CHAPTER 6

Preparation of Mn doped ZnO thin films by SILAR and their characterization

6.1 Preparation of films and thickness measurements

Preparation of Mn doped ZnO film was carried out from zinc chloride ($\text{ZnCl}_2$) solution as cationic precursor containing manganese (II) chloride as source of Mn ion and sodium hydroxide ($\text{NaOH}$) solution as anionic precursor. Efforts to synthesize Mn doped ZnO from sodium zincate as well as ammonium zincate bath failed possibly due to lowering of pH upon dopant addition. Although manganese chloride could be dissolve in low concentrations in these baths, no film formation took place.

The concentration of the zinc chloride ($\text{ZnCl}_2\cdot2\text{H}_2\text{O}$, Merck, Mol. Wt. 136.28) bath and sodium hydroxide bath was optimized at 0.1 M and 0.075 M respectively for synthesis of good quality adherent film. For concentrations more than 0.125 M for zinc chloride bath and for concentrations more than 0.1 M for sodium hydroxide bath, the growth process nonuniform resulting in poor quality and nonadherent films. The cationic precursor was at room temperature and the temperature of anionic precursor was optimized at 70°C.
One of the problems with zinc chloride solution is that complete dissolution of the solute does not occur and precipitate appears on standing. Addition of three drops of acetic acid (~ 0.3 cc by volume) gives a clear transparent solution. The pH of the transparent solution was 4.70 ± 0.05. Sodium hydroxide solution (0.075 M) was prepared by dissolving NaOH pellets (Merck, Mol. Wt. 40) in deionized water. The optimized pH of the sodium hydroxide bath was 11.10 ± 0.05. Alongwith bath concentrations, the pH and temperature of the baths were found to be optimum for getting adherent films on substrate.

Although adherent films could be obtained on glass substrate, it was found during the course of the experiment that adhesion of the films on quartz substrate was stronger compared to glass. The adherence of the ZnO films on glass substrate was found to be somewhat lesser compared to those deposited from sodium or ammonium zincate baths. Both microscope glass slides and commercially available quartz substrates were used for film deposition. For Mn doping, Manganese (II) chloride (MnCl₂·4H₂O, Merck, Mol. Wt. 197.9) was dissolved in zinc chloride solution. Addition of manganese chloride tetrahydrate gave the solution a slightly ash colouration. The resulting mixture was stirred using a magnetic stirrer for about 10 minutes. After stirring the manganese chloride salt gets completely dissolved in the solution. The manganese concentration was varied upto 5% in the zinc chloride solution for the preparation of doped films. For ≥10% dopant addition, the bath pH of the cationic precursor reduces resulting in slow growth rate and poor quality of the coated films. Accordingly the dopant addition was restricted to 5 atomic %.

The quartz substrate was cleaned, before deposition, by etching in 1% hydrofluoric acid (HF) for 24 hours followed by ultrasonic cleaning in equivolume acetone and alcohol and thorough rinsing in deionized water. The cleaned substrate was alternatively dipped in zinc chloride solution impurified with Mn (II) chloride and hot NaOH solution. Dipping for 2 s in each bath constitutes one complete dipping cycle.
The film thickness \( (t) \) was built up by increasing the number of dipping cycle. Fifty (50) dipping cycles were performed in the present experiments. The deposited films were subsequently annealed in air at 350°C for 2 hr. Figure 6.1 shows the dependence of film thickness (measured gravimetrically) on the number of dipping cycle \((N)\) for undoped ZnO films on quartz substrate.

It is seen from figure 6.1 that the film thickness follows a linear growth law with number of dipping cycle and the growth rate was found to be 0.021 µm/dipping. There is an overall variation of \( \pm 5\% \) in the film thickness data (shown as error bars against each data point of Fig. 6.1). The growth rate was found to be uniformly low for glass substrate.

![Figure 6.1: Dependence of film thickness on number of dipping cycle](image)

The film thickness was verified against cross sectional SEM. Some portion of the quartz substrate was acid etched to remove film from that area in order to create a step for thickness measurement. Figure 6.2 shows the cross-sectional SEM micrograph of undoped ZnO film of thickness 2.1 µm measured gravimetrically (obtained by 100 dipping). An average thickness of 2.56 µm was obtained from SEM micrograph.
The actual thickness determined from cross-sectional SEM is 22% higher than the gravimetric value (2.56 µm measured by SEM as opposed to 2.1 µm measured gravimetrically). The value was an average of several measurements on different portions. This indicates an average porosity of ~22% in the deposited films. The films are less porous compared to those from ammonium and sodium zincate baths (Section 4.2.4, Chapter 4).

![Cross-sectional SEM of ZnO film](image)

**Figure 6.2:** Cross-sectional SEM of ZnO film

The growth rate was found to decrease with Mn incorporation. For 50 dipping, the film thickness for pure ZnO was 1.05 µm. The corresponding thickness for 2% Mn:ZnO film was 0.94 µm and for 5% Mn:ZnO, the thickness was 0.82 µm. Thus the growth rate decreases with increasing Mn incorporation. The ZnO film was white in appearance and Mn doped films were slightly brownish with a good adherence to the substrate.

Table 6.1 shows the thickness and growth rate values for undoped and Mn doped films for 50 dipping on quartz substrate. The thickness of pure ZnO film was 0.80 µm and Mn doped film it was 0.71 µm on glass substrate.
Table 6.1: Thickness and growth rate for ZnO and Mn:ZnO films

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness (µm)</th>
<th>Growth rate (µm/dipping)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>1.05</td>
<td>0.021</td>
</tr>
<tr>
<td>2% Mn:ZnO</td>
<td>0.94</td>
<td>0.0188</td>
</tr>
<tr>
<td>5% Mn:ZnO</td>
<td>0.82</td>
<td>0.0164</td>
</tr>
</tbody>
</table>

6.2 Structural characterization: Evaluation of particle size and strain

The X-ray diffraction patterns of undoped ZnO and Mn doped ZnO films deposited on quartz substrate are shown in figure 6.3. The diffraction pattern for undoped ZnO is shown in figure 6.3 (a). Figure 6.3 (b) and 6.3 (c) shows the diffractograms for 2% and 5% Mn:ZnO films respectively. The films were heat treated at 350°C for 2 hr. prior to structural characterization. The materials were scanned in the range 25-65°. It is seen from figure 6.3 (a) that peaks appear at 31.70°, 34.397°, 36.183°, 47.516°, 56.551° and 62.88°. The corresponding values for 5% Mn:ZnO are 31.69°, 34.372°, 36.168°, 47.5°, 56.542° and 62.87°. The diffractogram of the sample reveals that all the peaks are in good agreement with the JCPDS data belonging to hexagonal ZnO structure. The corresponding reflecting planes are (100), (002), (101), (102), (110) and (103) respectively. The (002) peak appears with maximum intensity at 34.397°. Apart from ZnO characteristic peaks, no extra peaks due to manganese clusters, zinc or their complex oxides could be detected within the detection limit of XRD. This observation is an indication of the fact that the films do not have any phase segregation or secondary phase formation as well as Mn incorporation into ZnO lattice.

It is evident from figure 6.3 (a) that undoped ZnO film have a polycrystalline structure with preferred orientation along the (002) diffraction plane. Compared to undoped ZnO film, the intensity of (002) peak decreases for Mn:ZnO films. This results
in an increase of relative intensity of (101) peak with respect to (002) peak. The (101) peak appears with maximum intensity in ZnO powders with no preferred orientation (JCPDS Card No. 36-1451). Thus crystalline nature of films was affected due to enhancement of dopant concentration. Such loss of preferred c-axis orientation and enhancement of polycrystalline nature with Mn incorporation has been reported by Nirmala et. al [1]. The value of $T_C(002)$ for undoped ZnO is ~1.82 and it decreases to ~0.41 for 5% Mn:ZnO film [Evaluated using eqn. 3.5 (Section 3.2.1 of chapter 3) and following the method discussed in section 4.3 of chapter 4].

Figure 6.3: X-ray diffraction pattern of (a) ZnO, (b) 2% Mn:ZnO and (c) 5% Mn:ZnO.
The peaks of the diffraction pattern of the doped sample are slightly shifted to left compared to undoped ZnO. This is possibly because the ionic radius of $Mn^{2+}$ (0.83 Å) is larger than that of $Zn^{2+}$ (0.74 Å) [1]. A typical plot of MARQ2 analysis for 5% Mn:ZnO sample is shown in Figure 6.4.

Figure 6.4: Observed (dotted) and simulated (continuous) x-ray diffraction patterns of 5% Mn:ZnO on quartz substrate

The average value of particle size for undoped ZnO evaluated by x-ray line broadening method is 29.71 ± 0.01 nm. It decreases to 26.79 ± 0.01 nm for 2% Mn:ZnO and 23.76 ± 0.01 nm for 5% Mn:ZnO. Figure 6.5 shows the W-H plots of ZnO, 2% Mn:ZnO and 5% Mn:ZnO. The average microstrain in the films as determined from W-H plots is 0.0013, 0.00137 and 0.00146 respectively for pure, 2% Mn:ZnO and 5% Mn:ZnO films respectively. Thus the particle size decreases with increasing Mn incorporation and the strain increases. The decrease in average particle size with increasing Mn doping i.e. hindrance of grain growth upon Mn incorporation has been reported by other workers [2-102].
The decrease in crystal quality with Mn doping has been reported by Lee et al [5]. The decrease in average particle size might be due to development of strain because of Mn incorporation. Such enhancement of average microstrain with Mn incorporation has been observed in the present work. The enhancement of strain due to Mn incorporation might be due to larger ionic radius of Mn ion than Zn ion.

![Figure 6.5: W-H plots of (a) pure ZnO, (b) 2% Mn:ZnO and (c) 5% Mn:ZnO films](image)

The X-ray diffraction patterns of undoped ZnO and 5% Mn doped ZnO films deposited on glass substrates is shown in figure 6.6. The diffraction pattern for undoped ZnO is shown in figure 6.6 (a). Figure 6.6 (b) shows the diffractograms for 5% Mn:ZnO film. The films were heat treated at 350°C for 2 hr. prior to structural characterization. The step-scan data were recorded for the angular range 20° to 70°.
It is seen from figure 6.6 (a) that peaks appears at 31.7°, 34.42°, 36.2°, 47.46°, 56.56° and 62.84°. Similar observation of loss of preferred orientation along c-axis is evident from the figure. The preferred orientation of the films is governed by the total system energy, which is the summation of the strain and surface energies [6]. Thus increase in strain energy effects the preferred growth along c-axis since it is known that the driving force towards preferred orientation arises out of total energy minimization of the system.

6.3 SEM and EDX studies

Figure 6.7 shows the HRSEM micrograph of pure ZnO film prepared on quartz substrate. HRSEM study was undertaken in a FEI FEG Nova 600 Nanolab at 5 kV. The SEM image shows structure consisting of many spherical shaped nano particles with an
average size of ~31 nm. This is similar to the result obtained on glass substrate (chapter 4, Figure 4.18). The average particle size of ~31 nm matches well with that obtained using x-ray line broadening analysis of ~29.71 nm. Figure 6.8 shows the SEM image of 5% Mn:ZnO film on quartz substrate. Surface morphology of 5% Mn:ZnO film shows wrinkle structure with formation of nanorods in certain regions.

![HRSEM image of ZnO on quartz substrate](image)

**Figure 6.7:** HRSEM image of ZnO on quartz substrate

![SEM image of 5% Mn:ZnO thin film](image)

**Figure 6.8:** SEM image of 5% Mn:ZnO thin film
Similar observation of appearance of wrinkle structure due to Mn incorporation has been reported by Nirmal et al [1]. Srinivasan et al. [7] also reported microstructure consisting of nanorods with wrinkle structure for Mn doped films. Formation of such nanorods in Mn doped ZnO films have also been reported by Karamat et. al. [8]. Figure 6.9 shows the HRSEM image of 5% Mn:ZnO film on glass substrate with magnification $\times 25000$ [10].

Figure 6.9: HRSEM image of 5% Mn:ZnO

Figure 6.10 shows the energy dispersive X-ray spectrum of Mn:ZnO films prepared on quartz substrate. Figure 6.10 (a) shows the EDX spectrum of 2% Mn:ZnO and 6.10 (b) shows the spectrum of 5% Mn:ZnO. The EDX spectrum confirmed the presence of Zn, O and Mn elements in the deposited films i.e. incorporation of Mn in ZnO lattice. The silicon signal appears from the quartz substrate. Dopant concentration in these two cases was 2% and 5% in the starting solution. Accordingly the expected Mn/Zn ratio was 0.02 and 0.05 in the films. We actually obtained the Mn/Zn ratio in the films as 0.0131 and 0.0284 respectively indicating that the amount of Mn incorporation in the film is less than the amount of Mn in the starting solution. The real Mn content in the deposited films was 1.31% and 2.84% as obtained from EDX spectrum.
Figure 6.10. EDX pattern of (a) 2% Mn:ZnO and (b) 5% Mn:ZnO
Figure 6.11 reveals the EDX spectrum of 5% Mn:ZnO film on glass substrate. Trace amount of calcium (Ca) impurity was also detected in the film.

![EDX spectrum of 5% Mn:ZnO film](image)

**Figure 6.11:** EDX pattern of 5% Mn:ZnO

### 6.4 Evaluation of band gap from Optical absorption

The optical absorption spectra were recorded by using a similar quartz substrate as a reference and hence the absorption due to the film only was obtained. Figure 6.12 shows the dependence of optical absorbance ($\alpha$) on wavelength ($\lambda$). While figure 6.12 (a) shows the dependence of $\alpha$ on $\lambda$ for pure ZnO, figures 6.12 (b) and 6.12 (c) shows dependence of $\alpha$ on $\lambda$ for 2% Mn:ZnO and 5% Mn:ZnO respectively. Plot of $(\alpha h\nu)^2$ against $h\nu$ for undoped and Mn doped ZnO films was derived from figure 6.12 and is shown in figure 6.13. Figure 6.13 (a) shows the spectrum of undoped ZnO while figures 6.13 (b) and 6.13 (c) shows the spectrum of 2% Mn:ZnO and 5% Mn:ZnO respectively. The direct band gap is determined using this equation when linear portion of $(\alpha h\nu)^2$ against $h\nu$ plot is extrapolated to intersect the energy axis at $\alpha = 0$. 

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Figure 6.12. Plots of absorbance vs wavelength for (a) undoped ZnO; (b) 2% Mn:ZnO and (c) 5% Mn:ZnO

Figure 6.13: Plots of \((\alpha h \nu)^2\) vs \(h \nu\) for (a) pure ZnO; (b) 2% Mn:ZnO and (c) 5% Mn:ZnO
It is seen that with the increase of manganese doping level, the fundamental absorption edge decreases. The value of $E_g$ for undoped ZnO is $3.22 \pm 0.01$ eV. It decreases to $3.13 \pm 0.01$ eV for 2% Mn:ZnO and to $3.06 \pm 0.01$ eV for 5% Mn:ZnO.

The decrease in band gap value with increased Mn doping concentration has been accounted due to the sp-d exchange interactions and has been theoretically explained using the second–order perturbation theory [1, 9-10]. A decrease in band gap energy from 3.27 eV for undoped ZnO to 2.78 eV for 3% Mn doped ZnO has been reported by Senthilkumar et. al. [4] and has been attributed to s-d and p-d interactions giving rise to band gap bowing.

Similar results on glass substrate for undoped 5% Mn:ZnO film is shown in figure 6.14. The value of $E_g$ for undoped ZnO is 3.20 eV and it decreases to 3.04 eV for 5% Mn:ZnO. The data for drawing figure 6.14 was extracted from the data of $\alpha$ versus $\lambda$.

![Figure 6.14](image_url)

**Figure 6.14:** Plots of $(\alpha h \nu)^2$ vs $h \nu$ (in eV) for (a) pure ZnO and (b) 5% Mn:ZnO.
6.5 Discussion of results on Mn:ZnO thin films

The primary aim of this investigation was to explore the possibility of doping or impurifying ZnO with manganese by SILAR method. Mn doped ZnO films with different percentage of Mn content (upto 5%) could be successfully synthesized by suitable choice of cationic and anionic precursors under optimized deposition conditions. Zinc chloride bath with manganese chloride as source of Mn ion was used as cationic precursor and sodium hydroxide was used as anionic precursor. The film growth rate was found to increase linearly with number of dipping cycle. Better adherence of Mn:ZnO films were obtained on quartz substrate compared to glass substrate. More than 5% dopant addition was difficult to obtain due to lowering of stability of the cationic bath. Particle size evaluated using x-ray line broadening analysis shows a constantly decreasing trend with increasing manganese incorporation. The average particle size of ~29.71 nm for undoped ZnO evaluated by x-ray line broadening method matches well with HRSEM observation (~31nm). The average particle size reduces to ~26.69 nm for 2% Mn:ZnO and ~23.76 nm for 5% Mn:ZnO. The films are polycrystalline with an average porosity of ~22%. The polycrystallinity of the films as well as the average microstrain (evaluated using Williamson-Hall equation) increases with increasing Mn incorporation. Mn doping also influences the morphology of the films. The undoped films contained nearly spherical grains. On the other hand microstructure consisting of wrinkle structure was observed due to Mn incorporation. The observation was similar for both quartz and glass substrates. These observations along with EDX observation confirms the replacement of zinc ion by manganese ions in the ZnO lattice. The real Mn content in the deposited film was less than that in the starting solution as evident from EDX measurements. The oxidation state of Mn in ZnO is controversial and no experiment was taken up in this direction. This is important for magnetic properties on Mn:ZnO. Mn doping reduces the value of fundamental absorption edge from ~3.22 eV for pure ZnO to ~3.06 eV for 5% Mn:ZnO for films deposited on quartz substrate. Corresponding values on glass were 3.20 eV and 3.04 eV respectively. Incorporation of Mn has a strong effect on the structural, morphological and optical properties of ZnO.
References