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Structural and Optical Characterization of Magnesium Doped Zinc Oxide Thin Films Deposited by Spray Pyrolysis

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Abstract

Pure and magnesium (Mg) doped zinc oxide (ZnO) thin films were prepared onto clean glass substrate by spray pyrolysis (SP) technique at the substrate temperature of 300°C. Various optical parameters such as absorption co-efficient, band gap energy, refractive index, extinction co-efficient of the thin films were studied using UV-VIS-NIR spectrophotometer in the photon wavelength range of 300-2500 nm. Optical band gap increased from 3.24 to 3.46 eV with the increase of Mg concentration from 0 to 40%. Transmittance and refractive index of the Mg doped ZnO thin films decreased due to the increase of Mg concentration. The EDX spectra confirmed the increase of Mg and consequent reduction in Zn content in the Mg doped ZnO thin films. Pure and Mg- doped ZnO films were annealed at 425°C for 1 hour. X-ray diffraction (XRD) study of the annealed films showed hexagonal type of polycry-stalline structure with the preferred orientation along (101) plane with some other peaks (100), (002), (102), (110), (103) and (112). From the XRD patterns it was found that grain size decreased from 63.45 to 36.56 nm, lattice constant *a* and c remained almost constant with Mg doping concentration.

Keywords: Spray pyrolysis, Mg doped ZnO thin films, band gap energy, XRD analysis, EDX analysis.

I. Introduction

In recent years, zinc oxide (ZnO) has been studied extensively by several researchers[1-4] due to its interesting physical and chemical properties. It is a II-VI compound semiconductor with a direct and wide band gap (~3.3 eV) at room temperature and a large exciton binding energy (~60 meV) [5]. It is highly transparent in the visible and near infrared region of electromagnetic spectrum and shows high refractive index [6]. Such remarkable optical properties of ZnO make it useful in short wavelength photonic devices. It is used in UV-light emitting diodes, transparent electrodes, laser diodes, window layers, photovoltaic cells, varistors, thin film transistors, heterojunction solar cells, etc. [7, 8]. ZnO is capable to form alloy with nickel (Ni), cobalt (Co), iron (Fe), magnesium (Mg), cadmium (Cd), etc. Band gap tuning can be achieved in such alloys in thin film form by changing the doping concentration [9, 10]. Mg is one of the popular materials in preparation of doped ZnO thin films. Because, atomic radius of Mg is comparable to that of Zn and lattice distortion occurs by a small amount when Zn ion is replaced by Mg ion [11, 12]. ZnO has wurtzite and MgO has rock salt cubic type of crystal structure. Because of such a mismatch in crystal lattices a difficulty arises during tailoring of band gap in the alloy formed by them. However, several works have been reported on preparation of Mg doped ZnO thin films by various techniques and successfully overcome the difficulty. Molecular beam epitaxy (MBE) [13], chemical vapor deposition (CVD) [14], Sol-gel [15], spray pyrolysis (SP) [16], magnetron sputtering [17], etc. are the techniques often used for deposition of Mg doped ZnO thin films. Spray pyrolysis (SP) is a very simple technique which is commonly used for deposition of oxide thin films, but a few works are reported on spray deposited Mg doped ZnO thin films.

In this work, Mg doped ZnO thin films were deposited onto glass substrate by SP techniques at the substrate temperature 300ºC. Optical transmittance of Mg doped ZnO thin films were measured in the wavelength range 300-2500 nm by UV-VIS-NIR spectrophotometer. Absorption co-efficient, extinction co-efficient, refractive index and optical band gap of Mg doped ZnO thin films were calculated. Pure and Mg-doped ZnO films were annealed at the temperature 425°C for 1 hour in the air. Structural properties of the annealed pure and Mg doped ZnO thin films were studied by XRD. EDX spectra of the films were also studied to confirm the presence of Mg in the Doped ZnO films. Optical and structural characteristics of some other compound semiconductors such as ZnSe [18], CdTe [19], GaAs [20, 21], etc. were also studied by the authors previously.

II. Methods

Undoped and Mg doped ZnO thin films were deposited onto chemically (with acetone and distilled water) and ultrasonically cleaned and dried glass substrate by a simple spray pyrolysis (SP) set up. Zinc acetate [$Zn(CH_3COO)_2.2H_2O$] and Magnesium acetate [$Mg(CH_3COO)_2.4H_2O$] were dissolved in water at room temperature to prepare the working solution. The concentrations of source materials were adjusted relatively to increase Mg doping between 0-40% in ZnO. The distance between the spray nozzle and the substrate is to be maintained about 25 cm and the flow rate of the solution during spraying was adjusted to about 3 ml/min and kept constant throughout the experiment. The deposition time was 7 minutes. The substrate temperature was about 300^0C and was measured by a Copper-Constantan thermocouple. The possible chemical reaction that takes place on the heated substrate as follows:

$$[Mg(CH_3COO)_2.4H_2O] + [Zn(CH_3COO)_2.2H_2O]$$

$$\xrightarrow[\text{300˚C}]{\text{Decomposes to}}$$

$$MgZnO\downarrow + CO_2\uparrow + CH_4\uparrow + \text{steam}$$

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Optical transmittance and reflectance of undoped and Mg-doped ZnO thin films were measured for photon wavelength range 300- 2500 nm using a Shimadzu UV-3100 UV- VIS-NIR spectrophotometer. The energy dispersive X-ray (EDX) analysis was done by Quanta Inspect IS50 detector which is operated in the range of 0 eV to 30 keV.

The as deposited ZnO thin films were annealed at 425ºC for one hour in air. A two-circle (2θ-θ) X-ray powder diffractometer, X' Pert PRO XRD Philips PW3040 with angular range $20° \leq 2\theta \leq 80^{\circ}$ and CuK_{α} radiation, operated at input power of 60 kV and 55 mA was used to determine the structural parameters of the annealed thin films. "X'Pert Highscore" computer software was used to study 2θ values, d value and full width half maximum (FWHM).

III. Results and Discussion

The transmission spectra of pure and Mg- doped ZnO thin films exhibit that pure ZnO has transmittance in the visible range of about 55%-79% as shown in Fig. 1. Mg doping causes decrease in the optical transmittance of ZnO thin films [22]. Transmittance of the Mg- doped ZnO thin films reduces with the increase of doping concentration between 0% and 30%. But, for 40% Mg doping transmittance increased up to 79%. Thus transparency of the film changes due to Mg doping in ZnO. Decrease in transmittance may occur due to the increase of particle size because of the progression of Mg in the ZnO thin films [23].

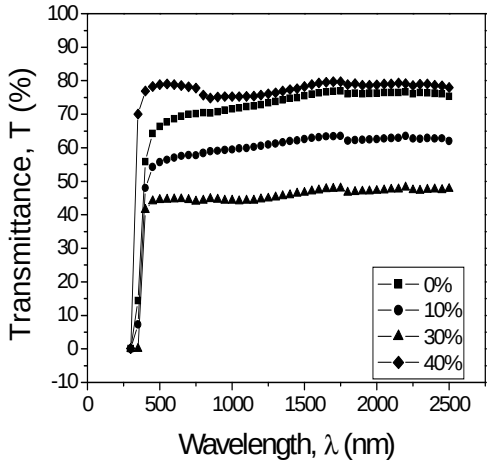

Fig.1. Transmittance versus wavelength graph for pure and Mg-doped ZnO thin films

The optical absorbance A is calculated from the following relation

$$A = \log_{10}\left(\frac{1}{T}\right) \quad (1)$$

Absorption co-efficient is then calculated from the relation

$$\alpha = 2.303\left(\frac{A}{t}\right) \quad (2)$$

Here, "t" represents the thickness of the films which is measured by Fizeau fringe interference method.

$$t = \frac{b}{a} \times \frac{\lambda}{2} \quad (3)$$

Where, λ is the wavelength of Na light, b is the fringe width and a is the fringe spacing.

Variation of absorption co-efficient with photon wavelength for pure and doped ZnO (Fig.2) shows higher absorption co-efficient in the ultra violet (UV) region and it falls sharply and then becomes almost constant in the vis-NIR region. Significant increase of absorption co-efficient with increasing Mg content in the ZnO thin films indicates improvement of optical absorption in the UV region. High values of absorption co-efficient (10^6-10^7 m^{-1}) are found for the films, which is important as it affects the solar conversion efficiency [24].

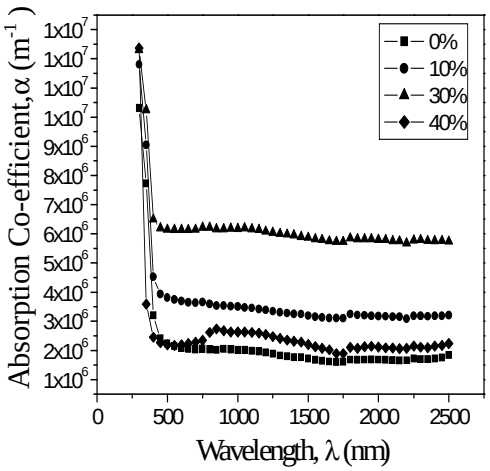

Fig. 2. Variation of absorption co-efficient with wavelength for pure and Mg-doped ZnO thin films

According to Tauc formula [25], absorption co-efficient α is related to the energy gap of a semiconductor as

$$\alpha h\nu = C\left(h\nu - E_g\right)^{\frac{1}{2}} \quad (4)$$

Where hν is the photon energy, n is an index related to the density of state (n= 1/2 for direct transition and n=2 for indirect transition) and E_g is the optical band gap of the semiconductor. Fig.3 shows the plot of $(\alpha h\nu)^2$ vs photon energy, the extrapolations of the straight portion of the graphs were used to estimate the band gap of ZnO thin films.

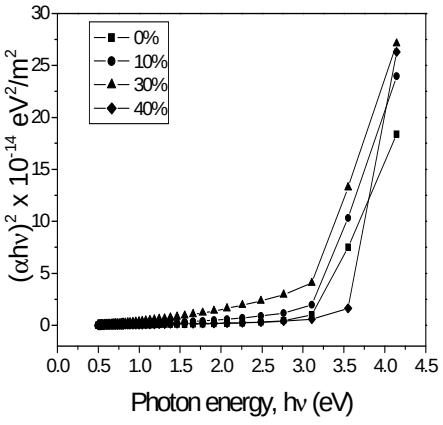

Fig. 3. $(\alpha h\nu)^2$ versus photon energy graph for pure and Mg-doped ZnO thin films

A direct band gap of 3.24 eV was found for pure ZnO films. The band gap increases from 3.31 eV to 3.46 eV with the increase of Mg doping concentration from 10% to 40%. It is evident that Mg^{2+} is incorporated into the ZnO lattice in the Mg- doped ZnO films grown by spray pyrolysis method. The reason of band gap increase may be considered as the consequence of replacement of Zn^{2+} by Mg^{2+} in the crystal lattice. Band gap widening can be elucidated by Burstein-Moss (BM) effect [26]. BM effect was explained for pure and doped ZnO thin films [27] and it was found from theoretical calculations that optical band gap of ZnO may increase up to 0.8-0.9 eV because of moderate and heavy doping. Experimentally the blue shift in band gap is always less than the values mentioned earlier [27].

Refractive index η was calculated using the relation

$$\eta = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (5)$$

Where k is the extinction co-efficient which was calculated using the following relation

$$k = \frac{\alpha\lambda}{4\pi} \quad (6)$$

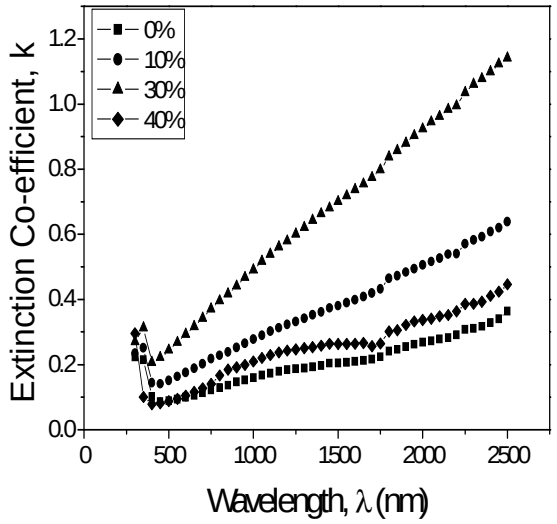

Fig.4. Variation of extinction co-efficient with wavelength for pure and Mg-doped ZnO thin films

Figure.4 shows that extinction co-efficient increases with photon wavelength for the pure and Mg doped ZnO thin films. Increase of Mg doping in ZnO thin films a shows raise in extinction co-efficient, signifying the increase of absorption in the films due to Mg incorporation. The plot of refractive index as a function of wavelength (Fig.5) for the Mg doped ZnO thin films exhibits decrease in average value of refractive index with the increase of Mg concentration. It may be attributed that Mg doping has decreased optical density of the medium. This is the direct effect of drop in transparency of ZnO thin films due to Mg doping.

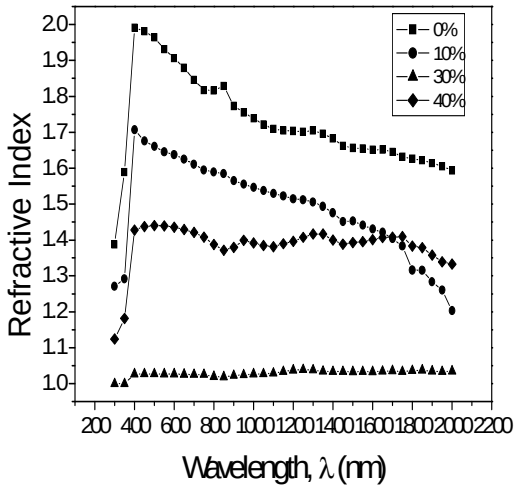

Fig. 5. Variation of refractive index with wavelength for pure and Mg-doped ZnO thin films

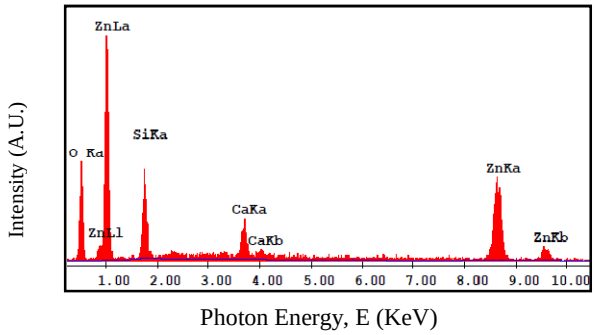

Fig. 6. EDX spectra of Pure ZnO thin film

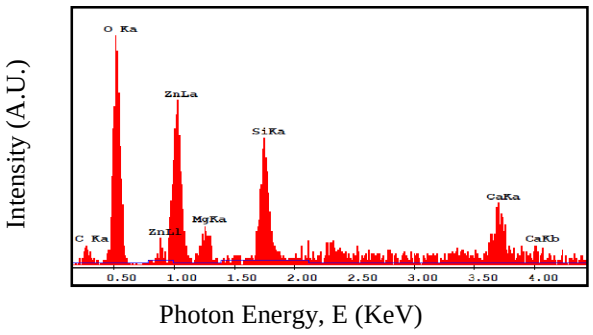

Fig. 7. EDX Spectra of as deposited 10% Mg doped ZnO thin film

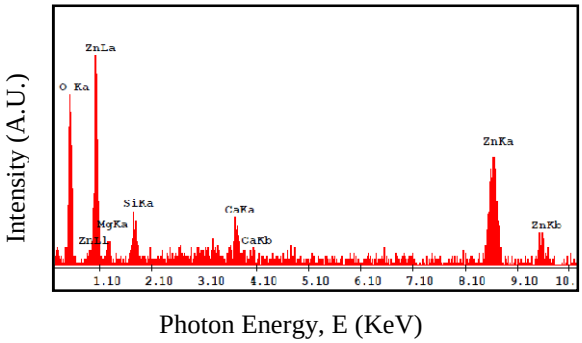

Fig. 8. EDX Spectra of as deposited 30% Mg doped ZnO thin film

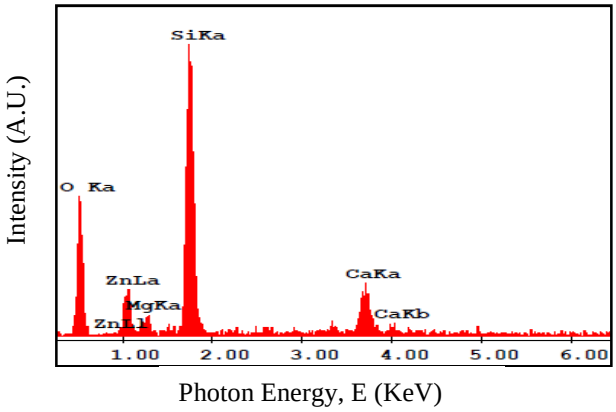

Fig. 9. EDX Spectra of as deposited 40% Mg doped ZnO thin film

Table 1. Quantitative results of Mg doped ZnO thin films from EDX analysis

Compositions of ZnO thin films	Element	Weight%	Atom%
Pure	O	6.85	21.49
	Zn	84.46	64.83
10%Mg doped	O	7.57	23.65
	Zn	86.24	66.07
	Mg	1.71	3.53
30% Mg doped	O	12.75	30.40
	Zn	71.08	51.47
	Mg	8.41	12.77
40% Mg doped	O	25.72	35.26
	Zn	61.54	43.49
	Mg	9.31	13.27

The quantitative results of Mg doped ZnO thin films from Table-1 show that the weight % for Mg increases with the increase of Mg doping. So, the doping concentration can be controlled precisely by the SP technique. It is observed that in all the spectra, there exist strong peak corresponding to O. There also exist peaks for Si and Ca due to the glass substrate ($CaSiO_3$). The results of the EDX analysis confirm that the deposited films are very close to the nominal composition.

The structural analysis of the pure and Mg- doped ZnO films were followed by X-ray diffraction measurements. The thin films were annealed at the temperature 425°C for 1 hour. All the films showed hexagonal wurtzite type of polycrystalline structure with the fundamental peaks for (100), (002), (101), (102), (110), (103) and (112) planes [23, 28]. There were slight shifts of the peak positions in the XRD reflections, but there was no peak in the XRD pattern corresponding to MgO or metallic Zn or Mg or any other phase. Thus, Mg doping does not cause any remarkable change in the wurtzite structure of ZnO. This may be due to the comparable ionic radii of Zn^{2+} and Mg^{2+} which made the substitution of Zn^{2+} easy with Mg^{2+} [29, 30].

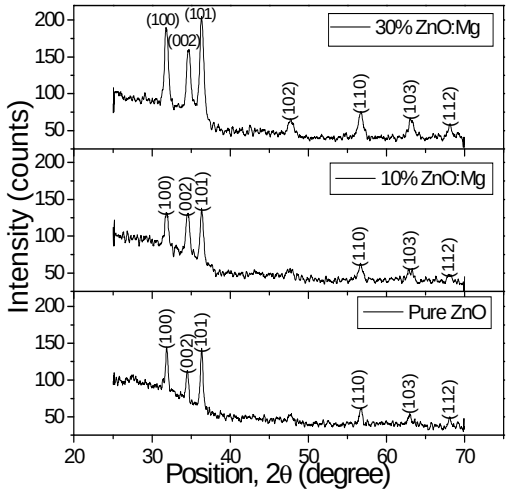

Fig. 10. XRD pattern of pure ZnO, 10% and 30% Mg doped ZnO thin film annealed at 425°C

The interplanar spacing for the hexagonal system is given as

$$\frac{1}{d_{hkl}} = \left[\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}\right]^{\frac{1}{2}} \quad (7)$$

Where, d_{hkl} is the inter planar spacing and it is related to the diffraction angle θ as

$$\frac{1}{d_{hkl}} = \frac{2\sin\theta_{hkl}}{\lambda} \quad (8)$$

The wavelength (λ) of X-ray was used 1.54178 Å for CuK_a line. The grain size, D, of the samples were determined quantitatively using the Scherrer formula[31]

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (9)$$

In general, β is obtained by measuring full width at half-maximum (FWHM) of a diffraction peak expressed in radians. k is a constant (=0.94). The values of *a*, c and D are shown in Table.2. The grain size in Mg-doped ZnO thin films was less than that of pure ZnO thin films, whereas the lattice parameters *a* and c were not affected much due to Mg doping. This is due to the fact that Mg^{2+} has smaller ionic radius than that of Zn^{2+}, thus it prefers to occupy the interstitial positions and as a result unit cell becomes compact [28, 32].

Table 2. Lattice parameters and grain size for pure and Mg doped ZnO thin films annealed at 425°C temperature for 1 hour

ZnO	Lattice parameter c (Å)	Lattice parameter *a* (Å)	Grain size D (nm)
Pure	5.264	3.229	63.45
10% Mg doped	5.264	3.229	49.35
30% Mg doped	5.268	3.231	36.56

IV. Conclusions

UV-vis-NIR spectroscopic analysis of the thin films showed reduction in transmittance and refractive index values and increase in absorption co-efficient, extinction co-efficient up to 30% of Mg doping. Optical band gap energy increased with the increase of Mg doping concentration. EDX spectra and XRD pattern of the ZnO thin films indicated the Mg^{2+} substitution in the thin films. Mg doping did not affect the hexagonal wurtzite structure of the undoped ZnO thin films. It was found from the XRD data that grain size decreased and lattice constants were almost constant with the increase of Mg doping. It can be concluded that Mg doping can make ZnO more useful for optical applications due to wide band gap.

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