Chapter 4

Structural, optical and magnetic properties of transition metal doped ZnO thin films grown by PLD

4.1 Introduction

Dilute magnetic semiconductors (DMS) have been of great interest in the last decade due to the combination of properties of the doped magnetic elements and the carriers of the host. Novel functions can be achieved using DMS, for example, in spin-field effect transistors or spin light emitting diodes, if the injection, transfer and detection of the carrier spin can be controlled electrically or optically [34, 106]. Magnetic properties of II-VI based and III-V based diluted magnetic semiconductors (DMS) have attracted much attention nowadays [33, 46, 107–110]. Spintronics is based
on concepts that utilize the quantum mechanical spin properties of carriers in addition to the carrier charge in realizing electronic functionality. The magnetic properties of a DMS are intimately coupled to the carrier concentration and carrier type within the material through the s-d and p-d exchange integrals. This is beneficial in that it allows external control over the magnetic properties by electronically or optically manipulating the carriers in the DMS. For example, this type of external control has been demonstrated in (In, Mn)As electric field-gated structure. While there has been much work on the III-V DMS materials, notably (In, Mn)As and (Ga, Mn)As, their ferromagnetic (FM) Curie temperatures (Tc) 90K for (In, Mn)As and 172K for (Ga, Mn)As. The realization of practical commercial or mobile devices will require the development of semiconductors that can retain their FM properties above room temperature. As a result, significant research effort has been focused on developing alternative DMS materials with higher Curie temperatures \cite{31, 32, 111}. Carrier spins are used to transport, store and process information in novel ways, providing both enhanced performance and new functionalities in traditional microelectronic devices.

Among the other DMS, ZnO is especially interesting because the valency and ionic radii of the cations match those of the magnetic transition metals. The wide band gap of ZnO (3.37 eV) and large excitonic binding energy (60 meV) are promising characteristics that the room temperature magnetic and transparent optical hybrid devices can be realized with a single compound \cite{106, 112}. This fact allows ZnO doping at high concentrations of magnetic ions. Moreover, some recent theoretical \cite{33, 39} and experimental \cite{113–117} reports have shown the room temperature FM in ZnO films highly doped with magnetic impurities. It is predicted that
n-type co-doping should reinforce the ferromagnetic ordering. Two principal approaches are used to introduce the transition metal ions into semiconductor materials. First the magnetic impurities are implanted into the host matrices [56]. Second the magnetic elements are introduced during the growth [118]. The second method is preferable for the growth of thin films and nanostructures.

This chapter is divided into two parts: first part deals with the growth and characterization of Co and Mn doped ZnO thin films and second part describes the synthesis and characterization of Ni and Cu doped ZnO thin films by PLD for spintronic applications.

4.2 Co and Mn doped ZnO thin films grown by PLD

The Co and Mn doped ZnO thin films have been prepared by various methods like rf-sputtering, chemical vapor deposition, sol-gel methods [33, 119–122]. Pulsed laser deposition (PLD) offers the advantages such as deposition at relatively high oxygen pressure, high deposition rate and growth of highly oriented crystalline films at low substrate temperature. One of the early works on cobalt-doped ZnO by Ueda et al. [46] showed that the material to be FM above 280K with 5-25% Co and 1% Al (added as an n-type dopant) without the secondary phases. Theoretical calculations by Sato et al. [38] and Yoshida et al. [39] predict that ZnO shows ferromagnetism for lower Mn doping concentration (5%) without any additional dopants for increasing the free electron concentration. Since then experimental and computational studies have been carried out on the origin of ferromagnetism in Co and Mn doped ZnO. Some groups observed room
temperature ferromagnetism in the absence of secondary phases or cobalt clusters [42, 48, 123, 124]. However, others report no ferromagnetism at room temperature [43, 125, 126] or that the observed ferromagnetism originates from metallic cobalt clusters [127] or manganese oxides [128]. The origin and reproducibility of the ferromagnetism are still controversial and the magnetic properties are very sensitive to thin film preparation methods and conditions.

During PLD the incorporation of the Co and Mn dopants into the ZnO lattice causes disorders, defects in the lattice and formation of secondary phases which can be analyzed by Raman spectroscopy [128–130]. The magnetic and optical properties strongly depend on the point defects and grain boundary defects arising in the thin film due to doping. In this chapter the magnetic, optical and structural properties of pulsed laser deposited Co and Mn doped ZnO films with dopant content up to 10 at.% are discussed. The intrinsic magnetic behavior and the origin of the defect induced Raman active modes in the Mn doped ZnO thin films were elucidated. The structural and magnetic properties can depend sensitively on film growth parameters and Co and Mn doping percentage. The crystal structure of the Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O thin films were confirmed by XRD and Raman analysis. XPS confirms the oxidation sates of Co and Mn dopants in the ZnO thin films.

4.2.1 Experimental

The properties of the deposited thin films depend on the specific synthesis route of the target. The targets were prepared by standard solid-state reaction. Stoichiometric amount of ZnO and Co$_3$O$_4$ powders were mixed in methanol medium for two hour and calcinated at 800°C for 15 hrs. The
Experimental powder was grounded again and pressed in the form of circular pellets of 1” diameter. These pellets sintered at 900 °C for 24 hrs were used as targets for laser ablation. In a similar method Zn$_{1-x}$Mn$_x$O targets were prepared by weighed amount of ZnO and MnO.

Co and Mn doped ZnO thin films were grown on fused silica substrates by pulsed laser deposition (PLD) technique. The fourth harmonic of Nd:YAG laser (266 nm) with repetition rate of 10 Hz and pulse width 6 - 7 ns was used for ablation. The laser beam was focused on the surface of the target kept inside the vacuum chamber through a quartz window. The ablation was carried out at laser energy density of 1.1 J cm$^{-2}$. The target was kept rotating during the ablation for uniform deposition and to avoid the pitting of the target surface. Fused silica substrate was placed in front of the target at a distance of 5.5 cm. The chamber was pumped down to a base pressure of 4×10$^{-6}$ mbar and then oxygen was introduced into the chamber through mass flow controller. The deposition parameter such as laser energy, substrate to target distance, substrate temperature and oxygen pressure were initially optimized to get good crystalline films. Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O thin films with various Co and Mn concentrations were grown at various substrate temperatures ($T_S = 350^\circ C - 650^\circ C$) varying the oxygen partial pressure ($P_{O_2} = 0.05 - 5\times10^{-4}$ mbar). The deposition duration was 1 hr for the growth of all thin films resulting a thickness $\sim$ 230 nm.

The crystalline nature of Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O bulk powders and thin films were investigated by Rigaku D-max C x-ray diffractometer with Cu K$\alpha$ (1.5418 Å) line. Stylus profiler (Dektak 6M) was used for thickness analysis. The surface morphology of the thin films were analyzed by Agilent 5500 series atomic force microscopy and scanning electron
microscopy. The transmission spectra of the films were recorded using UV-vis-NIR spectrophotometer (JASCO-V 570). Raman measurements of the Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O bulk powders and thin films were performed by Lab RAM HR spectrophotometer (HORIBA JOBIN YVON) using 514.5 nm Ar$^+$ laser. The magnetization of all the samples was carried out using Vibrating sample magnetometer and Quantum design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.

### 4.2.2 Results and discussion

![XRD pattern](image)

**Figure 4.1:** XRD pattern of (a) Zn$_{1-x}$Co$_x$O and (b) Zn$_{1-x}$Mn$_x$O targets for (x= 0-0.15).
The properties of the deposited thin film depends on the growth conditions and also on the specific synthesis route of the target. The Co and Mn doped ZnO thin films for magnetic studies were grown at a lower $T_S$ of 450 °C and PO$_2$ ($5 \times 10^{-4}$ mbar) to avoid the possible formation of CoO, Co$_2$O$_3$ in Zn$_{1-x}$Co$_x$O thin films and MnO, Mn$_2$O$_3$ in the Zn$_{1-x}$Mn$_x$O thin films. The x-ray diffraction pattern of Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O ($x = 0, 0.01, 0.03, 0.05, 0.10, 0.15$) targets are shown in figure 4.1, which confirms the wurtzite hexagonal phase for all the compositions. No secondary phases were detected by XRD upto 10 at.% of Co and Mn doped ZnO bulk powders.

Figure 4.2: XRD pattern of (a) Zn$_{1-x}$Co$_x$O and (b) Zn$_{1-x}$Mn$_x$O thin films ($x = 0-0.10$) grown by PLD at $T_S$ of 450 °C and 0.005 mbar PO$_2$.

The XRD pattern of Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O thin films deposited by PLD at $T_S$ of 450 °C and 0.005 mbar PO$_2$ with different Co and Mn concentrations are shown in figure 4.2. The Co and Mn doped ZnO films show only the (002) diffraction peak indicating the films growth along the c axis perpendicular to the substrate surface. None of Zn$_{1-x}$Co$_x$O or Zn$_{1-x}$Mn$_x$O films show any impurity phases i.e., no peaks corresponding to either cobalt or cobalt oxides and manganese oxides appear in the diffraction pattern. The (002) diffraction peak is shifted slightly to lower angles with increase of
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dopant concentration. The very small increase in the c axis lattice constant is due to the substitution of relatively large ionic radii Co$^{2+}$ and Mn$^{2+}$ ions at Zn$^{2+}$ site in ZnO.

The formation of secondary phases in Zn$_{0.95}$Co$_{0.05}$O thin films were ruled out from the XRD analysis. The oxidation state of the dopant are further examined by XPS measurements. Figures 4.3 (a),(b) and (c) shows the Zn (2p), O (1s) and Co (2p) core level XPS spectra of the Zn$_{0.95}$Co$_{0.05}$O thin film. Two strong peaks appear at 1021.2 eV and 1044.4 eV, which are in agreement with the binding energies of Zn 2P$_{3/2}$ and Zn 2P$_{1/2}$, respectively [88]. The two peaks have narrow line widths, indicating that Zn$^{2+}$ ions are dominant in the thin films. The O (1s) peak is asymmetric and stronger peak at 530.2 eV may be attributed to O$^{2-}$ ions in Zn-O and Co-O bonds [88, 131]. The incorporation of Co is clearly demonstrated by the core level spectra of Co (2p). The Co 2P$_{3/2}$ peak appears at 782 eV. No XPS signals from metallic Co was detected [131]. These results indicate that the doped Co ions are in divalent state. Two XPS peaks of Co$^{2+}$ ions with satellite peaks confirms the uniform incorporation into the ZnO host lattice without any secondary phases.

Figure 4.3: XPS spectra of (a) Zn 2p (b) O 1s and (c) Co 2p core levels from Zn$_{0.95}$Co$_{0.05}$O thin film.
Figure 4.4: XPS spectra of (a) Zn 2p (b) O 1s and (c) Mn 2p core levels from Zn$_{0.97}$Mn$_{0.03}$O thin film.

Figure 4.4 (a-c) shows the Zn (2p) and Mn (2p) and O (1s) core level XPS spectra of the Zn$_{0.97}$Mn$_{0.03}$O thin film. Two strong peaks appear at 1021.2 and 1044.4 eV, which are in agreement with the binding energies of Zn 2P$_{3/2}$ and Zn 2P$_{1/2}$ respectively. The two peaks have narrow line widths, indicating that Zn$^{2+}$ ions are dominant in the thin films and the influence of Mn impurities is negligible. We got stronger peak of O (1s) at 530.2 eV may be attributed to O$^{2-}$ ions in Zn-O and Mn-O bonds. The peak at 531.8 eV associated with the loosely bound oxygen (e.g.,adsorbed O$_2$,OH) chemisorbed on the surface and/or grain boundary of polycrystalline film [132] was not observed. The incorporation of Mn is clearly demonstrated by the core level spectra of Mn (2p). The Mn 2P$_{3/2}$ peak appears at 640.5 eV. No XPS signals from metallic Mn (637.7 eV) were detected. These results indicate that the doped Mn ions are in divalent state [133] without any metallic Mn. The XPS peaks of Mn$^{2+}$ ions were very weak, implying the low incorporation of Mn ions into the ZnO lattice.

SEM images of Zn$_{1-x}$TM$_{x}$O (TM=Mn,Co) thin films deposited on fused silica at substrate temperature 400°C and 0.05 mbar partial pressure of oxygen is shown in figure 4.5. SEM images shows that the ZnO morphology
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Figure 4.5: SEM images of (a) ZnO b) Zn$_{0.97}$Co$_{0.03}$O and (b) Zn$_{0.97}$Mn$_{0.03}$O thin films deposited at $T_S$ of 400°C and 0.005 mbar PO$_2$. is in the form of grains but Zn$_{0.97}$Co$_{0.03}$O thin film show dendrite like growths. The Zn$_{0.97}$Mn$_{0.03}$O thin films show uniformly placed small grains.

Figure 4.6: AFM images of Zn$_{1-x}$Co$_x$O thin films, (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.05$ and (d) $x = 0.10$ deposited at $T_S$ of 450°C and 0.005 mbar PO$_2$.

The film thickness was measured using Dektak stylus profiler. The average thickness of the film was found to be $\sim$ 230 nm. AFM images of Zn$_{1-x}$Co$_x$O thin films ($x = 0-10$) on fused silica substrate at 450°C and 0.005 mbar oxygen partial pressure is shown in figure 4.6. The undoped
ZnO film having uniformly distributed smaller grains with RMS roughness of about 6 nm. The Zn$_{0.97}$Co$_{0.03}$O films have densely packed columnar growth with RMS roughness of 9 nm and at higher doping become randomly distributed grains. The AFM images of Mn doped ZnO thin films prepared under the same condition shows smaller grains (fig. 4.7). The Zn$_{0.97}$Mn$_{0.03}$O film has uniformly distributed smaller grains and the highest RMS roughness observed was 10 nm. At higher Co and Mn doping concentration the morphology of the films changed and RMS roughness increased with Co and Mn concentration. The texture and the crystal quality of Co and Mn doped ZnO films analyzed by AFM measurement.

Figure 4.7: AFM images of Zn$_{1-x}$Mn$_x$O thin films grown by PLD at 450$^\circ$C $T_S$ and 0.005 mbar PO$_2$ (a) $x = 0.03$, (b) $x = 0.05$, (c) $x = 0.10$.

The structurally characterized Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O films transparency, band gap and defect emissions were analyzed by transmission and photoluminescent studies. The optical transmission spectra of Co and Mn doped ZnO films for ($x$=0-0.100) are shown in figure 4.8. The colour of the Zn$_{1-x}$Co$_x$O films changes from light green to dark green on increasing the Co content but in the case of Zn$_{1-x}$Mn$_x$O it changes from light yellow to amber on increasing the Mn content due to the change in their optical properties. All samples have an average transmittance greater than 80%
indicating good optical quality of the deposited films with low scattering or absorption losses. The green colour of the Zn$_{1-x}$Co$_x$O film is assigned to typical d-d transitions of high spin states Co$^{2+}$ 3d$^7$(4F) in tetrahedral oxygen coordination. In its neutral charge state, the Co$^{2+}$ ions have an [Ar] 3d$^7$ electron configuration. The atomic 4F ground state splits under the influence of the tetrahedral component of the crystal field in to $^4$A$_2$ ground state and $^4$T$_2$+$^4$T$_1$ excited states. The absorption around 1.89, 2.03 and 2.19 eV are in agreement with the Co$^{2+}$ d-d transitions $^4$A$_2$(F)→$^2$A$_1$(G), $^4$A$_2$(F)→$^4$T$_1$(P) and $^4$A$_2$(F)→$^2$E$_1$(G) respectively [134]. The appearance of these transitions clearly confirms that the Co$^{2+}$ ions are in tetrahedral crystal field symmetry. However the transparency of Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O films fades away when the Co and Mn dopant concentration increases.

**Figure 4.8:** Transmission spectra of (a) Zn$_{1-x}$Co$_x$O and (b) Zn$_{1-x}$Mn$_x$O thin films (x = 0-0.10) at 450°C T$_S$ and 0.005 mbar PO$_2$.

The variation of band gap energy with Co and Mn concentration in the Zn$_{1-x}$TM$_x$O thin films are shown in figure 4.9. The ZnO film shows a sharp absorption edge at 3.35 eV. The band gap estimated from transmission spectra shows a blue shift with increase in Co and Mn concentration.
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Figure 4.9: Band gap variation of Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O with concentrations (x = 0-0.10).

[125, 135, 136]. The band gap of the Co doped ZnO varies from 3.35 eV to 3.78 eV as the cobalt concentration increases from 1-10 at.%. In the case of Mn the band gap is blue shifted from 3.35 eV to 3.92 eV. The absorption takes place in a wide range, therefore it is more reasonable to assign this absorption to the charge-transfer transition between donor ionization levels of Mn ions and the band continuum as observed in (ZnMn)S and (ZnMn)Se based on the Anderson impurity model [43]. The observed blue shift was attributed to the Burnstein-Moss effect due to increase of carrier concentration. The Hall measurement confirms the increase of carrier concentration with Co and Mn doping. The band gap is defined as the separation in energy between the top of the valence band and the unoccupied energy states in the conduction band. The shift arises because the Fermi energy ($E_F$) lies in the conduction band for degenerate n-type doping (or in the valence band for p-type doping). The filled states therefore block thermal or optical excitation. Consequently the measured band gap determined from the
onset of interband absorption moves to higher energy - a blue shift. Similar observations of band gap widening on Co and Mn doping in ZnO have been reported in literature [135, 136].

![Figure 4.10: PL spectra of Zn$_{0.97}$TM$_{0.03}$O thin films grown at T$_S$ of 450 °C and 0.005 mbar PO$_2$ ($\lambda_{exc} = 325$ nm).](image_url)

The photoluminescence (PL) spectra of the Zn$_{1-x}$TM$_x$O films are shown in figure 4.10. All the PL spectra have an emission band in ultraviolet (UV) region at 380 nm. The intensity of near band energy (NBE) emission depends strongly on the crystalline quality of ZnO films. The crystalline quality of Co and Mn doped ZnO films decreases with increase in TM concentration. As a result, the intensity of the UV emission also decreases [96, 137]. The NBE emission results from the exciton related recombination [96, 138]. So the intensity and the FWHM of the UV emission strongly depend on the microcrystalline structure of the Zn$_{1-x}$TM$_x$O films.

Raman scattering is one of the effective technique to investigate the crystal structure, phase purity and defects in the thin films. Upon Co and Mn doping, the overall shape of the Raman spectrum changes, due to the loss of symmetry conservation leading to the appearance of ‘silent’ and mixed Raman modes from points off the center of the Brillouin zone.
Wurtzite ZnO belongs to the C\textsubscript{6v} [103] space group with two formula units per primitive cell. At the G point of the Brillouin zone, the A\textsubscript{1}+E\textsubscript{1}+2E\textsubscript{2} modes are Raman active based on the group theory analysis. Polar A\textsubscript{1} and E\textsubscript{1} modes exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) phonons, because of the macroscopic electric field associated with the LO phonons. The non polar E\textsubscript{2} modes have two frequencies, namely E\textsubscript{2\text{\textsuperscript{high}}} and E\textsubscript{2\text{\textsuperscript{low}}}.

![Figure 4.11: Raman spectra of (a) Zn\textsubscript{1-x}Co\textsubscript{x}O and (b) Zn\textsubscript{1-x}Mn\textsubscript{x}O targets (x = 0-0.10).](image)

Raman spectra of the Zn\textsubscript{1-x}Co\textsubscript{x}O and Zn\textsubscript{1-x}Mn\textsubscript{x}O bulk powders are shown in figure 4.11. The characteristic optical modes of wurtzite ZnO are
observed at $E_{2}^{\text{low}}$ (99 cm$^{-1}$), $E_{2}^{\text{high}}$ (436 cm$^{-1}$), $A_{1}^{\text{TO}}$ (376 cm$^{-1}$) and $E_{1}^{\text{LO}}$ (584 cm$^{-1}$) [103, 139]. Apart from the normal modes of vibrations of ZnO two additional modes at 332 cm$^{-1}$ ($I_{1}$) and 525 cm$^{-1}$ ($I_{2}$) are observed. The modes $I_{1}$ and $I_{2}$ are assigned as multi-phonon scattering considering the two-phonon process in the disordered lattice due to Co and Mn doping. The modes are identified as $(E_{2}^{\text{high}} - E_{2}^{\text{low}})$ and $(E_{2}^{\text{high}} + E_{2}^{\text{low}})$, respectively [139]. The oxygen sub-lattice vibrational optical mode ($E_{2}^{\text{high}}$) was found shifted toward lower frequency compared to the ZnO bulk powder samples. A broad band ranging from 500 to 600 cm$^{-1}$ appears at higher Co and Mn concentration, the defect induced modes. The intensity of the broad band increases significantly with Co and Mn doping concentration. When Co and Mn is substituted the Zn lattice site in ZnO, it forms the ternary alloy of Zn$_{1-x}$Co$_{x}$O and the allowed region for the optical phonon becomes finite than the ZnO host lattice. The atomic substitution leads to the structural disorder and breaks the translational symmetry of the allowed phonons. The disorder induced effect causes the phonon line shapes become broadened and shifted towards lower frequency [103, 128, 129, 139, 140].

The Raman spectra of the Co and Mn doped ZnO thin films are shown in figure 4.12. The Zn$_{1-x}$Co$_{x}$O thin films show three predominant modes at $E_{2}^{\text{low}}$ (99 cm$^{-1}$), $E_{2}^{\text{high}}$ (436 cm$^{-1}$), $A_{1}^{\text{LO}}$ (581 cm$^{-1}$) and one silent mode at $B_{1}^{\text{low}}$ (268 cm$^{-1}$). But in Mn doped ZnO thin films we got three modes $E_{1}^{\text{LO}}$, $E_{2}^{\text{high}}$ and $A_{1}^{\text{LO}}$ modes and are presented only in highly c-axis oriented thin films. The broadening of the $E_{2}^{\text{high}}$ modes and its red shift indicates the substitution of Co and Mn into the ZnO sub-lattice [141]. The structural disorder due to the atomic substitution breaks the translational symmetry of the zone centered (k=0) optical phonons of the host lattice, which leads to the contribution of (k$\neq$0) phonons to the finite size effects. Thus
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Figure 4.12: Raman spectra of (a) Zn$_{1-x}$Co$_x$O and (b) Zn$_{1-x}$Mn$_x$O thin films (x= 0-0.10) at 450°C T$_S$ and 0.005 mbar PO$_2$.

Raman spectra confirm the incorporation of Co into the ZnO lattice. The E$_{2}^{\text{low}}$ mode of ZnO was shifted toward higher frequencies and there was an increase in FWHM on Co and Mn substitution into ZnO lattice. A broad band ranging from 340 to 600 cm$^{-1}$ appears at higher Mn concentration and its intensity increases significantly with increase of doping percentage. Similar observations are reported in literature [142, 143]. The multi-peak-fitting result reveals that at 10% Mn doping, the broad band could be
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deconvoluted into five peaks, denoted as P₁-P₅ (figure 4.13).

![Raman spectra of Zn₀.₉₀Mn₀.₁₀O thin film and the inset shows the multi-peak fitting results.](image)

**Figure 4.13:** Raman spectra of Zn₀.₉₀Mn₀.₁₀O thin film and the inset shows the multi-peak fitting results.

The disorder-induced effects of $E_{2low}$ mode in Zn₀.₉₀Mn₀.₁₀O can be explained by alloy potential fluctuations (APF) using a spatial correlation (SC) model. Using an ab initio calculation, Manjun et al. [144] predicted that the $B_{1low}$, $2B_{1low}$ and $B_{1high}$ silent modes of wurtzite ZnO occur at 261, 522 and 552 cm⁻¹, respectively. The peaks, $P_2$ (434 cm⁻¹), $P_3$ (485 cm⁻¹) and $P_4$ (552 cm⁻¹/$B_{1high}$) and $P_5$ (620 cm⁻¹/$E_{1LO}$) are present only in heavily Mn-doped ZnO films. Generally, the $A_{1LO}$ mode is weak because of two opposing contributions from the Frohlich interaction and the deformation potential [144]. However, the breakdown of translational symmetry due to structural disorder caused by a random incorporation of the dopants will lead to alloy potential fluctuations. The spatial correlation
function of the phonon becomes finite which results in the enhancement and broadening of the $A_{1}^{LO}$ mode. These results are comparable with other groups findings, Hu et al. [129] and Wang et al. [145]. The defect induced Raman active modes arises due to two major types. The first one is the disorder-induced effects arising on the incorporation of Mn into the ZnO lattice, $P_2$ (434 cm$^{-1}$), $P_3$ (485 cm$^{-1}$) and $P_4$ (552 cm$^{-1}$/$B_{1}^{high}$) and surface phonon modes. The second one is due to the native lattice defects $P_5$ (620 cm$^{-1}$/$E_{LO}$) [129, 144–146].

Figure 4.14: M-H curve of (a) Zn$_{1-x}$Co$_x$O ($x = 0.05, 0.10$) and (b) Zn$_{1-x}$Mn$_x$O ($x = 0.03, 0.10$) bulk powder samples.

Magnetic properties of Zn$_{1-x}$TM$_x$O powders and thin films were investigated using vibrating sample magnetometer (VSM) and quantum design SQUID magnetometer respectively. Figure 4.14 shows the field dependent magnetization (M-H) of the Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$Mn$_x$O pellet at 300 K. The Zn$_{0.95}$Co$_{0.05}$O pellet shows ferromagnetic hysteresis loop with coercivity of 540 Oe but at higher Co concentrations Zn$_{1-x}$Co$_x$O pellets show a paramagnetic behavior. Metallic cobalt, CoO, Co$_2$O$_3$ and nanoclusters of Co are responsible [131] for the reduction of ferromagnetism in Zn$_{1-x}$Co$_x$O.
bulk powders. In the case of Mn doped samples, the Zn$_{0.97}$Mn$_{0.03}$O pellet shows hysteresis loop at room temperature. The magnetic moment of Zn$_{0.97}$Mn$_{0.03}$O increases with increase in external applied field, indicating a paramagnetic nature with the ferromagnetic loop. The oxides of Mn (MnO, Mn$_2$O$_3$) are responsible for the reduction of ferromagnetism at higher Mn doping concentrations [54, 145].

Figure 4.15: M-H curve for Zn$_{0.95}$Co$_{0.05}$O film at 300K. Inset shows (a) magnified view near zero field and (b) M-H curve of the ZnO film.

The M-H curve of the Zn$_{0.95}$Co$_{0.05}$O thin film is shown in figure 4.15. The samples were prepared and handled carefully to avoid any possible magnetic contamination. Theoretical modeling shows that Co$^{2+}$ - oxygen vacancies are capable of producing long-range ferromagnetic ground state in ZnO [131, 147]. The M-H curve (figure 4.15) of the Zn$_{0.95}$Co$_{0.05}$O thin films exhibits coercivity of 450 Oe. The saturation magnetic moment of the Zn$_{0.95}$Co$_{0.05}$O thin film is 0.41µ$_B$/Co atom. The high spin moment (3d$^7$) of
Co$^{2+}$ is $3\mu_B$, while that of metallic cobalt is $1.7\mu_B$. The ZnO film prepared under the same condition shows diamagnetic nature (inset figure 4.15). Recent studies show that antiferromagnetic oxides below certain critical sizes can exhibit ferromagnetism [131, 147]. In the case of Zn$_{1-x}$Co$_x$O thin films nanoclusters of Co and oxides (CoO, Co$_2$O$_3$) suppress the room temperature ferromagnetism.

The magnetization curve of the Zn$_{0.97}$Mn$_{0.03}$O thin film at 300K is shown in figure 4.16 and the magnified view near zero field shown in the inset. It clearly shows the ferromagnetic loop at lower magnetic field with coercive field of 150 Oe. The curve shows the room temperature ferromagnetism for Zn$_{0.97}$Mn$_{0.03}$O thin film [148, 149]. The saturation magnetic moment of the Zn$_{0.97}$Mn$_{0.03}$O thin film is $0.37\mu_B$/Mn atom. At higher doping percentages the Mn clusters or oxides(MnO,Mn$_2$O$_3$) suppress the room temperature ferromagnetism in Zn$_{1-x}$Mn$_x$O thin films and paramagnetism is observed [40]. Increased number of n-type carriers and clustering of Mn at higher concentrations in the Zn$_{1-x}$Mn$_x$O thin films deviate the system from achieving room temperature ferromagnetism [40, 149].

The shape of the M-H curve reveals that there is some trace of paramagnetism in the Zn$_{0.97}$Mn$_{0.03}$O and Zn$_{0.95}$Mn$_{0.05}$O thin film also. According to Ruderman-Kittel-Kasuya and Yosida (RKKY) interactions the concentration of free electrons plays a major role in stabilizing the magnetic phase in the Co and Mn doped ZnO thin films. At lower atomic doping concentrations the possibilities of secondary phases in the thin films are over ruled by XRD and Raman measurements [142, 143, 146]. At higher Co and Mn doping concentration, the possible origin of paramagnetism is due to the increase of nearest neighbor interactions among the dopant (Mn$^{2+}$ and Co$^{2+}$) ions in the ZnO matrix [40, 131, 147, 150].
4.2.3 Conclusion

The structure and magnetic properties of Co and Mn doped ZnO films were studied in respect to the Co and Mn concentration and growth conditions. All the films show a wurtzite crystal structure with c axis orientation. The surface morphology of the synthesized samples was characterized by atomic force microscopy. The $\text{Zn}_{1-x}\text{Co}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin film shows blue shift in the band gap with increase in cobalt and manganese concentration respectively. The presence of non-polar $E_2^{\text{high}}$ and $E_2^{\text{low}}$ Raman modes in thin films indicates that Co and Mn doping did not change the wurtzite structure of ZnO. $\text{Zn}_{0.95}\text{Co}_{0.05}$ thin films shows ferromagnetic behavior at room temperature with a saturation magnetization of 0.41$\mu_B$/Co. In the case of Mn doped ZnO we got magnetization at lower Mn doping (3 at.%) with saturation magnetization of 0.37$\mu_B$/Mn atom. Oxygen va-
cancies created during growth are likely necessary for the observed ferromagnetism. The magnetic properties rely on intricate combination of transition metal dopants and material defects such as oxygen vacancies which are difficult to characterize. XPS spectra confirms the incorporation of Co$^{2+}$ and Mn$^{2+}$ into the ZnO lattice. The formation of secondary phases in Zn$_{0.95}$Co$_{0.05}$ and Zn$_{0.97}$Mn$_{0.03}$O thin films were overruled by XPS analysis. Hence the observed RTFM in Co and Mn doped ZnO thin films were intrinsic in nature.

4.3 Ni and Cu doped ZnO thin films grown by PLD

4.3.1 Introduction

Transition metal-doped ZnO is a promising candidate for spintronics. In order to realize spintronic devices we have to obtain room temperature ferromagnetism in single phase materials without any secondary phases. After the theoretical prediction of RTFM in transition metals doped ZnO thin films the experimental and computational studies have investigated on the origin of ferromagnetism in Ni and Cu doped ZnO. The morphological, optical and magnetic properties of ZnO can be modified by doping with Ni or Cu. The Cu dopant was considered as the origin of green emission in ZnO:Cu thin films [116]. The intrinsic magnetic and Raman spectra of the Ni and Cu doped ZnO thin films and nanostructures have gained much attention recently [113–117].

In this section the structural, optical and magnetic properties of pulsed laser deposited Ni and Cu doped ZnO films with dopant content up to 15%
were discussed. The origin of the defect induced Raman active modes in the Ni and Cu doped ZnO thin films elucidated. The Ni and Cu doping will affect the lattice dynamic properties of the host material and the Raman scattering will provide the information about the crystal structure. The parameters of the Raman modes such as peak width and peak positions is useful in analyzing lattice dynamics. Optical and structural characterizations are used to explore the origin of defect induced photoluminescence in Cu doped ZnO thin films. The formation of defect levels and optical transitions in pure ZnO, Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O thin films were elucidated using UV-vis absorption and PL studies. The structural information were gathered by XRD and Raman analysis and the oxidation states of the Ni and Cu dopant is confirmed by XPS analysis. Magnetic studies confirms the intrinsic origin of room temperature ferromagnetism in Ni and Cu doped ZnO thin films.

4.3.2 Experimental

Ni and Cu doped ZnO pellets were used as target for the deposition of Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O thin films. The Zn$_{1-x}$Ni$_x$O composite targets were obtained by the standard solid-state reaction. Appropriate amount of ZnO (Alfa Aesar, 99.999%) and NiO (Alfa Aesar, 99.999%) were first weighed, mixed with a few drops of poly vinyl alcohol (PVA) as binder and ground along with methanol for 1 hour. Similarly Zn$_{1-x}$Cu$_x$O targets were prepared by conventional solid state reaction using ZnO (Alfa Aesar, 99.999%) and CuO (Alfa Aesar, 99.999%). The mixed powder was blended mechanically again so that the mixture become homogeneous. The mixture was then calcined at 800°C in air for 12 hours. The resultant powder was grounded again and was pressed into round pellets with 1” diameter and 5
mm thickness. The targets were finally obtained after sintering the pellets in oxygen at 900 °C for 24 hours.

Q-switched fourth harmonic Nd:YAG laser (266 nm) with repetition rate of 10 Hz and pulse width of 6-7 ns was used for the laser assisted film deposition. The ZnO films and Ni and Cu doped ZnO films were deposited on quartz substrate by ablating sintered ZnO, Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O targets. Before starting deposition the chamber was evacuated to a pressure of $10^{-6}$ mbar. The ablation was carried out at laser energy density of 1.1 J cm$^{-2}$. The target was kept rotating during the ablation for uniform ablation and to avoid the pitting of the target surface. The film properties were investigated by depositing them at various substrate temperatures keeping the substrate to target distance 5.5 cm and varying the oxygen pressure to obtain crystalline film.

The structural characterization of as prepared Ni and Cu doped ZnO thin films were carried out by PANalytical X’Pert PRO X-ray diffractometer using Cu Kα line (1.5418 Å). The thickness of the as prepared thin films were measured by Stylus Profiler (Dektak 6M). The surface morphology of the thin films was examined by Agilent 5500 series atomic force microscopy. The transmission spectra of the films were recorded using UV-vis-NIR spectrophotometer (Jasco-V 570). The photoluminescent and Raman measurements of the Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O thin films were analyzed by Lab RAM HR spectrophotometer (HORIBA JOBIN YVON). An excitation wavelength of 325 nm for the PL measurements and 514.5 nm for Raman studies were used. The magnetic measurements were carried out by Quantum Design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.
4.3.3 Results and discussion

![Figure 4.17](image)

**Figure 4.17:** XRD pattern of (a) $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ and (b) $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ targets for ($x = 0$ to 0.15).

The properties of the deposited thin films not only depend on the growth conditions but also on the target preparation conditions. The phase purity of the target and films has been investigated by X-ray diffraction (PANalytical X’pert PRO). The x-ray diffraction pattern of $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ and $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x = 0$ to 0.15) targets sintered at 900 $^\circ$C are shown in figure 4.17. All the diffraction peaks agreed with the reported ICSD data file.
Results and discussion

The presences of any other secondary phases were not detected by the XRD upto \( x = 10 \), but on 15\% Ni doping in ZnO we got an additional (002) peak of Ni\(_2\)O\(_3\). No secondary phases were detected in Zn\(_{1-x}\)Cu\(_x\)O targets upto \( x = 0.15 \). The colour of the pellets become greenish blue and light green by the increase of Ni and Cu concentration. These structurally characterized pellets were used as the targets for the PLD technique.

![Figure 4.18: X-ray diffraction pattern of (a) Zn\(_{1-x}\)Ni\(_x\)O and (b) Zn\(_{1-x}\)Cu\(_x\)O thin films grown by PLD at \( T_S \) of 450\(^\circ\)C and 0.005 mbar PO\(_2\).](image)

The structural properties of the Ni and Cu doped ZnO thin films were investigated by depositing them at various substrate temperatures and different substrate to target distance. The x-ray diffraction pattern of highly oriented Zn\(_{1-x}\)Ni\(_x\)O and Zn\(_{1-x}\)Cu\(_x\)O thin films grown at substrate temperature (\( T_S \)) 450\(^\circ\)C and oxygen partial pressure (PO\(_2\)) 0.005 mbar are shown in figure 4.18. No peaks corresponding to either CuO or Cu\(_2\)O appear in the diffraction patterns of Zn\(_{1-x}\)Cu\(_x\)O. The Zn\(_{1-x}\)Ni\(_x\)O thin films do not show any sign of impurity phases ie. no peaks corresponding to NiO, NiO\(_2\) or Ni\(_2\)O\(_3\) were observed. The (002) diffraction peak is shifted slightly to higher angles with increase of Ni and Cu concentration. The grain size and c axis lattice constant of Ni and Cu doped ZnO shows a small decrease...
due to the substitution of relatively smaller ionic radii of \{\text{Ni}^{2+}(0.55 \, \text{Å})\} or \text{Cu}^{2+}(0.57 \, \text{Å})} dopants at \text{Zn}^{2+} \text{ site (0.60 Å)} in \text{ZnO} \text{ wurtzite network [56, 152]. This confirms that the disordering increases with the increase in Ni and Cu concentration in Zn}_{1-x}\text{Ni}_x\text{O} \text{ and Zn}_{1-x}\text{Cu}_x\text{O} \text{ thin films resulting in small grain growth. The incorporation of 3d transition metal has reported generally to deteriorate the crystallinity of ZnO [152].}

**Figure 4.19:** XPS spectra of (a) Zn 2p, (b) O 1s and (c) Ni 2p and (d) Cu 2p core levels from Zn$_{0.97}$Ni$_{0.03}$O and Zn$_{0.97}$Cu$_{0.03}$O thin film.

The XPS measurements were carried out to study the bonding nature and oxidation state of the \text{Cu} into the Zn$_{0.97}$Cu$_{0.03}$O thin films (fig. 4.19 d). The \text{Zn}^{2+} shows strong peaks at 1021.2 eV (2P$_{3/2}$) and 1044.4 eV (2P$_{1/2}$) [153]. The sharp peaks indicate the dominance of \text{Zn}^{2+} ions in the thin films (fig. 4.19 a). The O(1s) shows (fig. 4.19 b) a symmetric
sharp peak at 530.2 eV, it may be attributed to \( O^{2-} \) ions in Zn-O bond [154]. The incorporation of Cu is clearly demonstrated by the core level spectra of Cu(2p) and have two peaks located at 932.88 eV (2p\(_{3/2}\)) and 952.68 eV (2p\(_{1/2}\)). So the formation of metallic copper is over ruled by the XPS analysis [56]. Similarly in Zn\(_{0.97}\)Ni\(_{0.03}\)O thin films we observed sharp peaks of Zn\(^{2+}\) and O\(^{2-}\). The incorporation of Ni is clearly demonstrated by the core level spectra of Ni (2p) (fig. 4.19 c). The peaks of Ni 2p\(_{3/2}\) are located at 853.5 eV and 859.8 eV. No XPS signals from metallic Ni (858.9 eV) was detected. These results indicate that the doped Ni ions are in divalent state [155].

![AFM images of Zn\(_{1-x}\)Cu\(_x\)O thin films deposited at T\(_S\) 450 °C and 0.005 mbar PO\(_2\) (a) x = 0, (b) x = 0.03, (c) x = 0.05 and (d) x = 0.10.](image)

**Figure 4.20:** AFM images of Zn\(_{1-x}\)Cu\(_x\)O thin films deposited at T\(_S\) 450 °C and 0.005 mbar PO\(_2\) (a) x = 0, (b) x = 0.03, (c) x = 0.05 and (d) x = 0.10.

The surface morphology and thickness of the Ni and Cu doped ZnO thin films have direct impact on the its optical and magnetic properties. So the thickness of the Zn\(_{1-x}\)Ni\(_x\)O and Zn\(_{1-x}\)Cu\(_x\)O films grown by PLD...
were measured by stylus profiler (Dektak 6M). The average thickness of the films were found to be \( \sim 230 \text{ nm} \). The surface morphology of the Ni and Cu doped thin films on fused silica substrate deposited at a substrate temperature 450 °C and oxygen partial pressure of \( 5 \times 10^{-3} \text{ mbar} \) were analyzed using Aglient 5500 series AFM in non-contact mode. The RMS roughness of the undoped ZnO is 6 nm and that of 15% Cu doped ZnO is 10 nm (figure 4.20). \( \text{Zn}_{1-x}\text{Cu}_x \text{O} \) films have uniformly placed smaller grains. The surface morphology of the \( \text{Zn}_{1-x}\text{Ni}_x \text{O} \) thin films were shown in figure 4.21. The \( \text{Zn}_{0.97}\text{Ni}_{0.03} \text{O} \) film have uniformly distributed smaller grains and the highest RMS roughness observed was 8 nm. At higher Ni and Cu doping concentration the morphology of the films changed. The RMS roughness of the Ni and Cu doped ZnO films increase with doping percentage. The morphological variation of the ZnO thin films with Ni and Cu doping indicates the incorporation of the transition metals into the ZnO host lattice. These results are consistent with the smaller grain growths observed by XRD analysis.

![AFM images of Zn\(_{1-x}\)Ni\(_x\)O thin films deposited at TS 450 °C and 0.005 mbar PO\(_2\) (a) x = 0.03, (b) x = 0.05 and (c) x = 0.10.](image)

The optical transmission spectra of \( \text{Zn}_{1-x}\text{Cu}_x \text{O} \) (x = 0, 0.03 and 0.15) and \( \text{Zn}_{1-x}\text{Ni}_x \text{O} \) (x = 0, 0.01, 0.03 and 0.10) thin films were recorded in
the wavelength range 300-1200 nm using Jasco-V 570, UV-vis-NIR spectrophotometer (figure 4.22). All the films have an average transmittance greater than 75% in the visible region indicating good quality of the deposited films with low scattering or absorption losses. The colour of the Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O films become light green and light blue with increase of the dopant concentration. The oscillations in the spectra are caused by multi-reflections at the film-air and film-substrate interfaces. The ZnO film shows a sharp absorption edge at 380 nm. However the transparency of Ni and Cu doped ZnO thin films fade away with increase of the dopant. Zn$_{1-x}$Ni$_x$O thin films show predominant visible d-d transitions in the tetrahedral geometry. The absorptions were around 2.10, 2.26 and 2.39 eV, the corresponding d-d transitions $^3$A$_2$(G)→$^3$T$_2$(G), $^3$A$_2$(G)→$^3$T$_1$(G) and $^3$A$_2$(G)→$^3$T$_1$(P). So these d-d transitions clearly indicate that Ni is occupying the tetrahedral lattice points in the ZnO host lattice [156].

![Transmission spectra of (a) Zn$_{1-x}$Ni$_x$O and (b) Zn$_{1-x}$Cu$_x$O thin films at T$_S$ 450°C and 0.005 mbar PO$_2$.](image)

**Figure 4.22:** Transmission spectra of (a) Zn$_{1-x}$Ni$_x$O and (b) Zn$_{1-x}$Cu$_x$O thin films at T$_S$ 450°C and 0.005 mbar PO$_2$. 

The optical absorption coefficient of a direct band gap semiconductor near the band edge for photon energy $h\nu$ greater than the band gap en-
ergy of the semiconductor is given by \( \alpha \nu = \text{constant} \times (h\nu-E_\text{g})^{1/2} \) [157].

The band gap of Zn\(_{1-x}\)Ni\(_x\)O and Zn\(_{1-x}\)Cu\(_x\)O thin films can be calculated by plotting \((\alpha \nu)^2\) as a function of photon energy \((h\nu)\). The band gap of the Zn\(_{1-x}\)Cu\(_x\)O films decreases from 3.35 eV to 3.24 eV with increase of Cu concentration upto 10%. In the case of Zn\(_{1-x}\)Ni\(_x\)O thin films the band gap reduces to 3.17 eV at 10% of Ni doping (figure 4.23). The reduction of optical band gap in Zn\(_{1-x}\)Cu\(_x\)O and Zn\(_{1-x}\)Ni\(_x\)O thin films at room temperature may attributed to the sp-d exchange interaction between the band electrons and the localized d electron of the Ni\(^{2+}\) and Cu\(^{2+}\) ion substituting Zn\(^{2+}\) ions [125, 158–160]. The s-d and p-d exchange give rise to negative and positive corrections to the conduction band and the valence band respectively, leading the band gap narrowing [156, 161]. The decrease of absorption edge suggests an increase in the disorder in Zn\(_{1-x}\)Cu\(_x\)O film. The Ni and Cu substitution in ZnO host lattice creates impurity level in the forbidden energy region of ZnO. Hence the transmission spectra and band gap analysis confirms the Ni and Cu incorporation into the ZnO lattice and its crystalline nature too.

The room temperature photoluminescence (RTPL) measurements of the Zn\(_{1-x}\)Ni\(_x\)O and Zn\(_{1-x}\)Cu\(_x\)O films using an excitation wavelength of \( \lambda_{\text{ex}} = 325 \) nm are shown in figure 4.24. All the PL spectra have ultraviolet (UV) emission band at 380 nm region. The RTPL shows that the UV emission is red shifted with increase of Ni and Cu concentration. The UV emission is attributed to the near band-edge free-excitation transition and its depends strongly on the crystalline quality of ZnO films. The crystalline quality of Ni and Cu doped ZnO films decreases with increase in Ni and Cu concentration in agreement with the XRD and AFM analysis. The intensity of the UV emission also decreases with increase of Ni and Cu
Results and discussion

Figure 4.23: Band gap variation of Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O with concentrations (x= 0-0.10).

content in the ZnO thin films [113–115, 162]. The NBE emission results from the exciton related recombination. The green emission (545 nm) was observed in Zn$_{1-x}$Cu$_x$O thin films for x>1% and it is quenched at high Cu doping. Samanta et al. [117] and Sakaguchi et al. [113] reported that decrease in green emission is due to the formation of point defects, which will act as nonradiative centers. The surface defects, Cu impurities and oxygen vacancies are responsible for the observed green emission [163]. The incorporation of Cu in Zn lattice site will create donor level at 0.17-0.19 eV below the bottom of the conduction band [163, 164]. This Cu impurity center behaves like a trap for non-equilibrium holes or electrons. The radiative recombination of the exciton gives rise to green emission in the spectrum [164–166]. So the intensity and the FWHM of the UV emission strongly depend on the microcrystalline structure of the Zn$_{1-x}$Ni$_x$O and Zn$_{1-x}$Cu$_x$O films.

Raman scattering is one of the effective technique to investigate the
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Figure 4.24: Room temperature PL spectra of (a) Zn\(_{1-x}\)Ni\(_x\)O (x=0-0.10) and (b) Zn\(_{1-x}\)Cu\(_x\)O thin films (x=0-0.15). Inset in fig b shows the magnified view of green region.

crystallization, structure and defects in the thin films. The wurtzite structure of ZnO has the space group C\(_{6v}\) with two formula units per primitive cell with all atoms occupying C\(_{6v}\) sites. Each Zn\(^{2+}\) atom is tetrahedrally coordinated to four O atoms and vice versa. The number of optical modes for the ZnO structures is given by A\(_1\) + E\(_1\) + 2B\(_1\) + 2E\(_2\), where B\(_1\) modes are silent in Raman scattering, A\(_1\) and E\(_1\) modes are polar and hence, exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical
(LO) phonons. The non polar $E_2$ modes have two frequencies, namely $E_{2}^{high}$ and $E_{2}^{low}$ associated with the motion of oxygen atoms along with zinc sub lattice vibrations [21, 103, 167].

Figure 4.25: Raman spectra of (a) Zn$_{1-x}$Ni$_x$O ($x = 0-0.10$) and (b) Zn$_{1-x}$Cu$_x$O ($x = 0-0.15$) bulk powder samples.

Raman spectra of the Ni and Cu doped ZnO bulk powders are shown in figure 4.25. In Zn$_{1-x}$Ni$_x$O powders we observed normal modes at $E_{2}^{low}$ (100.5 cm$^{-1}$) and $E_{2}^{high}$ (438 cm$^{-1}$), other modes are suppressed [21, 167]. But in the case of Zn$_{1-x}$Cu$_x$O powders the characteristic optical modes of wurtzite ZnO are observed at $E_{2}^{low}$ (99 cm$^{-1}$), $E_{2}^{high}$ (436 cm$^{-1}$), second phonon line (332 cm$^{-1}$), $A_{TO}$ (376 cm$^{-1}$) and $A_{LO}$ (575 cm$^{-1}$) [103, 166]. The oxygen sub-lattice vibrational optical mode ($E_{2}^{high}$) of the Zn$_{1-x}$Cu$_x$O bulk powder samples were found shifted toward lower wave number compared to that of the ZnO bulk powder. When transition metal is substituted the Zn lattice site in ZnO, it forms the ternary alloy of Zn$_{1-x}$TM$_x$O and the allowed region for the optical phonon becomes finite than the ZnO host lattice. The atomic substitution leads to the structural disorder and breaks the translational symmetry of the allowed phonons. The disorder induced
effect causes the phonon line shapes become broadened and shifted towards lower wavenumber [33, 117, 140].

Figure 4.26: Raman spectra of (a) Zn$_{1-x}$Cu$_x$O (x = 0-0.15) and (b) Zn$_{1-x}$Ni$_x$O (x = 0-0.10) thin films.

The Raman spectra of the Zn$_{1-x}$Cu$_x$O thin films (figure 4.26 a) shows three predominant modes at $E_2^{low}$ (99 cm$^{-1}$), $E_2^{high}$ (435 cm$^{-1}$) and $A_1^{LO}$ (575 cm$^{-1}$). These modes are present only in highly c-axis oriented thin films. The broadening of the $E_2^{high}$ modes and its red shift indicates the substitution of Cu into the ZnO sub-lattice [114, 117, 168]. The disappear-
ance of the $A_1^{LO}$ mode and red shift of the $E_{2}^{high}$ mode at higher Cu doping is due to the formation of mixed crystal states [114, 117]. Thus Raman spectra confirms the incorporation of Cu into the ZnO lattice and all the films are oriented along the c-axis.

The Raman spectra of the $Zn_{1-x}Ni_xO$ thin films are shown in figure 4.26 b. The $E_{2}^{low}$ mode of ZnO was shifted towards lower frequencies and there was an increase in FWHM up to 10% of Ni substituted ZnO. The shift of $E_{2}^{low}$ mode was detected as 1.05 cm$^{-1}$ compared to the bulk value. The FWHM was found to increase with nickel concentration in $Zn_{1-x}Ni_xO$ thin films. The atomic substitution of Ni in ZnO host lattice induces structural disorder. The disorder induced effect (lower frequency shift and broadening) in $Zn_{1-x}Ni_xO$ thin films were explained by alloy potential fluctuations (APF) using a spatial correlation (SC) model [103, 140, 169]. When the crystal is alloyed the spatial correlation region of the phonons become finite owing to the potential fluctuation of the alloying disorder, which gives rise to the relaxation of $q=0$ selection rule in Raman scattering. A broad band ranging from 300 to 700 cm$^{-1}$ appears at higher Ni concentration and its intensity increases significantly with increase of doping percentage. Similar observations are reported in literature [152, 167]. The multi-peak-fitting result reveals that at 10% Ni doping broad band could be deconvoluted into five peaks, denoted as P$_1$-P$_5$ (figure 4.27).

The disorder induced effects of $E_{2}^{low}$ mode in $Zn_{1-x}Ni_xO$ can be explained by alloy potential fluctuations using a spatial correlation model. Manjon et al. [144] predicted that the $B_{1}^{low}$, $2B_{1}^{low}$ and $B_{1}^{high}$ silent modes of wurtzite ZnO occur at 261, 522 and 552 cm$^{-1}$, respectively. In our case, the peaks, P$_2$ (434 cm$^{-1}/E_{2}^{high}$), P$_3$ (485 cm$^{-1}/I_{1}$) and P$_4$ (552 cm$^{-1}/B_{1}^{high}$) and P$_5$ (620 cm$^{-1}/E_{1}^{LO}$) are present only in heavily Ni-doped ZnO films.
Figure 4.27: Room temperature Raman spectra of Zn$_{0.90}$Ni$_{0.10}$O thin films and inset shows multi-peak fittings.

Generally, the A$_1^{LO}$ mode is weak because of two opposing contributions from the Frohlich interaction and the deformation potential [56]. The defect induced Raman active modes arise due to two major types of lattice disorders. The first one is the disorder induced effects arising on the incorporation of Ni into the ZnO lattice, P$_2$ ($434$ cm$^{-1}$/E$_2^{high}$), P$_3$ ($485$ cm$^{-1}$/I$_1$) and P$_4$ ($552$ cm$^{-1}$/B$_{1}^{high}$) and surface phonon modes. The second one is due to the native lattice defects P$_5$ ($620$ cm$^{-1}$/E$_1^{LO}$).

The decrease of crystalline nature, formation of defect induced Raman active modes and reduction of optical band gap confirms the uniform incorporation of Ni and Cu into the ZnO host lattice. If the doping percentage is above 5 at.%, the reduction of the UV emission (for Ni and Cu doping) and the green emission (for Cu doping) occurs. According to the above structural and optical characterization and in view of spintronic applica-
Results and discussion

The study focuses on the magnetic studies of the thin films below 5 at.% only. Room temperature magnetic properties of Ni and Cu doped ZnO thin films were investigated using Quantum Design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.

Figure 4.28: Room temperature M-H curve of the (a) Zn$_{0.97}$Ni$_{0.03}$O and (b) Zn$_{0.97}$Cu$_{0.03}$O thin films. Inset shows the magnified view near zero field.

The magnetic behaviour of the Zn$_{0.97}$Ni$_{0.03}$O and Zn$_{0.97}$Cu$_{0.03}$O thin films prepared at 450°C and 5×10$^{-4}$ mbar are shown in figure 4.28 a and b respectively. The magnetization field (M-H) curve reveals an obvious
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hysteresis loop, indicating the room temperature ferromagnetic ordering existing in the films. The saturation magnetization \( (M_S) \) and coercive field \( (H_C) \) of the 3 at.% Cu doped ZnO films are 0.28 \( \mu_B/Cu \) and 190 Oe respectively. But the Ni doped ZnO films shows better saturation magnetization (0.34 B/Ni atom) and coercive field (640 Oe). The ZnO thin films prepared at the same condition shows diamagnetic nature. Zn\(_{0.97}\)TM\(_{0.03}\)O thin films prepared at 450°C and 0.05 mbar oxygen pressure shows lower saturation magnetization than one prepared at 5x10\(^{-4}\) mbar pressure. This support the assumption that magnetism is due to the exchange interaction between local spin polarized electrons and conduction electrons. According to Ruderman- Kittel- Kasuya and Yosida (RKKY) interactions the concentration of free electrons plays a major role in stabilizing the magnetic phase in the Zn\(_{0.97}\)Ni\(_{0.03}\)O or Zn\(_{0.97}\)Cu\(_{0.03}\)O thin films. ZnO is n-type material, due to oxygen vacancies and zinc interstitials. Higher oxygen pressure result in less oxygen vacancies and reduce the carrier concentration. At higher concentrations the TM clusters and transition metal oxides suppress the room temperature ferromagnetism in Zn\(_{1-x}\)TM\(_x\)O thin films and paramagnetism is observed. The possibilities of metallic Ni and Cu and secondary phases (NiO, Ni\(_2\)O\(_3\), CuO) is over ruled by XRD and Raman measurements [33, 152]. In the application point of view we can use these lower at.% doped ZnO materials for spintronic devices.

In Zn\(_{1-x}\)Cu\(_x\)O thin films magnetization is reduced by the formation of secondary phases - CuO and Cu\(_2\)O. The theoretical magnetic moment of Cu\(^{2+}\) ion is \( \sim 1 \ \mu_B \). At higher Ni concentration in Zn\(_{1-x}\)Ni\(_x\)O thin films increased number of metallic Ni, NiO and Ni\(_2\)O\(_3\) deviate the system from achieving room temperature ferromagnetism [47, 152, 167]. The decrease of saturation magnetization at higher Ni and Cu doping due to increased
number of Ni and Cu atom occupying adjacent cation site resulting anti-ferromagnetic alignment \[47, 170\].

4.3.4 Conclusion

Pulsed Laser Deposition technique is one of the physical methods for the preparation of highly oriented compound semiconductors and doped semiconductors. The thin films morphology and optical properties can be tuned by varying the laser fluence and background pressure. Phase pure $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0-10$) and $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x=0-15$) thin films were grown by PLD technique. The PLD targets were synthesized by solid state reaction. The wurtzite structure of the targets were confirmed by XRD. The structural, morphological, optical and magnetic properties of TM doped ZnO films were analyzed. XRD pattern reveals that all the Ni and Cu doped ZnO films have c-axis orientation normal to the substrate. The surface morphology characterized by atomic force microscopy shows $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ and $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ films have uniformly placed smaller grains and larger gains at higher doping percentages. The TM doped ZnO films have transmittance greater than 75% in the visible region. The band gap of the ZnO thin films shows red shift with increase of Ni and Cu concentration in thin films. The Cu doped ZnO thin film shows green PL emission at 542 nm and the band edge emission at 385 nm. The defect induced Raman active modes in Ni and Cu doped ZnO thin films and bulk sample is also elucidated. The presence of non-polar $E_2^{\text{high}}$ and $E_2^{\text{low}}$ Raman modes in thin films indicates that Ni and Cu doping didnt change the wurtzite structure of ZnO. The intensity of $E_2^{\text{high}}$ high mode and the peak position shifted towards the lower wavenumber with increase of Ni and Cu concentration. The XPS confirm the incorporation of Cu$^{2+}$ and Ni$^{2+}$ ions into the ZnO.
lattice. Room temperature ferromagnetism is obtained for lower doping concentrations of Ni and Cu. The combination of photoluminescent and magnetic properties of Zn$_{1-x}$Cu$_x$O thin films make them attractive for spin light emitting diodes.