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Effect of Concentration of Ti Doping on Optical Properties of $Zn_{1-x}Ti_xO$ (where x=0.0, 0.1, 0.3, 0.5, 0.7 and 0.9) Thin Films Deposited by Spray Pyrolysis

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Abstract **-Ti doped $Zn_{1-x}Ti_xO$ (where x=0.0, 0.1, 0.3, 0.5, 0.7 and 0.9) thin films have been deposited on Indium Tin Oxide (ITO) coated glass substrate at 450^0 C. The effects of Ti doping concentration on the optical properties in ZnO films have been studied. The deposited films are characterized by Field Emission Scanning Electron Microscope (FESEM), Energy-Dispersive X-ray Spectroscopy (EDS), UV-Visible Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The FESEM studies reveal that the particle size decreases from 16 nm to 9 nm with increase in Ti concentration from x=0.0 to 0.9. Analysis of UV- visible spectra shows that the optical direct band gap increases from 3.92 eV up to 4.68 eV with increase in Ti doping concentration x=0.0 to 0.9. The FTIR spectra of the films shows Zn-O absorption band in between (450-487) cm^{-1}. The peaks also appear in between (3000-4000) cm^{-1}, (2885 -2100) cm^{-1} and at 530 cm^{-1} due to O-H, N-H and Ti-O bond stretching respectively. EDS result shows that Zn, O and Ti elements are present as per their stoichiometric ratio in all the prepared samples.**
Keywords: **Thin films, ZnO, Doping, Spray Pyrolysis.**

I.INTRODUCTION

Since last five to six decades ZnO semiconductor has been a material of great interest owing to its unique properties e.g. large band gap (3.27 eV) and large exciton binding energy (60 meV) [1]. It makes ZnO a superior candidate for applications in display devices such as LEDs and flat panel displays, laser diodes etc. Since the band gap of ZnO lies in the near UV region, therefore the band gap of the ZnO can be manipulated in such a way so that it lies in visible region. Hence it can be used in display devices [2]. The biocompatibility and nontoxic nature of ZnO make it a suitable candidate for using in cosmetics and sun screen lotions. It also absorbs the harmful ultraviolet radiations itself and does not let them to penetrate in the skin. ZnO is used mostly in paints as pigments [3]. Compared to other transparent conductive oxides (TCO), ZnO is being widely used on the account of its properties viz. high chemical stability, mechanical stability etc. The other TCO materials are ITO, SnO_2 etc [4]. ZnO is commonly used as a gas sensor [5]. ZnO thin films are used to coat the spectacles that are used while welding is performed and also for the wavelength selection to carry out a particular experiment e.g. to study the effect of wavelength or frequency of light on photoelectric effect [6]. The size, shape and crystallinity of the thin film should be controlled for using the thin films for a particular application. Therefore, there are various techniques for the deposition of good quality thin films such as Sol-Gel, Pulsed laser deposition (PLD), Sputtering etc. But spray pyrolysis technique has been used here since it is a very simple and cost effective technique for the deposition of thick and thin films. The very high quality targets and chemicals are also not required in this technique [7]. In the present paper, effect of Ti doing in ZnO thin films deposited on ITO substrate by Spray Pyrolysis technique on the structural and optical properties have been reported.

II.EXPERIMENTAL DETAILS

The Zn $(NO_3)_2.6H_2O$ was dissolved in ethanol to prepare a solution of molar concentration of 0.15 M. The solution was stirred for some time to ensure the complete solubility of $Zn(NO_3)_2.6H_2O$. The prepared solution was used to deposit the pure ZnO thin film on the ITO substrate using Spray Pyrolysis method. The films were deposited by Holmarc Spray Pyrolysis equipment (model: HO-TH-04). The parameters were optimized to obtain good quality films. Temperature of the substrate was fixed at 450^0C. The substrate to nozzle distance was kept 22 cm. The pressure of the carrier gas was fixed at 0.6 bar. The flow rate was kept at 0.5 ml/s. Before the deposition, ITO substrate was first cleaned with distilled water and then dipped in acetone solution to remove any impurity then again cleaned and dried. For the purpose of doping of Ti, the titanium isopropoxide $Ti\{OCH(CH_3)_2\}_4$ solution was taken. The solution was prepared as per the formula $Zn_{1-x}Ti_xO$ (x=0.0 0.1, 0.3, 0.5, 0.7 and 0.9). Then the respective solution was sprayed for two minutes on the heated ITO substrate. The thin films were sintered, after deposition, for two hours in the furnace at a temperature of 400^0 C. The sintered films were used for the further characterizations. The surface morphological analysis was done with Field Emission Scanning Electron Microscope (FESEM) (model: Carl Zeiss, Merlin Compact). The energy dispersive X ray Spectroscopy (EDS) was done using same equipment to detect the composition of various elements present in the films. The optical transmittance spectra were observed by UV- Visible spectrophotometer (model: UV-240, Krüss). The band gap was calculated using data of transmittance and the wavelength applying Tauc's extrapolation method. FTIR analysis was done to determine the vibrational bond stretching due to various bonds present in the sample (model: Bruckr Tensor 27). All the measurements were carried out at room temperature.

III.RESULTS AND DISCUSSIONS

FESEM Analysis: FESEM analysis of pure and doped ZnO thin films is done to get information regarding surface morphology and the particle size. The FESEM image of $Zn_{0.7}Ti_{0.3}O$ sample is shown in Fig. 1. The inset of Fig. 1 shows the histogram between particle size and frequency of occurrence of particles. By Gaussian curve fitting of the histogram, the average particle size is found 13 nm. It is also observed that most of the nanostructures are spherical in shape (See Fig. 1). It is also found from FESEM image analysis that the crystallinity of the films decreases with increasing Ti concentration [8]. The average particle size decreases with increase in the concentrations of Ti. This is due to Ti^{3+} ions which act as grain growth inhibitors [9]. The obtained values of the average particle sizes are 16, 16, 13, 11, 10 and 9 nm for the value of x=0.0 to 0.9 respectively.

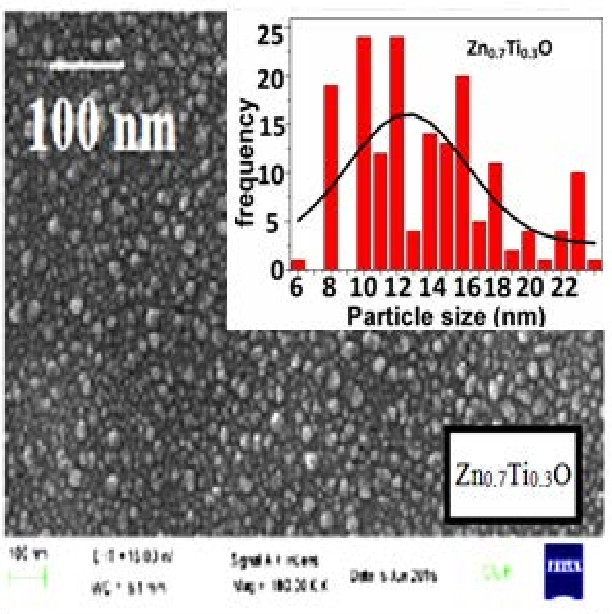

Fig.1 FESEM image of $Zn_{0.7}Ti_{0.3}O$ sample. Inset shows the histogram and its Gaussian curve fitting.

EDS spectra confirm that the theoretical and experimental values of weight and atomic percentages of different samples are equal within the experimental error.

UV- Visible Analysis: The UV-Visible spectra are obtained of the undoped and Ti doped ZnO thin films. The maximum transmittance lies in the range of 75-80%. It indicates that the good qualities of films have been deposited. An estimation of band gap is done from the absorption band edge of the films present in the UV-Visible spectra. The absorption coefficient for direct transitions is given by

$$\alpha(\upsilon)h\upsilon = B\,(h\upsilon - Eg)1/2$$

where α is absorption coefficient , h is Plank's constant, υ is incident radiation frequency, and B is constant. The direct band gap 'E_g' is obtained by plotting the quantity hν (the energy of the light) on the abscissa and the quantity $(\alpha h\nu)^{1/n}$ on the ordinate, then by extrapolating the linear region up to x-axis gives intercept on the x-axis that yields the band gap (See Fig. 2).

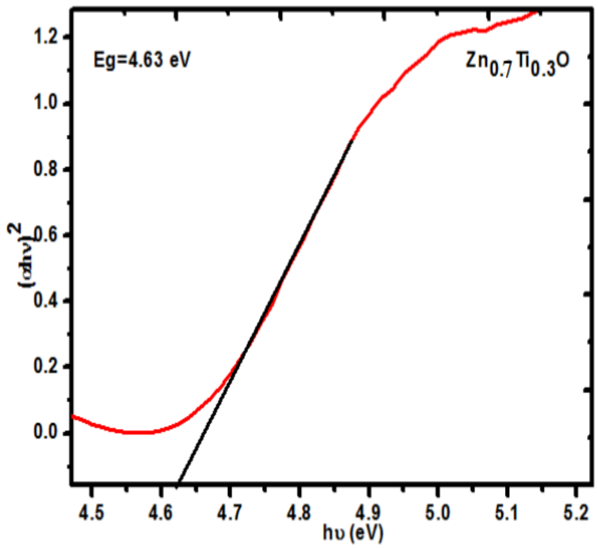

Fig. 2 Band gap calculation of $Zn_{0.7}Ti_{0.3}O$ sample.

It is also found that the band gap increases from 3.92 eV to 4.68 eV with increase in the Ti doping concentration form x=0.0-0.9. This kind of change in band gap can be attributed to Burstein Moss band filling effect [9-12]. It happens because the excessive charge carriers that are induced by Ti doping fill the conduction band. It results in increase in the band gap. Increase in the Ti concentration also leads to formation of amorphous phase. It leads to large increase in band gap due to formation of various defects [9], [10].

FTIR Analysis: Fig. 3 shows the FTIR Spectrum of the $Zn_{0.7}Ti_{0.3}O$ thin film.

FTIR investigates the vibrational properties in which the positions of the bands and absorption peaks are dependent not only on the chemical composition and structure but also on the morphology of the films [11]. The FTIR spectrum is analyzed to find out the functional group present in the films. The increase in transmittance from 75-80% is observed with increase in the Ti concentration. The FTIR spectra of the films shows Zn-O absorption band in between (450-487) cm^{-1}. The peaks also appear in between (3000-4000) cm^{-1}, (2885 -2100) cm^{-1} and at 530 cm^{-1} due to O-H, N-H, and Ti-O bond stretching respectively.

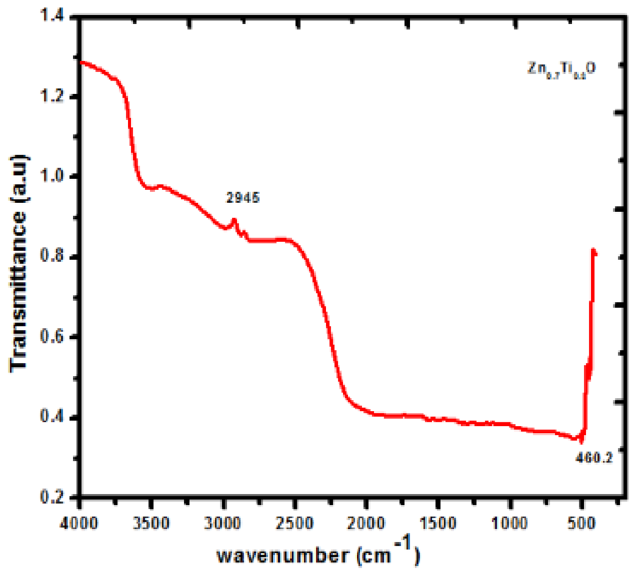

Fig. 3 FTIR Spectrum of the $Zn_{0.7}Ti_{0.3}O$ sample.

IV. CONCLUSION

In the present paper, the Ti doped ZnO thin films i.e. $Zn_{1-x}Ti_xO$ (where x=0.0, 0.1, 0.3, 0.5, 0.7 and 0.9) have been deposited on ITO coated glass substrate using spray pyrolysis method. The optical properties of the deposited sample have been studied. The films show the increase in transmittance in the range of 75-80% with Ti doping. These films are suitable for use in optoelectronic devices and solar cells. The band gap of ZnO thin films increases with increasing Ti concentration due to Burstein Moss effect. Furher, with increasing Ti content, more amorphous phases are formed which leads to fromation of various defects. Therefore, the films can be used as a good dielectric for energy storage devices since the semiconducting behavior of ZnO has been changed to insulating behavior due to Ti doping. Due to high band gap and transmittance it can also be used in the field of transparent conducting oxides such as solar cells, flat panel displays, touchscreens etc.

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