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In-doped $SnO_2$for Humidity Sensor at Room Temperature Obtained by Ultrasonic Nebulizer Method

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Abstract: In/SnO_2, the thin films have been prepared at T_s for 400°C by variation of In doping. The effect of doping on structural and humidity sensor properties was studied. XRD data indicated the formation of tetragonal polycrystalline (SnO_2) thin films with a preferred orientation along (110), and (In^{3+}) ions entering the lattice substitutionally. The crystallite size was found to be decrease with increasing In concentration. The Average grain size is slightly decreased with the increase of In concentration, which has been investigated by Scanning Electron Microscopy (SEM).The humidity sensor showed that the sensitivity increase with In doping concentration increasing. The result also showed that the humidity sensitivity of doped films is higher than undoped.

Keywords: SnO_2, In, thin films, humidity sensors.

1- 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 [1], gas sensors [2], transistor [3], optoelectronic devices [4], lithium batteries [5] , 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 [6], ultrasonic spray pyrolysis [7], chemical vapour deposition [8], activated reactive evaporation [9], ion-beam assisted deposition [10], sputtering [11] • , and sol–gel methods [12]. Among these, we will focus more particularly in this paper on the spray 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 In doping on the structural and sensing properties of SnO_2 thin films deposited by ultrasonic nebulizer method.

2- Experimental details

The indium doped SnO_2 thin films were prepared by Ultrasonic Nebulizer Deposition (UND) technique. Using $SnCl_2.2H_2O$ (Alfa Aesar, purity: 97 %) as the source for tin dioxide and $InCl_3$ (HPLC, purity: 98 %) as the source for indium. The starting solution is composed with 0.2 molarity. The latter was varied in the range of 0% - 8%. The prepared solution is then sprayed on the heated glass substrates, the temperature was fixed to 400 °C.

In order to get good quality films and complete combustion all the deposition parameters such as the distance between the substrate and the nozzle, the distance between nozzle and substrate was kept at 10 cm.Film thickness (t) measured by weight difference method.

The structural properties of the films were characterized by X-ray diffraction (XRD) using PHILIPS diffractometer patterns of the samples are recorded with Cu Kα radiation (λ= 1.5406 Å) operated at 40 kV and 30 mA. All samples were scanned in the range (20-80 deg) with a scan speed of (8 deg/min). Surface morphology of In doped SnO_2 thin films were performed by Scanning electron microscopy (SEM). The humidity sensing properties were evaluated at various RH%, by measuring the changes of resistance of the sensor.

3- XRD Patterns

The structure and lattice parameters of SnO_2 and SnO_2: In films of different doping concentrations (2,4,6 and 8%) prepared by ultrasonic nebulizer method at substrate temperature of (400°C) were analyzed by X-ray diffraction. Fig (1) show that all peaks are identically with the tetragonal SnO_2 standard peaks with

preferred orientation along (110) direction at 2θ around (26.5°) and another peaks were observed compared with standard (JCPDS) SnO_2 card. From this figure, it is clear that the X-ray diffraction spectra possess sharp and very fine peaks indicate a good crystallization and In peaks do not appear even after adding a higher quantity of In into the SnO_2 films.It is seen that the peaks are more broadened and shifted toward the decrease in diffraction angle when the film doping increase. This result is attributed to the replacement of relatively bigger In^{3+}ions by the relatively smaller Sn^{4+} ions [13], resulting in the increasing of lattice constant (a) and interplaner spacing (d), this result is agreement with previous studies [14,15].

The lattice constants 'a' and 'c', for tetragonal phase structure, are determined by the following relation [16].

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

Where d□ is the interplanar spacing and h, k, l are the Miller indices.The values of lattice constants are listed in the table (1). The lattice constants were found to be in a good agreement with standard values and it is found increase with increase doping concentration.

The crystallite size of SnO_2 thin films was evaluated using the following Debye-Scherer formula [16]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \text{.....(2)}$$

where D is the mean crystallite size, k' is a dimensionless factor around 0.9, β is the full width at half maximum of the diffraction line, θ is diffraction angle, and λ is the X-ray wavelength, and estimated as shown in table (1), was found to be decreased from (32.2-27.6)nm by adding In to pure SnO_2 films, which may be due to residual tensile stresses in the film or substitution of elements of large size for small size, or internal stress and defect when increasing In concentration in the films [13].

The texture coefficient $T_{c(hkl)}$ for the (hkl) orientations were estimated from the following relation (3) [16]

$$Tc = \frac{I(hkl)/I_o(hkl)}{N^{-1}\sum_N I(hkl)/I_o(hkl)} \quad \text{.....(3)}$$

Where $I_{(hkl)}$ is the measured intensities, $I_{o(hkl)}$ corresponding to recorded intensities according to the JCPDS. N is the number of diffraction peaks and n is the number of diffraction peaks. The calculated texture coefficients$T_{c(hkl)}$ are tabulated in Table (1). From the texture coefficient calculations it was found that the preferential orientation of deposited films was along (110) plane.

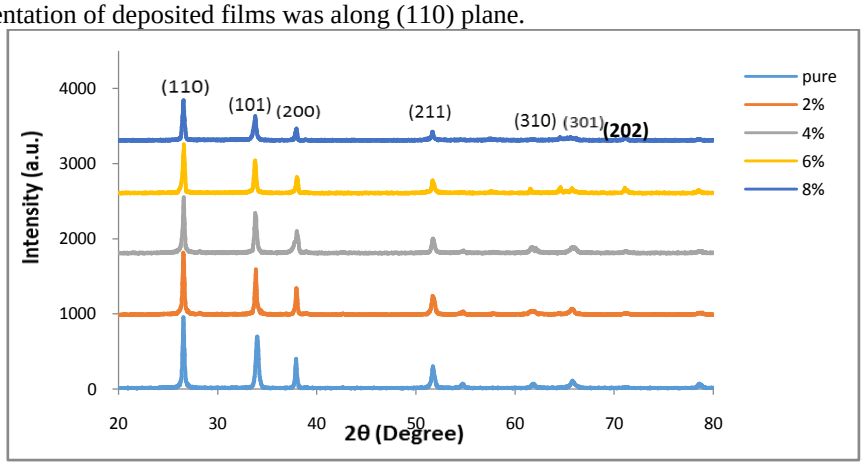


Fig:(1).XRD patterns of SnO_2 films and doped with In (2,4,6,8%)

Table (1) The D, T_s and Lattice constant for the SnO_2 and SnO_2: In thin films.

x	hkl	FWHM (XRD)	D nm	Tc	a (Å)	c (Å)	a ASTM (Å)	c ASTM (Å)
pure	(110)	0.2643	32.2	1.9538	4.7347	3.1877	4.7382	3.1871
	(101)	0.1779	48.7	1.4545				
	(200)	0.1928	45.5	0.9608				
	(211)	0.2199	41.9	0.6475				
	(110)	0.2750	31.0	1.8738	4.7393	3.1890		

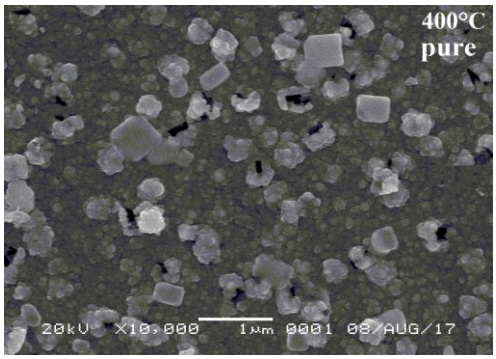
2%	(101)	0.1898	45.7	1.2487				
	(200)	0.2330	37.6	0.7925				
	(211)	0.2488	37.0	0.5099				
4%	(110)	0.2800	30.4	16474	4.7451	3.l934		
	(101)	0.2200	39.4	1.0867				
	(200)	0.2470	35.5	0.5873				
	(211)	0.2688	34.3	0.4256				
6%	(110)	0.2894	29.4	1.5181	4.7506	3.1948		
	(101)	0.2403	36.1	0.9835				
	(200)	0.2580	34.0	0.4974				
	(211)	0.2831	32.5	0.3030				
8%	(110)	0.3086	27.6	1.3250	4.7534	3.1996		
	(101)	0.2518	34.4	0.9582				
	(200)	0.2834	30.9	0.3885				
	(211)	0.3211	28.7	0.28064				

4- Scanning electron microscopy

The structure surface morphology of undoped and In doped SnO_2 thin films were studied by scanning electron microscopy as shown in fig.(2). This structure peats throughout the materials with closely packed to each other indicating good adhesiveness of film with the substrate.As clear in SEM images and table (2) the grain size was decreased from 87.31nm to 70.44nm with the increase of In doping concentration, the decrease of grain size due to substituted of In^{3+} in the locations of Sn^{4+} in SnO_2 structure and also some porosity is observable on the surface. This result is agree with the result of XRD and AFM. Similar studies was reported [14,15].

Table (2) The average grain size of pure SnO_2 and doped with In.

In (%)	Average grain size (nm)
pure	87.31
2	81.22
4	77.43
6	73.52
8	70.44



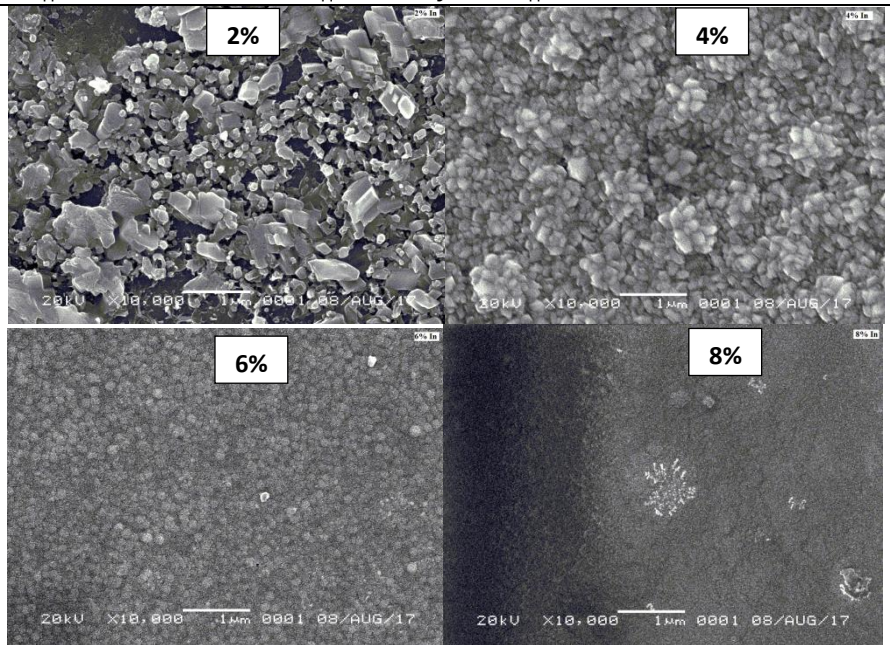


Fig:(2). SEM picture of pure SnO_2 and doped with In

5- Humidity sensors

Fig.(3) shows the effect of resistivity of thin film with variation of humidity. From the graph, it indicates that the resistance decrease with increasing of humidity. At low humidity levels the resistance of the sensing layers is high. The doping with In leads to the decrease in resistance comparing with the undoped films, thus, the decrease in substantial resistance could be attained through optimal doping.

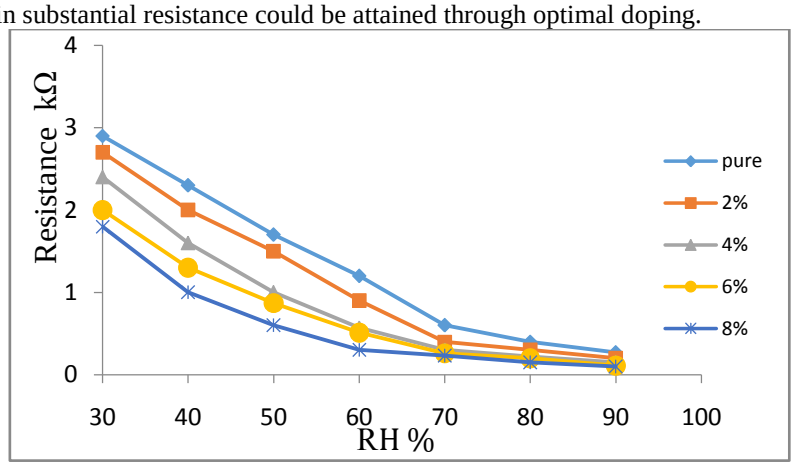


Fig. (3) Resistance of SnO_2 with different In doped vs. RH%.

The sensitivity is shown that in fig.(4) indicates undoped SnO_2 and In-doped SnO_2 thin films were linearly sensitive to humidity range (30-90%RH). It can be seen that the sensitivity increases with the increasing of humidity due to more water vapour has been absorbed. The graph shows the sensitivity increase with the increase of In doping concentration, it can be seen that the sample at 8% In doping concentration shows the higher sensitivity comparing with the undoped SnO_2 films, which may be attributed to the increase in roughness and the ability of absorb water vapour from the surroundings. Similar behavior is reported by Sin (2013) when SnO_2 doped with different concentration of Zn [17].

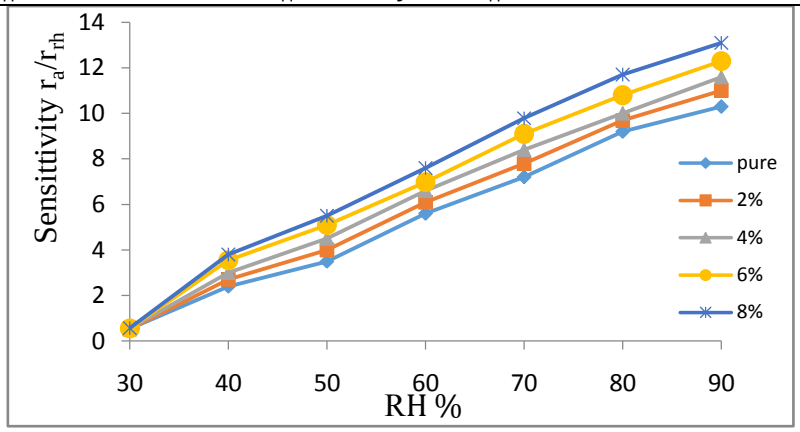


Fig: (4) Sensitivity of SnO_2 with different In doped vs. RH% .

The stability of the sensor was measured at 90 RH% as shown in fig.(5). The resistance was slightly the same when exposed to humidity every one hour. There are almost no changes in the resistance, which indicates good stability of the sensor. The sensor has clear stability and is quite promising for a practical humidity sensor. Similar studies was reported [17].

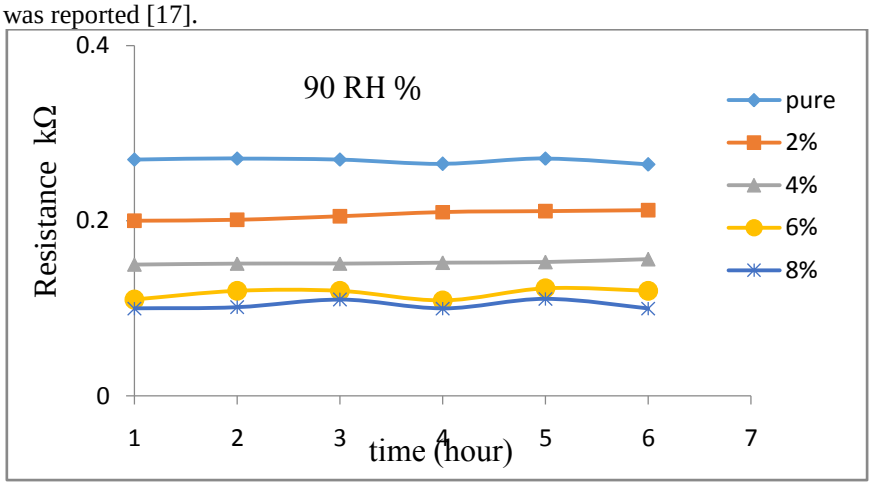


Fig: (5) Resistance of SnO_2 with different In doped vs. time.

Conclusions

Tin Oxide (SnO_2) thin films have been successfully deposited using local-made the ultrasonic nebulizer spray pyrolysis method.

1- The doping has caused the increased sensitivity of the thin films and decreasing the response and recovers time, but the operating temperature was not affected by the doping.
2- The sensing characteristics towards humidity indicate the highest sensitivity for the 8% In doped SnO_2 film which was prepared at 400℃ substrate temperature.

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