Chapter VI

Physical Properties of Transition Metal (Mn, Co, Ni) doped ZnO

6.1 Introduction

II–VI semiconductor materials at nanometer scale plays key role in various applications due to their great potential. ZnO is an important II–VI semiconductor having room-temperature (RT) ferromagnetism (FM) when doped with transition metals (TM) [Liu Yanmei et al., 2011, Huilian Liu et al., 2008]. This makes ZnO one of the most promising materials for potential applications in spintronics and as diluted magnetic semiconductor (DMS) material. Among doped ZnO materials, 3d transition metals doped ZnO [Xueyun Zhou et al., 2008] producing high quality DMS. In this chapter, Mn, Co and Ni doped ZnO nanocrystalline film preparation and their characterizations are discussed.

6.2 Experiment

Zinc acetate dehydrate (Zn (CH₃COO)₂.2H₂O.) precursor, (Dopant ions from manganous acetate (CH₃COO)₂Mn.4H₂O, cobaltous chloride(CoCl₂.6H₂O.), nickel chloride (NiCl₂.6H₂O), in appropriate proportions were dissolved in ethanol and diethanolamine solution and stirred at 50°C for 1 h and then aged for one day. Then the sol is spin coated on cleaned glass substrate at 200°C and the coating was repeated for 8 times and finally annealed at 450°C.

6.3 Characterizations

The crystalline structure was analyzed by X-ray diffraction (XRD) using CuKα radiation (1.5405 Å) diffractometer operating at 40 kV, 30 mA for angles between2θ=10 and 80° in 0.02° steps. The surface morphology was investigated using a field emission scanning electron microscope FESEM ((JOEL-6460F). X-ray photoelectron spectroscopy (XPS) was carried out at room temperature to identify the elements present. The optical transmittance was determined using UV-Vis-NIR spectrophotometer in the wavelength range from 300 to 1000 nm. The photoluminescence spectra were measured using a light
source of xenon lamp with the excitation wavelength of 280 nm at room temperature. The magnetization measurements were made on a Vibrating Sample Magnetometer (Lakeshore-7404)

6.4 Structural Properties

6.4.1 XRD Analysis of ZnO:Mn films

The X-ray diffractograms of manganese doped ZnO nanocrystalline film coated by the spin coating technique are depicted in Fig 6.1. The characteristic peaks of ZnO (100), (002), (101), (102), (110), (103) and (112) are determined in the investigated...
diffractograms. Similar peaks are observed in manganese doped ZnO prepared using chemical vapour deposition by Shuang et al., 2007 and sol gel process by Xiaolu Yan et al., 2011. It was found that for various samples, the phase wurtzite structure is formed. All peaks match the hexagonal ZnO structure and the lattice constants ‘a’ and ‘c’ are given in Table.6.1.

Table.6.1: Lattice constant for Mn doped ZnO films.

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>ZnO thin film</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1% Mn doped</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.25109</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.20982</td>
</tr>
</tbody>
</table>

Obviously, in 2 wt% manganese doped sample trace of glass (substrate) peak appeared. From XRD study, no trace of manganese metal, oxides, or any binary zinc manganese phases are observed. The XRD diagrams show a very strong (101) diffraction peak indicating a strong texture of the films with a preferential orientation parallel to this direction. In addition, the width of the (100), (002) and (101) peaks increases with increasing doping concentration, which indicates the decrease of the particle size. The manganese-doped film has the peak intensity of (002) plane less than that of the pure zinc oxide film. This indicates that dopant incorporation deteriorates the crystallinity of films, which may be due to the ion size difference between zinc and dopant. By using Scherrer’s relation [3.4] between the grain diameter D and the FWHM, the grain size for 1 wt% manganese doped ZnO is 26 nm along the (002) direction and for 3 wt% manganese doped ZnO is 17 nm along the same direction. The crystallite size D is presented in the Table.6.2. It is also observed that the size of the crystallites is least (17 nm) for 3wt% of Mn doped ZnO.

The texture coefficient of the films was calculated to determine the preferred orientation of the polycrystalline thin films using the formula proposed by Barrett and Massalski(1980) and it was reported in the literature [Usman Ilyas et al., 2011].
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The value, $TC_{(hkl)} = 1$, represents the film with randomly oriented crystallites, while higher value indicates the abundance of grains oriented along (101) direction. The variations of TC for manganese doped ZnO at different Mn concentrations are presented in Table 6.3. The highest TC value has been found for 3 wt% Mn doped ZnO film along (101) plane and lowest TC value has been found along (002) plane.

6.4.2 XRD Analysis of ZnO:Co films

Fig 6.2 shows the X-ray diffraction pattern of cobalt doped ZnO nanocrystalline samples. The result demonstrates that the nanocrystalline films have the hexagonal wurtzite structure. It can be seen from XRD patterns that all films were polycrystalline with mixed orientation and strongly textured. There are three dominant peaks at 31.7°, 34.4° and 36.2° corresponding to the (100), (002) and (101) planes respectively of hexagonal wurtzite structure. In addition, several diffraction peaks were detected along the (102), (110), (103) and (112) planes. XRD results indicate that the doping concentration influences the crystalline phases of ZnO films deposited on glass substrates. It is observed that, though the intensity of all the peaks decreases with the increase of dopant concentration, the intensity of (002) peak alone increases again from 2% to 3% change in concentration. In the radio-frequency magnetron sputtering derived cobalt doped ZnO [El Mir et al., 2007] and Co doped ZnO nanoparticles synthesized by DC thermal plasma method [Nirmala et al., 2011], the peaks obtained were similar to the present work and the most dominant peak is (101) in all the doped ZnO films. Lattice constants ‘$a$’ and ‘$c$’ are calculated for all the doping concentration and given in Table 6.4.

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>ZnO thin film</th>
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<tbody>
<tr>
<td></td>
<td>1% Co doped</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>3.24973</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.20788</td>
</tr>
</tbody>
</table>
The effect of cobalt doping concentration on the orientation of polycrystalline ZnO:Co films was investigated by evaluating the texture coefficient ($TC_{(hkl)}$) of the (hkl) plane using Eq.[3.3]. It is seen that the value of texture coefficient approaches unity for random orientation, while $TC_{(hkl)}$ is greater than unity when the (hkl) plane is preferentially oriented. It is clear that the lower value of texture coefficient represents that the films have poor crystallinity and 1wt % cobalt doped shows high texture coefficient and it shows the better crystallinity. Further increase in cobalt concentration, the value of texture coefficient slightly decreases as shown in Table 6.5.
In order to obtain more structural information, the mean grain size (D) of the films was evaluated using the Scherrer equation [3.4] and given in Table 6.6. The crystallite size was estimated for the standard (100), (002) and (101) reflections. It is seen that, as the dopant concentration increases the size of the crystallites decreases and the lowest crystalline size (19 nm) is observed for 3% concentration for the prominent (100) peak.

### 6.4.3 XRD Analysis of ZnO: Ni films

![XRD graphs of Ni doped ZnO nanorods.](image)

Fig 6.3 XRD graphs of Ni doped ZnO nanorods.

The XRD patterns of the 1wt % Ni doped, 2 wt % Ni doped and 3 wt % Ni doped ZnO are shown in Fig.6.3 a, b and c respectively. The sharp and intense peaks indicate that the samples are highly crystalline and ZnO nanocrystalline films have polycrystalline...
structure. The XRD peaks for (100), (002), (101), (102), (110), (103) and (112) planes indicates the formation of phase pure wurtzite structure of ZnO.

Lattice constants ‘a’ and ‘c’ are calculated from the XRD data and shown in Table 6.7. It shows good agreement with the standard value (a=b=3.249 Å, c=5.206 Å)[JCPDS-36-1451]. It also matches with the values given in literature [Prashant K. Sharma et al., 2009].

**Table 6.7: Lattice constant ‘a’ and ‘c’ of ZnO:Ni**

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>ZnO thin film</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1% Ni doped</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.24955</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.20686</td>
</tr>
</tbody>
</table>

The crystallite size of Ni-doped ZnO is calculated using Scherrer's formula [3.4] and given in Table 6.8. It is seen from the figure 6.3, for all the samples dominant peaks are (100), (002) and (101). For 1 wt% Ni doped ZnO the full width half maximum (β) of the above dominant peaks are 0.3097, 0.3313 and 0.3261, while for 2% Ni doping the (β) of the peaks become 0.3973, 0.3641 and 0.3619. However, that the intensities of diffraction peaks decline as the Ni$^{2+}$ ion concentration increases, i.e. the nickel doping within the films causes the ZnO crystallinity to deteriorate. Since the intensity of diffraction peaks becomes weaker and the half-peak width becomes wider with the increase of dopant concentration, the Ni$^{2+}$ ions inhibit the aggregation of ZnO nanocrystals [Nina V et al., 2011] and affect the crystallization of ZnO. For further increase of nickel that is 3 wt% Ni doped ZnO the (β) of the peaks become 0.2769, 0.2629 and 0.2930 and the crystallite size increases. (002) peak is found to be dominant for all Ni doped ZnO films for lower dopant concentration. For 3% dopant concentration the grains have preferential growth along (101) plane by making the corresponding peak with the higher intensity. The degree of orientation can be illustrated by the relative texture coefficient, given by equation [3.3].

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The calculated texture coefficients $TC$ are presented in Table 6.9. It can be seen that the highest $TC$ is obtained for the (002) plane of the ZnO film doped with 1 wt% Ni. The higher values of texture coefficient reveal that the 1 wt% nickel doped zinc oxide film crystallinity is strong.

6.5 Morphological studies

6.5.1 FESEM micrographs of ZnO:Mn films

The SEM images of Mn doped ZnO are shown in Fig 6.4 (a-c). The incorporation of Mn at Zn site was found to influence the surface morphology of the films. The Mn-doped ZnO film shows the formation of many spherical particles all over the surface. It is interesting to note that the grain sizes observed from SEM is different from the grain size determined by using XRD.

![FESEM image of Mn$^{2+}$ (1 wt %) doped ZnO nanoparticles.](image)

**Fig 6.4a** FESEM image of Mn$^{2+}$ (1 wt %) doped ZnO nanoparticles.
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Fig 6.4b FESEM image of Mn$^{2+}$ (2 wt %) doped ZnO nanoparticles.

Fig 6.4c FESEM image of Mn$^{2+}$ (3 wt %) doped ZnO nanoparticles.
These shows the grains seen in the SEM are the domains formed by aggregation [Srinivasan et al., 2008] of nanosize crystallites. For the 2 wt% Mn doped ZnO films more agglomeration is seen on the picture. Higher grain size might be attributed to the migration of grain boundaries causing the coalescence of smaller grains at higher doping concentration.

6.5.2 FESEM micrographs of ZnO:Co films

FESEM surface micrographs shown in Fig. 6.5 (a-c) reveal that the surface morphology was more or less similar for the Co-doped ZnO films prepared at various cobalt concentrations. All film shows worm shaped micro-rods. Particle size from SEM is consistent with the particle size from XRD pattern. However, regular grains can be seen clearly in all the films having uniform size distribution in the range of about 30-35 nm.

Fig 6.5 (a) FESEM image of the 1 wt% Co doped ZnO
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Fig 6.5b FESEM image of the 2 wt% Co doped ZnO

Fig 6.5c FESEM image of the 3 wt% Co doped ZnO
The value of grain size is in good agreement with the value calculated from XRD. Furthermore, the surface topography of ZnO thin films becomes smoother with increase in cobalt content, as Co incorporation causes regular grain size resulting in the formation of more uniform thin films. It is apparent from the electron micrographs that all of the morphology of the thin films has tightly packed grains and relatively smooth surfaces without any voids and crack.

6.5.3 FESEM micrographs of ZnO:Ni films

The FESEM images of Ni doped ZnO are shown in Fig. 6.6 (a-c). It clearly indicates that the transformation of spherical particles into rod shape with particle size confinement as a result of nickel doping. Fig. 6.6 (a-c) shows the FESEM images nickel doped nanoparticles, which indicates that the rod like structure of nanoparticles accompany with spherical particles.

![FESEM image of the 1 wt% Ni doped ZnO](image)

Fig 6.6a FESEM image of the 1 wt% Ni doped ZnO
Fig 6.6b FESEM image of the 2 wt% Ni doped ZnO

Fig 6.6c FESEM image of the 3 wt% Ni doped ZnO
The Ni atoms may have disturbed the growth process resulting in the formation of nanosize rods. Low Ni content doped ZnO samples have very less density of nanorods than high Ni content doped samples, which means that Ni doping can increase the even nucleation rate of Ni doped ZnO nanorods. Doping of nickel for the formation of ZnO thin films results in the formation of nanorod like structure as reported by Liu Yanmei et al., 2011. The above said literature reports that high Ni doped ZnO decrease the nanorod nucleation, which in turn shows the controversial report to the present work.

6.6 XPS Analysis

6.6.1 XPS Analysis of Mn doped ZnO films

**Fig 6.7** XPS spectra of (a) Zn 2p\(_{3/2}\), Zn 2p\(_{1/2}\) and (b) O1s peak in Mn doped ZnO film

**Fig 6.7** (c) XPS spectra of 1, 2 and 3 wt% Mn doped films
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Physical Properties of Transition Metal (Mn, Co, Ni) doped ZnO

The XPS spectra were measured for studying the composition and chemical bond configuration of manganese doped ZnO films. XPS spectra confirmed the high chemical purity of the manganese doped ZnO thin films, consisting solely of Zn, Mn, and O. In Fig 6.7(a-b) the Zn 2p_{3/2}, Zn 2p_{1/2} and O1s spectra of Mn-doped films are shown. The presence of sharp and high symmetric peaks of Zn 2p_{3/2} and Zn 2p_{1/2} core-level centered at 1020.85 and 1043.66 eV, respectively, with a spin–orbital-splitting (Δ) of 22.81 eV in Mn doped ZnO samples confirmed that Zn exist as Zn^{2+} [Barick et al., 2010, Xiaolu Yan et al., 2011] and the binding energy position of the spectra closely match with the standard data of zinc oxide [Wagner et al., 1979]. In the O 1s spectra of Mn doped ZnO films the peak centered on 531.7 eV. For 1, 2 and 3 wt% Mn doped ZnO there is no shifting of peak position and no increase of peak intensity of Zn 2p_{3/2}, Zn 2p_{1/2} and O1s peaks.

To determine the oxidation state of the implanted manganese ions, XPS spectra were taken from Mn-doped ZnO nanoparticles with 1, 2 and 3 wt % doping level. The Mn (Auger) spectra were asymmetric (broadened towards lower energy side) and not deconvoluted into peaks. The results clearly showed that the element Mn peak intensity increases with the increase in doping concentration, which is shown in the Fig 6.7(c). The Mn peak position is 851.61, 851.43 and 852.24 eV for 1, 2 and 3 wt% Mn doped ZnO films respectively. But Polat et al., 2011 observed Mn 2p_{1/2} peak in the Mn doped ZnO using spray pyrolysis.

6.6.2 XPS Analysis of Nickel doped ZnO films

XPS survey spectra were recorded on the surface of the 1, 2 and 3 wt% Ni doped ZnO films are shown in Fig 6.8 (a-c). The most important peaks are denoted. As seen in Fig. 6.8 a, the peak of Zn 2p_{3/2} and Zn 2p_{1/2} appears at 1020.53 and 1043.59 eV, confirming that Zn exists only in the form of Zn^{2+} linked to a nickel atom. Fig 6.8 b shows the O 1s peak centered around 531.76 eV, which are in good agreement with the standard value. The XPS oxygen peak also indicates that only one oxygen species is present at the surface. For all the above concentration of Ni there is no change in peak intensity and no shifting of peak in Zn and O 1s spectra.
Fig. 6.8c shows Ni 2s spectrum of Ni-doped ZnO thin films. The binding energy position of Ni 2s in 1, 2 and 3 wt% nickel doped ZnO is 1008.95, 1008.73 and 1008.79 eV which indicates the slight variation of binding energy with doping concentration and intensity of the peak also increases. The peak obtained in this study is different from the peak obtained by [Xiaolu Yan et al., 2011, Pandey et al., 2008].

Fig. 6.8 (a-c) XPS spectra of Nickel doped ZnO films, (a) Zn2p\textsubscript{3/2} and Zn 2p\textsubscript{1/2} (b) O1s, (c) Ni 2s for 1, 2 and 3 wt% of Ni doped ZnO films respectively.
6.7 Optical Properties

6.7.1 Optical Properties of Mn doped ZnO thin films

Figure 6.9a and b shows the optical transmission and absorption spectra of spin-coated manganese doped ZnO nanocrystalline films. The important optical parameter is the band-gap of materials. Plotting \((\alpha h\nu)^2\) against photon energy \(h\nu\), the band-gap value can be determined by extrapolating the straight line portion at \(\alpha = 0\) as indicated in the plots in Fig. 6.9c. The values of band-gap energy, \(E_g\) of doped ZnO thin films for different doping rates were then obtained by extrapolation method. First of all, from the plot it was determined that the film has direct band gap, and this property is suitable for photovoltaic applications \([\text{Ergin et al.}, 2008]\). Secondly, the optical direct band-gap value of 1, 2 and 3wt % Mn-doped films varied from 2.63 to 2.72 eV. The effect of dopant on higher band semiconductors like ZnO has the effect of decreasing the band-gap to the visible region so that they can be used in the fabrication of solar cells.

Fig 6.9 (a) transmittance and (b) absorbance spectrum of the Mn-doped ZnO films.
Fig 6.9c Evaluation of the \((\alpha h\nu)^2\) versus \(h\nu\) curves of manganese doped ZnO thin films.

6.7.2 Optical Properties of Co doped ZnO thin films

Fig 6.10a shows the optical transmittance of the cobalt doped ZnO nanocrystalline films on the pure glass substrate. UV–Vis analysis revealed a high optical transparency (>80%) in visible light region for all the ZnO films doped by cobalt in different concentration.

Figure 6.10 (a) transmission (b) absorption spectra of Co-doped ZnO films
It is observed that the average transmittance increases as the doping concentration increases. Fig 6.10b shows the absorption spectrum of Co doped ZnO nanostructures. A shift in the absorption edge was observed with the increase in doping concentration. The shift in the absorption edge is due to well-known Burstein-Moss shift and is related to carrier density. Plots of \((ahv)^2\) vs. the photon energy \(h\nu\) for films of varying doping concentrations are shown in figure 6.10c. Linearity of the plots indicates that the material is of direct band-gap nature. Extrapolation of linear portion of the graph to the energy axis at \(\alpha = 0\) gives the band-gap energy \(E_g = 3.27\) eV for the 1% doped film. Further it is found to get narrower with increasing Co doping concentration up to 3.23 eV for 3% Co-doped ZnO thin films. For 2% cobalt doping \(E_g=3.24\) eV. This narrowing of the bandgap with doping concentration is consistent with the observation of red-shift in the absorption tail of the transmittance spectra. Higher band gap value semiconductors are used as window layer in fabrication of solar cell [Asogwa, 2011].
6.7.3 Optical Properties of Nickel doped ZnO thin films

Fig 6.11 (a) transmittance spectrum of the Ni-doped ZnO.

Fig 6.11 (b) absorbance spectrum of the Ni-doped ZnO.
Fig 6.11c Plot of $(ahv)^2$ and energy of the incident photon for films prepared at different Nickel doping concentration in the starting solution.

The minima and next maxima in the transmittance curve is used to estimate the film thickness and the film thickness is given by

$$t = \frac{\lambda_{max} \lambda_{min}}{4n(\lambda_{min} - \lambda_{max})} \quad (6.1)$$

Where $n$ is the refractive index of the film (2.049), $\lambda_{min}$ and $\lambda_{max}$ are the values of the wavelength at a certain minima and next maximum respectively. The estimated value of the film thickness is about 800 nm. The transmission and absorption spectra of the Ni-doped ZnO thin films on glass substrate prepared at room temperature is shown in figure 6.16 a. In the visible region, film with 1 and 2% nickel doped shows high average transmittances that are more than 80% at wavelengths above 500 nm. Increment in the direct band gap value of nickel doped ZnO films may be attributed to the Burstein–Moss effect [Lee et al., 2004] in which the optical direct band gap increased followed by heavy
dopant concentration. When it is doped with 3% Ni the transmittance reduces rapidly. Quantum confinement leads to the initial rise in the optical band gap. On increasing the carrier concentration to the critical value, the potential at the grain boundaries collapse, leading to an abrupt decrease in the optical band gap. Above this carrier concentration the films behave according to existing many-body theories [Babu et al., 2010]. Figure 6.16 c shows plot of $\alpha^2$ as a function of photon energy against $h\nu$ of the Co doped films. The values of the optical energy gap ($E_g$) is determined by extrapolating the linear portion of the curves to $\alpha = 0$. The optical gap of the films for 1, 2 and 3% nickel doped ZnO are 3.24, 3.29 and 3.18 eV respectively. The obtained results are reported in Fig. 6.11c. When doping increases the band gap increases may be due to Vegard’s law (dopant) [Yuonesi et al., 2010]. According to this law it is a normal physical phenomenon. Again increasing the doping results in decrease of band-gap, it is an abnormal behaviour, which may be due to exchange interaction between the localized d-shell electrons of the magnetic ions and the delocalized band states (s,p) of the ZnO material [Yuonesi et al., 2008].

6.8 Photoluminescence

6.8.1 Photoluminescence of manganese doped ZnO thin films

The room temperature PL (Fig 6.12) analysis was carried out to study the effect of doping of Mn and doping concentration on the structural defects and the band gap energy of ZnO thin films. The samples with 1, 2 and 3 wt% Mn doped samples have a weak ultraviolet emission peak centered at about 386.5, 384.9 and 384.3 nm, blue emission peak centered at 415.8, 417.3 and 416.6 nm respectively. But all the samples show a sharp and more intense peak at 491.8 nm and there is no change in their peak position for all the above Mn concentration. The emission peak at 386.5, 384.9 and 384.3 nm have a blue-shift which is originated from the exciton recombination corresponding to the near band edge (NBE) exciton emission of the wide band gap ZnO. This recombination takes place through an exciton–exciton collision process at room temperature [Yang et al., 2009, Usman Ilyas et al., 2011]. The less intense UV emission band in Mn doped ZnO nanocrystalline films is due to Mn incorporation in to ZnO lattice and Mn is a strong quencher of the band edge emission of ZnO [Sharda et al., 2010, Norberg et al., 2004,
Wang et al., 2006]. PL emission peak in the blue region (415.8, 417.3 and 416.6 nm) is due to Zn vacancy [Sharda et al., 2010]. The sharp deep level emission (DLE) at 491.8 nm appears for all the samples, which strongly manifests a polycrystalline structure [Abrarov et al., 2006, Usman Ilyas et al., 2011] of ZnO, is due to a high density of native defects such as zinc vacancy (V\textsubscript{Zn}), oxygen vacancy (V\textsubscript{O}), interstitial zinc (Zn\textsubscript{i}) and interstitial oxygen (O\textsubscript{i}). It is very interesting to note that when doping of Mn increases peak corresponding to violet and blue emission increases and shifts slightly, but the peak corresponding to deep level or blue green emission increases in intensity and there is no shift in peak position.

**Fig 6.12** PL of Mn doped ZnO films.

For doped samples, the DLE emission spectrum can be attributed to both native (intrinsic) and foreign (extrinsic) defects. The tetrahedrally coordinated Mn\textsuperscript{2+} ion gives a blue green emission by forming a weak crystal field [Jagannatha Reddy et al., 2011]. In the present study, the emission at 491.8 nm is typical blue green emission. The emission
process from manganese doped ZnO is attributed to a d-level spin-forbidden transition for the Mn$^{2+}$ ions acting as an activating center.

6.8.2 Photoluminescence of cobalt doped ZnO thin films

![Graph showing photoluminescence spectra of cobalt doped ZnO thin films.](image)

**Fig 6.13** Room temperature photoluminescence spectra of cobalt doped ZnO thin films.

Fig 6.13 shows the room temperature photoluminescence (RTPL) spectra of samples with different (1, 2 and 3wt %) cobalt doping concentrations. Each sample has a very sharp and symmetrical emission peak in the range of 350–500 nm. For undoped and doped ZnO nanocrystalline samples, the near-band emission (NBE) appears around 380-390 nm. This is due to a recombination of bound excitons which might be a characteristic peak as reported by Mikhail Pashchanka *et al.*, 2011, Ruan *et al.*, 2011, Tao Wang *et al.*, 2011. PL spectra of all the samples contain three peaks located at 385, 418 and 492.5
nm corresponding to violet, blue and blue green emission. The violet emission peak located around 385 nm is generally ascribed to the near band edge emission (NBE), while the other two deep level emissions 418 and 492.5 nm in the visible region are usually related to Zinc interstitials (Zn_i) and oxygen vacancies (V_O) defects in ZnO. When doping concentration increases the intensity of NBE peak and blue emission enhances constantly but blue green emission peak of all concentration falls in the same position and are merged. The deep level emissions result from the recombination of electrons with holes trapped in singly ionized oxygen vacancies (V_O^+) [Nguyen Viet Tuyen et al., 2009].

Prasanth K. Sharma et al., 2010 have explained the mechanism of the observed emission as follows: the net charge of the singly ionized oxygen vacancy (V_O^+) in the ZnO is negative. Such negative centers in ZnO produce a repulsive defect potential and create an acceptor state (holes) by pushing the valance band levels higher into the band-gap. Due to the weak repulsive potential, an energy level of the acceptor state is created by singly ionized oxygen vacancies (V_O^+) when they are acting as luminescence centers. This results in the recombination of electrons, trapped at the oxygen vacancy (V_O^+), with the holes created in the valance band. This gives rise to the defect mediated blue green emission at 492.5 nm from the synthesized ZnO nanoparticles.

6.8.3 Photoluminescence of nickel doped ZnO thin films

PL measurements are conducted to investigate the optical properties of the synthesized thin films. Fig 6.14 shows the PL spectra of the nickel doped films. The PL spectrum of the film had a weak emission peak in the UV region centered around 383-390 nm. Weak UV emission was considered due to the increase of the non-radiative defects and decrease of ZnO nanorod size [Umar et al., 2005]. This UV emission peak was attributed to exciton recombination [Al-Harbi et al., 2011]. The peak position of violet emission is shifted slightly, which might be due to the morphological and size differences between the nanorod–nanoflake structures in the film [Qin et al., 2010]. For the increase in dopant concentration, the NBE peak position blue shifts from 390 nm to 383 nm. Two sharp visible emission peaks with a high intensity centered at 417 and 491.6 nm are appearing in the spectrum, which might be due to structural and surface
defects, such as oxygen vacancies, zinc interstitials and the presence of OH groups on the surface of the nanorods [Zhang et al., 2003, Zhou et al., 2008]. In fact, there are different mechanisms have been reported for the visible light emission of ZnO. Oxygen vacancies occur in three different charge states: the neutral oxygen vacancy, the singly ionized oxygen vacancy and the doubly ionized oxygen vacancy. For the increase of nickel doping the blue green emission peak steadily increases. The origin of blue-green luminescence peak at 491.6 nm is related to the defect levels introduced due to substitution of Ni$^{2+}$ in the Zn$^{2+}$ site by doping. This result is in conformity with the result obtaind by Gayen et al., 2010.

![PL spectra of nickel doped ZnO films](image)

**Fig 6.14** PL spectra of the (a) 1wt % (b) 2wt % (c) 3wt % nickel doped ZnO films
6.9 Magnetic Properties

6.9.1 Magnetic Properties of Mn doped ZnO films

Fig 6.15 M–H curves of (a) 1wt % (b) 2wt % (c) 3wt % Mn doped ZnO samples.

Magnetic measurements on manganese doped zinc oxide nanocrystalline films were performed at room temperature using vibrating sample magnetometer. Fig 6.15 shows the magnetization versus magnetic field ($M$–$H$) loops for different concentration of manganese incorporated into ZnO. All the samples show clear RTFM and with the Mn concentration increases, the saturated magnetic moment $M_s$ decreases. Similar results in Fe doped ZnO was demonstrated by Huilian Liu et al., 2008. The magnetic behaviour of the DMS materials is explained based on the carrier mediated exchange interactions. RKKY [Ruderman and Kittel 1954, Kasuya 1956, and Yosida 1957] interaction is one among them which explains the magnetic phases based on the concentration of free carriers apart from the concentration of magnetic ions. The saturated magnetic moment $M_s$ for 1, 2 and 3 wt% Mn doped ZnO is 0.0082, 0.0022 and 0.0017 emu/cm$^2$ respectively. If the origin of room-temperature magnetism derived from any impurity phase then there may be increase in magnetic moment. Thus an enhancement of the magnetism is suspected to be seen, but this phenomenon is not observed in the magnetic
behaviour of Mn doped ZnO samples as shown in Fig 6.15. Babi et al., 2008 and Duan et al., 2008 have reported ferromagnetism arose from the interaction between the Mn$^{2+}$ ions and defects. Only the concentration of Mn$^{2+}$ ions and defects within an appropriate range can produce strong ferromagnetism [Coey et al., 2005, Yang et al., 2010]. When the doping concentration increases, there may be agglomeration in ZnO matrix, which will be antiferromagnetic and severely suppress the overall ferromagnetic order in Mn-doped ZnO nanocrystalline films. Bulk crystals and thin films doped with the same dopant often show different magnetic behaviour. This suggests that the ferromagnetism observed in these materials is quite sensitive to growth technique and growth conditions. Similar result was obtained by Jayakumar et al., 2006 and Yang et al., 2010 but John Kennady Vethanathan et al., 2011 and Sharma et al., 2011 have reported the result which is contradictory to the present result.

6.9.2 Magnetic Properties of Co doped ZnO films

Fig. 6.16 Magnetisation(M) vs.Field (H) curves for Cobalt doped ZnO samples

Fig 6.16 shows the $M-H$ curves of the 2 and 3wt% cobalt doped zinc oxide thin films. Both the samples exhibit hysteresis loops at room temperature and shows ferromagnetism. The origin of room-temperature ferromagnetism in Co-doped ZnO DMS
is not clear yet. From the hysteresis loop, the coercive field \( (H_c) \) values are found to increase with increase in Co doping concentrations. The coercivity and saturation magnetic moment for the 2 wt% cobalt doped ZnO is about 606.6 Oe and 0.004emu/cm\(^2\) and for 3 wt% cobalt doped ZnO is about 633.1 Oe and 0.013emu/cm\(^2\). Inset shows the variation of coercivity \( H_c \) with the doping concentration. Many researchers believed that the room-temperature ferromagnetism just attributed to a secondary phase. Zhang et al., 2009 showed that ZnO nanoparticles have intrinsic ferromagnetism when doped with cobalt. Bouloudenine et al., 2005 and Rao et al., 2004 have reported absence of ferromagnetism in cobalt doped ZnO. An enhancement of magnetism is expected when the doping of transitional metal impurity increases which is observed in the present work. Similar result was observed by Shadie Hatamie et al., 2010. Ming Wei et al., 2006 and Patra et al., 2009 reported that increase in impurity decrease the magnetization. Mukta V. Limaye et al., 2011 presented that the origin of RTFM is associated with vacancies/defects present on the surface of nanorods. The magnetic properties of nanoparticles strongly depend on the preparation method [Garcia et al., 2007].

6.9.3 Magnetic Properties of Ni doped ZnO films

Fig 6.17 shows the magnetization measurements (M-H) of the samples. Before carrying out magnetic measurements on the doped ZnO films, the undoped film ZnO has been subjected to magnetization studies at RT, to ensure that the precursors are devoid of any magnetic impurity. The magnetization (M) vs. applied field (H) measurement of the film reveals the paramagnetic relationship of undoped ZnO, suggesting that no detectable ferromagnetic impurities are present in the starting precursor. The magnetization studies of ZnO films indicate that it has been possible to induce RTFM, with a maximum saturation magnetic moment of 0.0035emu/cm\(^2\) in 2% nickel doped ZnO.
RTFM of variable magnitude exist for Ni concentrations ranging from 1 wt% to 3 wt% which is shown in the Fig 6.17. However, all the nickel doped thin films show clear hysteresis loops (inset of Fig 6.17) revealing room temperature ferromagnetism. From 1 wt% to 2 wt% Ni concentration, ferromagnetism is enhanced significantly due to the higher Ni^{2+} concentrations. However, when the Ni^{2+} concentration in reactive solution reaches 3 wt % Ni concentrations, ferromagnetism decreased rapidly. Very interestingly, it has been observed that for 1 % and 3 % nickel doping, the saturation magnetization (Ms) of the films are more or less same. Similar result was observed by Prashant K. Sharma et al., 2009 and Dianwu Wu et al., 2009. From the hysteresis loop for 2 % nickel doped ZnO film, it is observed that the coercivity is 470 oesterd and the residual magnetic induction is 0.0005emu/cm^2. Pandey et al., 2008 reported the ferromagnetic behaviour in these systems arises due to two possibilities, one due to clustering of metallic Ni and another due to intrinsic ferromagnetism in the presence of charge carriers. El-Hilo et al., 2009 reported that the FM in the Ni-doped ZnO could be due to the exchange coupling between localised d-spins on the Ni ions mediated by free delocalized carriers.
6.10 Summary

Doping of ZnO with different transition elements has been achieved. XRD of all the films contain (100), (002), (101), (102), (110), (103) and (112) peaks, which indicate that are all polycrystalline in nature. FESEM images of Mn doped ZnO thin films exhibit the spherical grains with few agglomerations, cobalt doped ZnO thin films show worm like nanorods and ZnO:Ni films contain nanorods having nanograins aligned in a straight line like beads in a string. It is seen that the transition metal doped ZnO nanocrystalline thin films have violet, blue, and blue-green emission peaks. The band-gap energy value of manganese doped ZnO films are varied from 2.63 to 2.72 eV. All the films show ferromagnetic behaviour.
References


Chapter VI

Physical Properties of Transition Metal (Mn, Co,Ni) doped ZnO


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