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To cite this article: Auday H Shaban *et al* 2018 *J. Phys.: Conf. Ser.* **1003** 012101

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Doping And Annealing Effect On Evaporation Of ZnO Thin Films

Auday H Shaban[*]**, Samir A. maki, Shahd A. hussain,**

Department of physics/ College of Education For Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq

auday.h.s@ihcoedu.uobaghdad.edu.iq[*]

Abstract. The present study carried out to show the structure and optical properties of doped ZnO:Sn thin films that have been deposition on a glass substrate by thermal evaporation (using Zn metal). The percentage of dopant is (3, 5, 7, & 9)%. The annealing temperature was 200 oC fixed for one hour annealing time. The result of XRD shows the presence of (100), (002) and (101) are the diffraction peaks of all thin films. The crystalline size was found to be increased with Sn doping. The FWHM values of the peaks were found to increase with doping. The direct optical band gap was calculated and found to be (3.24, 3.21, 3.2, 2.72, 2.88) e.V for pure and doped thin films respectively.

Keywords ZnO, optical properties, Sn doping, thermal evaporation.

1.   Introduction

The transparent conducting oxides (TCO) has an interest wide range of application in solar cells, gas sensors, light emitted diode (LED), etc. Zinc Oxide can prepare by spray pyrolysis [1], sol-gel, chemical vapor deposition (CVD) and reactive evaporation. Among these methods, the thermal evaporation technique is a simple method and low-cost procedure [2]. Zinc Oxide is a semiconductor from II-VI group. it has a direct band gap 3.37 e.V and free excitation energy 60 Me.V [3]. Generally, it has polycrystalline with Wurtzite hexagonal structure [4]. In present study Tin (Sn+4) have a chosen as doping in ZnO matrix of ZnO as it will easily replace the (Zn+2) ions with (Sn+4) ions and create two more electron vacancies. In such condition, it will produce good conductivity and also alter some structural properties. It is known that the substitution of Sn does not produce large lattice distortion parent matrix (ZnO) because of its almost equal radius. Much of previous studies on pure ZnO and Sn-doped ZnO thin films with various concentration (3, 5, 7 & 9)% were deposited by thermal evaporation technique on the effect of the annealing process[5]. The properties of the deposited ZnO and ZnO:Sn films depend on the deposition parameters such as substrate temperature, the evaporation rate of Zinc metal and Tin concentration.

2.   Experimental techniques

Thermal evaporation was used to deposit pure Zn at room temperature and under vacuum about 10^{-5} (mbar) using Edward coating unit. The thin films were coated on a glass substrate at thickness 200 nm. The distance between the substrate to the source was 8 cm and the metal was placed in a molybdenum boat in thermal evaporation system. After deposition of Zn metal on a glass slide, the films were followed by thermal oxidation in air using furnace at temperature 400 C° with flow rates of oxygen 2.5 litters/ min for two hours to form ZnO thin films. After oxidation the samples were cooled at room temperature. The doping percentage of Tin varies (0 - 9) % were deposited on ZnO thin films then diffused by heating temperature 140 C° for one hour. All the pure and doped thin films were annealed at 200 C°. The structural properties were studied by X-ray diffraction using a (model (E306) with Cu Kα radiation (λ_{cu} = 0.154056 nm) as the source. The crystalline size was studied from Scherrer's formula. The influence of annealing time on the structure of thin films was investigated. The optical transmission and absorption of pure and doped ZnO were studied by UV-visible spectrophotometer with range (300-1100) nm.

3.   Result and discussion:

1-   The effect of doping:

A-   Structural properties

'Figure (1)' shows the X-ray diffraction of pure ZnO and doped thin films at different doping percentage. The peaks of XRD show that thin films are polycrystalline with a hexagonal structure (ASTM-00-019-1365) with orientation peaks (100), (002) and (101). With increase Sn content. The changes of peaks intensity depend on the level of Sn Doping. The value of the preferred orientation for pure ZnO thin film is (100) which is agree with **[3],** the peaks intensity is the domain orientation with respect to (002) and (101).
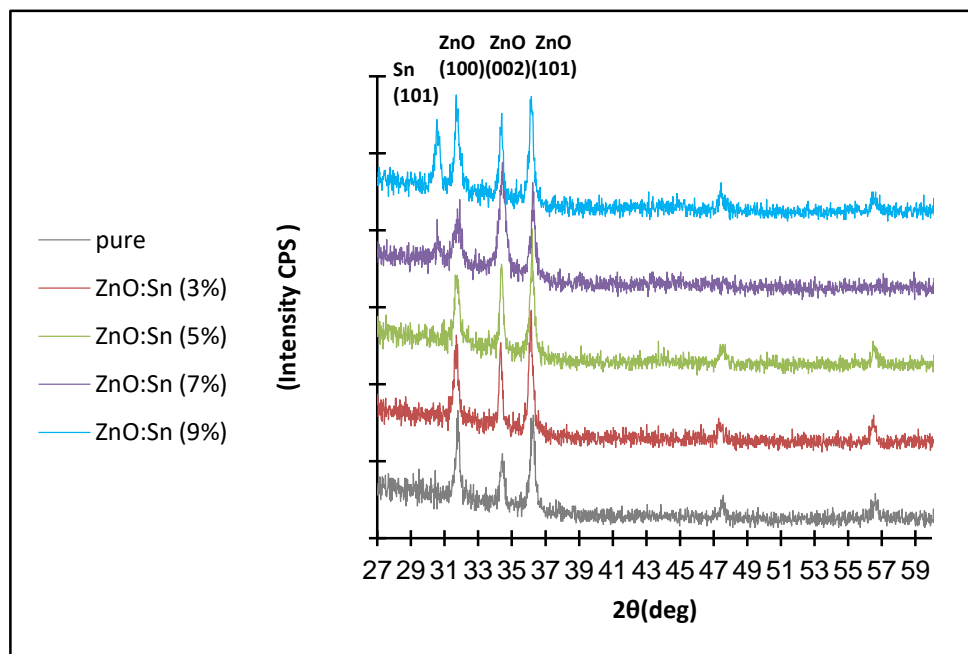

Figure 1. X-ray diffraction of ZnO:Sn thin films with different doping.

Table (1) shows the variation of intensity is dependent on the rate of the Sn impurities. The preferred orientation direction depends on Sn content. The value of pure ZnO films I(100) is a high intensity compared to both I(002) and I(101). At doping (3%) the value of I(100) is reducing until we reach (7%) compared to pure ZnO. the value of I(101) for doping (5%) continues to increase and the domain orientation becomes (101). At doping (7%) the value of I(002) is increased compared to (5%) and the value of I(101) decrease, therefore, the preferred orientation is (002). At doping (9%) the value of (002) decrease compared to (7%) while I(100) increased then the value of I(002), I(101), therefore again a preferred orientation along I(100) similar to pure ZnO. It is clearly noticed that was a peak appeared for Sn at (7%) and this peak increased at (9%). These results match the ASTM cards (00-019-1365) for Sn. The previous results refer to (impurities with limit percentages improves the crystalline structure) because it will reduce the crystal defects. The impurities atoms made their own atomic states except at 9% doping, where at this percentage, a reverse impact appears on the structural properties.

Table 1. shows the variation of intensity of XRD doping thin films.

Sn %	$I_{(100)}$	$I_{(002)}$	$I_{(101)}$	Preferred orientation	Sn $I_{(101)}$
o	166	110	156	100	
3%	164	154	194	101	
5%	140	150	202	101	
7%	140	188	162	002	114
9%	176	152	174	100	144

Table (2) indicates the diffraction angle (2θ), full width at half maximum (FWHM) and crystallite size (D) was calculated by using Scherrer's equation (1): **[6]**

$$C.S = \frac{0.9\,\lambda}{\beta \cos\theta} \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where **λ**: is the wavelength (A)
β : is the full width at half maximum (FWHM) of diffraction peak.
θ : Bragg angle.
The number of dislocation was calculated by equation (2):

$$\delta = \frac{1}{(C.S)^2} \ldots\ldots\ldots\ldots\ldots(2)$$

Where **δ** : dislocation density (Dislocation line/nm^2).
C.S: crystalline size (nm^2).
That obtained by x-ray diffraction for all peaks. The crystal size was decreased with increasing impurities except for 9% and an increase of dislocation δ. The dislocation is an indication of the crystals quality and Crystallization Level. The relation between dislocations and square particale size is [δ∝D^{-2}] **[7]** through a table (2) appears an increasing of layers with increasing impurities.

Table 2. X-ray diffraction of the peaks of ZnO thin films.

Sample	β (deg)	D (nm)	δ * 10^{14} (line.m^{-2})
ZnO (pure)	0.27	29.91	11.3
ZnO:Sn (3%)	0.27	31.2	11.09
ZnO:Sn (5%)	0.27	30.4	11.5
ZnO:Sn(7%)	0.28	29.3	11.7
ZnO:Sn(9%)	0.44	19.1	30.1

b-   Optical properties

'Figure 2' illustrated the optical transmittance spectra with respect to wavelength for ZnO: Sn thin films. The films show high transmission and low absorption and reflection. The transmittance of ZnO thin films decreases with increasing doping percentages. This behavior happened because of the creation of local states, gained from the impurities, at energy gap between valance and conduction bands, which increase absorption. It is also shown from the figure that the highest transmission was for pure Zinc Oxide thin films, reaching Its transmission is about (90)% of the wavelengths within the infrared region (800-900) nm **[4]** and this is the least absorption. The previous behavior makes the ability to use the properties of ZnO thin film as a transparent material for vehicles and airplanes windows, also as IR detector shields **[8]**.
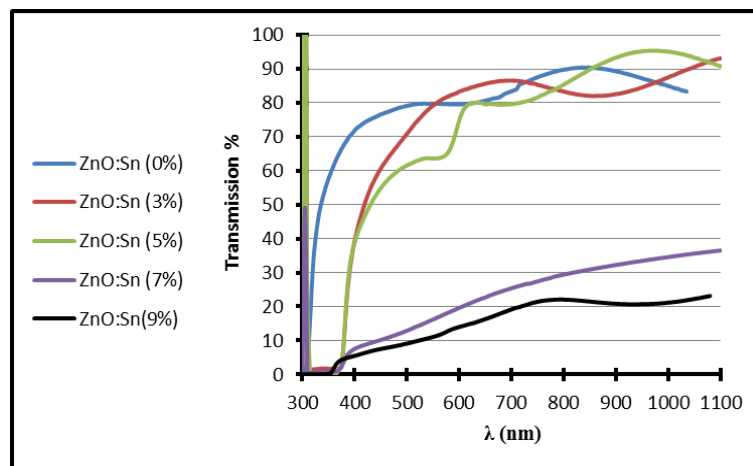
Figure 2. Transmittance spectra as a function of wavelength.

'Figure 3' , 'Figure 4' illustrated the increasing of absorption and reflection curve with increasing doping percentages. The reason for this behavior is the increasing of local states at energy gap **[8]**. Doping thin films were recorded with a precipitation rate of (9) % in the study that showed higher absorption compared to the absorption of the thin films prepared from pure and doping.
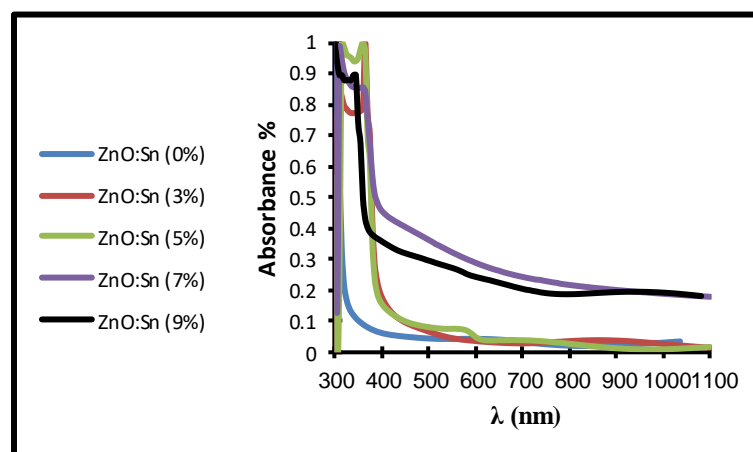

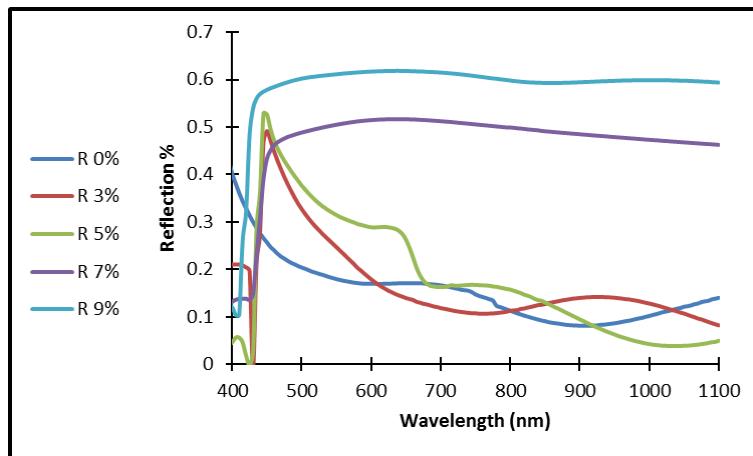**Figure 3**. Absorbance spectrum as a function of wavelength.

Figure 4. Reflection spectrum as a function of wavelength.

'Figure 5' illustrates the changes in the absorption coefficient as a function of the photon energy. The absorption coefficient generally begins a gradual increase as photon energy increases at ranges (2.2 - 2.9) eV for doping thin films. By increasing doping rate the absorption coefficient increases with low photonic energy. The higher value of absorption coefficient is greater than (10^4) cm^{-1}, indicate to direct electronic transitions between the valence and conduction bands at these energies. The absorption coefficient has a maximum value at $(9*10^4)$ cm^{-1}. At the energy range (2.85 - 3.3) eV, the absorption coefficient remains almost constant.
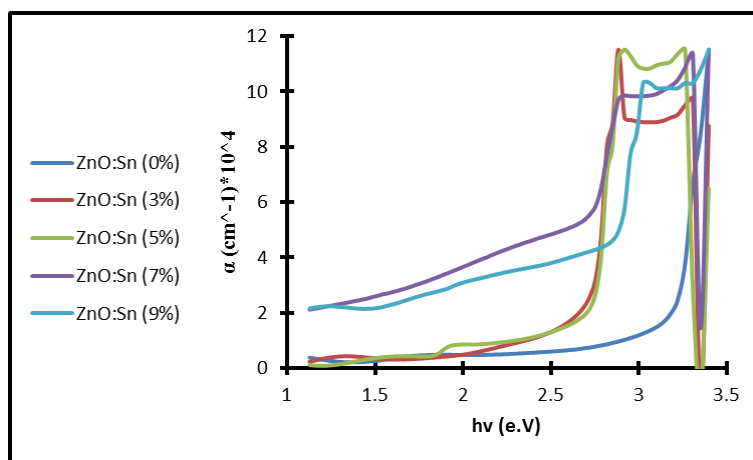

Figure 5. Absorption coefficient with different percentages.

The optical energy gap between the thin films material is the standard path to use these materials in industries. ZnO has a direct band gap dependence of the absorption coefficient can be calculated by Tauc's equation (3) [9]:

$$\alpha h\nu = B(h\nu - E_g)^n \ldots\ldots\ldots(3)$$

where α: is absorption coefficient.
hν: the photo of energy.
B: constant.
Eg: the energy gap.
n: constant the type of electronic transition.

'Figure (6)' illustrated the relation between (hν) and (αhν)^2 and the modification process to achieve the intercept with X-axis.

The band gap of the pure ZnO thin films is 3.24 eV **[10].** After doping the band gap is decrease to (2.72 eV) for (7 %) dopant this due to additional levels below the conduction band **[9]**. At level (9%) the energy gap is increases because of increase in the band tail width **[6].** Table (3) illustrates the variation value of energy gap with doping concentration.

Table 3. the change of energy gap with different doping.

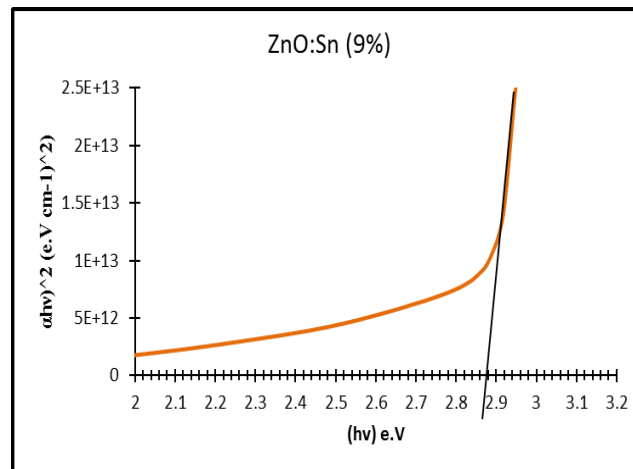| sample	Energy gap (e.V)
pure	3.24
3%	3.21
5%	3.2
7%	2.72
9%	2.88
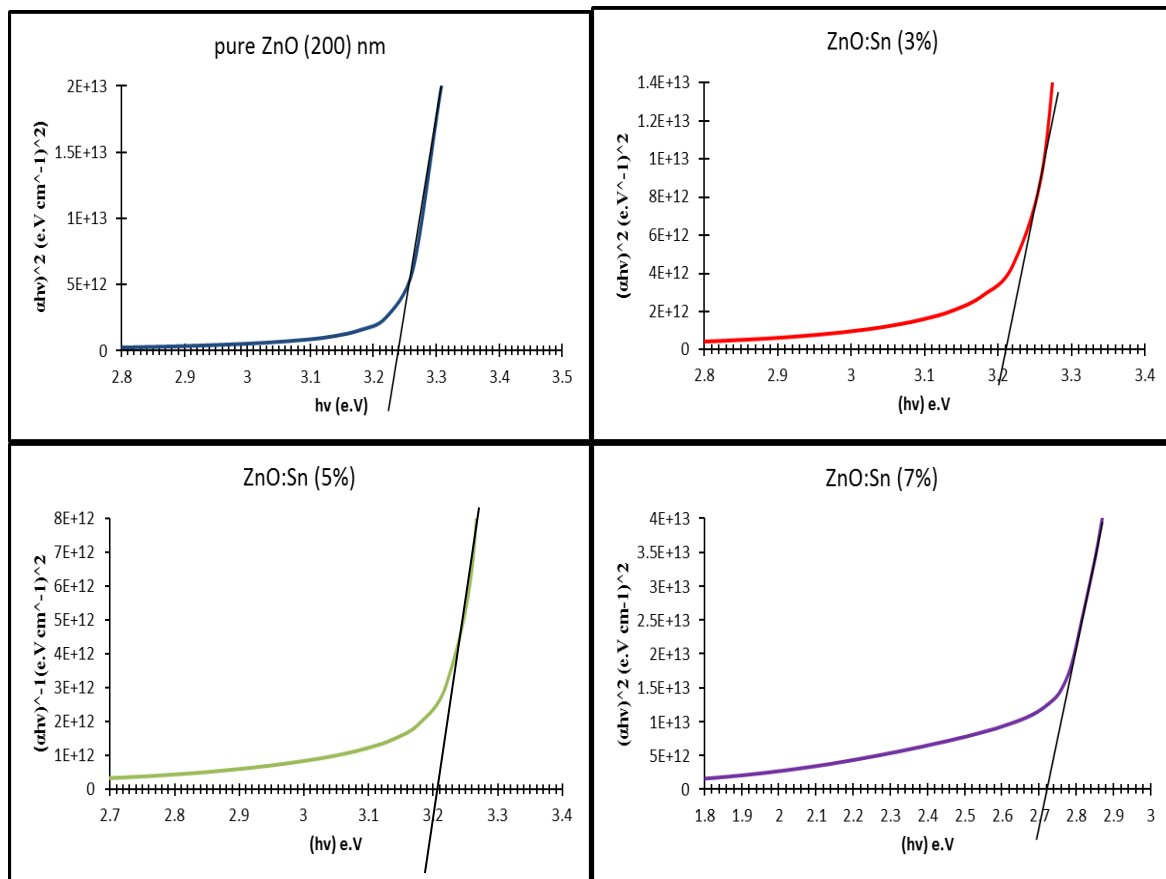
Figure 6. Energy gap for pure and doped ZnO thin films.

a- *The effect of annealing*
b- *Structural properties*

'Figures 7' illustrate X-ray diffraction of doping Zinc Oxide thin films after annealing. It show the effects on the domain peak which make it higher and more crystal order. Comparing the results between XRD and ASTM, which appear to be matched, before annealing. Table (4) shows the comparing values. This behavior gained from annealing process which makes the atoms with bigger energies and reorders the structure. The reason behind reduce the peaks, except the domain one, is the reorder process done with the domain direction.
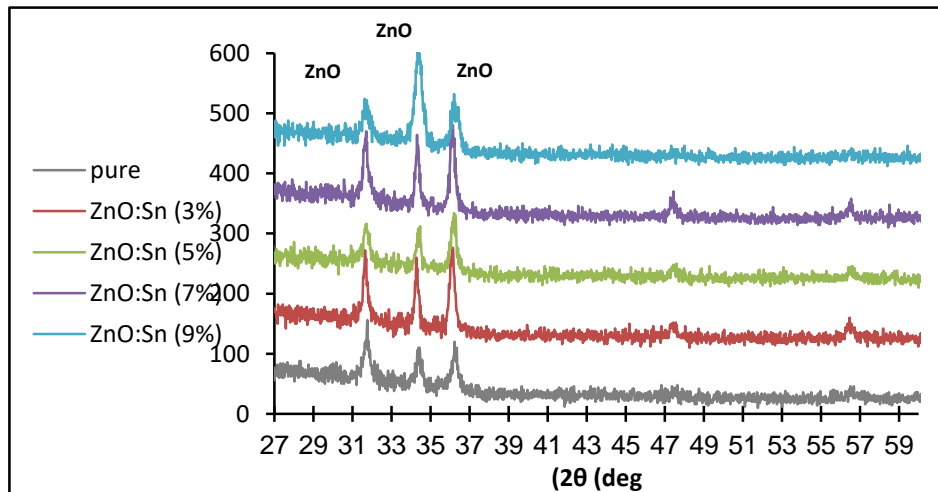

Figure 7. X-ray diffraction for ZnO thin films after annealing.

Table (4) shows the diffraction angle (2θ), full width at half maximum (FWHM) and crystalline size (D) was obtained by x-ray diffraction for all peaks. Table (4) illustrate Improved thin films the pure and doped with percentage 5 & 9%.

Table 4. X-ray diffraction for doped ZnO:Sn thin films after annealing.

Samples	FWHM (deg)	D (nm)	$\delta * 10^{14}$ (line.m^{-2})
ZnO (pure)	0.33	24.9	16.1
ZnO:Sn (3%)	0.27	30.6	10.8
ZnO:Sn (5%)	0.31	26.3	15

| ZnO:Sn (7%) | 0.27 | 30.7 | 10.8 |
| ZnO:Sn (9%) | 0.45 | 18.02 | 30.8 |

Table (6) illustrated the grain size for 9% was less size than after annealing. The FWHM curve is wider at the middle based on Scherer equation, which shows a nanocrystaline structure.

  c- Optical properties

Optical measurements of doped thin films after annealing were performed. The transmission decrease of pure ZnO thin films after annealed at 200 C° was below 70%. Figure shows the transmittance increase with increasing wave length. The transmittance values decrease with increasing impurities. The annealing effects on the transmittance and makes them decrease than before annealing **[11].**
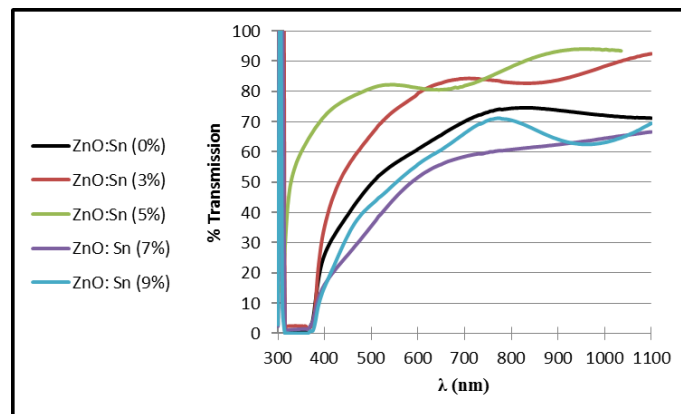

Figure 8. Transmission spectra forZnO:Sn films after annealing.

'Figure (9) & (10)' illustrated the absorption and reflection spectra for ZnO pure and doped thin films after annealing with respect to photon energy. This figure shows the increase of absorption and reflection with annealing and displacement of optical absorption edge to the region of higher wave length. The absorption spectra for ZnO thin films gradually decrease with increasing impurities, except for the pure sample which shows an increase in transmittance.
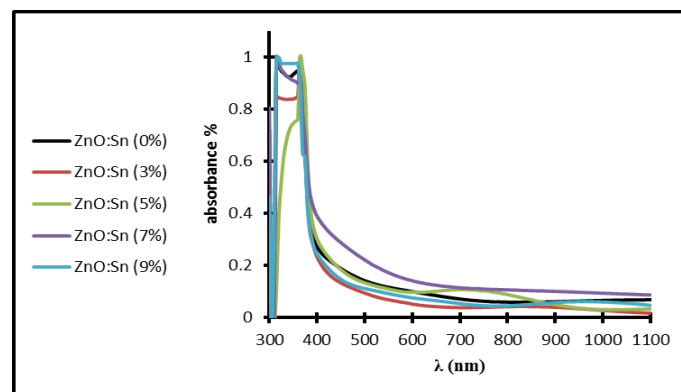

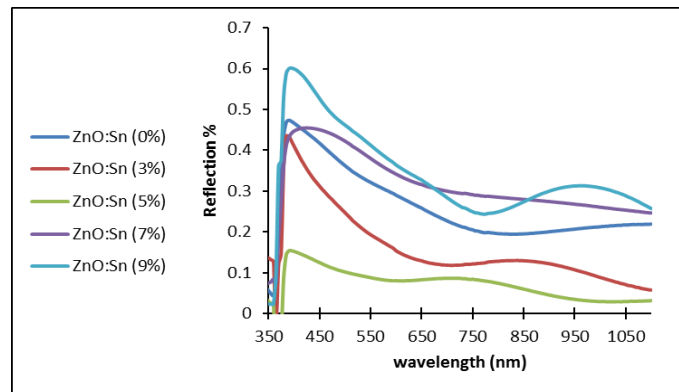**Figure 9.** Absorbance spectra for pure and doped ZnO filmsafter annealing.

Figure 10. Reflection spectra for pure and doped ZnO films after annealing.

The absorption coefficients appear to be increase gradually with increasing photon energy. The absorption coefficients reduce with increasing impurities. The higher value appears at 9% after annealing. This figure shows that the absorbance coefficient values for pure and doped thin films after annealing is ($\alpha > 10^4$ cm^{-1}) indicate that the electronic transition is of the direct type.
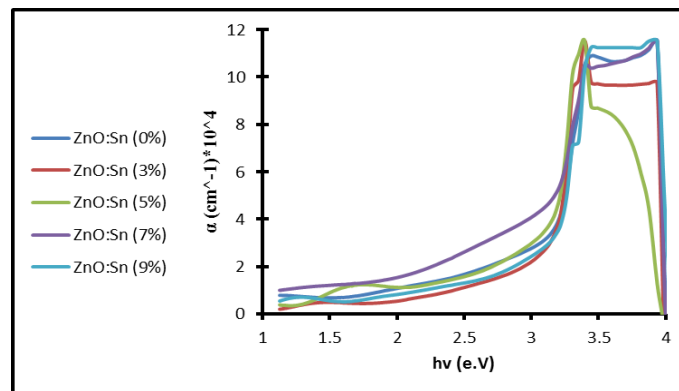

Figure 11. Absorption coefficient forZnO:Sn after annealing.

'Figure (12)' illustrate the changes of energy gap for pure and doped thin films after annealing. The figure shows the decrease of energy gap directly compare with energy gap before annealing because appearance of band tail resulting from defects associated with the presence of cavities and surface roughness **[3].** Table (5) illustrates the variation value of energy gap with doping concentration after annealing.
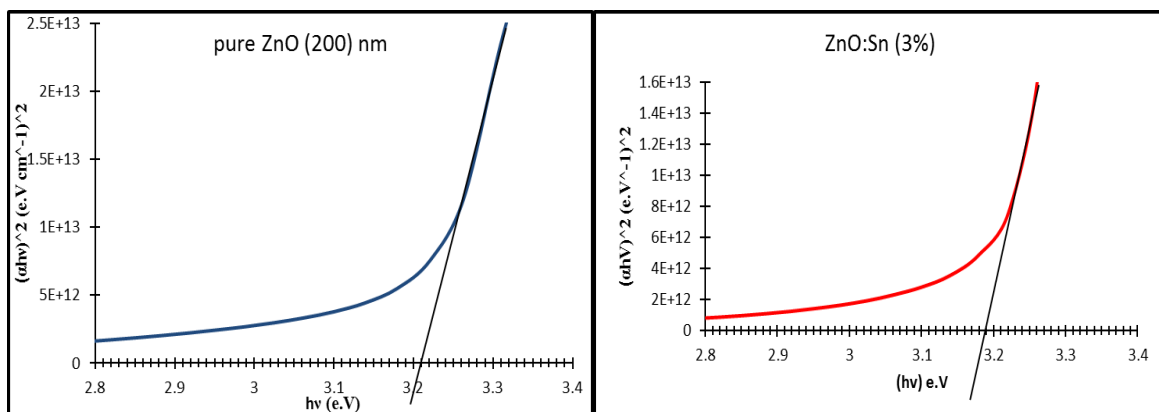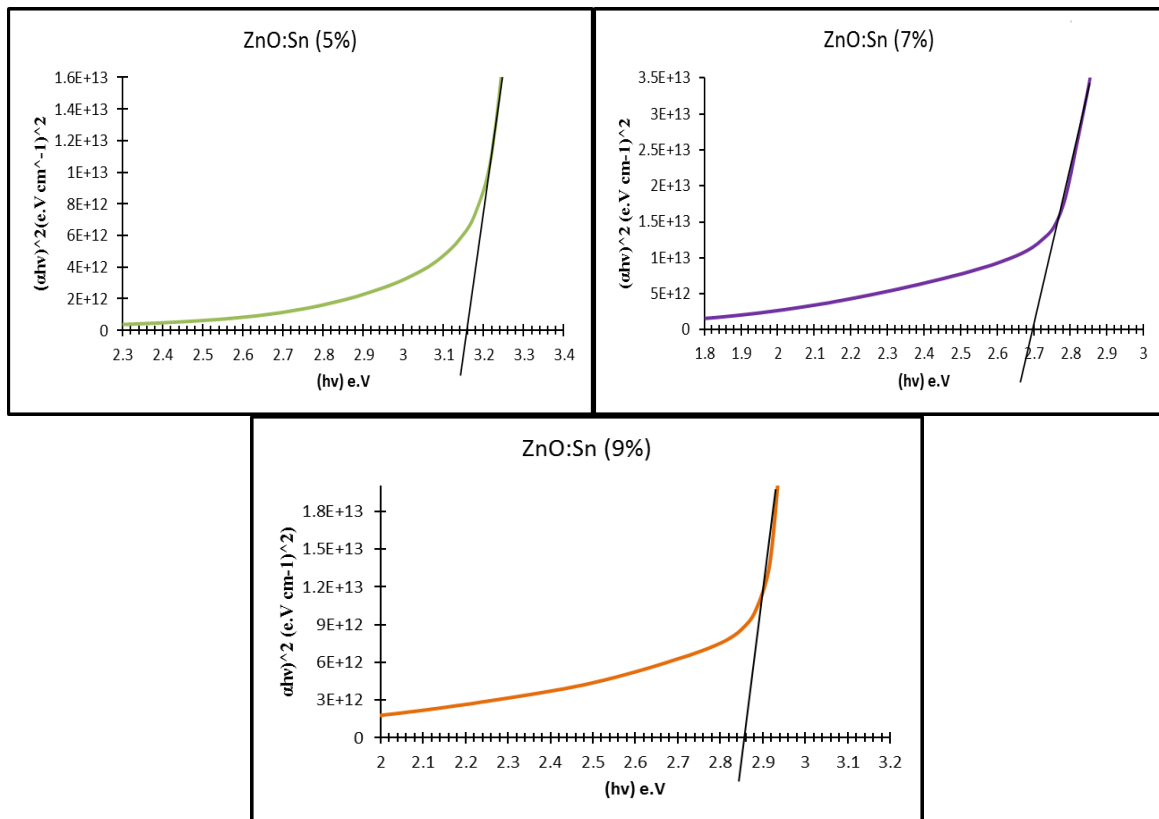
Figure 12. Energy gap for ZnO:Sn thin film after annealing.

Table 5. The change of energy gap after annealing.

sample	Energy gap (e.V)
pure	3.21
3%	3.19
5%	3.16
7%	2.7
9%	2.86

4. Conclustion

The films are apolycrystalline hexagonal structure wurtzite, and the preffered orientation for pure ZnO is (101) and varied with increase doping due to change of growth orentation. it is observed the value of crystaline size for (0, 3 and 5) % do not change, while at percantage (7 & 9) % shows increase the crystalline size. After annealng shows improvements for pure and doped at (5 & 9) % increase the crystalline size and decrease the FWHM. From optical properties show the best transmission for the effect of doping is about 95% for ZnO that due to complete oxidation of films, after anealing the transmission enhanced for thin films doping. The optical band gap decrease with doping reach to 5% then observe wideing due to Burstein –Moss effect. After annealing thin films show decrease the band gap effect of narrowing is attributed to film disorder.

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