Impact of different Compositions on Structural and Optical Properties of Indium Zinc Oxide thin films.

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Abstract

Thin films of composite Zinc Indium Oxide (ZIO) are grown on glass substrates by thermal vapour evaporation technique. Thin films with different ratios of $ZnO:In_2O_3$= (90:10, 80:20,70:30,60:40 and 50:50) wt% were prepared and annealed at 500 ^{0}C for 2 hours. The X-ray diffraction(XRD) patterns reveal that the ZIO films are crystalline initially but as we increase the percentage of Indium Oxide, the Crystanllity of films decreases Significantly. X-ray photoelectron spectroscopy (XPS) provides information about the binding energies of deposited materials and the atomic percentage of elements of composite thin films. The SEM results indicate that the Doping of Indium Oxide changes the film's morphology. UV visible spectroscopy of the films indicates that band gap is reduced with increased concentration of In in the mixture and transmittance is also decreased at higher indium concentration.

Keywords: Composite ZIO thin films, XRD, SEM, XPS, Optical band gap.

1. Introduction:

Transparent Conducting Oxides (TCOs) have been praised as the inevitable successor material for microelectronic devices, providing the most efficient and cost-effective use of a broad array of applications. The physical, chemical and electrical aspects of TCOs are fascinating. A significant increase in the literature on the usefulness of thin-film TCOs (In_2O_3, SnO_2, ZnO) has occurred in the last three to four decades (Hong, et al 2009, Lozano, et al 2007, Dong, et al 2011, Yadav, et al 2015).

The TCOs thin film has higher visible transparency, wide bandgap, and good electrical conductivity due to oxygen vacancies in the lattice. These features are required by transparent heating elements for aircraft and car windows, solar cells, gas sensors, and transistors. Optical properties are as important as electrical properties like resistivity, mobility, and conductivity.

Semiconductor thin films with good optical properties are needed for optoelectronic devices. Optical characterisation of thin films can disclose physical properties including bandgap energy, band structure, and optically active defects. Several factors, including film thickness, dopant type, annealing temperature, and the deposition process itself, have a significant impact on optical properties (Fallah, et al 2010). There are several other important factors to consider when developing thin films for optical devices like crystallinity, smooth surface morphology and uniform film thickness. Annealing-induced changes in crystallinity affect the optical properties of a thin film in a significant way. In addition, annealing often improves the uniformity of a film's thickness by smoothing out its surface (Yang, et al 2008). To minimise the optical loss due to light scattering and optical transmission degradation, homogeneous and smooth surface morphology is essential (Dulgheru, et al 2012). Surface morphology, minimal signal loss, and fewer defects/void forms are all required for use in optical devices as an optical coating thin film. Several investigations have been made on multi-component oxides, and ternary systems like IZO for various applications.(Kim, et al 2009,Morikawa, et al 2000,Lee, et al 2005). TFTs, solar cells, and transparent electrodes have been explored using IZO as a semiconducting oxide layer. (khan, et al 2010,Parthiban, et al 2012,Xiao, et al 2011).

TCOs based on In_2O_3, ZnO, IZO, AZO, and GZO thin films have been prepared using a variety of deposition techniques (Zhou, et al 2011, Chen, et al 2015, Yan, et al 2011, Faraj, et al 2011,Kim, et ai 2015). There are two common deposition techniques for high-quality thin films: physical and chemical deposition. Physical deposition techniques include evaporation and sputtering. Sol-gel, chemical bath, spray pyrolysis, plating, and chemical vapour deposition are examples of chemical deposition techniques (CVD).

The following characteristics of thermal evaporation technology make it a suitable tool for obtaining good quality films. Thermal evaporation has many advantages, including large area coating, high film deposition rates, less substrate surface damage, excellent film purity, cost-effectiveness, adhesion to glass substrates, and uniform film formation.

Zinc Indium Oxide (ZIO) is a useful binary oxide for various applications. ZIO optical band gap is observed to depend on the percentage of Indium Oxide doping in it (Mary, et al 2017). The aim of this work is to synthesise high-quality mixed oxide films ($ZnO+In_2O_3$) and study their optical properties to determine their suitability as transparent electrodes in solar cells.

In the present study, thin films grown on glass substrates using the thermal vapour evaporation technique have been investigated for five different ratios of ZnO: In_2O_3 = 90:10,80:20, 70:30,60:40 and 50:50 wt.% at room temperature. We used XRD, XPS, SEM, and UV-Visible to characterize the samples.

2. Materials and Methods

ZnO and In_2O_3 in powder form with 99.9% purity were obtained from Sigma Aldrich (USA).

Thermal vacuum evaporation is used to develop ZIO thin films on glass substrates by using a HINDHI vacuum coating set up (Smart Coat 3.0A Thermal Evaporation System, Hind High Vacuum Co. Pvt. Ltd., Banglore) with a turbo molecular pump maintaining the pressure of 10^{-6} torr.

3. Experimental details

A mortar and pestle were used to mix ZnO and In_2O_3 powders with 99.9% purity at different concentrations (90:10, 80:20,70:30,60:40 and 50:50 wt.%) for about 5 hours. A molybdenum boat was inserted into the HINDHI vacuum coating unit to hold this mixture. The distance between target and source was fixed to 10 cm. A quartz crystal thickness monitor was used to determine the thickness of the prepared films. The measured thickness ranged from 500 Å to 650 Å for the films prepared. For uniform deposition of composite (ZIO) thin films, the experimental conditions were not altered. The films were then annealed in a muffle furnace at 500^{o}C for 2 hours to obtain crystalline ZIO films. This is the optimum temperature for annealing films because films begin to degrade above this temperature.

3.1Characterizations: The crystanallity of films was examined by employing an X-ray diffractometer (Bruker Lynx Eye detector) using Cu-Kα radiation (0.154 nm). Compositional analysis and study of bonding states of the ZIO films were carried out by using X-Ray Photoelectron Spectroscopy (Omicron DAR 400, Germany) with MgKα (1.2536 keV) radiation, the pressure being kept 5x10^{-10} torr. Optical properties of the ZIO films were studied in the wavelength range 300-800 nm by using a UV-vis- near infrared spectrometer (Perkin Elmer, Lambda 750, USA). The surface morphology of the films was imaged by using Nova Nano FE-SEM 450 (FEI) Model Scanning Electron Microscope (SEM).

4.Results and discussion

4.1 Structure Analysis (XRD)

Fig.1 shows the XRD pattern of ZIO thin films. The films are polycrystalline with hexagonal ZIO structure at a peak $2\theta=23.1^{0}$ (JCPDS file=00-020-1442) with preferred orientation along (006) plane, two more peaks has been observed at $2\theta=31.7^{0}$ (JCPDS file=00-036-1451) at the plane (100) and 42.2^{0} (JCPDS file=01-077-8351) at the plane (105) respectively for Wurtzite Hexagonal structure of ZnO and orthorhombic In_2O_3 for all the five samples. Moreover, as the In content increases, the intensity of the(100) peak diminishes, causing the reorientation of the crystal (Shinde, et al 2008). When the percentage of In_2O_3 exceeds 30%, very weak peaks appear, indicating that the films are alike amorphous in nature. Insoluble Indium atoms split at grain boundaries at higher doping levels, preventing the growth of ZnO: In crystals.(Mary, et al 2017). The overall picture shows how the crystallinity of the films degrades as the concentration of In increases. The grain size is observed to vary from 15nm to 36nm for different indium Concentrations. The above findings are in conformity with the findings reported recently.

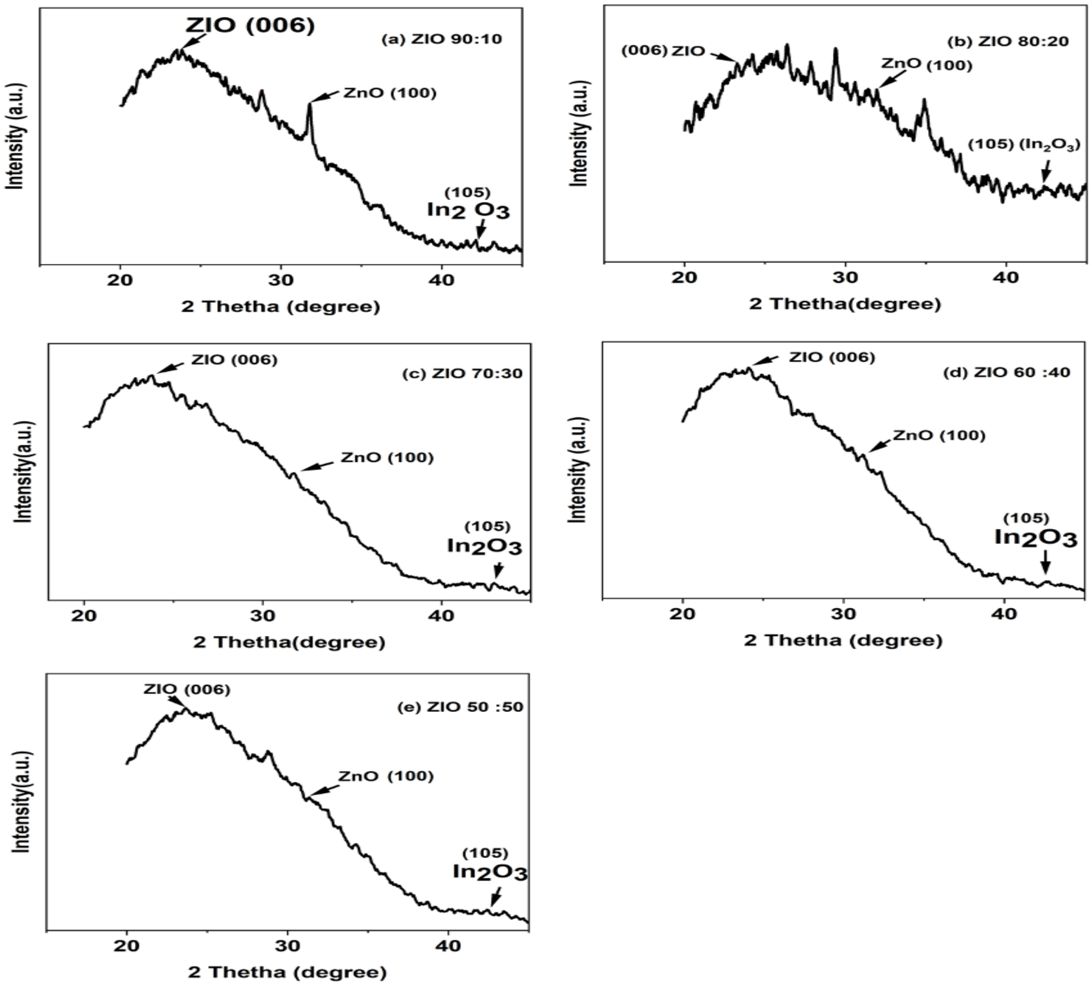

Fig.1: XRD profile of Composite ZIO thin films.(a) ZIO (90:10),(b) ZIO (80:20),(c) ZIO (70:30),(d) ZIO (60:40) and (e) ZIO (50:50).

4.2 Surface Morphology (SEM)

SEM micrographs of ZIO thin films at x20K magnification are shown in the Fig.2 Scanning electron microscopy (SEM) was used to analyze the film’s surface morphology . The Indium doping concentration modifies the film morphology, as seen in SEM micrographs. Increased grain sizes in ZIO films, as defined by SEM images, imply that particle aggregation has occurred, resulting in increased grain size. It is evident that indium doping has a significant impact on the microstructure of the films. Image J software was used to examine the particle size distributions of these particles. A smooth surface with uniform spherical shape morphology is required for optical applications (Sugumaran, et al 2016). It's hypothesised that In is spread unevenly on the surface, preventing nanoparticles from forming an organised configuration(Farid,et al 2019). At 40% and 50% indium content, there seems to be an unequal distribution of material.

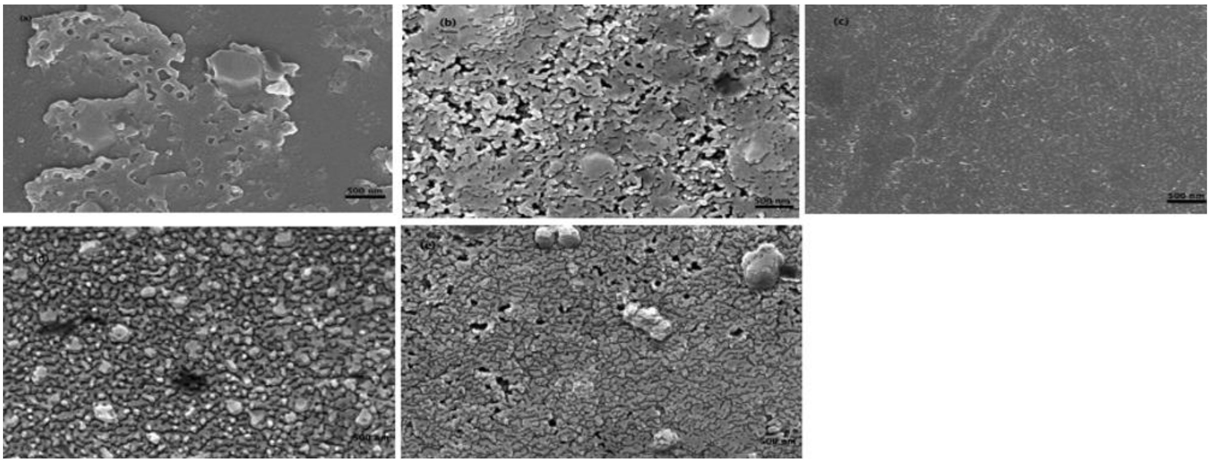

Fig.2: SEM image of Composite ZIO thin films.(a) ZIO (90:10),(b) ZIO (80:20),(c) ZIO (70:30),(d) ZIO (60:40) and (e) ZIO (50:50).

4.3 X-Ray Photoelectron Spectroscopy analysis (XPS)

The XPS spectra for ZIO films are depicted in Fig.3. The measured binding energy values of $In3d_{5/2}$ Zn (2p) O (1s) in ZIO thin films are in agreement with the reported values (Minami, et al 1998). Charge-induced shifts are compensated by adjusting binding energies and setting the C 1s signal to 284.6 eV. The current study of ZIO thin films reveals that as the concentration of Indium oxide in the mixture is increased, the concentration of Zn on the surface of the film decreases, but the opposite is true for In. This demonstrates that Zn has a stronger tendency to agglomerate in surface states than In, as previously documented. Furthermore because Zn is more chemically active, it oxidises to ZnO, hence ZnO rather than pure Zn is found on the surface of ZIO films. The survey scan process is used to produce quantitative estimations of atomic sensitivity factors for distinct atoms' core states in a compound (Wagner, et al 1979). Fig.4 shows the variation of % composition of contents with the concentration of In_2O_3 of ZIO thin films.

The appearance of the In peak validates the incorporation of indium ions into the ZnO lattice. Peaks identified between 440 and 460 eV correlate to the In3d orbital. The peaks if In3d appear at 445.4eV and 453.1eV, which belong to $In3d_{3/2}$ ions and $In3d_{5/2}$ respectively. These peaks correspond to In (+ 3) state (Reddy, et al 2017). The peaks of Zn2p centred at 1022.6 eV and 1045.7 eV which belong to Zn2p3/2 and Zn2p1/2 respectively. They can be attributed to the Zn–O and Zn–O–In-related contributions respectively (Medjaldi, et al 2018). This finding confirms that Zn exists as Zn 2^+ (Medjaldi, et al 2018).In light of this, we draw the conclusion that the In ions were successfully absorbed into the host ZnO lattice as In3d. The peak of O1s was identified at 531.1 eV, indicating oxygen in the OH groups or the medium state between O_2 and dissociated oxygen (Haung, et al 2000,Biswas, et al 2006).

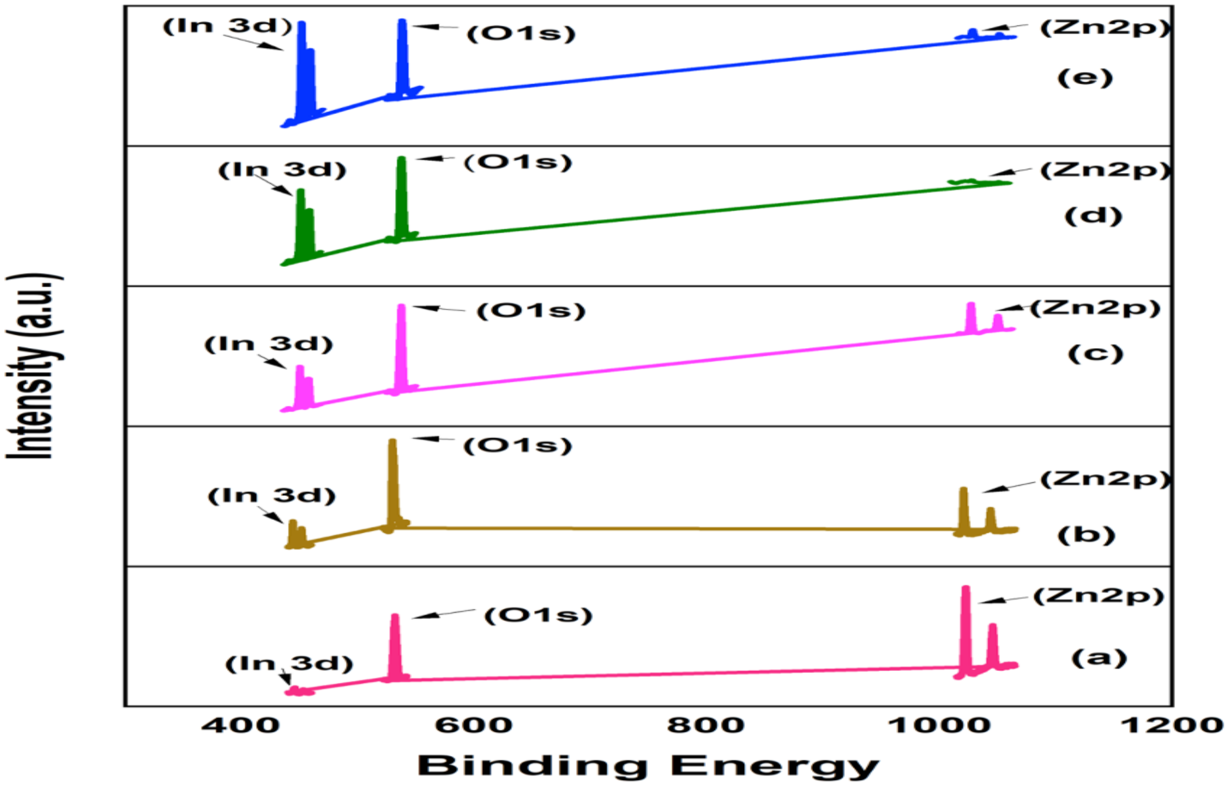

Fig. 3: XPS profile of composite ZIO thin films. (a) ZIO (90:10),(b) ZIO (80:20),(c) ZIO (70:30),(d) ZIO (60:40) and (e) ZIO (50:50).

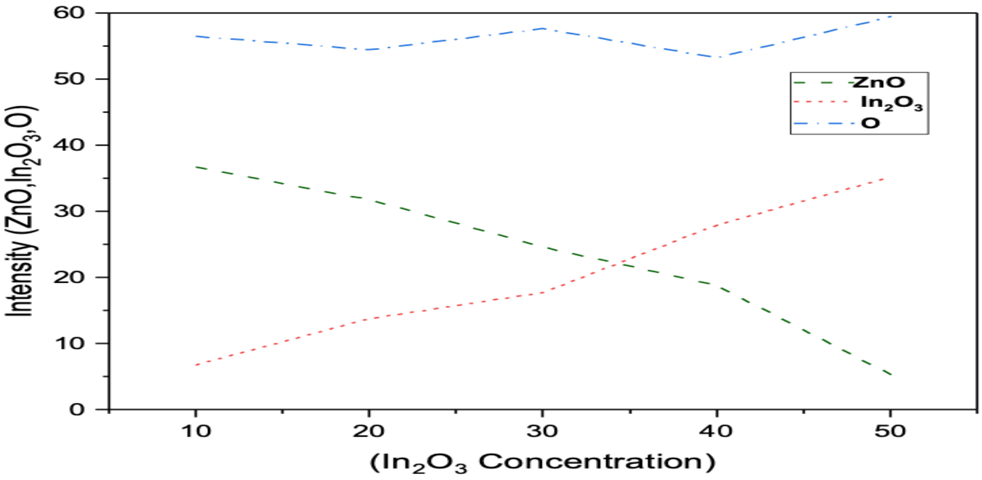

Fig.4: The variation of % composition of contents with concentration of In2 O3 of ZIO thin films.

Table 1: % Composition of In, Zn and O obtained on surface of ZIO films.

% Composition	**Film Type**	**Annealed at 500^0 C**
Zinc Oxide	90:10	36.72
	80:20	31.76
	70:30	24.62
	60:40	18.81
	50:50	5.39
Indium Oxide	90:10	6.77
	80:20	13.79
	70:30	17.72
	60:40	27.95
	50:50	35.17
Oxygen	90:10	56.51
	80:20	54.45
	70:30	57.66
	60:40	53.24
	50:50	59.44

4.4 Optical Analysis

By using Beer-Lambert law (Belkhalfa, et al 2016) given below, the absorption coefficient (α) of thin films can be estimated:

$$\alpha = -\frac{\ln(T)}{t} \qquad (1)$$

Here t and T represents the thickness and transmittance of the thin films respectively. Since ZnO is a direct band gap material permitting direct allowed transitions, it is used to study the relationships between the optical absorption coefficient (α), and the band gap of material (Viezbicke, et al 2015).

Tauc relation can be used to calculate the optical band gap of ZIO thin films.

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

Where n= ½ for direct allowed transition and E_g is the transition energy across the band gap and hν is the photon energy, α is the absorption coefficient for the film and A is a constant.

The band gap energies are found to range from a high of 3.91 eV for 10% Indium doping to a low of 3.68 eV at 50% indium doping. The general trend reported is band gap narrowing, which means that the value of E_g diminished as indium concentration increased. This observation is in part agreement with the findings of Tang and Xie.

(Tang,et al 2013,Xie, et al 2012). The reduction in band gap energy was due to an alteration in the nanostructure, which enhanced film defects (Dalven, et al 1973).The optical transmittance of ZIO thin films were measured using a UV-VIS spectrophotometer. The transmittance of the films are greater than 90% with an almost flat response for ZIO (90:10) and ZIO (80:20). For higher concentrations of indium oxide, the transmittance reduces. This could be owing to an increase in optical scattering as a result of segregation produced by the addition of dopant. (Farid,et al 2019).

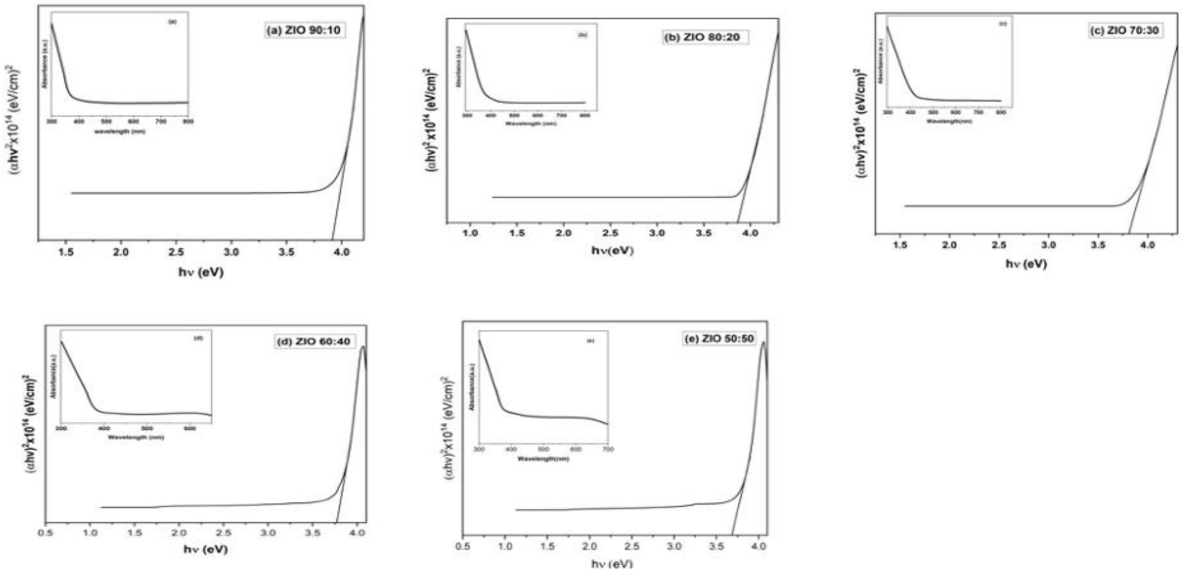

Fig.5: The optical band gap of composite ZIO thin films. (a) ZIO (90:10),(b) ZIO (80:20),(c) ZIO (70:30),(d) ZIO (60:40) and (e) ZIO (50:50).

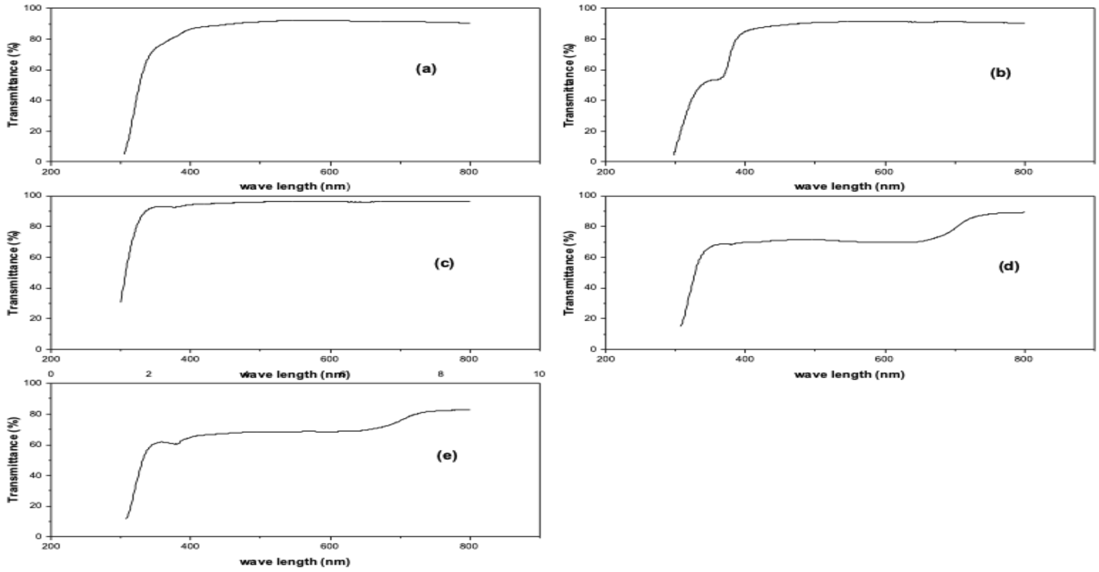

Fig.6: Transmission spectra of composite ZIO thin film. (a) ZIO (90:10),(b) ZIO (80:20),(c) ZIO (70:30),(d) ZIO (60:40) and (e) ZIO (50:50).

Table 2:Optical band gap of ZIO thin films.

S.NO.	Sample Name	Ratio	Band gap
1.	ZIO	90:10	3.91eV
2	ZIO	80:20	3.86 eV
3	ZIO	70:30	3.81 eV
4	ZIO	60:40	3.77 eV
5	ZIO	50:50	3.68 eV

5. Conclusion

The XRD results indicate that when the concentration of In_2O_3 reaches at 30%, the film indicates an amorphous alike nature. SEM reveals that the concentration of indium doping changes the morphology of the films. The results of XPS show that as the concentration of Indium oxide in the mixture increases, the concentration of Zn on the surface of the film decreases, but the opposite is true for In. The optical band gap of the composite ZIO thin films decreases on increasing the concentration of In_2O_3 in ZnO. The transmittance also decreases for higher concentrations of Indium Oxide.

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