(c): 3 wt%



(d): 5 wt%



(e): 7 wt%

Fig. 5: SEM micrographs of (a) undoped, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt% Mg doped SnO_2 thin films.

From figure 5(a) it can be observed that pure SnO_2 film possess uniform, spherical grains and its almost homogeneously distributed. We observe with increasing Mg doping level until 3 wt% that grains size decreases and gets smooth. By increasing the Mg dopant to 5 wt% the grains size gets bigger and has nearly spherical shape then decreases at 7 wt%.

5. Conclusion

This paper presents a study of structural properties of Mg doped SnO_2 thin films deposited by spray pyrolysis technique on glass substrates at 450°C. X-ray diffraction patterns confirm that the films have polycrystalline nature with tetragonal structure and show presence (110), (101), (200), (211), (301) planes in all pure and Mg doped tin oxide thin films. The SnO_2 film has preferred orientation along (101) plane. Upon increasing Mg concentration the preferred orientations change to (301) and (211) planes. The average of crystallite size is within the range [22.42-9.48 nm] for all films. It was defined that the lattice constants a, c for all the films, were almost identical with JCPDS values, and the ratio c/a remained constant with increasing Mg dopant concentration. It was found by studying SEM micrographs, that the form of grains is spherical and almost homogeneously distributed, and by Increasing doping level, the form of grains changed.

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