CHAPTER - V
THICKNESS AND STRUCTURAL STUDIES ON UNDOPED AND DOPED ZnO THIN FILMS

5.1 Introduction

Characterization of double dip synthesized thin films is a vital field in thin films research. The primary object of this section is to discuss the results of the investigations on the undoped and doped ZnO thin films grown by double dip technique. The effects of molar concentrations on the resulting of ZnO film thickness, structural and microstructural properties are studied. In addition to this, the effect of nickel (Ni), manganese (Mn) and co-doping (Mn & Ni) of ZnO thin films are discussed. X-ray diffraction technique is now a most powerful and versatile method to reveal micro structural parameters of ‘thin film’ in a qualitative as well as quantitative manner. The primary object of this section is to discuss the results of the investigations on the undoped and doped ZnO thin films grown by double dip technique.

5.2 Microstructural Parameters

The structural parameters like micro strain, dislocation density, stacking fault probability and texture coefficients were evaluated along with crystallite size using the formula as given under.

1. Crystalline size (D):

This parameter can be calculated using Scherer’s formula from Full width at half Maximum (FWHM) [1],

\[
D = \frac{k \lambda}{\beta \cos \theta} \tag{5.1}
\]
Where the constant ‘k’ is the shape factor = 0.94, ‘λ’ is wavelength of X-rays (1.5406 ÅCuKα) ‘θ’ is the Bragg’s angle and ‘β’ is FWHM.

2. Dislocation density (δ)

Dislocations an imperfection in crystal associated with the misregistry of lattice existing in different parts of crystal. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections (i.e.) thermodynamic considerations are inadequate to account for their existence in observed densities. This can be evaluated from crystalline size (D) by following relation

\[
\delta = \frac{1}{D^2}
\]  
\(5.2\)

The origin of microstrain is related to lattice misfit which is related to lattice misfit which in turn depend upon the deposition condition.

3. Microstrain

The microstrain (ε) developed in thin films can be evaluated from the relation

\[
\varepsilon = \left( \frac{\lambda}{DCos\theta} - \beta \right) \frac{1}{\tan\theta}
\]  
\(5.3\)

4. Stacking fault probability (α)

The relation connecting stacking fault probability (α) with peak shift Δ(2θ) was given by

\[
\alpha = \left( \frac{2\pi^2}{45\sqrt{3}} \right) \frac{\Delta(2\theta)}{\tan\theta}
\]  
\(5.4\)

where D is crystallite size, β is full width at half maximum, α stacking fault probability and λ wavelength of the X-ray diffraction respectively.
5. Texture coefficient

The X-ray diffraction peak of films corresponding texture coefficient \( (T_c) \) is estimated using an expression [2]

\[
T_c(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[ \frac{1}{n} \sum I(h_i k_i l_i) \right]^{-1} \tag{5.5}
\]

where \( I_0 \) represents the standard intensity, \( I \) is the observed intensity of \( (h_i k_i l_i) \) plane and \( n \) is the reflection number.

5.3 Undoped ZnO thin films

5.3.1 Thickness studies of ZnO thin films

Thickness is the most significant film parameter. It may be measured either by in-situ monitoring of the rate of the deposition or after the film is taken out of the deposition chamber. In the present study stylus profilometer is used to determine the film thickness [3]. Figure 5.1 describes the growth of undoped thin film as a function of the rinsing time such as 5, 10, 15 and 20sec, respectively. Film thickness is estimated against various molar concentrations ranging from 0.01 to 0.03 M at different rinsing time of ZnO thin films. Fig. 5.1 shows that the growth rate linearly increases with increase of rinsing time. In the case film thicknesses the film growth slows down after 80dippings. The faster growth is observed upto15 sec rinsing time and film grows to a thickness at 610nm at 0.03 M zinc sulphate. In the initial stage, the source materials are sufficient and the solution has high complexity. The process of deposition plays a more important role than the dissolution process which leads to increase in film thickness. With the deposition time being prolonged, the thickness of the film increases, at the same time the resistance of the film increases. Therefore, after a particular time of deposition, the dissolution process predominates over the
deposition thereby resulting in a decrease in film growth. After about 20 immersion cycles, the solutions were substituted with fresh ones. The maximum value of film thickness is obtained at 620 nm at 20 sec rinsing time. The rinsing step employed between the rinsing in the SILAR process is meant to eliminate the transport of surface tension held solution layer to and fro the baths and hence avoids precipitation of semiconductor clusters and pigments in the bath. The reaction in such a case takes place only with the adsorbed ion layer leading to the deposition of thin films of relatively higher quality. However fig. 5.1 describes the rinsing also leads the lower growth rate of undoped ZnO film. The duration of immersions ranging from 5s to 20s were employed. It was found that durations longer than 15s do not result in a higher film thickness. Hence 15s in each of the solutions was chosen as the standard immersion period in the present case.
**Fig. 5.1:** Film thickness as a function of dipping time of undoped ZnO thin films
5.3.2 Structural studies of ZnO thin films

The structural properties are studied using X-ray diffraction patterns for undoped ZnO thin films prepared at various molar concentrations. The polycrystalline nature of undoped ZnO thin films, whose c-axis was preferentially, oriented normal to the glass substrate [4]; in other words, that grains of undoped films are mainly grown with c-axis vertical to the glass substrate. Hence, the multiple-coating or the piling up of each film was considered not to disturb the overall growth of the films with c-axis orientation. Therefore, the c-axis orientation may be a common phenomenon in the ZnO film deposition by chemical process. Figure 4.1 (a) shows XRD patterns of ZnO thin films for various zinc sulphate concentrations. From this figure the predominant orientation of the film is (002) and its corresponding Bragg’s angle 34.41º. The 0.01 M zinc sulphate concentration prepared film possesses polycrystalline nature of XRD patterns as shown in fig. 5.1(a). The diffraction peaks are observed at an angle 34.43º, 36.23 º, 47.37 º and 62.95º and corresponding crystallographical planes are (101), (002), (102) and (103), respectively. The peak intensities are increases and some new peaks are emerged at 0.02 molar concentration of zinc sulphate prepared ZnO thin film. The crystallographical plane (100), (110) and (112) are newly emerged diffraction line as shown in fig. 4.1(b). The peak intensities are increases for increase of zinc sulphate concentrations from 0.02 to 0.03 M prepared ZnO film as shown in fig. 5.1(c). Also no other new peak is emerged in this molar concentration prepared film.

The crystallite size of the ZnO thin film is estimated using relation (5.1). Figure 52 shows the variation of crystallite size and micro strain values of various molar concentrations prepared ZnO thin films. It is clear that the crystallite size
increases with respect to molar concentration of zinc sulphate. The maximum value of crystallite size is achieved at 29 nm and it may be due to the number of Zn atoms occupies oxygen vacancies. The microstrain of the film is calculated using above mentioned relation (5.2) [5]. The microstrain value variation is plotted against molar variations as shown in fig. 4.2. From this figure microstrain values are linearly decreases with zinc sulphate concentrations. The lower value of microstrain is observed at $1.79 \times 10^{-3}$ lines$^{-2}.m^{-4}$. The dislocation density values are linearly decreases with molar concentrations which may be due to increase of crystallite size. The stacking fault probability values are slightly decreases with increase of molar concentrations. The predominant peak is shift towards standard peak values. This may be due to change of atomic percentage ratio of various molar concentrations prepared ZnO thin films.

The X-ray diffraction peak of ZnO films texture coefficient ($T_C$) is estimated using an equation (5.5). The crystallite shape of ZnO film is strongly related to the texture coefficient of the film. The texture coefficient of different lattice planes of ZnO thin films are shown in figure 4.1. The maximum texture coefficient value is obtained in higher zinc sulphate concentration because intensity of the peaks is increased with increasing the zinc sulphate concentration. The predominant plane orientation of the film has high texture coefficient value. It has been reported for copper oxide film [6] earlier that texture coefficient is higher than 1 indicates preferential orientation and also indicates the abundance of grains in a given $(h,k,l)$ direction.
### Table 5.1

Microstructural properties of undoped ZnO thin films

<table>
<thead>
<tr>
<th>Zinc sulphate concentrations (M)</th>
<th>Crystallite size (nm)</th>
<th>Micro strain (ε)</th>
<th>Dislocation density ( \delta \times 10^{15} ) lines/m²</th>
<th>Stacking fault probability (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>26.62</td>
<td>0.00188</td>
<td>1.31</td>
<td>0.04638</td>
</tr>
<tr>
<td>0.02</td>
<td>27.55</td>
<td>0.00187</td>
<td>1.30</td>
<td>0.02898</td>
</tr>
<tr>
<td>0.03</td>
<td>29.23</td>
<td>0.00179</td>
<td>1.17</td>
<td>0.00307</td>
</tr>
</tbody>
</table>

**Fig. 5.2:** XRD patterns of ZnO thin films prepared at various molar concentration such as (a) 0.01 M (b) 0.02 M and (c) 0.03M
Fig. 5.3: Variation of crystallite size and microstrain values of ZnO thin films prepared at various molar concentrations.

Fig. 5.4: Variation of dislocation density and stacking fault probability values of ZnO thin films prepared at various molar concentrations.
Fig. 5.5: Texture coefficient values of ZnO thin films prepared at various molar concentrations
5.4 Nickel doped (Ni) ZnO (NZO) thin films

5.4.1 Nickel sulphate molar variation of NZO thin films

The thickness of the Ni doped ZnO (NZO) thin film is estimated using surface profilometer. Figure 5.6 describes the growth of Ni doped ZnO (NZO) thin film as a function of the deposition time such as 5, 10, 15 and 20sec, respectively. Film thickness is estimated against various molar concentrations of NiSO$_4$. Fig. 4.6 shows that the growth rate linearly increases with increased deposition time. In the case film thicknesses the film growth slows down after 15 sec of rinsing time. The faster growth is observed upto 15 sec rinsing time and film grows to a thickness at 630nm at 15mM NiSO$_4$. In the initial stage, the source materials are sufficient and the solution has high complexity. The doping element concentration increases film thickness as well as rinsing time increase the thickness of the film. The process of deposition plays a more important role than the dissolution process which leads to increase in film thickness. The rinsing step employed between the immersions in the SILAR process is meant to eliminate the transport of surface tension held solution layer to and fro the baths and hence avoids precipitation of semiconductor clusters and pigments in the bath. The reaction in such a case takes place only with the adsorbed ion layer leading to the deposition of thin films of relatively higher quality.
Fig. 5.6: Film thickness as a function of rinsing time of NZO thin films
The doping molar concentrations mainly affect the crystallinity of the film and also change the microstructural properties of the NZO films. Fig. 5.7 (a) shows the X-ray diffraction patterns of Ni doped ZnO films with various molar concentrations such as 5, 10 and 15mM. The ‘d’ (interplanar spacings) values of the XRD reflections were compared with standard ‘d’ values taken from JCPDS diffraction file (No. 89-0511). Good agreement between the observed and standard ‘d’ values suggests that the material deposited is Ni doped ZnO with hexagonal structure. The doping molar concentration of the films produces a considerable improvement in crystallinity, showing more intense and sharper XRD peaks. The predominant peak at 34.51° indicates that NZO thin film is preferentially oriented along (002) plane. The lattice parameter values are \( a = 3.249 \, \text{Å} \) and \( c = 5.205 \, \text{Å} \). The sharpened X-ray line profile and higher intensity of (002) plane is observed at 5mM to 10mM of nickel sulphate concentration. There is no other new peak is observed in this molar concentration as shown in fig. 5.7 (b). The predominant peak orientation is shift from (002) plane to (101) plane for 15mM prepared NZO thin film. Also (002) and (100) plane peaks intensities are slightly suppressed due to increase of doping molar variations. No other typical peaks were appeared in increasing the doping molar variations. It is indicated that the phase transformation did not take place when the Ni concentrations increased NZO thin films.

Fig. 5.8 shows that crystallite size and microstrain with their corresponding peak of FWHM and ‘2θ’ values. The crystallite size ‘D’ of the films was calculated from the Debye-Scherer’s formula using FWHM. The larger full-width at half-maximum (FWHM) observed 5 mM prepared NZO film and calculated crystallite size is in the range of 47 - 57 nm. The maximum broadening of peak is observed in lower
doping concentration because FWHM value inversely proportional to the crystallite size. Crystallite size of the film increase with doping concentrations is as shown fig. 5.8. Because it may be due to Ni atoms incorporate with ZnO atoms in NZO thin films. The microstrain (ε) was calculated from the slope of βcosθ versus sinθ. Figure 5.9 shows dislocation density and stacking fault probability of various molar concentration prepared NZO thin films. Also it is observed that the microstrain value is depending on the crystallite size of the film. So that microstrain and dislocation density of the films is decrease with increase doping concentration. Due to the removal of defects in the lattice with increase in doping concentration of themicrostrain in the films get released and attained a minimum value at 15mM of NiSO₄. A sharp increase in crystallite size and decrease in dislocation density with doping concentration is shown in figure. The stacking fault probability value is mainly depending on diffraction angle shift compared with standard JCPDS values as shown in fig. 4.9. The doping concentration is increase predominant orientation angle shift towards high may be due to increase of Ni atomic percentage in ZnO thin films. So that stacking fault probability of the NZO thin films increases with doping molar concentrations. The NZO thin film with lower microstrain and dislocation density is improves the stoichiometry of the films which in turn causes the volumetric expansion of thin films.

The texture coefficient was calculated using an equation (5.4) [7]. The crystallite shape of the Ni doped ZnO film is strongly related to the texture coefficient of the film. The doping molar variation of texture coefficient values for different lattice plane Ni doped ZnO thin films are shown in figure 5.10. $T_c(h,k,l)$ has to be bigger that 1 to determine the preferential orientation, if $T_c(h,k,l)$ approximately 1 for
all the \((h,k,l)\) planes considered at X-ray diffraction patterns, the films are randomly oriented \(T_c(h,k,l)\) values higher than one indicates the abundance of grains in a given \((h,k,l)\) direction. The (002) predominant plane orientation of the film has high texture coefficient value in 5 mM prepared NZO thin film. The texture coefficient of (002) and (112) plane are decreases with increase of doping concentrations. The other peak texture coefficient value of (100), (101), (110), (102) and (103) plane are increases with doping concentrations. The predominant peak orientation of (002) plane is changed as (101) plane and maximum value is estimated at 2.6.

### Table 5.2
Microstructural properties of various NiSO₄ concentrations prepared NZO thin films

<table>
<thead>
<tr>
<th>Nickel sulphate concentrations (mM)</th>
<th>Crystallite size (nm)</th>
<th>Micro strain (\varepsilon)</th>
<th>Dislocation density (\delta \times 10^{15} \text{ lines/m}^2)</th>
<th>Stacking fault probability (\alpha \times 10^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>29.5</td>
<td>0.00167</td>
<td>1.14</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>44.6</td>
<td>0.00117</td>
<td>0.51</td>
<td>7.06</td>
</tr>
<tr>
<td>15</td>
<td>45.2</td>
<td>0.00115</td>
<td>0.48</td>
<td>11.0</td>
</tr>
</tbody>
</table>
Fig. 5.7: XRD patterns of NZO thin films prepared at various molar concentrations such as (a) 5 mM (b) 10mM and (c) 15 mM

Fig. 5.8: Variation of crystallite size and microstrain values of NZO thin films prepared at various doping molar concentrations
Fig. 5. 9: Variation of dislocation density and stacking fault probability values of NZO thin films prepared at various doping molar concentrations

Fig. 5. 10: Texture coefficient values of NZO thin films prepared at various doping molar concentrations
5.4.2 Annealing effect of NZO thin films

The thickness of the film is calculated using surface profile meter. Figure 5. 11 describe thickness of the film with various annealing temperatures. The thickness of the film decreases with annealing temperatures. The lower value is observed at 629 nm of as-deposited NZO thin films. The thickness of the film decreases from 629 to 610 nm for 200°C prepared nickel doped zinc oxide thin films. The film thickness decreases from 640 nm to 585 nm for maximum value of annealing temperatures. The value of thickness decreases may be due to decrease of oxygen atomic vacancies.

Annealing properties mainly affect the crystallinity of the film and also change the microstructural properties of the NZO films. Fig. 5.12 shows the X-ray diffraction patterns of Ni doped ZnO films with various annealing temperature such as 0, 200, 300 and 400°C. The‘d’ (interplanar spacings) values of the XRD reflections were compared with standard‘d’ values taken from JCPDS diffraction file (No. 89-0511). The annealed films at 200, 300 and 400°C for 60 min in air produces a considerable improvement in crystallinity, showing more intense and sharper XRD peaks. The XRD patterns predict the increase annealing temperature 0 to 400°C increase the crystallinity and intensity of the film. The predominant peak at 36.28° indicates that Ni doped ZnO thin film is preferentially oriented along the (101) plane. The diffraction peak intensity of the NZO film is increased with annealed at 200°C. The predominant peak angle is shift to (002) plane at 300°C annealed film. The all the diffraction peak intensities are increases with increase of annealing temperatures. Also this same behavior has been observed at 400°C annealed film.
Fig. 5.13 shows that crystallite size and microstrain values of various temperatures annealed NZO thin film. The crystallite size $D$ of the films was calculated from the Debye-Scherer’s formula using FWHM. The maximum broadening of peak is observed in as-deposited film. Crystallite size of the film increase with annealing temperature is as shown fig. 5.13. Because post heat treatment to grow the crystallite of its thermal expansion properties. The strain $\varepsilon$ was calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$. The microstrain values are decreases with increase of annealing temperatures as shown in fig. 5.13. Due to the removal of defects in the lattice of microstrain in the film get released and attained a minimum value at 400°C. Figure 5.14 shows dislocation density and stacking fault probability with various annealing temperature. Also it is observed that the both of the microstructural properties are depend on the crystallite size of the film. So that microstrain and dislocation density of the films is decrease with increase annealing temperature. The stacking fault probability of NZO thin films are decreases with increase of annealing temperatures as shown in fig.5.14. The lower peak shift is observed at 400°C of NZO thin film. The lower value of microstrain, dislocation density and stacking fault probability of 400°C annealed film such as $8.8 \times 10^{14}$ lines$^2$.m$^{-2}$, $1.42 \times 10^{14}$ lines/m$^2$ and 0.0057, respectively. The texture coefficient values are calculated using relation (5.4) and the values are shown in fig. 5.15. The crystallite shape of the NZO film is strongly related to the texture coefficient of the film. The annealing effect of texture coefficient values for different lattice plane NZO thin films are shown in figure 5.15. The texture coefficient value of (002) plane is linearly increases may be due to highly texture peak observed at 400°C prepared NZO thin film. The (100) and (101) peak texture coefficient values are slight decrease for 200°C.
prepared film and then increases up to 400°C annealed NZO thin film. Also other peak texture coefficient values are increases for all the case of annealed films.

Table 5.3
Microstructural properties of annealed NZO thin films

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Crystallite size (nm)</th>
<th>Micro strain (ε $\times 10^{-3}$)</th>
<th>Dislocation density (δ $\times 10^{14}$)</th>
<th>Stacking fault probability ($\alpha \times 10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45.2</td>
<td>1.15</td>
<td>4.44</td>
<td>11</td>
</tr>
<tr>
<td>200</td>
<td>48.2</td>
<td>1.12</td>
<td>3.57</td>
<td>5.47</td>
</tr>
<tr>
<td>300</td>
<td>49.7</td>
<td>1.05</td>
<td>2.00</td>
<td>1.81</td>
</tr>
<tr>
<td>400</td>
<td>52.8</td>
<td>0.88</td>
<td>1.42</td>
<td>1.57</td>
</tr>
</tbody>
</table>
Fig. 5.11: Film thickness variations of annealed NZO thin films

Fig. 5.12: XRD patterns of as-deposited and annealed NZO thin films (a) as-deposited (b) 200°C (c) 300°C and (d) 400°C
Fig. 5.13: Variation of crystallite size and microstrain values of various temperatures annealed NZO thin films

Fig. 5.14: Variation of dislocation density and stacking fault probability values of various temperatures annealed NZO
Fig. 5.15: Texture coefficient variation of various temperatures annealed NZO thin films
5.5 Manganese (Mn) doped ZnO (MZO) thin films

5.5.1 Manganese sulphate variation of MZO thin films

Figure 5.16 describes the growth of Mn doped ZnO (MZO) thin film as a function of the deposition time such as 5, 10, 15 and 20sec, respectively. Film thickness is estimated against various MnSO\(_4\) concentrations ranging from 5 to 15 mM. Fig. 5.16 shows that the growth rate linearly increases with increased deposition time. The faster growth is observed upto 15 sec rinsing time and film grows to a thickness at 631nm at 15 mM MnSO\(_4\). In the initial stage, the source materials are sufficient and the solution has high complexity. The process of deposition plays a more important role than the dissolution process which leads to increase in film thickness. With the deposition time being prolonged, the thickness of the film increases, at the same time the resistance of the film increases. Therefore, after a particular time of deposition, the dissolution process predominates over the deposition thereby resulting a decrease in film thickness. After about 20 immersion cycles, the solutions were substituted with fresh ones. The maximum value of film thickness is obtained at 655 nm at 15 mM MnSO\(_4\) concentrations. The reaction in such a case takes place only with the adsorbed ion layer leading to the deposition of thin films of relatively higher quality. However fig. 4.16 describes the rinsing also leads the lower growth rate of MZO film. The duration of immersions ranging from 5s to 20s were employed. It was found that durations longer than 15s do not result in a higher film thickness. Hence 15s in each of the solutions was chosen as the standard immersion period in the present case.
Fig. 5.16: Film thickness variation as a function of rinsing time of MZO thin films prepared at various MnSO$_4$ concentrations
The structural properties are studied using X-ray diffraction patterns for Mn-doped ZnO (MZO) thin films prepared at various doping concentrations. The polycrystalline nature of MZO thin films, whose c-axis was preferentially oriented normal to the glass substrate. Hence, the multiple-coating or the piling up of each film was considered not to disturb the overall growth of the films with c-axis orientation. Figure 5.17 shows XRD patterns of ZnO thin films for various zinc sulphate concentrations such as 5, 10 and 15 mM MnSO$_4$. From this figure the predominant orientation of the film is (002) and its corresponding Bragg’s angle 34.48°. The 5 mM manganese sulphate concentration prepared film possesses polycrystalline nature of XRD patterns as shown in fig. 5.17(a). The diffraction peaks are observed at an angle 31.62°, 34.43°, 36.23 °, 47.37 °, 56.38°, 62.95° and 68.01° and corresponding crystallographical planes are (100), (002), (101), (102), (110), (103) and (112), respectively. The peak intensities are increases with increase of doping molar concentration of manganese sulphate for MZO thin films. The peak intensities are increases for increase of zinc sulphate concentrations from 10 to 15mM prepared MZO film as shown in fig. 5.17(c). Also no other new peak is emerged with increase of doping molar concentration prepared film.

The crystallite size of the MZO thin film is estimated using relation (5.1). Figure 4.18 shows the variation of crystallite size and micro strain values of various molar concentrations prepared MZO thin films. It is clear that the crystallite size increases with respect to molar concentration of manganese sulphate. The maximum value of crystallite size is achieved at 32.1 nm and it may be due to the Mn atoms incorporate with ZnO matrix. The microstrain of the film is calculated using above mentioned relation (5.2). The microstrain value variation is plotted against molar
variations manganese sulphate as shown in fig. 4.18. From this figure microstrain values are linearly decreases with manganese sulphate concentrations. The lower value of microstrain is observed at $1.09 \times 10^{-3}$ lines$^{-2}$m$^{-2}$. The dislocation density values are linearly decreases with molar concentrations which may be due to increase of crystallite size as shown in fig. 4.19. The stacking fault probability values are rapidly increases with increase of molar concentrations shown in fig. 5.19. The predominant peak is shift towards higher values due to incorporation of Mn atoms in ZnO matrix.

The texture coefficient was calculated using an equation (5.4). The crystallite shape of the Mn doped ZnO film is strongly related to the texture coefficient of the film. The doping molar variation of texture coefficient values for different lattice plane Mn doped ZnO thin films are shown in figure 4.20. $T_r(h,k,l)$ has to be bigger that 1 to determine the preferential orientation, if $T_r(h,k,l)$ approximately 1 for all the $(h,k,l)$ planes considered at X-ray diffraction patterns, the films are randomly oriented $T_r(h,k,l)$ values higher than one indicates the abundance of grains in a given $(h,k,l)$ direction. The (002) predominant plane orientation of the film has high texture coefficient value in 5 mM prepared MZO thin film. The texture coefficient of (002) predominant peak value is increases with increase of doping concentrations from 5 to 15 mM MnSO$_4$. Also other peaks texture coefficient value of (100), (101), (110), (102), (103) and (112) planes are increases with doping concentrations. The maximum value of predominant peak orientation of (002) is estimated at 2.66.
Table 5.2 Microstructural properties of various MnSO\(_4\) concentrations prepared MZO thin films

<table>
<thead>
<tr>
<th>Nickel sulphate concentrations (mM)</th>
<th>Crystallite size (nm)</th>
<th>Micro strain ((\varepsilon))</th>
<th>Dislocation density ((\delta)) x 10(^{14}) lines/m(^2)</th>
<th>Stacking fault probability ((\alpha \times 10^{-4}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>32.1</td>
<td>0.00154</td>
<td>9.69</td>
<td>9.91</td>
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<tr>
<td>10</td>
<td>40.9</td>
<td>0.00127</td>
<td>5.95</td>
<td>10.2</td>
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<tr>
<td>15</td>
<td>47.8</td>
<td>0.00109</td>
<td>4.36</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Fig. 5.17: XRD patterns of MZO thin films prepared at various molar concentrations of MnSO\(_4\) such as (a) 5 mM (b) 10 mM and (c) 15 mM
Fig. 5.18: Crystallite size and microstrain values variation of MZO thin films prepared at various molar concentrations of MnSO$_4$

Fig. 5.19: Dislocation density and stacking fault probability values variation of MZO thin films prepared at various molar concentrations of MnSO$_4$
Fig. 5.20: Texture coefficient variation of MZO thin films prepared at various molar concentrations of MnSO$_4$
5.5.2. Annealing effect of MZO thin films

Film thickness is estimated using surface profile meter. Figure 5.21 describe thickness of the MZO film with various annealing temperatures. The thickness of the film decreases with annealing temperatures. The lower value is observed at 631 nm of as-deposited NZO thin films. The thickness of the film decreases from 631 to 625 nm for 200°C prepared nickel doped zinc oxide thin films. The film thickness decreases from 625 nm to 590 nm for annealing temperature increased from 200°C to 400°C. The value of thickness decreases may be due to decrease of oxygen atomic vacancies [8].

Annealing properties mainly affect the crystallinity of the film and also change the microstructural properties of the MZO films. Fig. 5.22 shows the X-ray diffraction patterns of Mn doped ZnO films with various annealing temperature such as 0, 200, 300 and 400°C. The ’d’ (interplanar spacings) values of the XRD reflections were compared with standard ‘d” values taken from JCPDS diffraction file (No. 89-0511). The annealed films at 200, 300 and 400°C for 60 min in air produces a considerable improvement in crystallinity, showing more intense and sharper XRD peaks. The XRD patterns predict the increase annealing temperature 0 to 400°C increase the crystallinity and intensity of the film. The predominant peak at 34.58° indicates that Mn doped ZnO thin film is preferentially oriented along the (002) plane. The diffraction peak intensity of the MZO film is increased with annealed at 200°C. The predominant peak angle is shift to (101) plane at 300°C annealed film. However, the MZO thin film is subjected annealing at 400°C, some new properties are discovered. The (100) peak intensity is suddenly increased and act as a predominant orientation than other orientation. This shift may be due to the all the MZO atoms are try to
change other phase of MZO. The all the diffraction peak intensities are increases with increase of annealing temperatures.

Fig. 5.23 shows that crystallite size and microstrain values of various temperatures annealed MZO thin film. The crystallite size (D) of the films was calculated from the Debye-Scherer’s formula using FWHM. The maximum broadening of peak is observed in as-deposited film. Crystallite size of the film increase with annealing temperatures is as shown fig. 5.23. Because post heat treatment to grow the crystallite of its thermal expansion properties. The strain ε was calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$. The microstrain value is decreases with increase of annealing temperatures as shown in fig. 5.23. Due to the removal of defects in the lattice of microstrain in the film get released and attained a minimum value at 400°C. Figure 5.24 shows dislocation density and stacking fault probability with various annealing temperature. Also it is observed that the both of the microstructural properties are depend on the crystallite size of the film. So that microstrain and dislocation density of the films is decrease with increase of annealing temperatures. The stacking fault probability of NZO thin films are decreases with increase of annealing temperatures as shown in fig. 5.24. The lower peak shift is observed at 400°C of MZO thin film. The lower value of microstrain, dislocation density and stacking fault probability of 400°C annealed film such as $1.04 \times 10^{-3}$ lines$^{-2}$, $4 \times 10^{14}$ lines/m$^2$ and $4.68 \times 10^{-4}$, respectively. The texture coefficient values are calculated using relation (5.4) and the values are shown in fig. 5.25. The crystallite shape of the MZO film is strongly related to the texture coefficient of the film. The annealing effect of texture coefficient values for different lattice plane NZO thin films are shown in figure 5.25. The texture coefficient value of (100) plane is linearly
increases may be due to highly texture peak observed at 400°C prepared MZO thin film. Hence other peak texture coefficient values are slightly decreases with annealing temperature increases upto 400°C for MZO thin film.

Table 5.3 Microstructural properties of annealed MZO thin films

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Crystallite size (nm)</th>
<th>Micro strain ($\varepsilon \times 10^{-3}$)</th>
<th>Dislocation density ($\delta \times 10^{14}$)</th>
<th>Stacking fault probability ($\alpha \times 10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39.4</td>
<td>1.32</td>
<td>6.43</td>
<td>10.5</td>
</tr>
<tr>
<td>200</td>
<td>43.1</td>
<td>1.21</td>
<td>5.38</td>
<td>8.22</td>
</tr>
<tr>
<td>300</td>
<td>47.9</td>
<td>1.09</td>
<td>4.36</td>
<td>7.93</td>
</tr>
<tr>
<td>400</td>
<td>49.9</td>
<td>1.04</td>
<td>4.00</td>
<td>4.68</td>
</tr>
</tbody>
</table>
Fig. 5.21: Film thickness variations of annealed MZO thin films

Fig. 5.22: XRD patterns of as-deposited and annealed MZO thin films
(a) as-deposited (b) 200°C (c) 300°C and (d) 400°C
Fig. 5.23: Variation of crystallite size and microstrain values of various temperatures annealed MZO thin films

Fig. 5.24: Variation of dislocation density and stacking fault probability values of various temperatures annealed MZO thin films
Fig. 5.25: Texture coefficient variation of various temperatures annealed MZO thin films
5.6 Mn and Ni doped ZnO (MNZO) thin films

Figure 5.26 shows that film growth rate of co-doped (Mn& Ni) ZnO (MNZO) as a function of the deposition time such as 5, 10, 15 and 20 sec, respectively. Film thickness is estimated against various molar ratio of Zn:Mn:Ni. Fig. 4.26 shows that the growth rate linearly increases with increased rinsing time. The film growth rate rapidly increased from 5 to 15 sec rinsing time of prepared MNZO thin films. It may be due to the source materials are sufficient and the solution has high complexity in initially. The process of deposition plays a more important role than the dissolution process which leads to increase in film thickness. With the deposition time being prolonged, the thickness of the film increases, at the same time the resistance of the film increases. Therefore, after a particular time of deposition, the dissolution process predominates over the deposition thereby film growth rate is decrease. After about 20 immersion cycles, the solutions were substituted with fresh ones. The maximum value of film thickness is obtained at 655 nm at 100:3:3 of Zn:Mn:Ni molar ratio. The reaction in such a case takes place only with the adsorbed ion layer leading to the deposition of thin films of relatively higher quality. However fig. 4.26 describes the rinsing also leads the lower growth rate of MNZO film.
Fig. 5.26: Film thickness variations as a function of time of co-doped (Mn & Ni) ZnO thin films
Fig. 4.27 presents typical XRD spectra of MNZO thin films for various Zn:Mn:Ni molar ratio of such as 100:1:1, 100:2:2 and 100:3:3. The ‘d’ (interplanar spacing) values of the XRD reflections were compared with standard ‘d’ values taken from JCPDS diffraction file (No. 89-0511). The deposited films are polycrystalline nature with hexagonal structure. It shows that the MNZO films have preferred orientation of ZnO (002), indicating a perpendicular alignment of the c-axis of the grains. The predominant peak observed at an angle $2\theta = 34.41^\circ$ corresponds to the (002) reflection, the other peaks are at angles $2\theta = 31.47^\circ, 36.24^\circ, 47.12^\circ, 56.73^\circ, 62.32^\circ$ and $68.61^\circ$ corresponding to the (100), (101), (102), (110), (103) and (112) crystallographic planes, respectively. This peak has shifted towards higher diffraction angles for various molar ratio of Zn:Mn:Ni. The line width of (002) peak, 0.175$^\circ$ for 100:1:1 (Zn:Mn:Ni) molar ratio prepared MNZO films, increased largely with increase of molar ratio and reached 0.24$^\circ$, which implies that the crystallite size in MNZO films is decreased. All the patterns revealed that the wurtzite structure of ZnO is conserved for MNZO thin films. Because of this arguments we get increase the intensity of the peaks when addition to the Mn and Ni in ZnO matrix. The crystallographical plane of (002) is observed highly oriented peak for all case of prepared MNZO films. No other major variation has been observed in co-doped ZnO matrix. This may be due to the lower composition of Mn and Ni is incorporated with ZnO matrix. So that the structural properties does not change apparently in co-doped ZnO thin films. Both the co-doped metals are equally masked for its own structural properties. In the case of MZO and NZO thin films are structurally changed with doping molar variation, but MNZO films does not change in structurally due to the co-doped metals. This property is difficulty to observe in the ZnO matrix compared
with above mentioned results such as MZO and NZO thin films. We will discuss about the composition percentage of MNZO thin films in forthcoming chapter.

The crystallite size of the MNZO thin film is estimated Debye-Scherrer formula. Figure 4.28 shows the variation of crystallite size and micro strain values of various molar ratio of Zn:Mn:Ni prepared MNZO thin films. It is clear that the crystallite size decreases with respect to molar ratio of Zn:Mn:Ni. The minimum value of crystallite size is achieved at 26.5 nm for 100:3:3 molar ratio of Zn:Mn:Ni. This reduction of crystallite size is may be due to the Mn and Ni atoms are incorporate with ZnO matrix. Actually the undoped ZnO thin film crystallite size is observed nearly 29 nm and co-doped Zno thin film crystallite size is 26.5 nm. In this regard, we predicted that ZnO is dominated in this MNZO film which may be due to the co-doping elements are suppressed the doping properties in microstructural characteristics. The microstrain of the film is calculated using above mentioned relation (5.2). The microstrain value variation is plotted against molar ratio variations of Zn:Mn:Ni as shown in fig. 5.28. The microstrain values are linearly increases with co-doping molar ratio. The lower value of microstrain is observed at $1.23 \times 10^{-3}$ lines$^{-2}$.m$^{-4}$. The dislocation density values are linearly increases with molar ratio which is due to decrease of crystallite size as shown in fig. 5.29. The stacking fault probability values are rapidly decreases with increase of molar ratio shown in fig. 5.29. The predominant peak is shift towards higher values due to incorporation of Mn and Ni atoms in ZnO matrix.
The texture coefficient was calculated using an equation (4.4). The crystalline nature of the co-doped ZnO film is strongly related to the texture coefficient of the film. The doping molar variation of texture coefficient values for different lattice plane MNZO thin films are shown in figure 4.30. $T_c(h_kl_i)$ has to be bigger than 1 to determine the preferential orientation, if $T_c(h_kl_i)$ approximately 1 for all the $(h_kl_i)$ planes considered at X-ray diffraction patterns, the films are randomly oriented $T_c(h_kl_i)$ values higher than one indicates the abundance of grains in a given $(h_kl_i)$ direction. The (002) predominant plane orientation of the film has high texture coefficient value in all the cases of MNZO thin film. The texture coefficient of (002) predominant peak value is increases with increase of co-doped molar ratio.

Table 5.4: Various microstructural properties of MNZO thin films

<table>
<thead>
<tr>
<th>Zn:Mn:Ni molar ratio</th>
<th>Crystallite size (nm)</th>
<th>Micro strain $\varepsilon \times 10^{-3}$</th>
<th>Dislocation density $\delta \times 10^{14}$</th>
<th>Stacking fault probability $\alpha \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:1:1</td>
<td>42.2</td>
<td>1.23</td>
<td>5.59</td>
<td>0.512</td>
</tr>
<tr>
<td>100:2:2</td>
<td>37.1</td>
<td>1.4</td>
<td>7.25</td>
<td>1.040</td>
</tr>
<tr>
<td>100:3:3</td>
<td>26.5</td>
<td>2.12</td>
<td>1.42</td>
<td>1.881</td>
</tr>
</tbody>
</table>
**Fig. 5.27:** XRD patterns of co-doped (Mn & Ni) ZnO thin films prepared at various molar ratio of Zn:Mn:Ni such as (a) 100:1:1 (b) 100:2:2 and (c) 100:3:3

**Fig. 5.28:** Variation of crystallite size and microstrain values of co-doped (Mn & Ni) ZnO thin films prepared at various molar ratio of Zn:Mn:Ni
Fig. 5.29: Variation of dislocation density and stacking fault probability values of co-doped (Mn & Ni) ZnO thin films prepared at various molar ratio of Zn:Mn:Ni

Fig. 5.30: Texture coefficient values of co-doped (Mn & Ni) ZnO thin films prepared at various molar ratio of Zn:Mn:Ni
5.7 Conclusions

The structural and thickness properties investigations were performed for optimizing the film growth by chemical bath deposition employing double dip technique. It is observed that the films grown with aqueous solutions are much better than that grown using non-aqueous solvents. The Ni, Mn and co-doped ZnO thin films were achieved in aqueous bath. The detailed study on undoped ZnO thin films thickness and structural properties were studied. The film thickness was estimated by varying molar concentrations of zinc sulphate with respect to the rinsing time. The maximum value of thickness is observed at 610 nm for 0.03 M zinc sulphate concentration. The (002) crystallographical plane with hexagonal structure is observed all the case of ZnO thin film. The maximum value of crystallite size is about 29.3 nm at 0.03 M zinc sulphate concentration prepared ZnO thin film. In this way we have to choose the optimized deposition concentration is 0.03 M of ZnSO$_4$ for further depositions.

The NZO thin films were prepared at various doping concentration such as 5, 10 and 15 mM of NiSO$_4$. The film thickness with respect to various doping concentration prepared NZO were observed. The structural and microstructural properties were discussed with doping concentrations prepared film. The predominant peak orientation was observed at (002) plane for lower doping concentration and (101) for higher doping concentration prepared NZO thin films. Also, the structural and corresponding microstructural properties were studied for various temperatures annealed NZO thin films. The Mn doped ZnO thin films were prepared various doping concentrations. The film thickness and structural properties were studied doping molar variations prepared films. The higher doping concentration prepared
MZO films were employed with post heat treatment at 200-400°C and microstructural properties were discussed.

The film thickness and structural properties of MNZO thin films for various Zn:Mn:Ni molar ratio of such as 100:1:1, 100:2:2 and 100:3:3 were studied. The deposited films are polycrystalline nature with hexagonal structure. The predominant peak has shifted towards higher diffraction angles with increase molar ratio of Zn:Mn:Ni. The Mn and Ni as co-doped metals were equally masked for its doping element properties. In the case of MZO and NZO thin films are structurally changed with doping molar variation, but MNZO films does not change in structurally due to the co-doped metals masking properties. This is interesting phenomena in doping properties of ZnO thin films. The crystallite size was achieved at 26.5 nm for 100:3:3 molar ratio of Zn:Mn:Ni. This reduction of crystallite size is may be due to the Mn and Ni atoms are incorporate with ZnO matrix. The predominant peak is shift towards higher values due to incorporation of Mn and Ni atoms in ZnO matrix. The (002) predominant plane orientation of the film has high texture coefficient value in all the cases of MNZO thin film.
5.8 References