

# Optical Dispersion Characterization of Sprayed $Zn_{1-x}Mn_xO$ Thin Films

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## ABSTRACT

Uniform and adherent  $Zn_{1-x}Mn_xO$  films have been deposited by using spray pyrolysis technique on glass substrates. The optical properties and dispersion parameters of zinc oxide have been studied as a function of doping concentration with Mn. Changes in direct optical energy band gap of cobalt oxide films were confirmed after doping. The optical energy gap  $E_g$  increased from 3.13 eV for the undoped ZnO to 3.39 eV with increasing the doping concentration of Mn to 4 %. The changes in dispersion parameters and Urbach tails were investigated. An increase in the doping concentration causes a decrease in the average oscillator strength. The single-oscillator parameter has been reported.

**Keywords:** TCOs; Dispersion parameters; Spray pyrolysis; Zinc Oxide;  $Zn_{1-x}Mn_xO$

## 1. INTRODUCTION

ZnO is a well-known as transparent conductive oxide, which belongs to the wide-band-gap semiconductor family, with a relatively large exciton binding energy (60 meV). It is a promising material for ultraviolet nano-optoelectronic devices and lasers operating at room temperature<sup>[1]</sup>. As is well known, impurity-doping in semiconductors with selective elements greatly affects the basic physical properties, such as the electrical, optical, and magnetic properties, which are crucial for their practical. Among these materials, zinc oxide (ZnO) is a promising transparent oxide that has been extensively used for candidate for novel device applications, such as varistors<sup>[2]</sup>, sensors<sup>[3]</sup>, UV light emitting devices<sup>[4]</sup>, transparent transistors<sup>[5, 6]</sup> and laser diodes<sup>[7-9]</sup>.

Generally, selective elements as dopant materials in ZnO can be classified into two groups of materials. One group can substitute for Zn and the other can substitute for O. These different types of doping materials can exhibit different optical properties for ZnO due to the different treatments of Zn and O in the ZnO structure. Each exhibits very different behavior as dopant material in ZnO nanostructures<sup>[10]</sup>. Mn as a cation dopant can substitute for Zn. It can be applied as an impurity that changes the band-gap of ZnO. By alloying ZnO with another material of a different band-gap, the band-gap of ZnO can be fine-tuned.

Various techniques have been applied to study Mn-doping including RF magnetron sputtering, pulsed laser deposition, spray pyrolysis method, atmospheric barrier torch

discharge technique, chemical vapor deposition, and sol-gel process<sup>[11-17]</sup>. In this work, un-doped and Mn-doped ZnO films have been prepared by using the spray pyrolysis technique.

Owing to the influence of doping on the properties of materials, the controlled preparation of zinc oxide of different doping materials and concentrations are always the researcher's purpose. This paper reports the influence of doping with manganese on the preparation and properties of zinc oxide ZnO thin films by spray pyrolysis technique (SPT).

The accurate determination of the optical properties of these materials is important, not only in order to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications.

## 2. EXPERIMENTAL PROCEDURE

Thin films of zinc oxide have been prepared by chemical pyrolysis method. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 450 °C, the starting solution was achieved by an aqueous solutions of 0.1M zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) provided from Merck company/Germany and 0.1M manganese chloride  $\text{MnCl}_2$  from BDH/England, used as a doping agent with atomic concentration of 2% and 4%, these materials were dissolved in de-ionized water and ethanol, few drops of HCl were added to speed up the dissolving, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 sec lasted by a (3 min) wait to avoid excessive cooling.

The carrier gas (filtered compressed air) was maintained at a pressure of  $10^5 \text{ Nm}^{-2}$ , distance between nozzle and substrate was about 28 cm  $\pm$  1 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 0.3  $\mu\text{m}$ . Optical transmittance and absorbance were recorded in the wavelength range (300-1000 nm) using UV-visible spectrophotometer (Shimadzu Company Japan). Optical transmittance and absorbance were reported in order to find the effect of doping on the parameters under investigation.

## 3. RESULTS AND DISCUSSION

Information concerning optical transmittance is important in evaluating the optical performance of conductive oxide films. Transmittance spectra in the UV and visible wavelength regions of the films are shown in Fig. 1. It can be observed that in the visible wavelength region the optical transmission of both un-doped and Mn-doped ZnO films increases with increasing wavelength. Furthermore, the average values of the optical transmission in the visible range (400–800 nm) were estimated. The average transmittance values for the films were 59, 68, and 72% for ZnO, ZnO:Mn 2%, and ZnO:Mn 4% thin films, respectively.

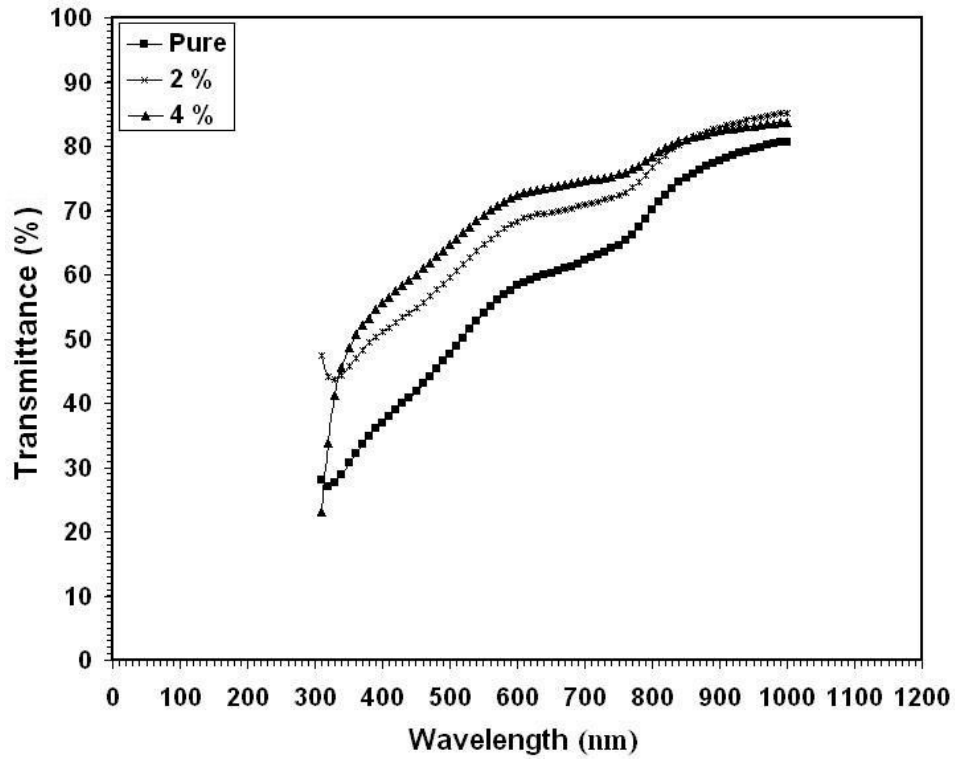


Fig. 1. Transmittance versus wavelength.

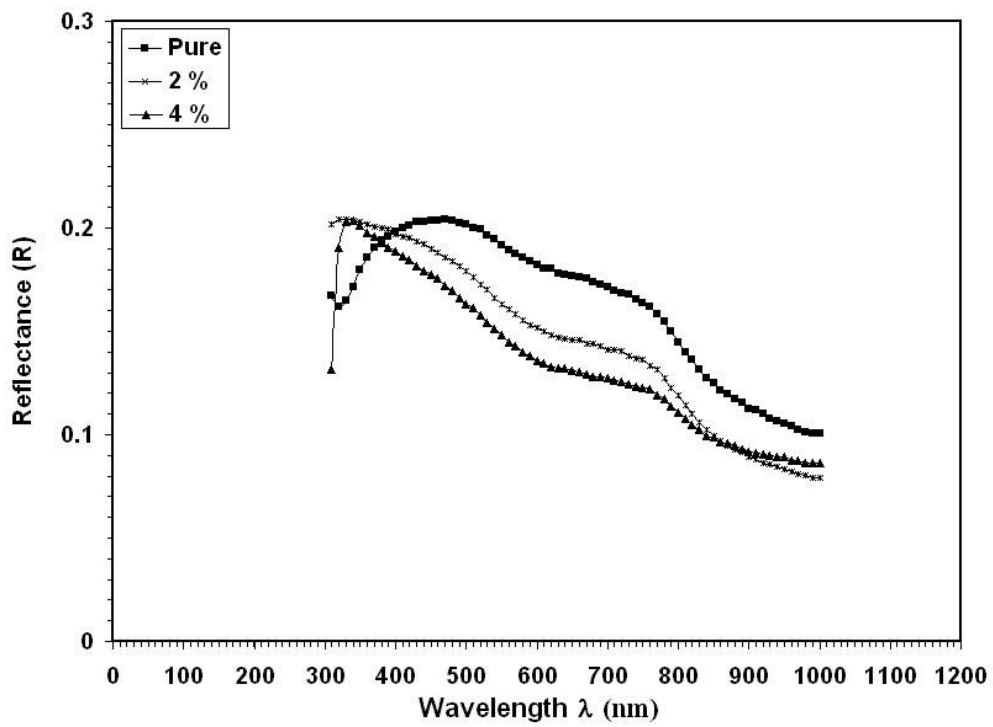


Fig. 2. Reflectance versus wavelength

Fig. 2. Shows that in the visible region, the reflectance values were observed between 0.12 % and 0.2 %. The reflectance of all films had a common tendency that the values decreased with the increase in the wavelength. It is seen that the reflectance is limited only by the surface reflectance of about 20% in the visible region. These results were in a good agreement with that obtained by Mandal et al. and Fukumara et al.<sup>[12, 18]</sup>.

The incorporation of impurity into the semiconductor often reveals the formation of band tailing in the band gap. The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach<sup>[19]</sup>. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as<sup>[20,21]</sup>:

$$\alpha = \alpha^{\circ} \exp (h\nu / E_U)$$

where  $\alpha^{\circ}$  is a constant,  $E_U$  is the Urbach energy, which characterizes the slope of the exponential edge. Figure 3 shows Urbach plots of the films. The value of  $E_U$  was obtained from the inverse of the slope of  $\ln \alpha$  vs.  $h\nu$  and is given in Table 1. The dopants change the width of the localized states in the optical band.  $E_U$  values change inversely with the optical band gap. The Urbach energy values of ZnO, ZnO:Mn 2 %, and ZnO:Mn 4 % films were calculated to be 666, 625, and 555 meV respectively. The decrease of  $E_U$  suggests that the atomic structural disorder of ZnO films increase by manganese doping. This behavior can result from increasing the concentration of point defects induced by the dissolution of Mn atoms in ZnO crystals and formation of solid solution. So, this decrease leads to a redistribution of states, from band to tail. As a result, both an increase in the optical gap and a narrowing of the Urbach tail are taken place.

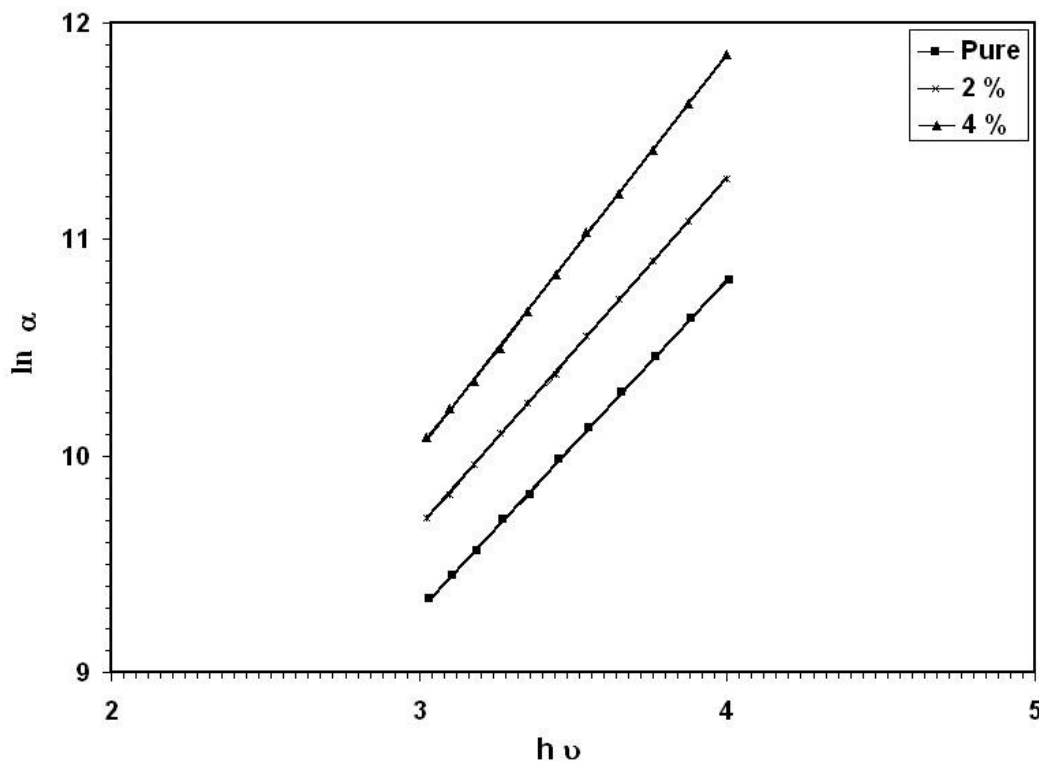


Fig. 3.  $\ln \alpha$  versus photon energy for ZnO and ZnO:Mn films.

The refractive index dispersion plays an important role in optical communication and designing of the optical devices. Therefore, it is important to determine dispersion parameters of the films. The dispersion parameters of the films were evaluated according to the single-effective-oscillator model using the following relation<sup>[22, 23]</sup>:

$$n^2 - 1 = [E_d E_o / E_o^2 - E^2]$$

The physical meaning of the single-oscillator energy  $E_o$  is that it simulates all the electronic excitation involved and  $E_d$  is the dispersion energy related to the average strength of the optical transitions<sup>[24]</sup>, which is a measure of the intensity of the inter band optical. This model describes the dielectric response for transitions below the optical gap.  $(n^2 - 1)^{-1}$  vs.  $(h\nu)^2$  plots for the films was plotted as shown in Fig. 4.  $E_o$  and  $E_d$  values were determined from the slope,  $(E_o E_d)^{-1}$  and intercept  $(E_o/E_d)$ , on the vertical axis and are given in Table 1.  $E_o$  values increased with the dopants as the optical band gap increase. According to the single-oscillator model, the single oscillator parameters  $E_o$  and  $E_d$  are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum  $M_{-1}$  and  $M_{-3}$  moments can be derived from the following relations<sup>[25]</sup>:

$$E_o^2 = M_{-1} / M_{-3}$$

$$E_d^2 = M_{-1}^3 / M_{-3}$$

The values obtained for the dispersion parameters  $E_o$ ,  $E_d$ ,  $M_{-1}$  and  $M_{-3}$  are listed in Table 1. The obtained  $M_{-1}$  and  $M_{-3}$  moments changes with the dopants.

For the definition of the dependence of the refractive index ( $n$ ) on the light wavelength ( $\lambda$ ), the single-term Sellmeier relation can be used<sup>[22]</sup>:

$$n^2(\lambda) - 1 = S_o \cdot \lambda_o^2 / 1 - (\lambda_o/\lambda)^2$$

Where  $\lambda_o$  is the average oscillator position and  $S_o$  is the average oscillator strength. The parameters  $S_o$  and  $\lambda_o$  in Eq. (4) can be obtained experimentally by plotting  $(n^2 - 1)^{-1}$  against  $\lambda^{-2}$  as shown in Fig. 5, the slope of the resulting straight line gives  $1/S_o$ , and the infinite-wavelength intercept gives  $1/S_o \lambda_o^2$ . The results shows an increase in the band gap which may be attributed to the presence of unstructured defects, that decrease the density of localized states and cause a narrowing in the Urbach tail and consequently increase the energy gap.

**Table 1.** The optical parameters

Sample	$E_o$ (eV)	$E_d$ (eV)	$E_g$ (eV)	$E_u$ meV	$\epsilon_\infty$	$n(o)$	$M_{-1}$ eV <sup>-2</sup>	$M_{-3}$ eV <sup>-2</sup>	$S_o \times 10^{13}$ m <sup>-2</sup>	$\lambda_o$ nm
Pure	6.26	34.75	3.13	666	6.56	2.56	5.56	0.142	1.97	356
2 %	6.47	28.12	3.23	625	5.35	2.31	4.35	0.104	1.15	422
4 %	6.78	24.2	3.39	555	4.57	2.14	3.57	0.078	1.08	430

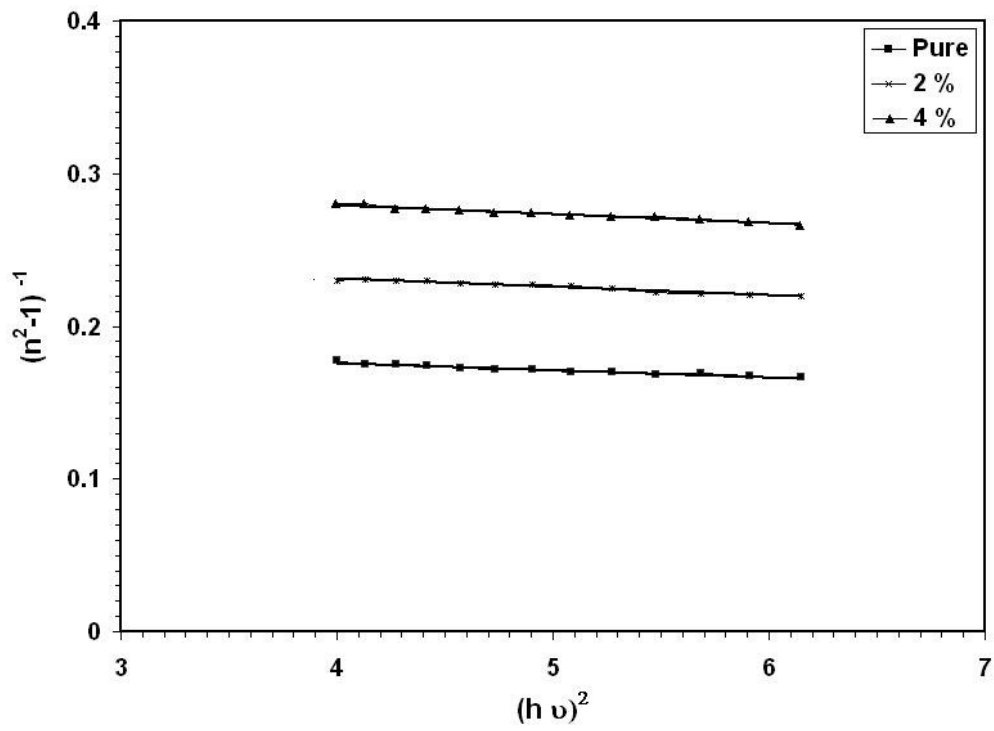


Fig. 4. Variation in  $(n^2 - 1)^{-1}$  as a function of  $(h\nu)^2$  for ZnO and ZnO:Mn films.

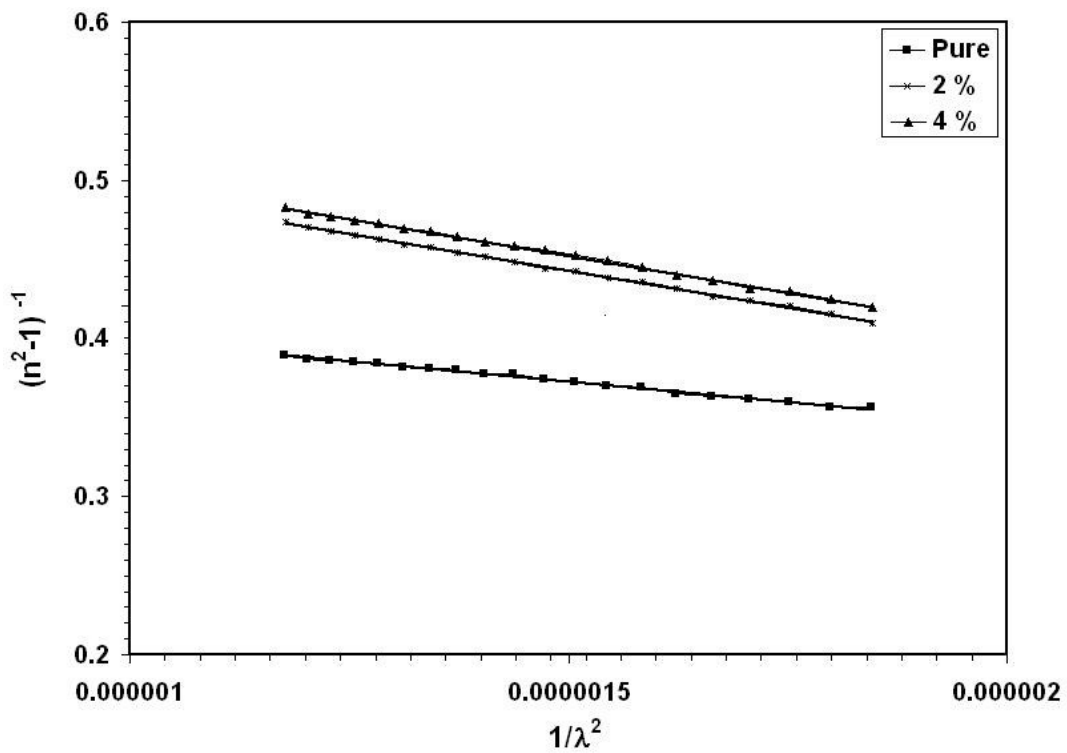


Fig. 5. Variation in  $(n^2 - 1)^{-1}$  as a function of  $(\lambda)^{-2}$  for ZnO and ZnO:Mn films.

#### 4. CONCLUSION

Zn<sub>1-x</sub>Mn<sub>x</sub>O thin films were prepared by using spray pyrolysis technique. Both doped and undoped samples were characterized. Optical band gap increased due to doping. Similarly optical transmittance was affected for moderate doping.

The single-oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model, the change in dispersion was investigated and its value increased from 6.26 for ZnO films to 6.78 for ZnO:Mn films with increasing the doping concentration to 4 %.

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