

## Physical Properties of Indium Tin Oxide (ITO) Nanoparticle thin films used as gas sensor

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### ABSTRACT

ITO/ Si gas sensor were fabricated by an efficient and size – controlled by using DC-Sputtering technique suitable for large deposition area and high quality thin films. Structural, optical and electrical properties of ITO thin films were investigated and analyzed extensively under different doping concentration. Structure and surface morphology of ITO thin films were characterized by X-ray diffraction, Atomic Force Microscope. XRD technique that showed these films is polycrystalline structure with a preferred orientation of (222),( 440),(400) the best orientation plain is (222) These been found crystalline size decrease with increasing doping concentration. The optical properties of ITO thin films were studied such as transmissions, energy gap The transmittance was measured in the wavelength range from(300nm to 900 nm) for all the films was highly transparent (greater than 85%). The optical energy band gap was increase with doping concentration in range from (3.9 to 4.15) eV. The electrical properties for ITO thin films include D.C electrical conductivity and Hall effect which shows that the type of films is (n- type), and the film has two activation energies in the rang (305-355)K, and the resistivity increase with doping concentration at 8wt%. The sensitivity toward NH<sub>3</sub>, NO<sub>2</sub> gas has been measured. In<sub>2</sub>O<sub>3</sub> doped with (Sn) has higher sensitivity to NH<sub>3</sub>, The sensitivity toward NO<sub>2</sub> gas has been measured, where In<sub>2</sub>O<sub>3</sub> doped with (Sn) has higher sensitivity to NO<sub>2</sub> than to NH<sub>3</sub>.

**Key Worde** D.C Sputtering, ITO, Gas sensor

الخصائص الفيزيائية لأكسيد الانديوم المشوب ذات الجسيمات النانوية واستخدامه كمتحسس غازي

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## الخلاصة

في هذا المشروع تم تصنيع متحسس غازي بطريقة تمتاز بكفاءتها وإمكانية السيطرة على الحجم الحبيبي للغشاء المحضر بطريقة التريز بالتيار المستمر والتي تعتبر طريقة غير مكلفة ومناسبة لترسيب اغشية ذات كفاءة ونقاوة عالية وتجانس تام للغشاء المرسب. , تبين من خلال دراسة حيود الاشعة السينية بان الاغشية ذات طبيعة متعددة التبلور وبتجاهية سائده (222,440,400) واتجاهية مفضلة (222), لوحظ تناقص بالحجم الحبيبي بازياد نسبة التشويب.اظهرت دراسة الخصائص البصرية للأغشية بوساطة قياس طيف النفاذية وفجوة الطاقة ان النفاذية قياست عند طول موجي يتراوح من (300 nm الى 900 nm) لجميع الاغشية وان جميع الاغشية الرقيقة هي شفافة للغاية بنسبة اكثر من (85%). بينما تدرجت فجوة الطاقة بزيادة تركيز الاشابة في مدى من eV (3.9 الى 4.15). الخصائص الكهربائية لأغشية اوكسيد الانديوم المشوب تضمنت التوصيلية المستمرة وتأثير هول حيث ان النتائج بينت ان الغشاء من نوع (n-type), يمتلك طاقتي تنشيط ضمن المدى الحراري (305-335)K , زيادة في المقاومة عند نسبة تشويب 8wt% تم حساب تحسسه الاغشية المشوبة لغاز NH<sub>3</sub> وغاز NO<sub>2</sub> , امتلكت الاغشية تحسسه عالية لغاز NO<sub>2</sub> من تلك التي تحسست غاز الامونيا.

## INTRODUCTION

Indium tin oxide (In<sub>2</sub>O<sub>3</sub>: Sn) has a wide band gap semiconductor with low resistivity, high optical transparency in the visible range of the spectrum it having a good adherence to the substrate surface and high chemical inertness, ITO can be appear in two stable modification as body centered cubic and rhombohedra (rh), they can be stabilized by choosing appropriate deposition on condition or synthesis method. [1]. Nanostructures of In<sub>2</sub>O<sub>3</sub>, particles were prepared by using physical method such as R.F sputtering, D.C sputtering, thermal evaporation and ion beam deposition were the most studied methods for preparation In<sub>2</sub>O<sub>3</sub>, [2] reported that most of applied recommended technique high –temperature treatment in order to fabricate good- quality polycrystalline films however, high temperature damages the surface of films and increases the interface thickness, which has a negative effect on the optical properties [2] D.C technique was successfully applied for growing quality In<sub>2</sub>O<sub>3</sub> thin Films. It plays a great roll in reducing the chemical contamination due to controlling of the composition of deposition structure, and in situ doping . Moreover, and it is a versatile and powerful tool for the production of nanopartical with desired size and composition, only by varying the deposition conditions [3]. ITO has been always applied as a gas sensing material to detect combustible, toxic and pollutant gases due to its high sensitivity, simple design and it is low cost [3]. Recently, researches have been focused on improving gas sensitivity in addition to reducing the operating temperature by introduction doping [4]

## Target Preparation

Indium oxide powder from Fluka company with high purity (99.99%) and tin oxide (Sn) with high purity (99.99%) in different doping concentration of (4%, 8% 12%). The powder was mixed mechanically for 6hours so that the mixture was uniformly distributed .The resulting powder was ground again and the additive material used as glue to make sure that the target was not crack ,the additive material which is the paraffin liquid evaporated in 125C without any effect on the target was added and was pressed under a 20 tons by using a compressor to make a target with 2.7cm diameter and 0.7cm thickness. Than the target was sintered at 800°C for 2 hours. The obtained target was as dense and homogenous as possible to ensure a good quality of the deposit

## Results and Dissection X-ray Diffraction Result

$\text{In}_2\text{O}_3$  films doped with tin metal oxide at different concentrations for (4,8 and 12 wt%) and at fixed annealing temperature of ( $400^\circ\text{C}$ ),the Figure(1,2,3)shows polycrystalline of cubic doped  $\text{In}_2\text{O}_3$  structure according to the JCPDS card No (6-416). The ITO films shows diffraction peaks of high intensity in plane (222), increasing in FWHM lead to decreasing in the main grain size as shown in Figure (2). At doping concentration of 8 wt% of ITO films which were annealed at  $400^\circ\text{C}$ , two diffraction peaks located at  $2\theta = 30.54$  and  $2\theta = 51.16$  which corresponding to the (222) ,(440) plan. As be seen decreasing in the intensity of peak of (222) with increasing doping concentration and the FWHM also increasing, and main grain size decrease with increasing doping consternation reported in the publication [5].As shown in Figure (3)12wt%:Sn concentration of tin metal doped with  $\text{In}_2\text{O}_3$ ,the films shows diffraction peaks at  $2\theta = 30.12$  and  $51.23$ which corresponding to the (440),(222) plane it can be concluded that 12wt% (Sn) doped films generally has smaller grain size the increasing doping level of 12wt% might have increasing potential energy of atomic diffusion barrier[6].Same workers attribute that to the presence of internal stress by doping of tin during sputtering deposition, which can alter the energetic balance between different crystal planes orientations such as [7] . The values of the FWHM and the main grain size of the samples are given in the Table (1).

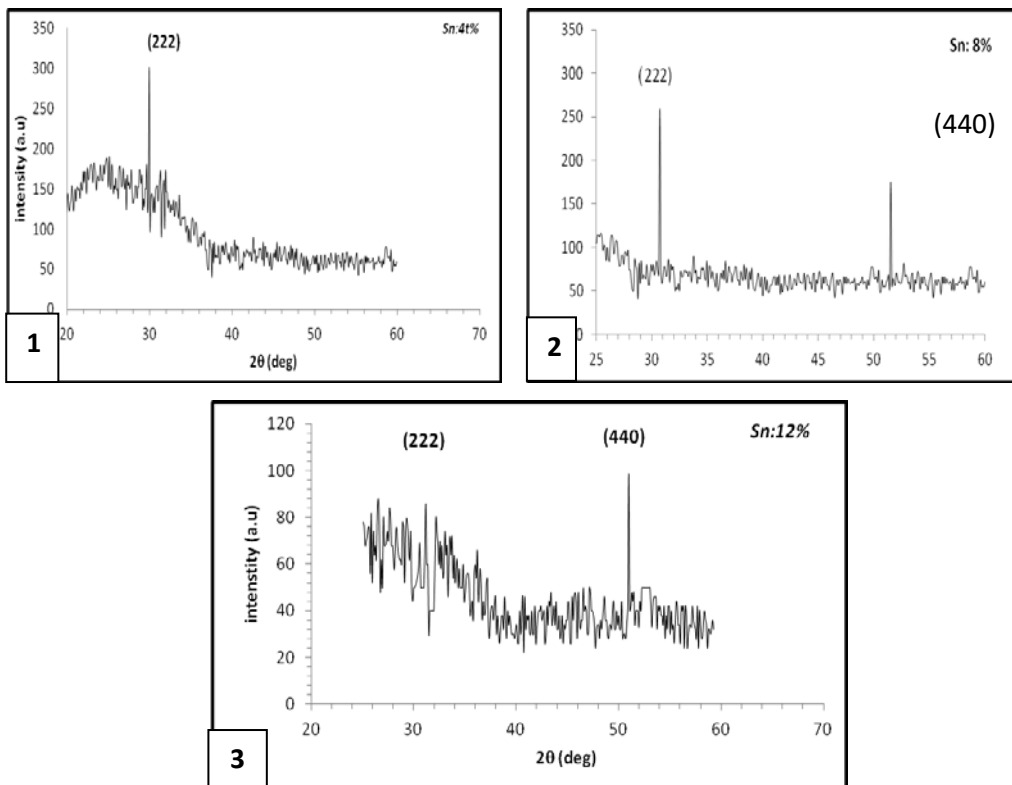
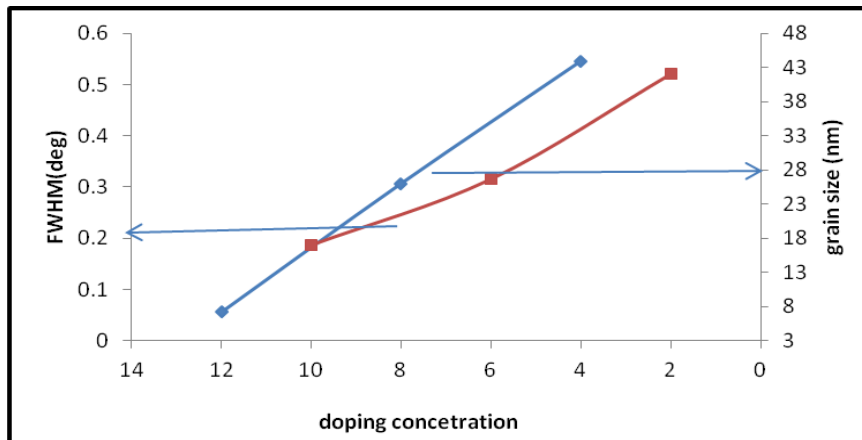


Figure (1,2,3): XRD of ITO thin film with doping concentration 4, 8,12wt% annealed at  $400^\circ\text{C}$



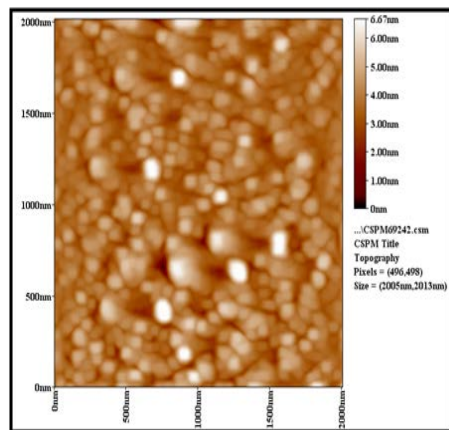
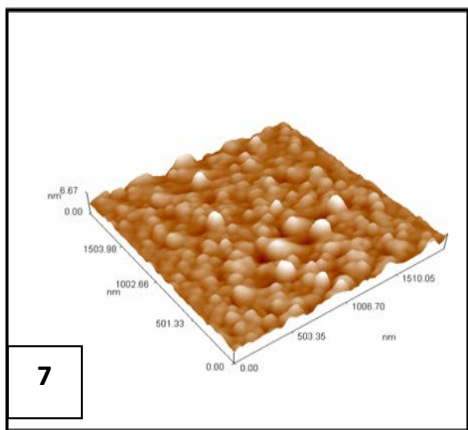
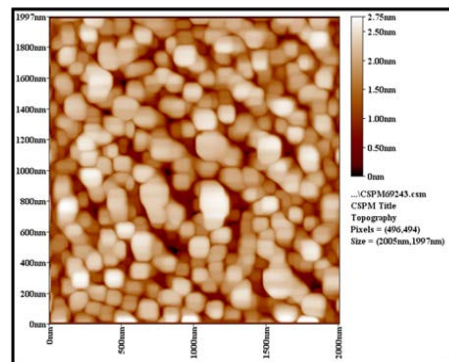
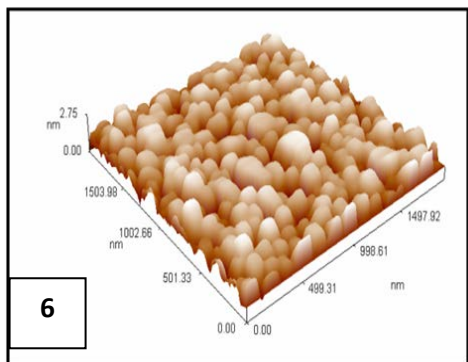
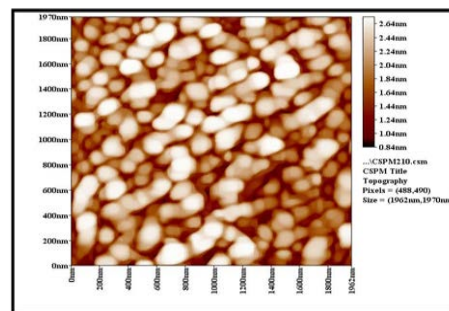
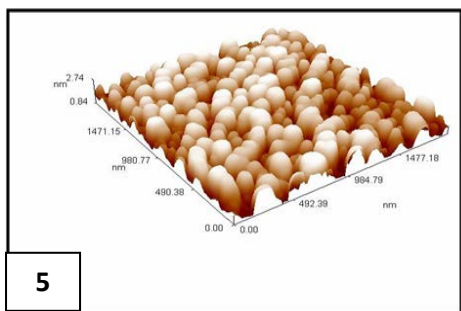
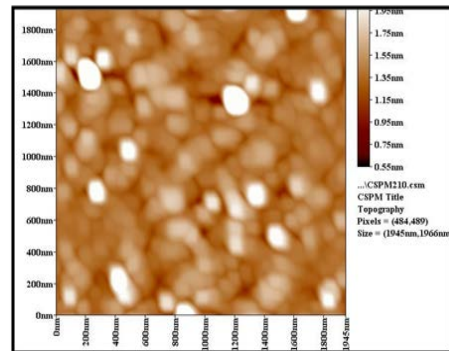
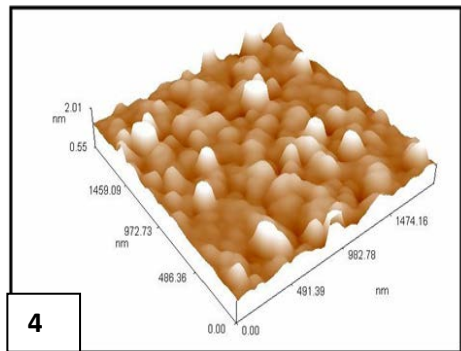
**Figure (1-2): The Full Width at Half Maximum (FWHM) and main grain size for  $\text{In}_2\text{O}_3$ : Sn (222) as a function of doping concentration**

**Table (1): The obtained result of the XDR for  $\text{In}_2\text{O}_3$ : Sn with 4,8,12wt% at annealing temperature  $400^\circ\text{C}$**

Doping concentration	2θ (deg)	Hkl	FWHMβ (deg)	Grain Size(nm)	Lattice constant(nm)	D(nm) XRD
$\text{In}_2\text{O}_3$ / $400^\circ\text{C}$	30.65	222	0.3252	21.8	10.118	2.530
	37.14	400	0.2630	33.2	10.119	2.532
	51.14	4400	0.208	30.5	10.120	2.528
Sn 4wt %	30.54	222	0.1875	43.9	10.112	2.258
Sn 8wt%	30.65	222	0.3162	26	10.118	2.5295
	51.20	440	0.4167	22.11	10.119	2.5299
Sn 12wt%	30.12	222	0.5210	7.19	10.116	2.528
	51.23	440	0.5466	5.13	10.116	2.528

### Surface Morphology Atomic Force Macroscopic (AFM)

The grain size (grain diameter) and average roughness and root mean square roughness (RMS) of pure and doped  $\text{In}_2\text{O}_3$  thin films for different doping concentrations (4,8 and 12wt%) are measured by using AFM as shown in Figure (4,5,6,7) and the result listed in Table (2). Shows the value of average roughness and root mean square roughness (RMS) and average grain size. It is observed from this table that the average roughness and root mean square roughness (RMS) value decreases with increasing the doping due to the rearrangement of atom in film and reduction in the vacancy defect, this result agrees with my result [7].



**Figures (4,5,6,7): Three- dimensional AFM images of the  $\text{In}_2\text{O}_3$  with different doping concentrations (4)  $\text{In}_2\text{O}_3$ pure,(5)4wt%,(6) 8wt%,(7) 12wt% thin films**

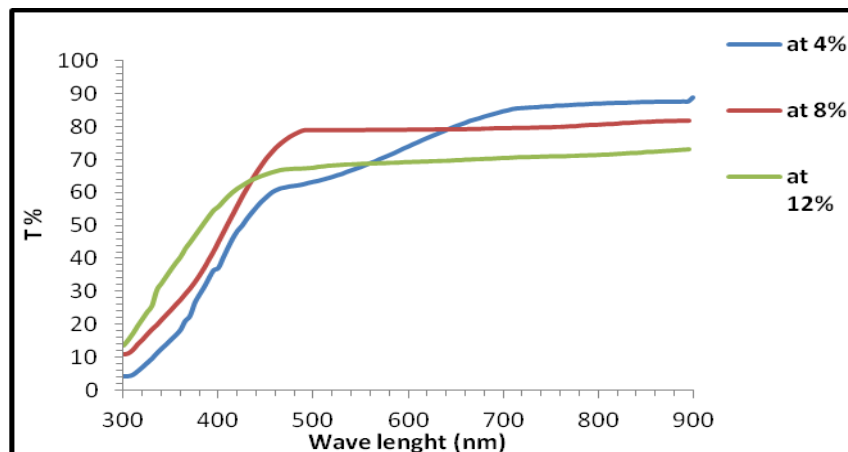
**Table (2): Variation of root mean square and grain size for doped  $\text{In}_2\text{O}_3$  at different doping concentrations of (4, 8,12wt %) and at fixed annealing  $400^\circ\text{C}$**

Doping concentration	Root mean square(nm)	Roughness(nm)	Grain size(nm)
Pure $\text{In}_2\text{O}_3$	55.2	40	24
4%	50	38	43.9
8%	42	24	26
12%	33	21.5	7.19

### Optical Properties

#### Transmission

Figure (8) shows the optical transmission for (4,8 ,12 wt % ) Sn doped  $\text{In}_2\text{O}_3$  deposited on glass substrate. The transmission in doped is found to decreases with increasing doping concentration .The decrease of transmission at doping concentration may be due to increased scattering of photons by crystal defects created by doping, which is in according with the finding of other workers[10].

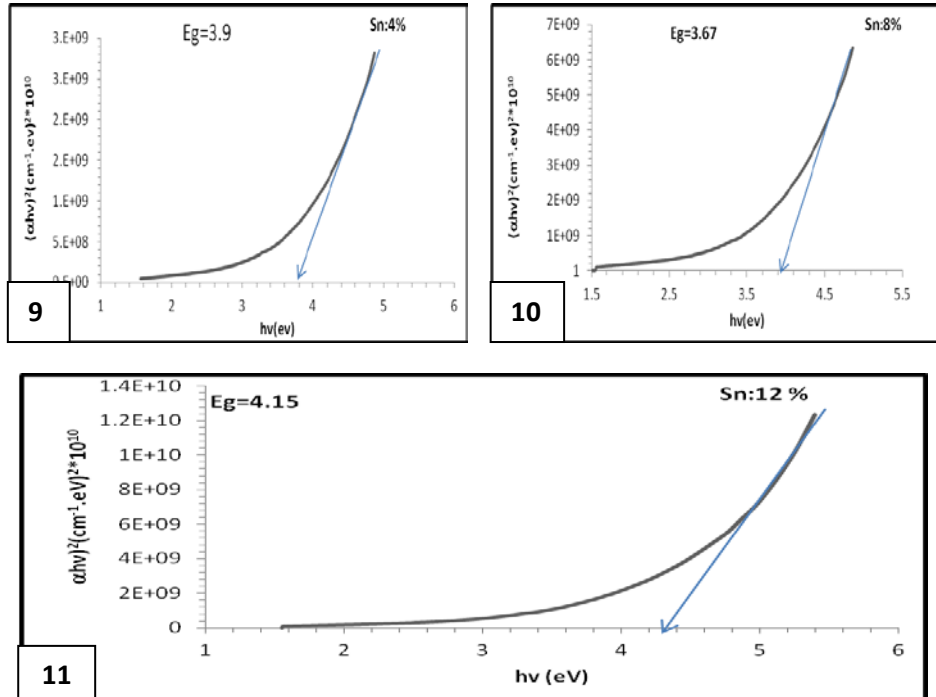


**Figure (8): UV-VIS transmittance spectra of  $\text{In}_2\text{O}_3$  / glass films at different doping concentrations of (4, 8,12wt %)**

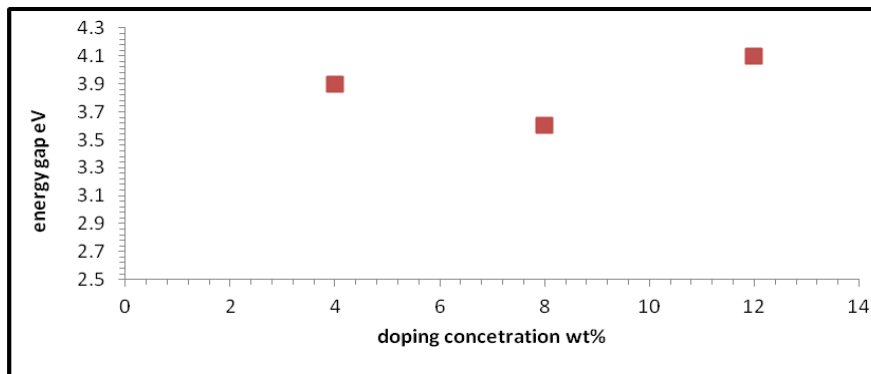
#### Energy Band Gap ( $E_g$ )

The direct band gap values for  $\text{In}_2\text{O}_3$ : Sn thin films at different doping concentrations at (4, 8,12wt %) was calculated the result shows at doping concentration 4% increases in the band gap as shown in the Figure (9), the band gap value related to the crystalline thin film. Thin film with concentration 8wt% show decreases in energy gap that can be due to the prohibited impurities that led to the formation of donor levels within the energy gap near the conduction band. thus, it will absorb photons of low energy, which is in according with finding of other works[11,12,13,14,15,] .While at doping concentration 4,12% as show in the figure (10) the energy gap increases because the widening of the band gap is due to the

increase in carrier density as a result of Sn doping[16,17], according to the Burstein-Moss model as shown in Figure (11,12)



**Figure (9,10,11): Plots of  $(\alpha hv)^2$  verses photon energy (hv) of doped  $\text{In}_2\text{O}_3$  thin films at different tin concentrations**

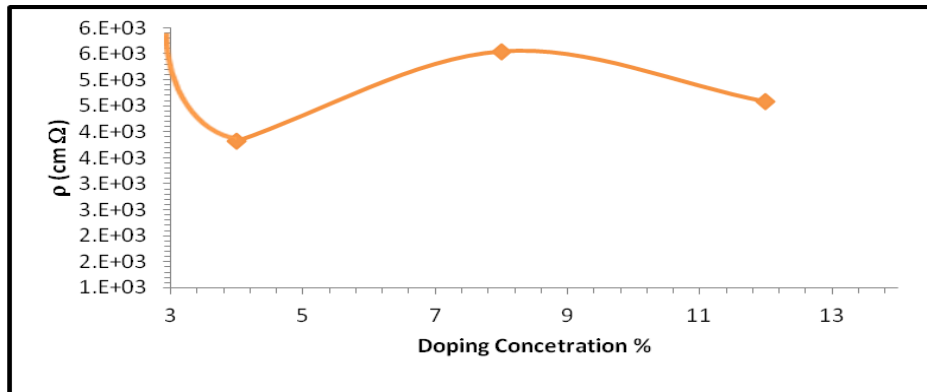


**Figure (12): Band gap as a function of different doping concentrations with tin.**

### The Electrical Properties

In order to investigate the effect of tin doping on some electrical properties of  $\text{In}_2\text{O}_3$  films, electrical resistivity is a function of doping concentration Sn as shown in Figure (13). Which shows that the electrical resistivity decreases with increasing doping concentration of Sn in  $\text{In}_2\text{O}_3$  thin films, indicating that the initial decrease in resistivity is very sharp with Sn concentration increasing from 0% to 12%, and subsequently, the resistivity tends to saturation with further increase in Sn concentration. This saturation is due to an increase in the density of electron traps introduced by more Sn dopants. On the other hand, the carrier mobility of the films

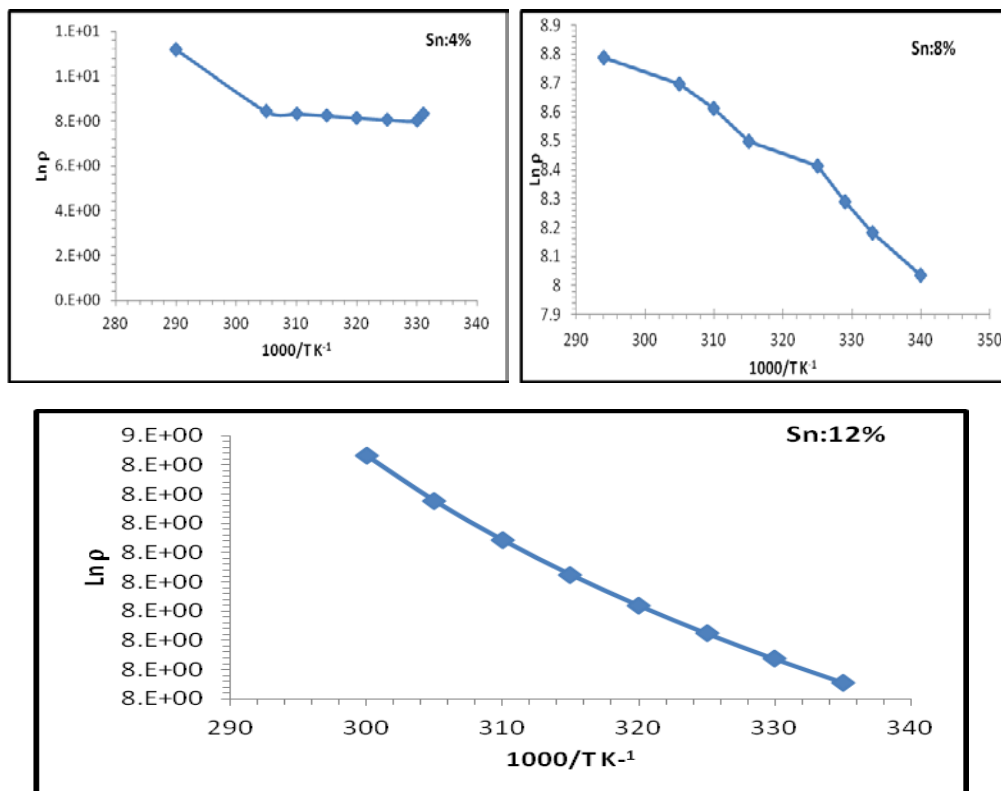
varies not monotonously with the Sn concentration initially [17]. As the Sn concentration increases further, ionized impurities in the crystal will increase gradually. In that case, ionized impurity scattering is dominant and causes the decrease in carrier mobility [18].



**Figure (13): The electrical resistivity as a function of different doping concentrations (4, 8, and 12%) with tin oxide**

#### Variation in Resistivity with Temperature

In order to investigate the effect of tin doping on some electrical properties of  $\text{In}_2\text{O}_3$  films, electrical resistivity used as a function of temperature for different doping concentrations as shown in Figure (1-9a, b, c). Table (4) which shows the activation energy  $E_{a1}$  and  $E_{a2}$  of the  $\text{In}_2\text{O}_3$  thin films doped with Sn. It is clear that the activation energies  $E_{a1}$  and  $E_{a2}$  increase with increasing doping concentration in the films [19].





**Figure (14,15,16) :  $\ln \rho$  as a function of  $1000/T(K)^{-1}$  for  $In_2O_3$  films at different doping concentrations with Tin**

**Table (4): Activation energies  $E_{a1}$  and  $E_{a2}$  for  $In_2O_3$  thin films for different doping concentrations with Tin.**

Doping with Sn	$E_{a1}(ev)$	$E_{a2}(ev)$
4%Sn: $In_2O_3$	0.030	-
8% Sn: $In_2O_3$	0.10383	0.1175
12% Sn: $In_2O_3$	0.1279	0.13383

### Hall Measurements

The results were obtained from Hall effect on Sn doping  $In_2O_3$  thin films and fixed annealing temperature at  $400^\circ C$  for 60 min were (n-type). The results shows increase in the value of electrical conductivity, accompanied by a clear increase in the values of charge carriers with the decrease in the values of both the mobility and Hall coefficient. The value of  $R_H$  decrease with the increases in doping concentration in the films Hall coefficient sign has not been changed by the increase in doping concentration which indicates that the electrons are the charge carriers and are responsible for the increased conductivity, as shown in Table (5). The mobility decreases with increasing doping concentration in  $In_2O_3$  thin films the results may be attributed to the average grain size decreasing with increasing doping concentration in the films Therefore doping concentration in  $In_2O_3$  thin films plays a vital role in determining its electrical properties[9].

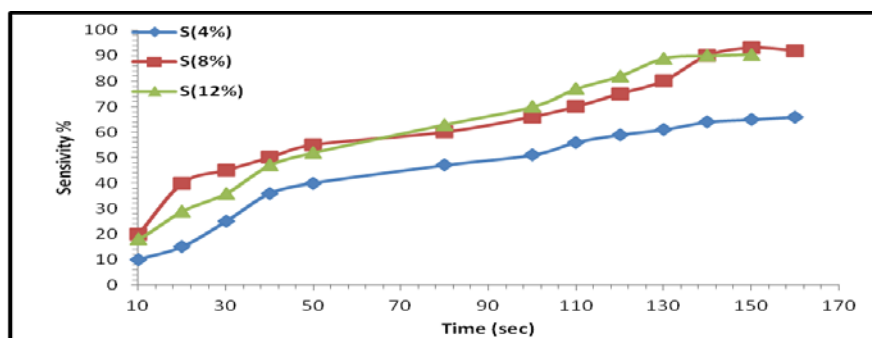
**Table (5): The obtained results of Hall measurement for  $In_2O_3$  doping with tin.**

Sample Thin	$R_H (cm^3/C)$	$n(cm)^{-3}$	$\mu_H (cm^2/v.s)$
4%Sn: $In_2O_3$	6.603	$9.45 \cdot 10^{18}$	$2.001 \cdot 10^{-1}$
8% Sn: $In_2O_3$	2.045	$5.975 \cdot 10^{19}$	$3.613 \cdot 10^{-2}$
12% Sn: $In_2O_3$	1.355	$4.687 \cdot 10^{19}$	$2.985 \cdot 10^{-2}$

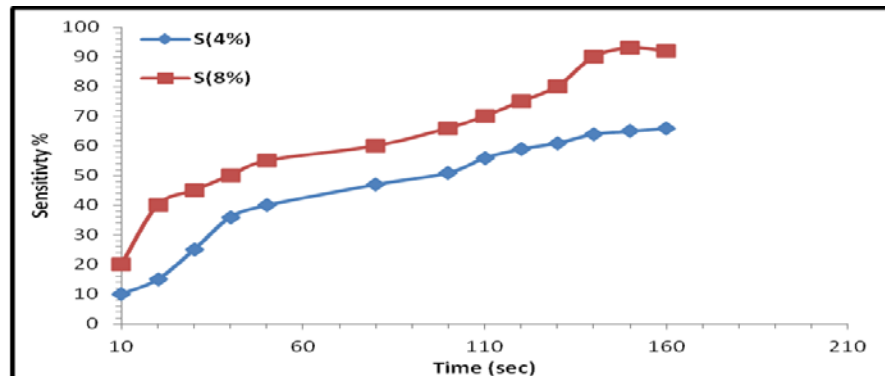
### Sensing Properties

#### Gas Sensitivity for $NH_3, NO_2$

The Figure (17) shows the gas sensitivity of Sn doped  $In_2O_3$  on silicon substrate at different concentration (4, 8, 12 wt %) s increases with increase in doping concentration because with increasing doping concentration the grain size decrease leading to increase in the sensitivity of film for  $NH_3$  gas [1]



In Figure (18) show the sensitivity of ITO with tin concentrations of 4,8wt% for NO<sub>2</sub> gas with concentration 5ppm it is clear that with increasing doping concentration the sensitivity is increasing because with increasing doping concentration the grain size decrease leading to increases in the sensitivity of film [1,2,3,4].



## CONCLUSION

The XRD results reveal that ITO as deposited is amorphous but the annealed ITO thin films at 400°C for 60 min have a good crystalline cubic structure. It is observed that the ITO films exhibit a polycrystalline structure having (222), (400) and (440) planes of high peak intensities. The structure of In<sub>2</sub>O<sub>3</sub> doped with tin (Sn) thin films becomes less crystalline than that of undoped samples. Transmittance of thin films doped increases with the increasing doping concentration. Energy gap increases with increase in doping concentrations, the electrical resistivity was found to decrease with increasing doping concentration. Hall measurements indicate that the ITO thin films have the same conduction type (n-type conductivity). In<sub>2</sub>O<sub>3</sub> doped deposited on silicon (p-type) has sensitivity to NH<sub>3</sub>, NO<sub>2</sub> gas, the sensor In<sub>2</sub>O<sub>3</sub> doped with Sn shows good sensitivity to NH<sub>3</sub>.

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