CHAPTER - 8
Summary and Conclusion

Mn doped ZnO thin films are prepared by SILAR technique. The films are annealed in air to improve the crystallinity and crystallite sizes. All the synthesized films are characterized for their structural, optical, surface morphological properties and estimates on, surface roughness, compositional analysis, magnetic analysis, spectroscopic analysis and hardness properties are presented. The salient features of the various studies carried out and the important findings are presented in this chapter. Zinc Oxide and doped (Mn) thin films find interesting applications in the field of gas sensor, solar cells, optoelectronic devices etc., Mn doped Zinc Oxide thin films are more suitable for gas sensor applications owing to their band gap. The aims of the present work are to

- Synthesis Mn doped ZnO thin films by SILAR technique and optimize the preparatory conditions for device applications.
- Characterize the films for structural, optical, morphological, magnetic, spectroscopic and hardness behaviour.
- Analyze the viability of using the films for gas sensor applications.

Mn doped ZnO thin films are prepared at various Mn doping level in the solution (Mn 1%, Mn 2% and Mn 3%) under different condition to obtain uniform pinhole free, thin film suitable for gas sensor applications.
Mechanical Studies (Hardness of the film)

The hardness of the film is varied with respect to the thickness and annealing temperature. The hardness value was measured for various Mn doping levels, thickness and annealing temperature 300 °C, 350 °C and 400 °C with uniform interval. The hardness value is found to vary from 64 – 95 Sh. N.

Structural studies

Structural studies of Mn doped ZnO thin films reveal several interesting features. The following observations are made from X-ray diffraction studies on ZnO thin films.

a) The films deposited at the precursors solutions at room temperature are found to be uniform; the layers are better crystallized and exhibit semiconducting properties.
b) The characteristic X-ray powder diffraction of the definite compounds are visible for hot water temperature at 95 °C.
c) When the films are post annealed at temperatures more than 500 °C the layers are found to be peeling off.

The stable structure of Mn doped ZnO is hexagonal (wurtzite). It is observed that a ZnO thin film grown by SILAR is of (hexagonal) structure. That indicates that the stable thin films of Mn doped ZnO are prepared by SILAR. Annealing at 300 °C – 400 °C for 30 minutes in air ambient revealed that the synthesized films are well crystalline. Since the cost of fabrication of stable, crystalline films is low the cost of fabrication of elements for gas sensors is very low.
ZnO films are always found to be n-type semiconductors and they are at the very beginning of the diffusion plateau region, that the best crystal quality and the best light conversion behaviour are achieved. The best performances are obtained with deposits, which are prepared under certain conditions giving simultaneously good crystallinity and nearly stoichiometric composition. The following results are obtained from the structural studies of Mn doped ZnO thin films. The structural properties are found to be influenced by the bath conditions during deposition.

**Compositional Studies**

It is observed from EDAX studies that nearly stoichiometric Mn doped ZnO film can be formed by adjusting the bath composition as Mn 1%, Mn 2% and Mn 3%. The EDAX studies indicated that Mn doped ZnO formation for films deposited at certain conditions may be altered by subsequent annealing. The following results are obtained from the structural studies of Mn doped ZnO thin films.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Dopant Composition in bath (%)</th>
<th>Annealing Temperature (°C)</th>
<th>Estimated % Mn in the thin film</th>
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<tbody>
<tr>
<td>1</td>
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<td>1</td>
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<td>5</td>
<td>2</td>
<td>400</td>
<td>2.16</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>400</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Morphological Studies

Morphological studies through AFM and SEM reveal’s excellent features. The SEM reveals a continuous surface with grains of different shapes and sizes, ranging from 30 nm to few hundred nanometers. The AFM studies reveal the surface to be of minimum roughness composed of spherical and hexagonal shaped grains. They are uniformly distributed throughout the surface exhibiting the superiority of the films. The films with 1% Mn annealed in 350 ⁰C is found to have unique morphology coupled with good transmission and photoluminescence behaviour. Interesting morphological variations are presented and that offers wide range of morphology tailoring. The extensive studies with SEM revealed that morphology can be tailored by altering deposition conditions and post annealing.

Optical Studies

Optical absorption indicated the shift in bandgap to be around 3.32 to 3.28 eV with respect to bandgap of ZnO matrix and refractive index to be around 2.33 and extinction coefficient around 0.09. The transmittance became lesser for Mn doped ZO films with increase in doping level. The optical studies reveal that the doped thin films are low absorbing for Mn(1%) doped samples annealed at 350 ⁰C. The refractive index value estimated by a novel algorithm developed revealed that the films are in the region typical of semiconductors.
Magnetic Studies

The Room temperature M-H hysteresis loop of various concentration of MZO thin films were studied. The Mn doped ZnO film exhibit the ferromagnetic property. On Mn doping the non-magnetic host ions are partially substituted by Mn$^{2+}$ ions, some new defects are introduced or the existing host-lattice defects such as oxygen vacancies might have become active. The Magnetization (Ms) value is around in the range of 34.688 – 100.01 X 10^{-6} emu. The Retentivity (Mr) value is in the range of 4.4137 - 11.862 X 10^{-6} emu. The results are in consistant with literature and can be explained by bound polarons.

Raman Studies

Mn doped ZnO thin films grown by SILAR with 100 number of dips and annealed at 350 $^\circ$C for 30 minutes were subjected to Raman studies and the Raman Shifts in the range of 300 – 1100 cm$^{-1}$ reveals peaks at 546, 572 and 692 cm$^{-1}$ with 640.3 I$_5$, 568.4 I$_4$, and 572.3 I$_3$. It may be noted that the mode at 577 cm$^{-1}$ is highly asymmetric with the lower energy side broader in comparison with the higher energy side.

Gas sensor studies

The typical gas sensitivity for Ethanol was found to have oscillating behavior. Samples annealed at 300 $^\circ$C and 400 $^\circ$C have less sensitivity. The gas sensitivity obtained are presented. The saturation region is more for 1% Mn doped ZnO thin films. The studies reveal the possibility of fabricating gas sensor with Mn doped ZnO thin films grown by SILAR method. This may provide a low cost solution to gas sensing.