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Electrical andOptical Study of Indium Doped Zinc Oxide (In:ZnO) Thin Film in Gas Sensor Applications.

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Abstract: *This study investigated the effect of doping concentration on the Thickness Electricaland Optical properties of undoped and Indium doped Zinc 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 In doped ZnO. The absorption coefficient and the extinction coefficient increase with increase in doping concentration to an optimum of 4 wt. %.*
Key Words*: Thickness, Optical, Electrical, Indium, Zinc Oxide*

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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]; [2]. 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 [3]. 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 [4]. ZnO is a member of hexagonal wurtzite class; it is a semiconducting, piezoelectric and optical wave guide material. ZnO is an n-type broad-band gap (3.3 eV) oxide semiconductor with high chemical and mechanical stability. ZnO 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 [5]; [6]. As such we investigate the effects of doping concentration on the thickness, electrical and optical properties of indium doped ZnO.

II. Materials and Method

2.1 Fabrication of Undoped ZnO

The fabrication of the undoped Zinc oxide (ZnO) was carried out using spray pyrolysis technique. An aqueous solution of 0.1 M $Zn(CH_3CO_2)_2$ was used as the source element. During the fabrication of undoped zinc oxide, 10 ml of $Zn(CH_3CO_2)_2$ solution, and 10 ml of distilled water were added to the solution container of the spray pyrolysis equipment after which it was switch on for the thin film deposition to begin. The thin films of ZnO 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 at 450 ^oC and the room temperature was 30 ^oC. The distance between the substrate and the spray nozzle was fixed at 15 cm throughout the fabrication process. The consumption rate or the spray rate was 1.76 ml/min. The time of deposition of the film on the glass slide was ten minutes because at that time, quality thin film, good for characterisation had already being deposited on the glass slide.

2.2 Fabrication of Indium Doped With Zinc Oxide

During the fabrication of the doped thin film, 10 ml of $Zn(CH_3CO_2)_2$ solution with indium chloride ($InCl_3$) as the dopant and 10 ml of distilled water was used and the thin film form of indium-doped ZnO were deposited on a glass substrate.

The Indium-doped ZnO was fabricated by doping from 1wt.% to 4 wt.% of In in the source material (ZnO) using the relation:

$$\frac{\mathrm{In}\ (g)}{In\ (g)+Zn\ (g)} = 1\ \%,\ 2\ \%,\ 3\ \%,\ 4\ \%$$

of the In by weight used for the doping. 1000 ml $Zn(CH_3CO_2)_2$ solution used contained 36.83 g of $Zn(CH_3CO_2)_2$; this implies 10 ml of $Zn(CH_3CO_2)_2$ solution used for the fabrication contained

$$\frac{10}{1000} \text{ X } 36.83 = 0.368 \text{ g.}$$

Table 1 shows the doping concentration of In from 1 to 4 wt.% in 0.36 wt. ZnO.

Table 1: In doped ZnO at 1 wt. % to 4 wt. %

Wt. of ZnO (g)	Wt. of In (g)	% of In	$InCl_3$ (ml)	$Zn(CH_3CO_2)_2$ (ml)
0.36	0.0036	1	0.267	9.733
0.36	0.0072	2	0.531	9.469
0.36	0.0108	3	0.790	9.210
0.36	0.0144	4	1.042	8.958

Avantes UV-Visible Spectrophotometer was used to determine the Transmittance T and the Reflectance R in the wavelength range of 420-760 nm. The Absorbance A, the Absorption coefficient α, and the Extinction coefficient of the Indium k of the indium doped ZnO thin films were determined from the Transmittance and Reflectance according to the following equations [8]

$$A = \frac{1}{\mathrm{T}} \qquad (1)$$

$$\alpha\lambda = \frac{1}{d} ln\frac{1}{\mathrm{T}} \qquad (2)$$

where d is the film thickness, $\lambda$is the wavelength and T is the Transmittance

$$k\lambda = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

A QUADPRO-301-6 four point probe was used to determine the sheet resistance and the resistivity of the deposited films, after which the conductivity was determine from the resistivity. The sheet resistant is given by

$$R_s = 4.53\frac{V}{I} \qquad (4)$$

Where V is the measured voltage between the two inner probes and I is the current passed through the outer probes. The resistivity was determine from the relation

$$P = R_s \text{ X } d \qquad (5)$$

WhereP is the resistivity, d is the thickness of the conducting layer and Rs is the sheet resistance.

From the value of P, the conductivity σ was determined using the relation:

$$\sigma = \frac{1}{P} \qquad (6)$$

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

III. Results and Discussion

3.1. 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. Figure 1-5 below gives the thickness for the undoped ZnO and 1 wt. % to 4 wt. % In doped ZnO respectively. The values of the thickness of the thin films were then used to calculate the resistivity of the thin film.

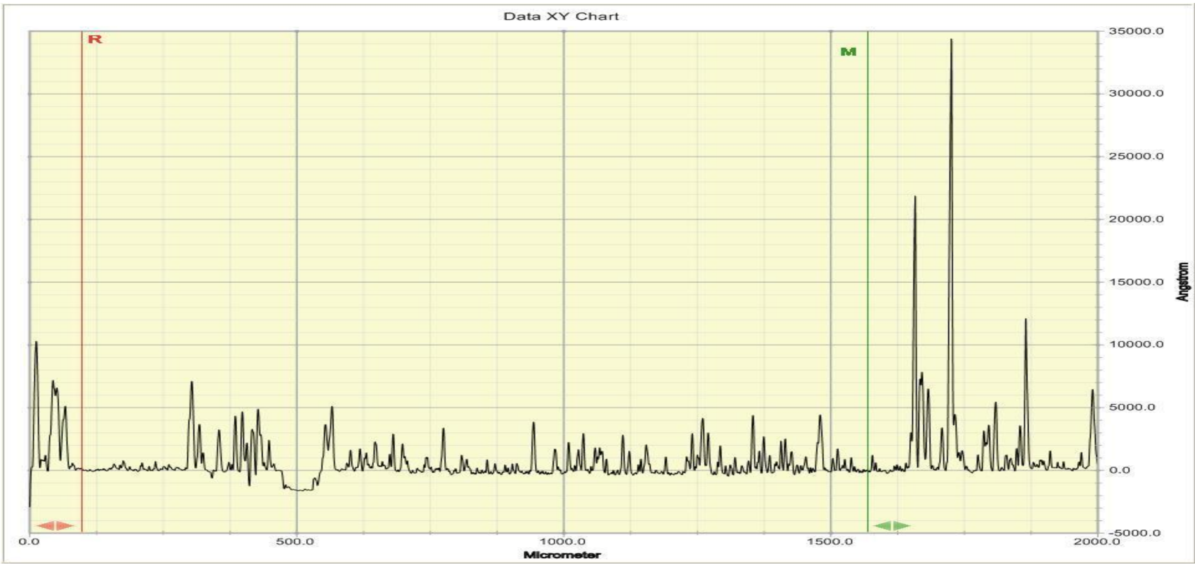

Figure 1: Spectra of Thin film thickness for undoped ZnO

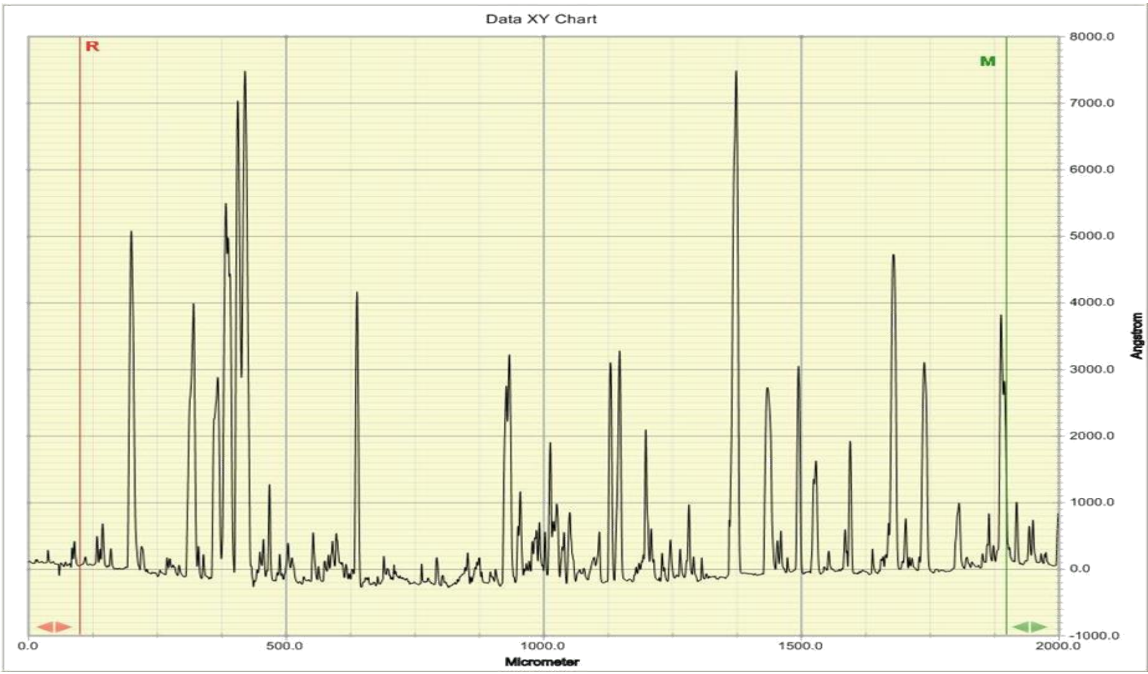

Figure 2: Spectra of Thin film thickness for 1 wt.% In:ZnO

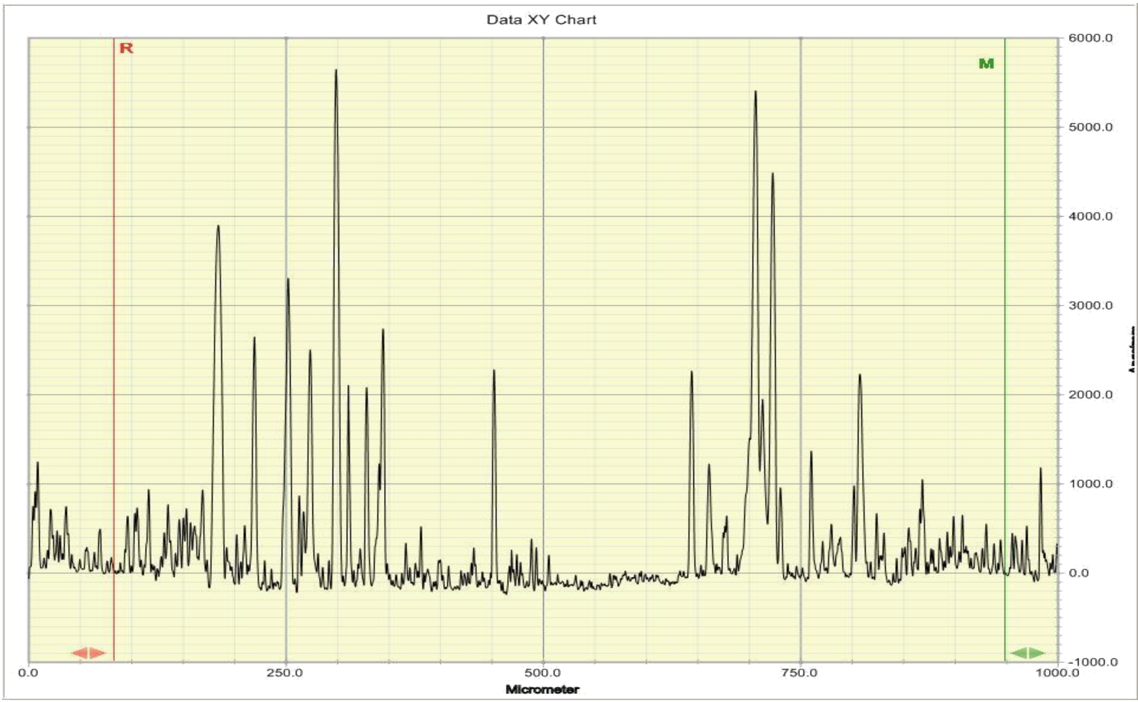

Figure 3 Spectra of Thin film thickness for 2 wt.% In:ZnO

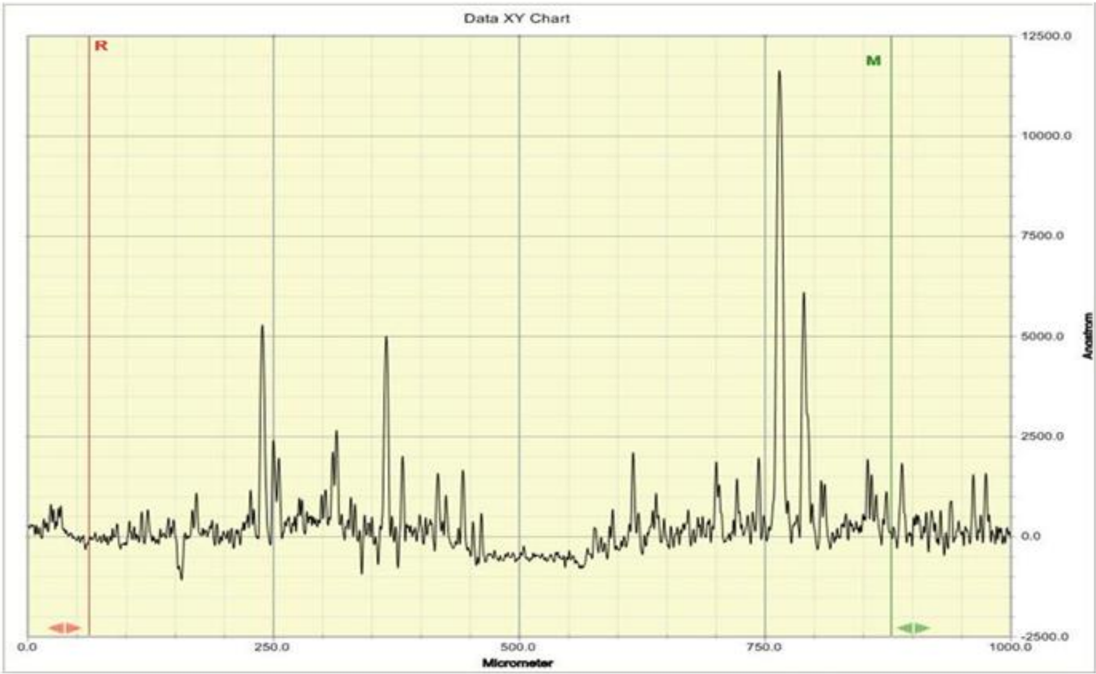

Figure 4: Spectra of Thin film thickness for 3 wt.% In:ZnO

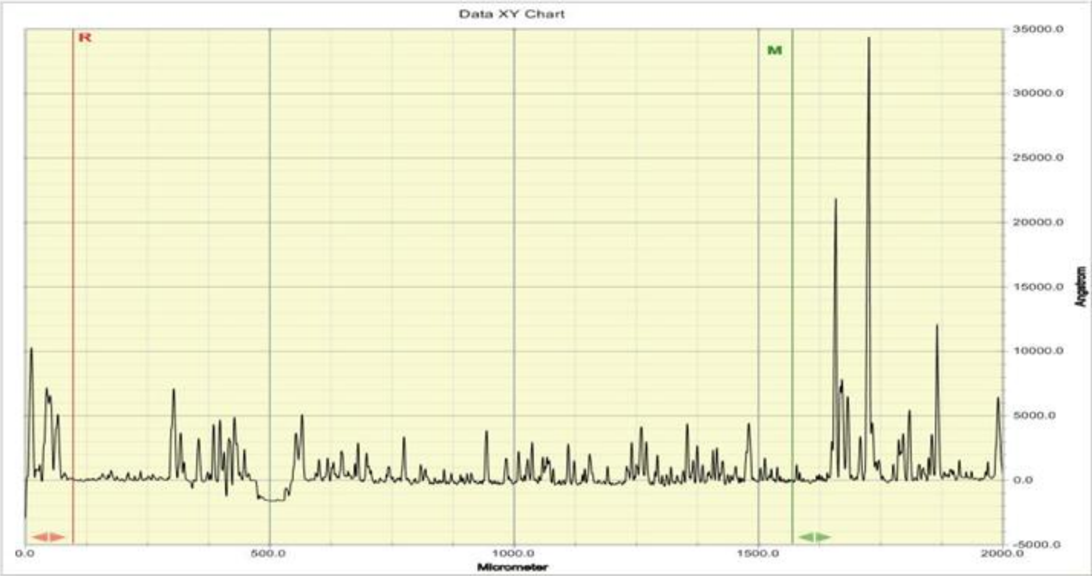

Figure 5: Spectra of Thin film thickness for 4 wt.% In:ZnO

Table 2 below gives the summary of the result of the thickness of the undoped ZnO and the 1 to 4 wt.% In doped ZnO thin film.

Table 2 Shows the Result of thickness for the thin film

Sample	Thickness of thin film (nm)
Undoped ZnO	110
1 wt.% In doped ZnO	60
2 wt.% In doped ZnO	45
3 wt.% In doped ZnO	30
4 wt.% In doped ZnO	28

Table 2 shows the result of the thickness of the undoped ZnO thin film and the 1 wt. % to 4 wt. % In doped ZnO thin film. It was observed that the thickness of the thin film decreases with increase in doping concentration of In. 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 3.0

Table 3.0 Summary of the results of the electrical properties showing the resistivity and conductivity of thin film

Sample	Doping Conc. (wt.%)	Resistivity (Ωm)	Conductivity (S/m)
Undopped ZnO	0	$2.43x10^{-2}$	41.15
1 wt.% In doped ZnO	1	$2.40x10^{-2}$	41.66
2 wt.% In doped ZnO	2	$1.88x10^{-2}$	53.10
3 wt.% In doped ZnO	3	$1.21x10^{-2}$	82.71
4 wt.% In doped ZnO	4	$8.45x10^{-3}$	118.34

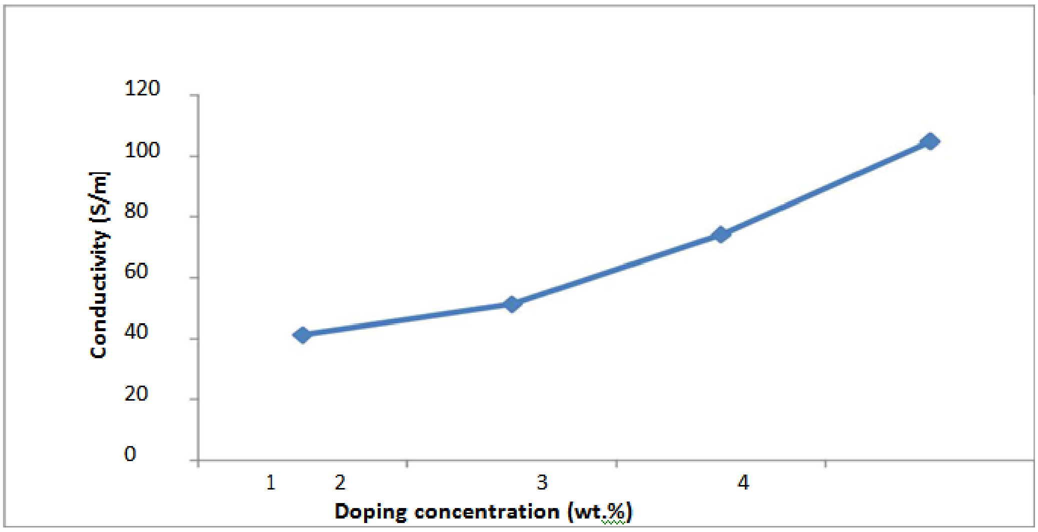

Figure 6: Graph of conductivity against doping concentration

From figure 6, the conductivity increases with increase in the doping 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 andmobility 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 In 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 undoped and In doped ZnO

The optical transmittance spectra of the deposited film were recorded. The result of absorption coefficient for the thin film is given in table 3.1. The transmittance and reflectance spectra are given in figures (7 and 8) respectively and the relationship between the absorption coefficient and the doping concentration of In doped ZnO thin film in figure 9. The result of extinction coefficient for the thin film is given in table 4 and the relationship between the extinction coefficient and the doping concentration of In doped ZnO thin film in figure 10.

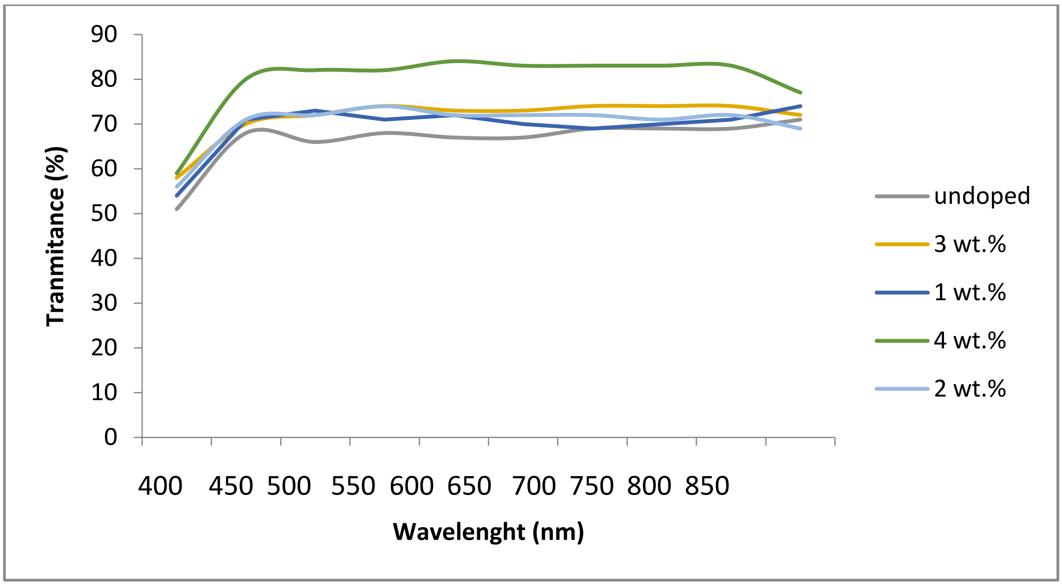

Figure 7 Transmittance spectra of undoped ZnO, 1 wt.% and 2 wt.%, 3 wt.% and 4 wt.% In doped SnO_2

Figure 7 gives the average transmittancefor the undoped and In doped ZnO. 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 [9]. 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 ZnOwas estimated to be 68.4%, for the 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% In doped ZnO 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 increase in doping concentration.

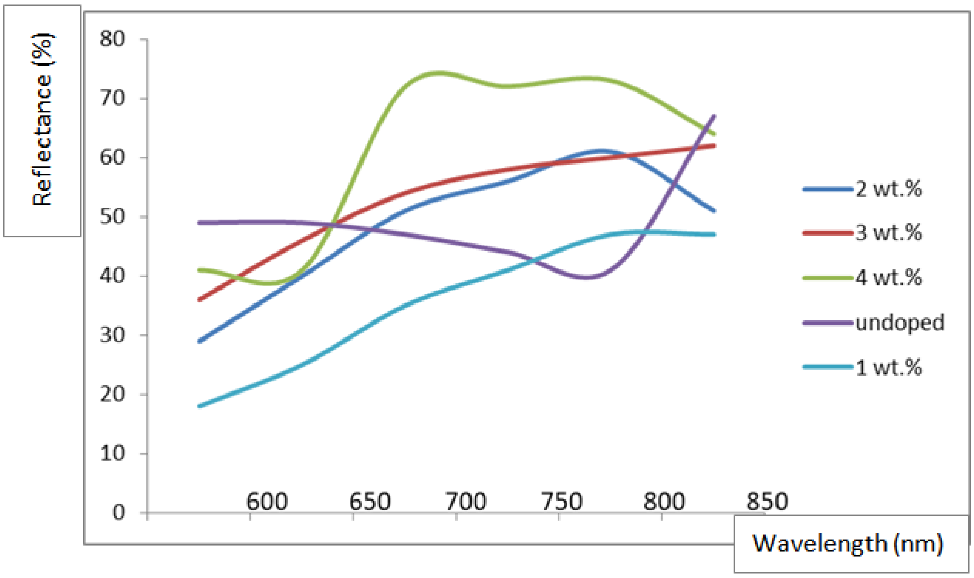

Figure 8 Reflectance spectra of undoped ZnO, 1 wt.% and 2 wt.%, 3 wt. % and 4 wt.% In doped ZnO

From figure 8, the average reflectance was estimated by taking the average of the reflectance within that wavelength range 400 -780. The average reflectance for the undoped ZnO was 33%, for the 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% of In doped ZnO, the average reflectance were estimated to be 46%, 49%, 58% and 48% respectively. The reflectance values increases as the In concentration increases except for 4 wt.% concentration. This is because the reflected fraction of the incident beam is probably more significant than the absorption fraction in the wavelength region 400 nm – 780 nm except at 4 wt.% In doped were reverse was the case. This could be explained by Plasmon absorption of the free electrons of In doped ZnO thin films, this is in agreement with [9].

Table 3.1 Result of absorption coefficient for the thin film

Sample	Absorption coefficient of thin film (cm^{-1})
Undopped ZnO	$3.27x10^5$
1 wt.% In doped ZnO	$2.15x10^6$
2 wt.% In doped ZnO	$2.61x10^6$
3 wt.% In doped ZnO	$2.39x10^6$
4 1 wt.% In doped ZnO	$2.75x10^6$

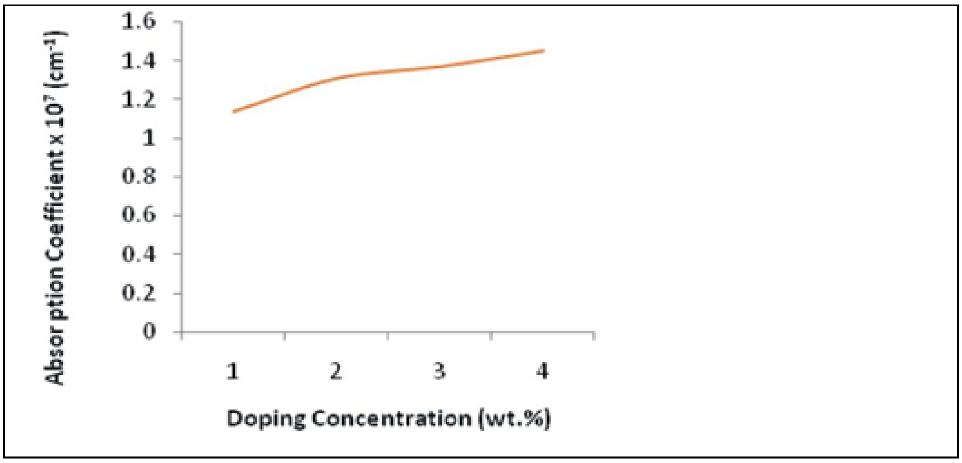

Figure 9 plot of the absorption coefficient and the doping concentration of In doped ZnO

Figure 9 gives the relationship between the absorption coefficient and the doping concentration of In doped ZnO thin film. There is increase in the absorption coefficient of the thin film with increase in the In concentration as shown in figure 9. 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 dependent on the conductivity which is a function of carrier concentration. Since increase in doping concentration increases 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.

Table 4 Shows the Result of extinction coefficient for the thin film

Sample	Extinction coefficient of thin film
Undopped ZnO	0.04
1 wt.% In doped ZnO	0.22
2 wt.% In doped ZnO	0.25
3 wt.% In doped ZnO	0.26
4 1 wt.% In doped ZnO	0.28

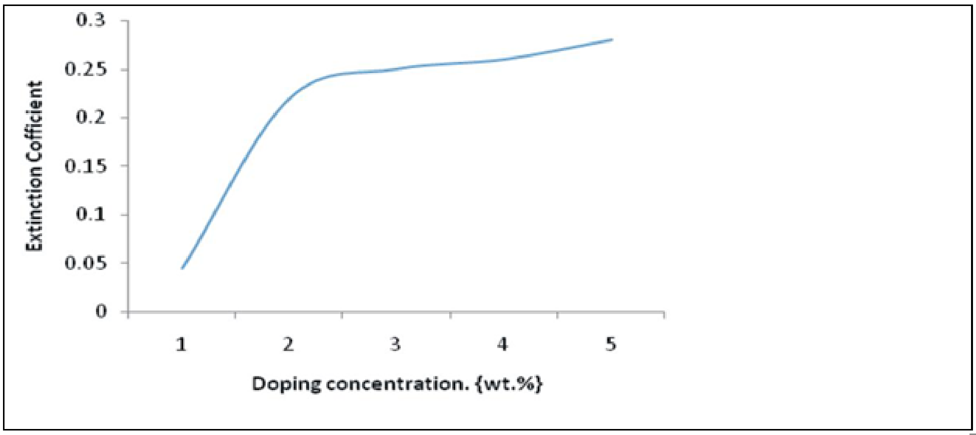

Figure 10 Plot of extinction coefficient against doping concentration

Figure 10 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 In doped ZnO 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.

IV. Conclusion

From the four point characterization, the resistivity values of the thin film decreases with increase in doping concentration. This is attributed to decrease in the thickness with increase in doping concentration. This implies that increase in doping concentration increases the conductivity of the ZnO thin film. The absorption coefficient and the extinction coefficient also increase with increase in the doping concentration of the zinc.

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