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Effect of Doping Concentration on the Electrical and Optical Properties of Zn: SnO_2

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Abstract: *This study investigated the effect of doping concentration on the Electrical and Optical properties of undoped and zinc doped tin oxide thin film, fabricated by Chemical spray pyrolysis technique. The doping was done at 1 wt%, 2 wt%, 3 wt% and 4 wt%. The film thickness decreases with increase in doping concentration of the Zn doped SnO_2. The band gap, the absorption coefficient and the extinction coefficient increase with increase in doping concentration to an optimum of 3wt%.*

I. Introduction

Transparent conducting oxides (TCOs) are solid- state oxides with low resistance and high transparency in the visible range of the electromagnetic spectrum. Most inorganic films typically are made up of a layer of transparent conducting oxides, generally in the form of Indium doped Tin IV Oxide (ITO), Fluorine doped Tin IV Oxide (FTO), Zinc doped Tin IV Oxide (ZTO), [1].TCOs are wide band-gap semiconductors that have relatively high concentration of free electrons in their conduction band which arises either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. Reduction of the resistivity involves either an increase in the carrier concentration or in the mobility [2]. The high-electron-carrier concentration causes absorption of electromagnetic radiation in both the visible and infrared portions of the spectrum. For the present purposes, it is the former that is the more important.

Transparent conducting oxides have band gaps with energies corresponding to wavelength which are shorter than the visible range of 380 nm to 700 nm. As such, photon with energies below the band gaps are not collected by these materials and these visible lights passes through [3].Tin dioxide (SnO_2) is an n-type broad-band gap (3.6eV) oxide semiconductor with high chemical and mechanical stability. SnO_2 which has exceptional optical, electrical and mechanical properties because of the low resistivity and high transmittance, is a multipurpose material and has wide usage as the most smart material for gas sensor applications, as a catalyst during the oxidation of organic compounds, as a crucial component in rechargeable Li batteries and as a master element in opto-electronic devices [4]. As such we investigate the effects of doping concentration on the electrical and optical properties of Tin IV Oxide (ITO) doped with Zinc.

II. Materials And Methods

2.1Fabrication of Undoped SnO_2

The fabrication of the undoped Tin dioxide (SnO_2) was carried out using Tin (IV) Chloride ($SnCl_4$) solution as the source element. During the fabrication of undoped tin (IV) Oxide, 10 ml of Tin (IV) Chloride solution, and 10 ml of distilled water were added to the solution container of the spray pyrolysis equipment after which is was switch on for the thin film deposition to begin. The thin films of Tin (IV) Oxide (SnO_2) were deposited on a glass substrate. During the fabrication of the doped thin film, 10 ml of the doped Tin (IV) Chloride solution with zinc acetate ($Zn(CH_3COOH)_2.2H_2O$) as the dopant and 10 ml of distilled water was used and the thin film form of tin (IV) Oxide doped with zinc, ($Zn.SnO_2$) were deposited on a glass substrate. The temperature of thermocouple of the chemical spray pyrolysis depositor set-up which was kept constant throughout the fabrications process was 420 ^{0}C and the room temperature was 30 ^{0}C. The distance between the substrate and the spray nozzle was fixed at 12 cm through the fabrication process. The consumption rate or the spray rate was 1.92 ml/min. The time of deposition of the film on the glass slide was five minutes because at that time, quality thin film, good for characterisation have already being deposited on the glass slide.

2.2 Fabrication of Tin (IV) Oxide Doped With Zinc

Tin (IV) Oxide (SnO_2) doped with Zinc was fabricated by doping from 1wt.% to 4 wt.% of Zn in the source material (SnO_2) using the relation;

$\frac{Zn\,(g)}{\{Zn\,(g)+Sn\,(g)\}}$ = 1%, 2%, 3% and 4% of the Zn by weight used for the doping.1000 ml $SnCl_4$ solution used contained 36.83g of $SnCl_4$; this implies 10ml of $SnCl_4$ solution used for the fabrication contain $\frac{10}{1000} \times 36.83 = 0.368$ g.

Table 1:SnO_2 doped with Zinc

Wt. of Sn (g)	Wt. of Zn (g)	% of Zn	Zinc Acetate (ml)	$SnCl_4$ (ml)
0.37	0.0037	1	0.269	9.731
0.37	0.0074	2	0.533	9.467
0.37	0.0111	3	0.790	9.210
0.37	0.0148	4	1.045	8.955

Avantes UV-Visible Spectrophotometer was used to determine the Transmittance T and the Reflectance R in the wavelength range of 420-760 nm at SHESTCO. The Absorbance A, the Absorption coefficient α, the Band gap E_g, Extinction coefficient k and Refractive index n of the Zinc doped SnO_2 thin films were determined from the Transmittance and Reflectance according to the following equations [2]:

$$A = \text{Log}\left(\frac{1}{T}\right) \quad (1)$$

$$\propto(\lambda) = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (2)$$

Where d is the film thickness and T is the Transmittance

$$k(\lambda) = \frac{\propto\lambda}{4\pi} \quad (3)$$

The band gap was determined from the Tauc's relation;

$$\alpha h\nu = B\,(h\nu - E_g)^m \quad (4)$$

Where B is band edge parameter and value of m determines the nature of optical transition ($m = \frac{1}{2}$ Indicates direct transition and $m = 2$ indicates indirect transition). Since SnO_2 has a direct transition (Islam and Podder, 2009) .The band gap of the films was calculated by plotting $(\alpha h\nu)^2$ versus hv followed by extrapolation of the linear region of the absorption edge to find the intercept with the energy axis.

A QUADPRO-301-6 four point probe was used to determine the sheet resistance and the resistivity of the deposited films at SHESTCO Abuja, after which the conductivity was determine from the resistivity. The sheet resistant is given by (Islam and Podder, 2009):

$$R_s = 4.53 \times \frac{V}{I} \quad (5)$$

Where V is the measured voltage between the two inner probes and I is the current passed through the outer probes. The resistivity was determined from the relation (Theraja, 2007):

$$\rho = R_s \times d \quad (6)$$

Where d is the thickness of the conducting layer, ρ is the resistivity and R_s is the sheet resistance. From the value of ρ, the conductivity σ was determined using the relation (Theraja, 2007) :

$$\sigma = \frac{1}{\rho} \quad (7)$$

A Profilometer (VEECO DEKTAK 150) was used to carry out measurement of the thickness of the deposited films at SHESTCO Abuja.

III. Results And Discussion

3.1. Surface thickness of the film

The surface thickness of the films was carried out using profilometer with stylus of 12.5 µm, length of 2000 µm, resolution of 0.333µm and duration of 10.0 second. The results are shown in table 2 for the undoped SnO_2 and 1 wt.% to 4 wt.% Zn doped SnO_2 respectively. The values of the thickness of the thin films are then used to calculate the resistivity of the thin film. Table 2 gives the result of the thickness of the thin film.

Table 2 Shows the Result of thickness for the thin film

Sample	Thickness of thin film (µm)
Undopped SnO_2	0.150
1 wt.% Zn doped SnO_2	0.030
2 wt.% Zn doped SnO_2	0.025
3 wt.% Zn doped SnO_2	0.020
4 wt.% Zn doped SnO_2	0.018

Table 2 shows the result of the thickness of the undoped SnO_2 thin film and the 1 wt.% to 4 wt.% Zn doped SnO_2 thin film. It was observed that the thickness of the thin film decreases with increase in doping concentration of Zn. This is due to the decrease in grain size of the thin film which as a result of increase in the grain boundary of thin film. The decrease in the thickness of the thin film is also attributed to Beer Lambert's

law which shows that as the transmittance increase the thin film thickness decrease at wavelength range of the visible portion of the electromagnetic spectrum between 400 nm and 780 nm for transparent conducting oxides.

3.2. Electrical properties of the film

The summary of the results of the electrical properties showing the resistivity and conductivity as the vary with doping concentration is given in table 3

Table 3: Summary of the results of the electrical properties showing the resistivity and conductivity values

Sample	Doping Conc. (wt.%)	Resistivity (Ωm)	Conductivity (S/m)
Undopped SnO_2	0	$1.43x10^{-1}$	8.70
1% Zn doped SnO_2	1	$1.97x10^{-2}$	50.60
2% Zn doped SnO_2	2	$1.32x10^{-2}$	75.61
3% Zn doped SnO_2	3	$4.52x10^{-3}$	221.24
4% Zn doped SnO_2	4	$3.45x10^{-3}$	289.85

Figure 1: Plot of resistivity against doping concentration

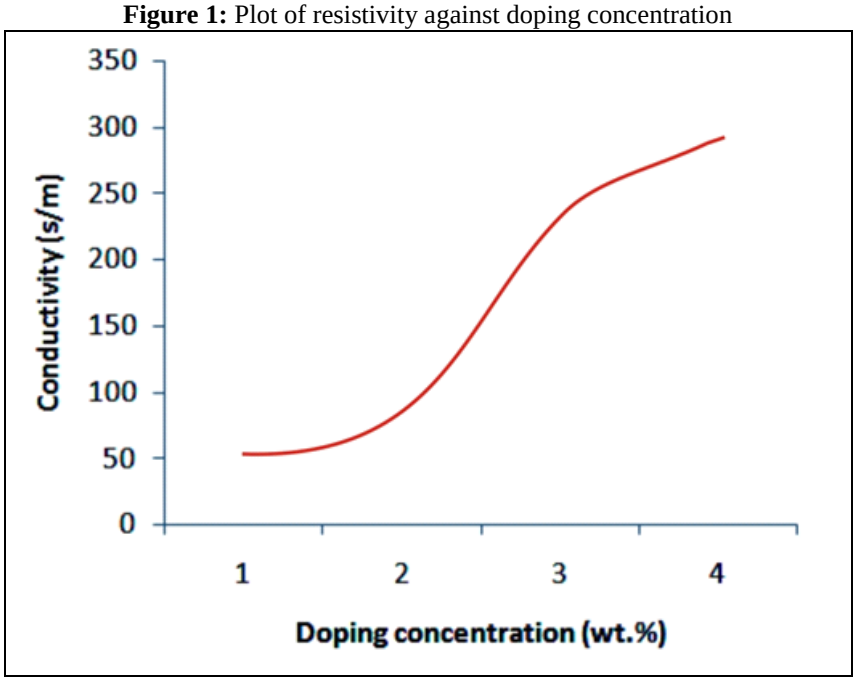

Figure 2: Graph of conductivity against doping concentration

From figure 1 the values of the resistivity decreases with increase in the doping concentration and from figure 2 the conductivity increases with increase in the doping concentration. This is because the ionic radius of $Sn^{4+}$is (r= 0.71 Å) and Zn^{2+} is (r = 0.74 Å), which clearly shows that they are close to each other. Therefore the replacement of one Sn^{4+} ion with Zn^{2+} ion, one broken bound (hole) is produced, which act as acceptor energy level near the valence band. This level accept electrons from the valence band and thus increase the hole concentration The resistivity of the films is a function of film thickness and minimum resistivity for these films is obtained at lower film thicknesses. The resistivity ρ is a direct result of concentration and mobility of free carriers in the films. Since the carrier concentration strongly depends on the doping level, the mobility is mainly influenced by grain boundary scattering, lattice defects and impurity scattering introduced by Zn dopants, therefore the resistivity of the thin film is decrease, which implies increase in the conductivity of the thin film.

3.3. Discussion on optical properties of the doped and undoped SnO_2

The optical transmittance spectra of the deposited film were recorded. The graph of $(\alpha h\nu)^2$ and $(h\nu)$ was plotted using excel for the determination of the band gap energy (Eg) of undope and Zn doped SnO_2 film by extrapolation of curve as shown in figure 3 and figure 4.

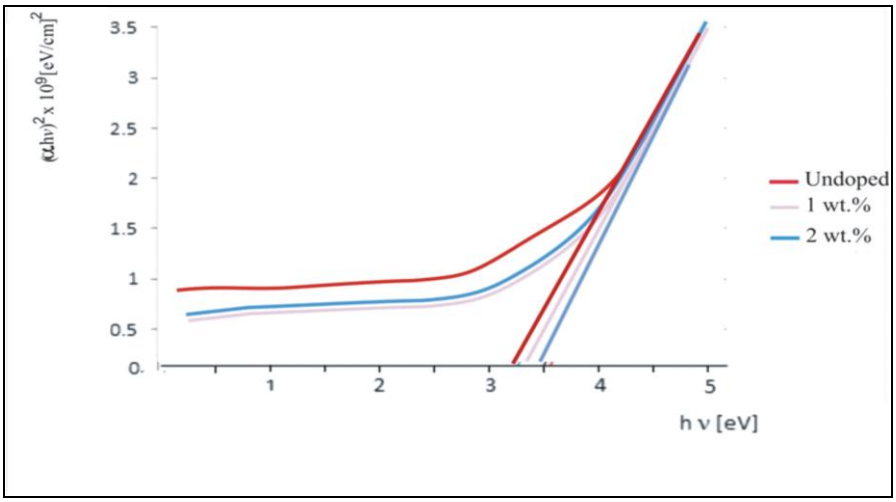

Figure 3: Band gap for SnO_2, 1% and 2% Zn doped SnO_2

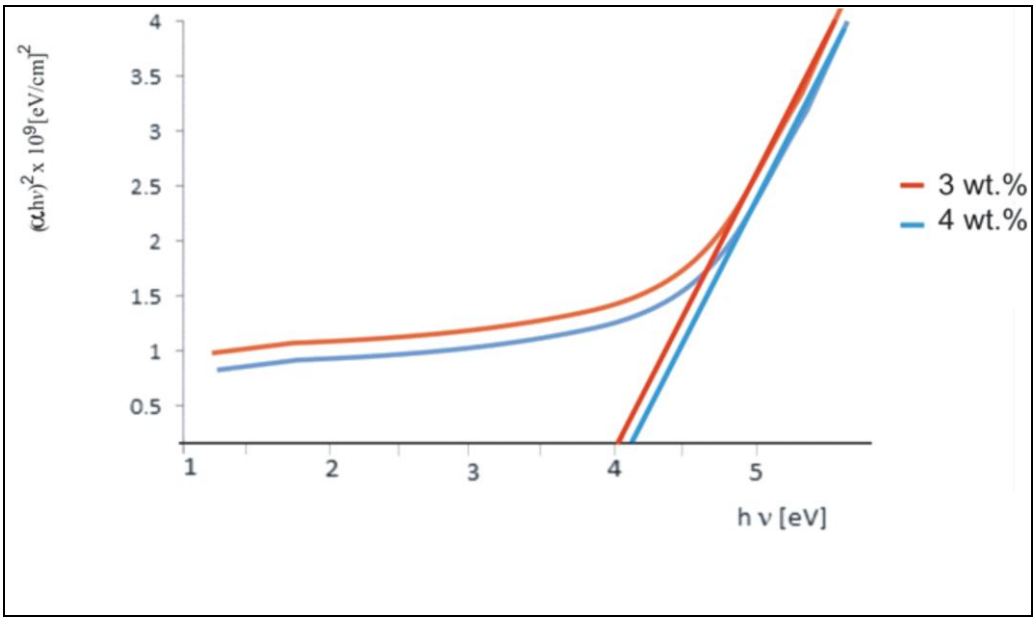

Figure 4: Band gap for 3 wt.% and 4 wt.% Zn doped SnO_2

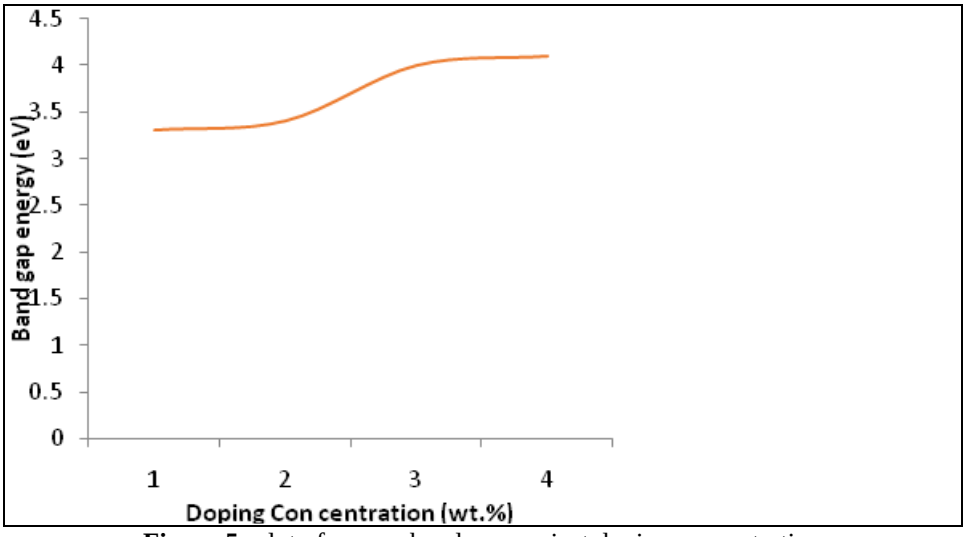

Figure 5: plot of energy band gap against doping concentration

The optical band gap was estimated by extrapolation of the curves in figure 3 and 4. The energy gap was estimated to be 3.2 eV for the undoped SnO_2 and 3.3 eV, 3.4 eV, 4.0 eV and 4.1 eV for 1 wt.%, 2 wt.%, 3 wt.%, and 4 wt.% Zn doped SnO_2 respectively.The increase in the band gap with increase in Zn doped SnO_2 is as a result of the effect of oxygen partial pressure on the optical band gap. This caused the extension of the band –tail into the band gap [7].Other factors such as the growth defect, charge impurities, disorder at the grain boundary could also havecaused by the increase in the energy gap due to decrease in the grain size of the thin film [8]. The increase in the band gap could also be due to Burstein Moss effect, where doping causes the conduction of TCOs to be partially filled and therefore broadens the band gap. This happens as a result of the Fermi level moving into the conduction band. Since Zn doping increases the carrier concentration in the conduction band, this implies the optical band gap energy increases as well.

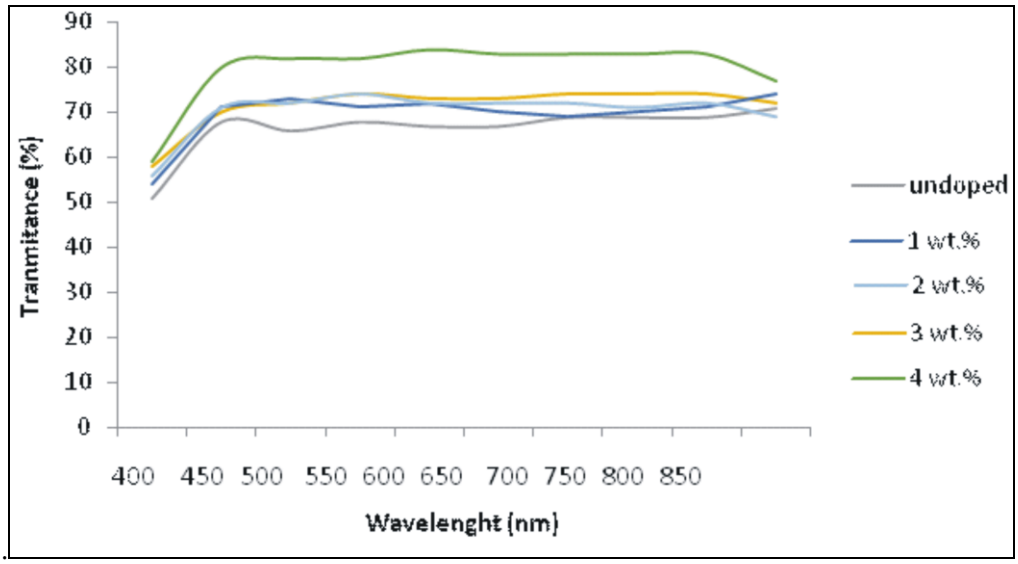

Figure 6: Transmittance spectra of undopedSnO_2 , 1 wt.% and 2 wt.%, 3 wt.% and 4 wt.% Zn doped SnO_2

Figure 6 gives the average transmittance for the undoped and Zn doped SnO_2. The average transmittance was estimated in the lower wavelength region between 400 nm and 780 nm because transparent materials posses' band gaps with energies corresponding to wavelength which are shorter than the visible light [1]. The average transmittance was estimated by taking the average of the transmittance at wavelength range 400 nm – 780 nm.The average transmittance for the undope SnO_2 was estimated to be 68.4%, for the 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% Zn doped SnO_2 were 69%, 72%, 73% and 81% respectively. The increase in the transmittance with increase in the doping concentration is due to the minimized light scattering with increasein doping concentration.

3.4. Discussion on absorption coefficient of the thin film

The result of absorption coefficient for the thin film is given in table 4

Table 4: Shows the Result of absorption coefficient for the thin film

Sample	**Absorption coefficient of thin film (cm^{-1})**
Undopped SnO_2	$2.47x10^6$
1 wt.% Zn doped SnO_2	$1.14x10^7$
2 wt.% Zn doped SnO_2	$1.31x10^7$
3 wt.% Zn doped SnO_2	$1.37x10^7$
4 wt.% Zn doped SnO_2	$1.45x10^7$

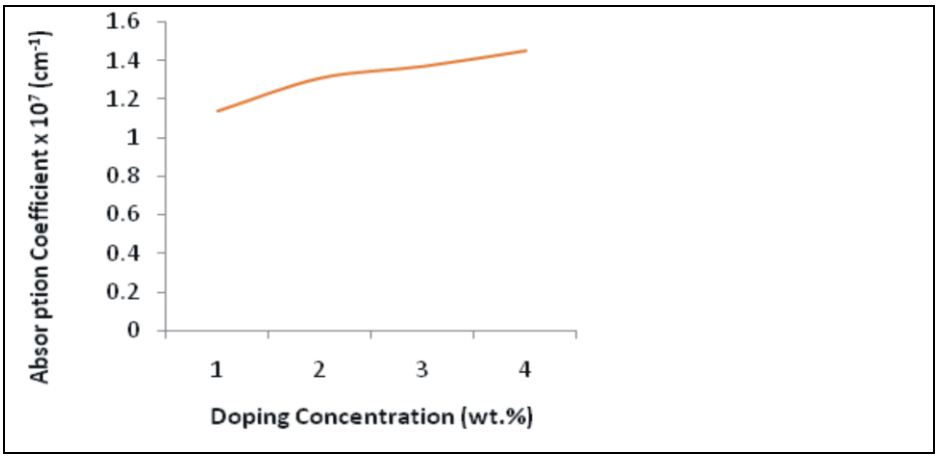

Figure 7: Plot of absorption coefficient against doping concentration

Figure:7gives the relationship between the absorption coefficient and the doping concentration of Zn doped SnO_2 thin film.There is increase in the absorption coefficient of the thin film with increase in the Zn concentration as shown in figure 5. This is because the edge absorption of the thin film increases with increase in the band gap energy. Since the absorption of light by thin film is as a result of the raising of electrons from the valence band to the conduction band and also by exciting the lattice vibration of the material by photon energy, this causes the absorption coefficient to be dependant on the conductivity which is a function of carrier concentration. Since increase in doping concentrationincreases carrier concentration, this implies increase in absorption coefficient of the thin film increase with increase in doping concentration at wavelength range of 400 nm and 780 nm in the visible portion of the electromagnetic spectrum.

3.5. Discussion on extinction coefficient(k) of the thin film

Table 5: Shows the Result of extinction coefficient for the thin film

Sample	**Extinction coefficient of thin film**
Undopped SnO_2	0.045
1 wt.% Zn doped SnO_2	0.22
2 wt.% Zn doped SnO_2	0.25
3 wt.% Zn doped SnO_2	0.26
4 wt.% Zn doped SnO_2	0.28

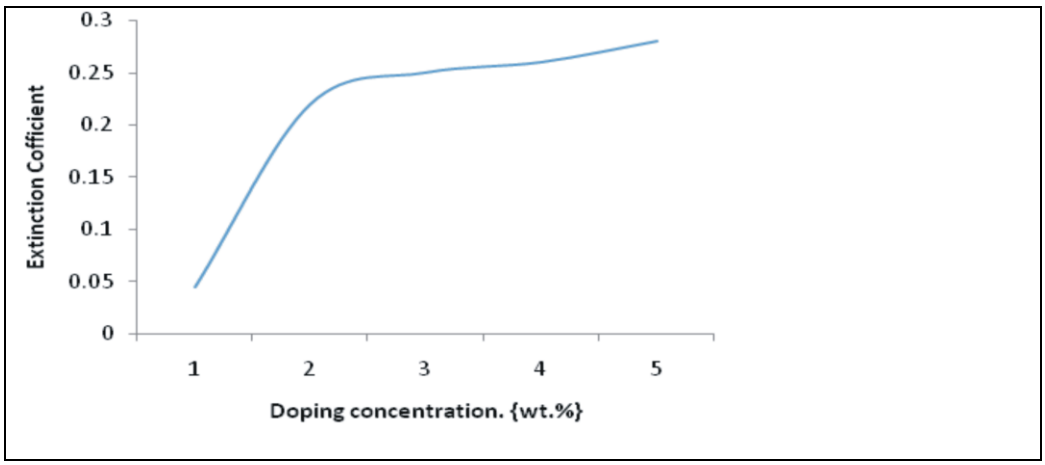

Figure 8: Plot of extinction coefficient against doping concentration

Figure 8 gives the variation of the extinction coefficient with doping concentration. The extinction coefficient describes the attenuation of light wavelength as it goes through the thin film material. In the visible range of the light spectrum, the extinction coefficient increases with increase in doping concentration of the Zn doped SnO_2 thin film. The increase in the extinction coefficient with increase in doping concentration is due to the combine action of the absorption coefficient and the scattering of light in the visible region of the electromagnetic spectrum. Increase in doping concentration increases the carrier concentration and decreases

light scattering in the wavelength region between 400 nm and 780 nm in the visible region of the electromagnetic spectrum for TCOs.

IV. Conclusion

From the four point characterization, the resistivity values of the thin film decreases with increase in doping concentration. This implies that increase in doping concentration increases the conductivity of the SnO_2 thin film. The optical band gap was estimated in lower wave length region of the visible light spectrum and it was found to increase with increase in doping concentration. It was also observed that, there was increase in transmittance of the thin film with increase in doping concentration of the zinc. The absorption coefficient and the extinction coefficient also increase with increase in the doping concentration of the zinc.

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