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# Ferromagnetism in sol-gel derived ZnO: Mn nanocrystalline thin films

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## ABSTRACT

This paper reports the growth of Mn doped ZnO thin films by sol-gel technique with different Mn concentration (0-20 %). Structural and vibrational properties have been measured by X-ray diffraction and Raman spectroscopy. The films exhibit crystalline nature with (002) preferential orientation. The crystallite size and lattice parameters have been estimated as a function of Mn concentration. The Raman spectrum of the ZnO film shows the peaks corresponding to  $E_2$  (high) mode at 434 cm<sup>-1</sup> assigned to Zn-O bond and  $A_1$  (LO) mode at 575 cm<sup>-1</sup>. The elemental analysis of the films have been performed using X-ray photoelectron spectroscopy confirms the presence of Zn, O and Mn in doped films. Surface morphology and roughness of the films are observed by atomic force microscopy. The optical bandgap is found to decrease with Mn concentration as estimated by Tauc's plots. Room temperature ferromagnetism has been obtained in ZnO: Mn thin films by superconducting quantum interference device. Copyright © 2016 VBRI Press.

Keywords: ZnO: Mn; dilute magnetic semiconductor; thin films; ferromagnetism.

## Introduction

Recent studies have shown that II-VI based diluted magnetic semiconductors (DMSs) are promising materials spintronic device applications. The principal for requirement in realizing spintronic devices is to develop single phase DMSs with ferromagnetism at or above room temperature. Doping of ZnO with transition metals (TM) into the cation sites illustrate promising results for devices such as non-volatile memory, logic devices, spin valve transistor, spin light-emitting diode, data storage and information processing devices [1-3]. The indispensability of ZnO lies in its properties like wide direct bandgap (3.34 eV), low toxicity and large exciton binding energy (60meV) at room temperature [4]. Theoretical simulations have suggested that doping in ZnO with TM can amend its electronic structure [5, 6]. The magnetic anisotropy of the dopant cation is proposed to be a signature of intrinsic ferromagnetism in dilute magnetic semiconductors [7]. The magnetic properties of TM doped ZnO are highly sensitive to the preparation method and conditions. In fact the distributions of Mn ions are very different due the different growth modes and mechanism which affects the structural and magnetic properties of Mn doped ZnO thin films. The low solubility of Mn in ZnO or the formation of secondary phases even at very low doping concentration is the main problem to find the origin of ferromagnetism. However, it has also been reported that the thermal solubility of Mn in ZnO thin films grown by pulsed laser deposition (PLD) is larger than 10 mol % [8]. The Mn-doped ZnO system is popular among researchers because of their high thermal

solubility and high magnetic moments at room temperature. Due to the closer radii of  $Zn^{2+}$  (0.074 nm) and  $Mn^{2+}$  (0.080 nm), the dopant ion can easily substitute the  $Zn^{2+}$  site without altering the original structure of ZnO. If not so, clustering or precipitation may be responsible for the ferromagnetic behavior. If the carriers do not mediate the ferromagnetic interaction, this can limit the usefulness of spintronics devices fabricated from such materials [9]. Inspite of the various studies there is no clear confirmation about the nature and origin of the ferromagnetic properties of ZnO based DMS [10].

Till now, various methods such as radio frequency magnetron sputtering [11], pulse laser deposition [12], reactive magnetron co-sputtering [13], laser molecularbeam epitaxy [14] and sol-gel method [15] have been used to deposit the ZnO: Mn nanostructure thin films. In this context, the sol-gel method is widely accepted because of its simplicity, low cost and easy control of chemical composition. In this paper sol-gel spin coating method is used to for the deposition of ZnO: Mn thin films onto the corning glass substrate. The structural, vibrational, optical and magnetic behavior of the ZnO:Mn thin films have been investigated with different Mn doping concentration.

# Experimental

## Material synthesis

ZnO and ZnO:Mn thin films were prepared on corning glass substrates (7059) using sol-gel spin coating technique. Precursor solutions were prepared by using zinc acetate dihydrate (ZnAc) [Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O, Alfa-aesar],

manganese acetate tetrahydrate (MnAc)  $[C_4H_6MnO_4.4H_2O,SRL],$ methanol [CH<sub>3</sub>OH] as solute, dopant and solvent respectively. 0.2 M sol was prepared by dissolving ZnAc in methanol. The mixture was stirred on a magnetic stirrer for 60 min at room temperature results in a milky solution. The monoethanolamine (MEA) [CH<sub>2</sub> (OH).CH<sub>2</sub>.NH<sub>2</sub>. Thomas Baker] was further integrated as a stabilizer in the prepared solution and again stirred for 30 min to obtain a clear transparent solution. For doping, another sol of 0.2 M of MnAc solution was prepared in the same way as ZnAc solution. Proportionate volumes of MnAc solution were added to the ZnAc solution in order to get desirable doping concentrations between 0-20 %. The modified sols were kept for 48 hrs for ageing before deposition of thin films. The sols were found stable even after one month. Before deposition the substrates were cleaned thoroughly by dipping in a mixture of deionized water (DI) and HCl, then cleaned ultrasonically followed by acetone and with DI water for 10 min respectively. Deposition of films was carried out in atmospheric air using spin coater with a spinning speed of 2500 rpm for 30 sec. For consummate evaporation of solvents, the films were preheated at a 300 °C temperature for 10 min on the hot plate. Since the MEA evaporates at 170 °C and ZnAc decomposes thermally at a temperature of 300 °C [16]. The overall process was reiterated 14 times to obtain homogeneous ZnO and ZnO: Mn thin films. The post deposition annealing was carried out at a 550 °C temperature for duration of 60 min for all the films.



Schematic 1. Steps involved in the growth of ZnO:Mn thin films.

## Growth mechanism

**Schematic 1** shows the main steps of preparation of thin films. The methods contains three major steps (i) preparation of precursor solution; (ii) deposition of prepared solution uniformly on the substrate and (iii) Heat treatment. It has been reported that there are two possible ways of describing the growth of ZnO crystals: Ostwald

ripening and aggregation [17]. The nucleation and growth process of the films involve nuclei formation, growth and coalescence. Sufficient energy is also required to start growth of the grains to initiate coalescence [18]. Moreover, it is believed that the kinetics of nucleation and growth are strongly dependent on the properties of solvent. Nucleation and growth are faster for shorter chain alcohol rather than longer one. In proposed sol-gel mechanism, zinc acetate dihydrate Zn (CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O would transform to mono-acetate when it was added in methanol. So when  $[CH_3COOZn]^+$  is formed, it makes a complex with MEA during the process. Then these complexes undergo transformation through hydrolysis and polymerization. After that, heat treatment will lead to formation of oxide. For doped ZnO, dopant salt, manganese acetate tetrahvdrate  $[C_4H_6MnO_4.4H_2O]$ was added with Zn (CH<sub>3</sub>COO)<sub>2</sub> in methanol. For stability,  $Mn^{2+}$  ions has to be substituted in place of  $Zn^{2+}$  without changing the original structure of ZnO which leads to the formation of Mn doped ZnO system.

# Material characterization

To analyze crystallinity and orientation of the films, X-ray diffraction (XRD) measurements were taken using a Bruker D8 X-ray diffractometer with CuKa radiation of wavelength 1.54056 Å. The diffraction pattern was recorded by varying the  $2\theta$  value in the range of 25-60°. Vibrational modes were analyzed by micro Raman system (Horiba Yvon Lab Raman spectrophotometer) having a 488 nm argon ion laser source. The thickness has been measured by Veeco Dektak 150 surface profiler with an uncertainty of 0.1 nm. The thickness of the films was found to be in the range of 150-200 nm. The X-ray photoelectron spectroscopy (XPS) was recorded at 15KV and 20 mA using Al anode by Multi-technique analysis system (OEM-Omicron Nanotechnology GmbH) equipped with AlKa monochromatic source with 1486.6 eV energy. Surface roughness and morphology of the films were obtained by atomic force microscope (AFM, JSPM-5200TM, JEOL). Optical transmittance measurements were obtained using Shimadzu solid spec 1500 UV-vis spectrophotometer in the wavelength range of 300-900 nm. The magnetic quantification was carried out at room temperature using super conducting quantum interference device (SOUID: Quantum design MPMS-5P) in a field up to 4000 Oe.

# **Results and discussion**

## Structural properties

**Fig. 1(A)** shows the XRD pattern of ZnO and ZnO:Mn thin films for different Mn concentration (0-20 %). The synthesis of ZnO can be confirmed by the presence of diffraction peaks at 31.7° (100), 34.5° (002) and 36.4° (101) corresponding to wurtzite hexagonal structure of ZnO. These peaks are well matched with JCPCD card (No. 36-1451) with lattice constant  $a_o = b_o = 3.250$  Å and  $c_o = 5.195$  Å. The films are crystalline in nature having c-axis orientation. The incorporation of Mn ion into the ZnO lattice results in the broadening of the peaks which degrades the quality of the films. No traces of Mn metal or clusters were observed below the solubility limit of Mn for less than 10 % in present work. However, at high Mn dopant concentration, small signal of secondary peaks was observed. The diffraction patterns of 10 %, 15 % and 20 % ZnO: Mn depicts the presence of two phases simultaneously i.e.  $MnO_2$  and  $Mn_2O_3$ .



**Fig. 1.** (A) XRD pattern of ZnO:Mn thin films with different Mn concentration (a) 0%; (b) 1%; (c) 2%; (d) 5% (e) 10%; (f) 15%; (g) 20%. (B) Variation of grain size, bond length and lattice parameters (Inset) as a function of Mn concentration.

The peaks at  $35.6^{\circ}$  (312) and 28.6 (122) could be indexed to  $Mn_2O_3$  commonly known as bixbyite having lattice structure (JCPCD (024-0508))orthogonal According to the JCPCD (024-0735), the peak at  $28.6^{\circ}$  (110) can also be related to MnO<sub>2</sub> having pyrolusite tetragonal structure. It has been reported that the low solubility of transition metals in ZnO results in the formation of secondary phases. However, different values of dopant solubility have been reported i.e. formation of Mn<sub>3</sub>O<sub>4</sub> phase at 3 at% Mn concentration has been observed in  $Zn_{1-x}Mn_xO$  thin film deposited on sapphire substrate by pulse laser deposition [19]. Whereas, no phases formation has been found by Yadav et al. [20]. This difference is most likely attributed to growth process and conditions, which allows different distribution of Mn within the ZnO structure. The crystallite size (D) corresponding to (002) peak was calculated by Scherrer's formula [21],

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where,  $\lambda$  is the X-ray wavelength of CuK $\alpha$  (1.54046Å),  $\theta$  is diffraction angle (in radians) and  $\beta$  is the full width at half maximum of the peak.

Crystallite size was found to be decreasing with the Mn doping concentration as shown in **Fig. 1(B)**. It has been observed that the addition of Mn concentration in the ZnO lattice can also affect lattice parameters and hence, the bond length. The ZnO bond lengths (*l*) for pure and ZnO: Mn thin films have been obtained by relation [22],

$$l = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2}$$

where, a and c are the lattice parameters and  $\boldsymbol{u}$  is the positional parameter in the wurtzite structure and defined as

$$u = \frac{a^2}{3c^2} + 0.25$$

The evaluated bond length and lattice parameters (inset) of the films are found to increase slightly with Mn dopant concentration as given in **Fig. 1(B)**. This can be due to the incorporation of  $Mn^{2+}$  at  $Zn^{2+}$  site into the films without affecting the structure up to the solubility limit.

#### Vibrational properties

Raman spectra of ZnO and ZnO: Mn films have been investigated as a function of doping concentration. The samples were illuminated by a 488 nm argon ion laser. The hexagonal wurtzite structure of ZnO belongs to  $C_{6v}^4$  space group, in Schoenflies notation. At the  $\Gamma$ -point of the Brillouin zone, the optical phonons have the irreducible representation  $\Gamma_{opt} = A_1 + 2B_1 + 2E_2 + E_1$  where E modes are two fold degenerate.  $A_1$  and  $E_1$  are polar phonons, exhibit different frequencies for the transverse-optical (TO) and longitudinal optic (LO) due to long-range electrostatic forces. E<sub>2</sub> is non-polar phonon modes have two frequency corresponds to E<sub>2</sub> (high) associated with oxygen atoms and  $E_2$  (low) is associated with Zn sub lattice whereas  $B_1$  is silent mode i.e. both Raman and infrared inactive. The Raman spectra of ZnO and ZnO: Mn thin film in the range  $200-1000 \text{ cm}^{-1}$  is shown in **Fig. 2.** 



Fig. 2. Raman spectra of ZnO:Mn thin films. Inset shows the intensity of peak at  $667 \text{ cm}^{-1}$  at high Mn concentration.



Fig. 3. AFM surface images of ZnO:Mn thin films (a) 0% and (b) 5%.

The sharpest peak observed at 434 cm<sup>-1</sup> and another peak at 576 cm<sup>-1</sup> is assigned to  $E_2$  (high) and  $A_1$  (LO) modes respectively, which confirms the wurtzite ZnO structure. However, doping of Mn in ZnO results in broadening of  $E_2$  (high) mode which confirms the successful incorporation of Mn ion into ZnO lattice. In addition, a peak at 667 cm<sup>-1</sup> was found in 5 % to 20 % Mn doped sample which was absent in undoped ZnO and low doping i.e, 1 % and 2 % thin films which can be attributed to local vibration mode. The intensity of 667 cm<sup>-1</sup> peak getting sharper with the increase in doping concentration upto 20 % as shown in inset of **Fig. 2**. The existence of 667 cm<sup>-1</sup> mode is controversial, however it has been reported that the local modes are possible for frequency above 600 cm<sup>-1</sup> i.e, above optical mode [**23**].

Also, at M-Brillouin point zone the combination of TA+LO is assigned to 666 cm<sup>-1</sup>. On the other hand, the tetragonal rutile type  $MnO_2$  has been characterized by a Raman band at 667 cm<sup>-1</sup> having  $A_{1g}$  symmetry. The tetragonal structured  $MnO_2$  with a space group of P4<sub>2</sub>/mmm allows eleven optical phonons,  $A_{1g}+A_{2g}+A_{2u}+B_{1g}+B_{2g}+E_g+2B_{1u}+3E_u$  out of which  $1A_{1g}+1B_{1g}+1B_{2g}+1E_g$  are Raman-active. Hence, the XRD

#### Surface morphology

The surface morphology of ZnO and ZnO:Mn films were examined by atomic force microscope (AFM). The three-dimensional (3D) surface images are presented in **Fig. 3**. The incorporation of Mn dopant in ZnO lattice affects the normal growth of the grains, which is probably due to large strain in the films. The surface roughness were found to be 6.19 nm for ZnO thin film which further decreases with the Mn dopant concentration.



Fig. 4. XPS survey spectra of ZnO:Mn thin films (a) 0 % (b) 5 %. Inset shows the enlarged view of  $Mn2p_{3/2}$  for doped film.

## XPS analysis

The XPS spectra were recorded for ZnO and ZnO: Mn (5 %) thin films in order to investigate the chemical composition and state of the films. The Fig. 4 shows the survey spectra of ZnO and ZnO: Mn thin films in the binding energy range 0-1050 eV. The carbon 1s peak positioned at 284.8 eV is used as internal reference for correcting the data. XPS spectra confirmed the presence of Zn, O and Mn elements in the films. The detailed scans for Zn, O and Mn have also been observed with a step size of 0.1 eV. It was observed that the peaks of  $Zn2p_{1/2}$  and Zn2p<sub>3/2</sub> are located at 1021.0 eV and 1044.1 eV respectively. The energy separation (~ 23.1 eV) between these peaks is consistent with divalent Zn. The results are in good agreement with the standard data of zinc oxide and also consistent with other reported work [25]. However, a small shift in the binding energy corresponding to  $Zn2p_{1/2}$ and  $Zn2p_{3/2}$  was observed while maintaining the energy separation of 23.1 eV for ZnO: Mn thin film, which can be due to the substitution of  $Mn^{2+}$  ion in place of  $Zn^{2+}$  and the formation of Zn-Mn bonding structure. The peak at ~530.0 eV can be assigned to oxygen lattice O<sup>2-</sup> into ZnO whereas the binding energy side at 531.7 eV is attributed to the oxygen vacancy (V<sub>o</sub>), oxygen interstitial (O<sub>i</sub>) and oxygen antisite  $(O_{Z_n})$ . It has been reported that these defects plays a significant role in luminescence and magnetic properties of ZnO [26, 27]. The detailed scan corresponding to Mn is also shown in inset of **Fig. 4**. The results exhibit that the binding energy of  $Mn2p_{3/2}$  is located at ~641.6 eV for ZnO: Mn (5 %) thin film, which is attributed to divalent Mn state and in agreement with the earlier reported data [**28**].



**Fig. 5.** (a) Transmittance spectra of ZnO:Mn thin films. (b) Tauc's Plot:  $[((\alpha hv)]^2$  versus photon energy (hv) of ZnO:Mn thin films. Inset shows the variation of Eg with Mn Concentration.

#### **Optical properties**

Optical transmission spectrum of ZnO and ZnO:Mn thin films have been observed by varying the wavelength range from 350-900 nm. **Fig. 5(a)** shows the typical transmission spectrum of the ZnO and ZnO: Mn thin films. The transmittance of all ZnO: Mn thin film decreased with Mn dopant concentration. This is due to the decrease in the crystallite size with Mn concentration leading to higher density of grain boundaries which in turn increases the scattering of light and reducing the optical transmittance of the films [**29**].

The absorption coefficient has been estimated using the relation,

$$\alpha = \left(\frac{1}{d}\right) \ln \left(\frac{1}{T}\right)$$

where, T is the transmittance and d is the film thickness. The bandgap was evaluated using the tauc's plot

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where, A is a constant, hv the photon energy and  $E_g$  is the bandgap.



Fig. 6. M-H curve of ZnO: Mn thin film at room temperature. Insets show (a) the magnified M-H loop (b) ZFC and FC curve at 0.1 tesla field for ZnO: Mn (5 %) thin film.

The bandgap has been estimated by extrapolating the straight portion of  $(\alpha hv)^2$  versus hv plot to intersect the energy axis at  $\alpha = 0$  shown in Fig. 5(b) for ZnO and ZnO: Mn. The value of the E<sub>g</sub> for an ZnO thin film is found to be 3.25 eV and 3.12 eV for ZnO: Mn (5 %) thin film. The decrease in the band gap is mainly arise due to the sp-d exchange interaction between the ZnO band electrons and localized d-electron associated with Mn<sup>2+</sup> cation. This interaction leads to decrease in the energy band by lowering the conduction band and elevating the valence band. This can also be attributed to the increase in the density of Mn induced defect states with the higher concentration of Mn doping which leads to decrease in the bandgap [30]. Similar results of decreasing bandgap have also been reported on ZnO: Mn thin films prepared by other techniques [31, 32].

#### Magnetic properties

The Magnetization of ZnO: Mn thin film was measured at room temperature as a function of magnetic field (M-H curve) by SQUID. Fig. 6(a) shows the typical M-H curve for ZnO: Mn thin films after subtracting the diamagnetic contribution of corning glass substrate. Inset of Fig. 6(a) shows the magnified M-H loop of ZnO: Mn (5 %) thin film. No Mn metal or related oxides appear to be ferromagnetism at room temperature. The oxides of Mn like MnO and MnO<sub>2</sub> are antiferromagnetic except Mn<sub>3</sub>O<sub>4</sub> which is ferromagnetic with a curie temperature of 46 K in thin films [33]. This suggests, the ferromagnetic property observed by M-H curve at room temperature in the ZnO: Mn thin films is mainly due to the incorporation of Mn ion into the Zn site below the solubility limit. However, the presence of MnO<sub>2</sub> at high doping concentration leads to super-exchange antiferromagnetic coupling between Mn<sup>2+</sup> ions which increase with the doping concentration. As a result, the anti-ferromagnetism dominated over the ferromagnetic nature of the films. The origin of ferromagnetism cannot completely attribute to formation of secondary phases, since Mn itself is antiferromagnetic with a Neel temperature of 100K. Inset of **Fig. 6(b)** shows the zero field cooled (ZFC) and field cooled (FC) magnetization versus temperature (M-T) curve at 0.1 T field. It can be seen that ZFC and FC both traces the same path. The observation of clear hysteresis and behavior of M-T curve suggest room temperature ferromagnetism in ZnO: Mn thin films without the contribution of secondary phases. The variation of coercivity and retentivity with the Mn concentration is shown in **Fig. 7**. The coercivity of the films doped with higher concentration was found to be decreasing that can be attributed to the formation of secondary phases and clustering of Mn based-oxides which are antiferromagnetic in nature [**34, 35**].



Fig. 7. Variation of coercive field and ramanence with Mn doping concentration.

#### Conclusion

In summary, the ZnO: Mn nanocrystalline thin films with (002) preferred orientation have been successfully synthesized on corning glass substrate by low cost sol-gel spin coating process. XRD measurements have shown that the Mn doping concentration soluble in ZnO is less than 10 % without forming secondary phases. Above this solubility limit, the Mn dopant degrades the structure and quality of the films owing to the formation of Mn clusters or secondary phases that do not incorporate in the  $Zn^{2+}$  site of ZnO. Raman measurement has also revealed an additional mode at 667 cm<sup>-1</sup> due to high Mn doping concentration associated to formation of MnO<sub>2</sub> with A<sub>1g</sub> symmetry. XPS measurement confirmed the incorporation of divalent Mn state in ZnO lattice. The average optical transmittance for ZnO is above 85 % in the visible region and it reduces for ZnO: Mn thin films. The ferromagnetism has been observed in ZnO: Mn thin films at room temperature. This will be a useful step for the fabrication of semiconductor devices that can hold their ferromagnetic properties at or above room temperature. The ZnO: Mn thin films with high transmittance along with magnetic properties will also find applications in magneto-optic devices.

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#### Author Contribution

The authors contributed equally to this work. All authors read and approved the final manuscript. Authors have no competing financial interests.

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