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RESEARCH ARTICLE

Effect of Annealing on Structural, Compositional and Optical Properties of Composite ZIO Thin Films

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Abstract

In this work, the structural, compositional and optical properties of composite zinc indium oxide (ZIO), thin films grown on glass substrates using thermal vapor evaporation technique have been investigated for two different ratios of $ZnO:In_2O_3 = 90:10$ and 80:20 wt.% at room temperature. The films so obtained were annealed for 2 h at 500^0C. The ZIO films are amorphous before annealing and become crystalline after annealing for both the ratios, as revealed by the X-ray diffraction patterns. The study of the composition of the surface and oxidation states present there in made by using X-ray photoelectron spectroscopy, also provides information about the binding energies of deposited materials. The effect of thermal annealing on these mixed oxide thin films has also been studied by using UV visible Spectroscopy. The optical band gap is found to increase on annealing the ZIO thin films.

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

Introduction

Thin films of Zinc oxide (ZnO) are superior choice for optical applications due to their excellent properties. It is non toxic and reasonably less rare. It has tunable electronic conductivity (Biswal *et al.*, 2014). It shows high degree of transparency for UV-vis electromagnetic radiation (Kumar *et al.*, 2004).ZnO has common uses in flat panel screen (Chae,2001),in piezoelectric devices, as photo catalysts (Chang *et al.*,2016), as antimicrobial agent (Lefatshe *et al.*, 2017),in photovoltaic devices (Sharma *et al.*, 2015), and in electrode applications such as in light emitting and absorbing devices (Liu *et al.*, 2010). For surface deposition it does not require very high substrate temperature (Muchuweni *et al.*, 2016). By doping of some materials the optical performance of these materials can be made more appropriate for application in several optoelectronic devices. This may happen due to change in their crystal structure on doping with impurities (Moditswe *et al.*, 2016). Several researchers have examined the properties of ZnO doped with different doping elements, including indium, aluminum (Bedia *et al.*, 2015), copper (Muiva *et al.*, 2011), fluorine (Ariyakkani *et al.*, 2017), cobalt (Dhruvashi and Shishodia, 2016),tin (Sanchez-Juarez *et al.*, 1998), iron (Chava and Kang, 2017) and a few doping elements.

In its pure form, Zinc oxide is very resistant and researchers are making efforts to enhance its optical properties with deliberate doping. Dopant selection should be based on the ionic size and electro negativity, since both factors determine the effectiveness of the dopant element higher valence (group III) elements are generally preferred to improve the properties of ZnO like optical properties. Thin films of optimized zinc oxide are doped with indium and investigated for its effect on the structural, optical and electronic properties of thin films of ZnO. On the other hand Indium Oxide (In_2O_3) is well- known transparent conducting oxide and prepared both in the form of powder and thin films. It finds application in solar cells, sensors, opto-electronic devices and as a useful electrode material (Hartnagel *et al.*, 1995) and (Lewis and Paine, 2000) and (Elliott, 2005). Recently it has been studied for its properties in different Nano structure shapes, such as spherical (Kim and Park, 2004), rods, wires (Yu *et al.*, 2004) and Nano tubes (Zhu *et al.*, 2004), where the focus has been mainly on preparation in different shapes and their applications.

Zinc indium Oxide (ZIO) is a useful binary oxide for research in view of its practical application. With change of doping percentage of indium oxide in Zinc oxide, a change in optical band gap of ZIO is observed, as reported in (Jain *et al.*, 2010). The goal of the present work is to synthesis high quality films of mixed oxides ($ZnO+In_2O_3$) and to examine their optical properties, the

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knowledge of which can help to determine their suitability for use as a transparent electrode in solar cells. These materials have several other applications in the field of electronics, such as gas sensors, thin film transistors, for coating and in optoelectronic devices etc.

It has been observed that in the visible region with the wide band gap of the order ~3eV, ZIO films showed transmission above 80%. There are several methods to synthesize thin films, such as sputtering, spin coating, thermal vapor evaporation, sol gel deposition, chemical bath deposition, and many more. Thermal vapor evaporation technique is attractive as it is simple and produces uniform good quality thin films.

Materials and Methods

Thin films of ZIO are obtained by thermal vacuum evaporation method on glass substrates by employing HINDHI vacuum coating setup with turbo pump with pressure being maintained at 10^{-6} torr. High purity ZnO and In_2O_3 in powder with 99.9% purity obtained from sigma Aldrich were mixed at different concentrations (90:10, 80:20 wt.%) with the help of mortar-pestle for 5 hours. This mixture was placed in a molybdenum boat in the HINDHI vacuum coating unit. Distance was set at 10 cm between the target and the source, the target being kept at room temperature. A quartz crystal thickness monitor was used to measure the thickness of the prepared films, which was found to be varying from 975 Å to 1025 Å for the films prepared. Experimental conditions were kept unchanged for uniform deposition of composite (ZIO) thin films. The films thus obtained were annealed at 500°C for 2 h in muffle furnace in air as these values of annealing temperature and time have been reported to be satisfactory conditions for obtaining ZIO films in crystalline form.

The crystality of films was examined by employing X-ray diffractometer (Bruker Lynx Eye detector) using Cu-K 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 MgK_α (1.2536 keV) radiation, the pressure being kept $5x10^{-10}$ torr. The absorption characteristics 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).

Results and Discussion

X-ray Diffraction Analysis

XRD is used to characterize the composite ZIO thin films in as prepared and annealed forms. the XRD patterns of as prepared and annealed films are shown in Fig. 1(a) and 1(b) respectively for different concentration of In_2O_3 in ZnO. Fig. 1(a) and 1(b) show the XRD patterns of ZIO thin films for as prepared and after thermal annealing at 500°C for 2 hours. Fig. 1(a) reveals that the as prepared ZIO (90:10) film is amorphous in nature after annealing a peak appears at 28.7°, indicating that the structure of ZnO now becomes crystalline (JCPDS file 21-1486) and another peak (102) is obtained at $2\theta = 31.7°$indicating the hexagonal ZIO structure indicating formation of hexagonal $Zn_2In_2O_5$ structure (JCPDS file 00-20-1442). From Fig. 1 (b) it can be seen that the as prepared ZIO (80:20) film is also amorphous in nature as no Bragg reflection peaks are seen, but after annealing a peak (009) appears, at 13.6° and another sharp peak (0 0 12) is obtained at 18.3° indicating the presence of rhombohedral ZIO structure (JCPDS file 01-089-8974). In

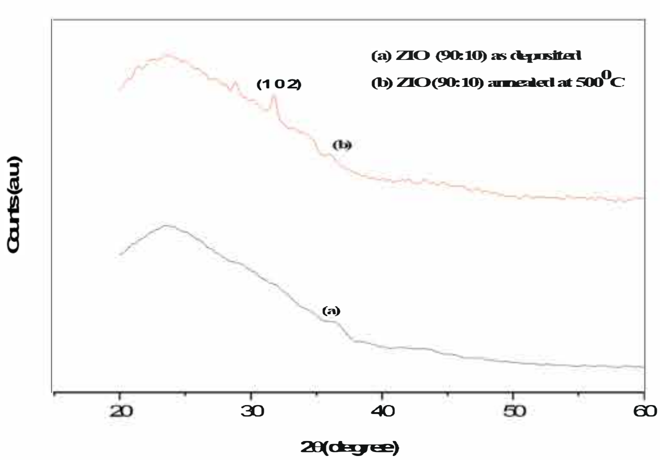

Fig.1(a)

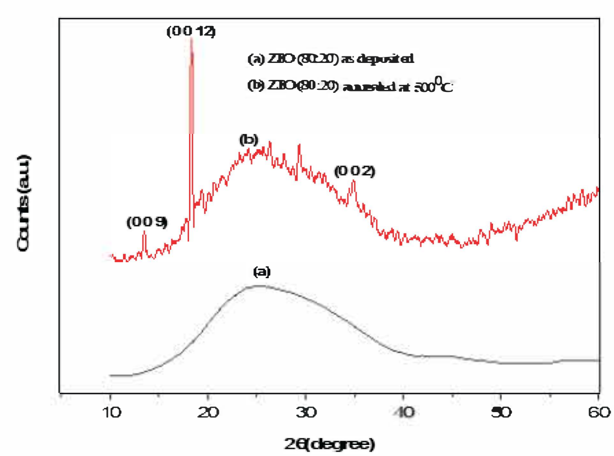

Fig.1(b)

Fig.1. XRD profile of (a) as-prepared and annealed ZIO (90:10) thin films and (b) as-prepared and annealed ZIO (80:20) thin films.

this case another peak (002) appears on the right side of the main peak of graph which can be seen at 34.8° indicating the presence of hexagonal ZnO structure (JCPDS file 01-074-9941). These ZIO peaks for 80:20 thin film might appear due to presence of compounds like $(ZnO)_{1-x}$,$(In_2O_3)x$,$(Zn_2In_2O_5)_{1-x}$ $(ZnO)_x$ and $(Zn_2In_2O_5)_{1-x}$ $(In_2O_3)_x$ which may be formed as a result of annealing, as also reported by (Naghavi *et al.*,2001). It is observed that as proportion of In_2O_3 in the mixture increases more intense peaks and large in number are obtained. It is also found that crystallization can occur with an increase in the content of In_2O_3 and post annealing processes as reported earlier.

The crystallite grain size of ZIO crystallites was calculated by using the Debye-Scherer equation:

$$D = 0.9\lambda / \beta\cos\theta \quad (1)$$

where λ represents the wavelength of the X-rays used, β is the full-width half-maximum

(FWHM) and θ represents the Bragg's diffraction angle.

On making calculations with above formula, the range of grain size is found to lie between 30 – 50 nm for ZIO (90:10) and for ZIO (80:20) it is found to lie between 25 – 60 nm.

X-Ray Photoelectron Spectroscopy Analysis

Investigations are made to determine the relationship, if any, between chemical composition of thin films and their opto-electronic properties (Wang and Hu,2001). In the present case XPS with MgK radiation of energy 1.2536 KeV is used to determine chemical composition and bonding states of as-prepared and annealed thin films of ZIO, obtained by sputtering with 2 KeV Ar^+ ions.

The XPS spectra for as-prepared and annealed ZIO films are shown in Fig. 2(a) and 2(b) respectively. The calculated binding energy values of In $(3d_{5/2})$ Zn (2p) O (1s) in ZIO thin films comply with the values reported by (Minami *et al.*, 1996). Present investigation on ZIO thin films show that in annealed films concentrations of Zn on the surface of the film is higher as compared to as prepared films, whereas an opposite behavior is observed for In this shows Zn has a higher tendency to aggregate in surface states as compared to In as reported earlier. Further Zn being more chemically active, oxidizes to ZnO and hence on the surface of ZIO films ZnO is found to be present instead of pure Zn. The survey scan technique is used to obtain quantitative estimates of the atomic sensitivity factors for the core states of different atoms in a compound (Wagner *et al.*, 1979).

Optical Properties

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

$$\alpha = \frac{-\ln(T)}{t} \quad (2)$$

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). The band gap energies obtained in the present case range from 3.8-3.99 eV for composite ZIO thin films. After annealing band gap is found to increase in both the cases (for 90:10 and 80:20). It may be

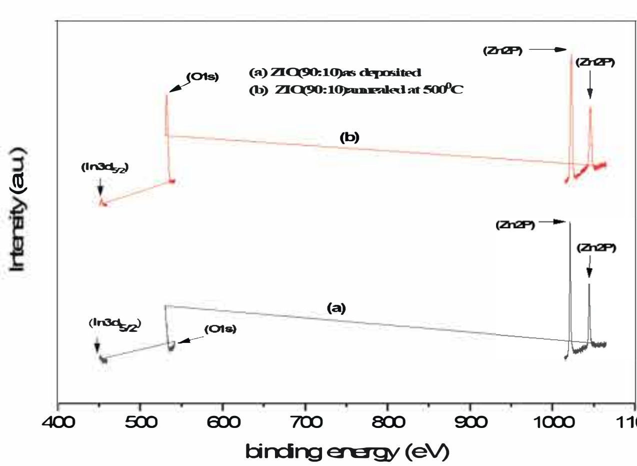

Fig.2(a)

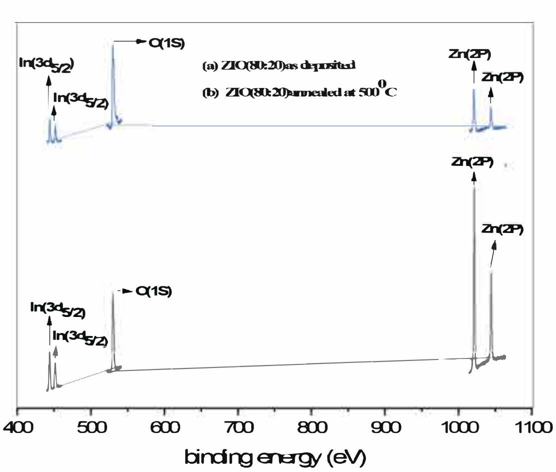

Fig.2(b)

Fig.2. XPS binding energy diagrams for (a) as-prepared and annealed ZIO (90:10) thin films and (b) as-prepared and annealed ZIO (80:20) thin films.

observed that as the concentration of In in ZIO increases, the band gap decreases. The results reported by (Tang *et al.*, 2013) and (Xie *et al.*, 2012) are partly in agreement with this finding. As observed by (Dalven, 1973), the decrease in band gap energy can be due to a modification in the crystalline structure of the film leading to increase in crystal defects.

The optical band gap of ZIO thin films can be evaluated by using Tauc relation.

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (3)$$

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 is found to increase on annealing the film, as shown in Fig. 3(a) and (b) and the relevant band gap values for as-prepared and annealed thin films assemble in Table 1 (Jain and Vijay, 2016).

Table. 1 Optical band gap of as-prepared and annealed ZIO thin films.

Ratio	Sample type	Band gap
ZIO (90:10)	As deposited	3.90 eV
	Annealed	3.99 eV
ZIO (80:20)	As deposited	3.80 eV
	Annealed	3.86 eV

Scanning Electron Microscope Analysis

The surface morphology of the films has been studied by scanning electron microscopy (SEM). For this study we took two samples, one as deposited thin films and the

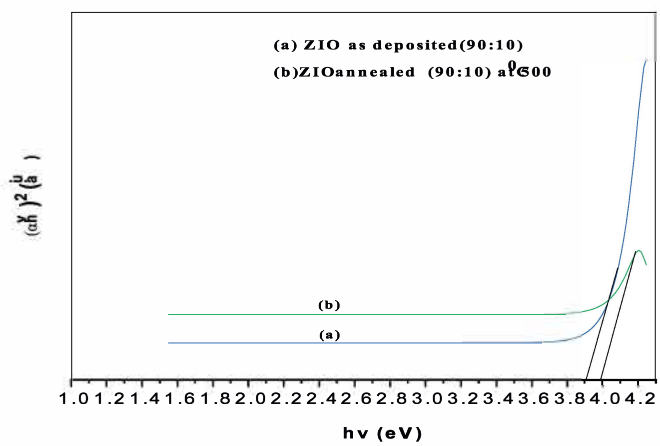

Fig.3(a)

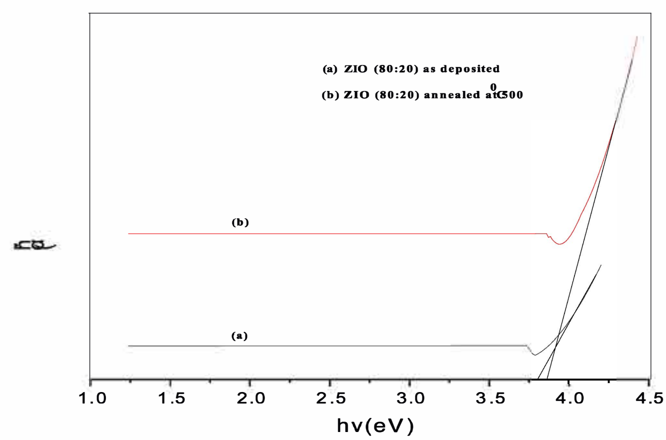

Fig.3(b)

Fig.3 Tauc relation diagrams for obtaining Optical band gap of (a) as-prepared and annealed ZIO (90:10) thin films and (b) as-prepared and annealed ZIO (80:20) thin films.

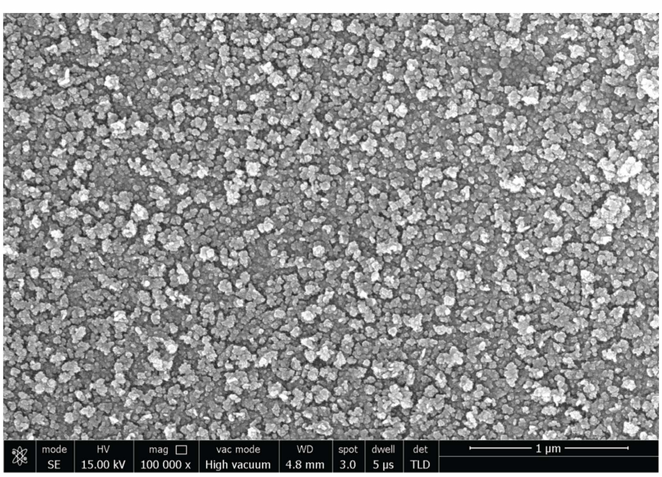

Fig.4(a)

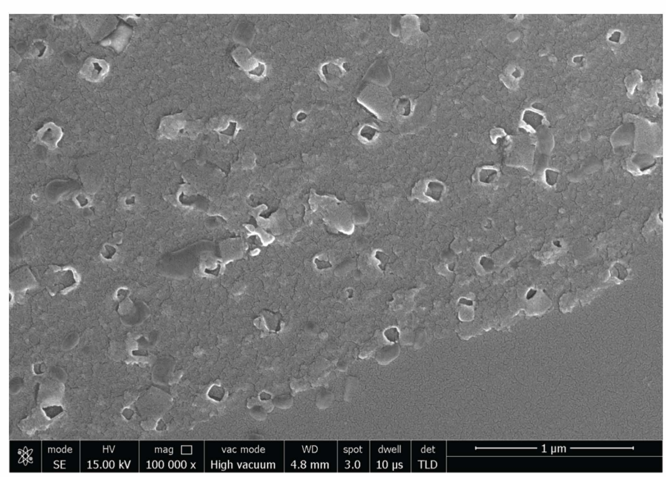

Fig.4(b)

Fig.4. Surface morphology of ZIO thin films as obtained by SEM (a) For as deposited, and (b) for ZIO films annealed at 500°C.

other ZIO film annealed at 500°C. Fig. 4 (a) and (b) shows SEM images of as- prepared and annealed ZIO (90:10 wt.%) films respectively. The images indicate that whereas the surface of film was rough before annealing, it becomes smooth after annealing. The average grain size calculated was about 30 nm to 60 nm for as prepared ZIO (90:10 wt.%). The similar trend of grain size was also observed in XRD analysis.

Conclusion

These XRD results indicate that after annealing thin films become crystalline whereas as-prepared films were amorphous in nature.XPS results help us in evaluating the chemical composition of the as-prepared as well as annealed films.The optical band gap of the composite ZIO thin films increases from its value for as- prepared consentration of In_2O_3 in ZnO. The SEM results indicate that whereas the surface of film was rough before annealing, it becomes smooth after annealing.

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