

Structural and Optical Studies of Magnesium Doped Zinc Oxide Thin Films

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The paper describes the structural and optical properties of Magnesium doped Zinc Oxide (Mg = 3.5 %, 6 %, 9 %, 12 % by weight) thin films prepared by pulsed laser deposition technique. The samples are characterized by X-ray diffraction technique, Ultra-violet visible absorption spectroscopy, X-ray photoelectron spectroscopy. X-ray diffraction results reveal the polycrystalline nature of samples with no impurity or secondary phase formation. Ultra-violet visible absorption spectroscopy studies show the blue shift in the optical band gap subsequent to Mg doping. X-ray photoelectron spectroscopy results reveal the replacement of Zn²⁺ cation by Mg²⁺ ion.

Keywords: Semiconductor, Thin films, Doping, Laser deposition.

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1. INTRODUCTION

Zinc Oxide (ZnO) is one of the most promising material from the view point of its exceptional physical and optical properties. It is a II-VI semiconductor with a direct wide band gap of 3.37 eV ($\lambda = 368$ nm) at room temperature and a large exciton binding energy of 60 meV. Such unique properties of ZnO make it a good candidate for short wavelength photonic devices. Success of ZnO as a semiconductor also depends on the possibilities of band gap engineering [1]. ZnO has ability to make alloys with MgO and CdO. In particular, alloys made from MgO and ZnO give wide band gap semiconducting material with a highly tunable band gap which can be easily controlled over a wide range by making Mg_xZn_{1-x}O alloy thin films [2-4]. Thus MgZnO alloys have been increasingly investigated due to UV luminescence ranging from 150-400 nm or alternatively wide band gaps from 3.3 eV to 7.8 eV.

ZnO crystallizes in hexagonal wurtzite crystal structure (P6) with tetrahedral coordination among the cations and the anions while MgO favors the cubic Rocksalt structure () with octahedral coordination for both anions and cations [5]. However the similarity in the ionic radii between Mg²⁺ (0.57 Å) and Zn²⁺ (0.60 Å) allows some replacement in either structure.

In this paper we have investigated the structural and optical properties of Mg_xZn_{1-x}O thin films with different Mg concentrations prepared by pulsed laser deposition technique, as this enables the growth of good quality films because of the stoichiometric transfer from the target to the film.

2. EXPERIMENTAL DETAILS

ZnO and MgZnO films were deposited on glass substrate by Pulsed laser deposited technique (PLD), where MgZnO pellets prepared by solid state reaction route method were used as the target material. The films were deposited in a vacuum chamber using a 248 nm KrF excimer laser. The pulse repetition rate was set at 10 Hz and the energy density of the laser beam was 2 J/cm². The vacuum chamber was pumped

down to a base pressure of 4 nbar and the partial pressure of oxygen was 1×10^{-4} mbar with target to substrate distance maintained at 5 cm and optimized substrate temperature of 400 °C. After deposition, substrates were cooled at 2 °C/min in the same environment as used during deposition.

The crystalline quality and crystal orientation of prepared thin films were investigated by the X-ray diffraction technique (XRD) using CuK α radiation source ($\lambda = 0.1540$ nm). All samples were scanned from 20° to 80° continuously. Ultra-violet visible absorption (UV-Vis) measurements were performed to determine the optical band gap. We also performed the X-ray photoelectron spectroscopy (XPS) to determine the core level positions in the samples. XPS measurements were carried out at angle Integrated Photo-electron Beam-line on INDUS-1 Synchrotron radiation source at RRCAT, Indore. All the data were recorded using AlK α (≈ 1486.6 eV) radiation. To reduce the contamination effect, all the samples were subjected to a surface clean procedure by Ar⁺ bombardment in the vacuum chamber equipped in the XPS instrument.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

Fig. 1 shows the XRD pattern of pure ZnO film, Mg_xZn_{1-x}O ($x = 3.5$ %, 6 %, 9 %, 12 %) films grown by PLD technique. All the samples are polycrystalline in nature and two major peaks are found corresponding to hexagonal wurtzite structure of pure ZnO with a preferred orientation in the (002) and (004) directions. Only ZnO-related peaks were observed and no other peak related to MgO or Mg were detected which suggests that the films don't have any phase segregation or secondary phase formation. The strongest (002) peak of all Mg_xZn_{1-x}O is shifted towards higher diffraction angles compared to pure ZnO. This conforms to the expectation from Bragg's law; as Mg²⁺ ions with radius 0.57 Å replace Zn²⁺ ions with larger radius, 0.60 Å, the contraction of the unit cell occurs [6]. The average grain size is estimated by using the Debye Scherrer's

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formula. The grain size is reduced in $Mg_xZn_{1-x}O$ thin films as compared to the pure ZnO film which can be attributed to the fact that there is a increase in the 2θ value with a simultaneous increase in the FWHM value indicating the decrease in the grain size value. The replacement of Zn by Mg induced a significant change in the lattice constant i.e c parameter in Mg_xZnO alloys compared to those of ZnO which is quite expected because of the relatively lower ionic radius of Mg^{+2} ion compared to Zn^{+2} ion. Table 1 exhibits the calculated values of c -axis lattice parameter and the particle size of the grown thin films.

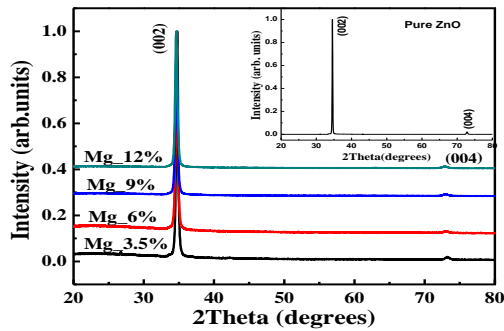


Fig. 1 – XRD pattern of the $Mg_xZn_{1-x}O$ ($x = 3.5\%$, 6% , 9% , 12%) and inset shows the XRD pattern of pure ZnO thin films deposited using PLD

Table 1 – Calculated c -axis lattice parameter and particle size of the grown samples

Sample	c -parameter	Particle size
Pure ZnO	5.180 Å	40.98 nm
$Mg_{0.035}Zn_{0.965}O$	5.159 Å	27.09 nm
$Mg_{0.06}Zn_{0.94}O$	5.173 Å	23.27 nm
$Mg_{0.09}Zn_{0.91}O$	5.175 Å	24.27 nm
$Mg_{0.12}Zn_{0.88}O$	5.176 Å	26.08 nm

3.2 Optical Properties

Fig. 2a and 2b shows the Optical absorption spectra of $Mg_xZn_{1-x}O$ ($x = 3.5\%$, 6% , 9% , 12%) thin films and optical band gap of as deposited thin films as a function of Mg concentrations, respectively. The band gap values of these materials can be determined using the following relation:

$$\alpha hv = K(hv - E_g)^{1/2},$$

where, K is a constant, $h\nu$ is the incident photon energy, α is the absorption coefficient, and E_g is the band gap energy. E_g is determined by extrapolating the straight line portion of the spectrum to $\alpha hv = 0$.

The measurements reveal that the films are highly transparent in the visible region. It has been observed that the absorption edge showed a blue shift for Mg doped ZnO film i.e band gap widening is due to the Mg doping. The optical band gap calculated from absorption spectra of ZnO, ZnO:Mg thin films are 3.24, 3.35, 3.42, 3.53 and 3.62 eV, respectively. The increase of optical band gap energy with Mg doping can be attributed to the so-called Moss-Burstein effect [7].

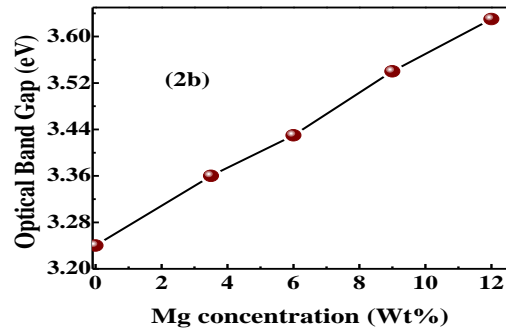
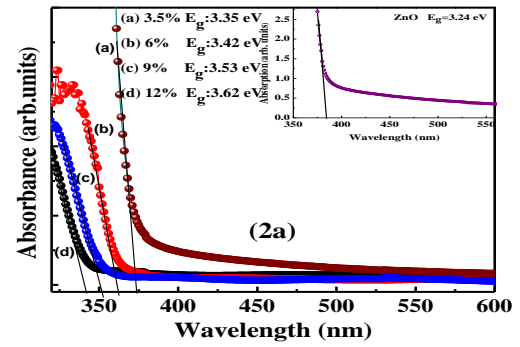


Fig. 2 – Optical absorption Measurement of $Mg_xZn_{1-x}O$ ($x = 3.5\%$, 6% , 9% , 12%) thin films deposited by PLD and inset shows the absorption spectra of pure ZnO (a), 2b shows linear variation of the band gap with Mg concentration, respectively

Substitution of Zn^{2+} by Mg^{2+} results in an increase in oxygen vacancies and electron concentration due to the electronegativity and ionic radius difference between Zn and Mg. This increase in carrier density results in the lifting of the Fermi-level towards the conduction band of the degenerate semiconductor and a consequent band gap widening.

3.3 XPS Results

XPS core level spectra of Zn $2p_{3/2}$ in ZnO and $Mg_{0.035}Zn_{0.965}O$ thin films is shown in Fig. 3. All the CL peaks have been fitted using Tougaard background and voigt profile. The addition of Mg to ZnO can either replace Zn^{2+} or form MgO secondary phase [6]. All XPS spectra were calibrated by the C 1s peak (284.6 eV) to compensate the charge effect.

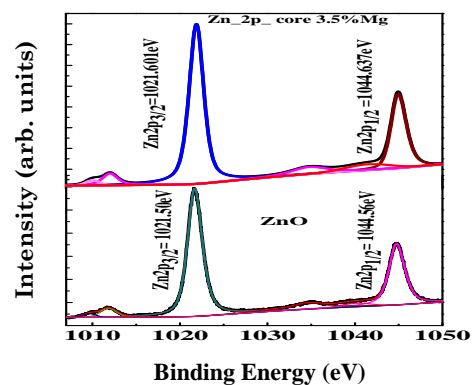


Fig. 3 – Zn $2p_{3/2}$ core X-ray level spectrum of undoped and 3.5 % Mg-doped ZnO thin films

In the case of pure ZnO, the Zn $2p_{3/2}$ XPS peak appeared at 1021.50 eV represents the formation of Zn-O bonds while in case of Mg doped ZnO films, the Zn $2p_{3/2}$ peak shifted towards higher binding energies, which results from the replacement of Zn^{2+} by Mg^{2+} and an added Zn-O-Mg binding energy.

Fig. 4 shows the core level spectra of Mg $2p_{3/2}$ in $Mg_{0.035}Zn_{0.965}O$ thin film. The Mg $2p_{3/2}$ XPS peak in the Mg doped ZnO thin film centered at around 49.5 eV can

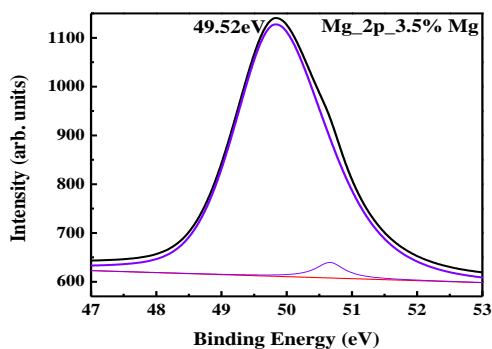


Fig. 4 – Mg $2p_{3/2}$ core X-ray level spectrum of 3.5 % Mg-doped ZnO thin films

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be ascribed to the presence of Mg^{2+} replacing Zn^{2+} . No positive Mg $2p_{3/2}$ binding energy shift toward the Mg $2p_{3/2}$ (MgO) binding energy of around (50-51) eV was identified, which was in correlation with absence of MgO phase.

4. CONCLUSION

XRD measurement shows that all the films so prepared were oriented to the c axis of wurtzite ZnO structure and no other features related to Mg & MgO were observed. The optical band gap calculated from UV-Vis absorption spectra of the thin films increases with the increase of Mg content. XPS studies confirmed the substitution of Zn^{2+} by Mg^{2+} in Mg doped ZnO samples and the absence of MgO phase.

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