4.1 Introduction ............................................................................................................ 123
4.2 Experimental Details of ZnO:B thin films ......................................................... 123
  4.2.1 Film Synthesis ................................................................................................. 124
  4.2.2 Characterization Techniques ......................................................................... 125
4.3 Results and Discussion ....................................................................................... 125
  Section (A)
  4.3A Effect of concentration variation on properties of B:ZnO Thin Films 125
    4.3A.1 X-ray diffraction Studies ................................................................. 125
    4.3A.2 Surface morphology ............................................................................. 129
    4.3A.3 AFM studies .......................................................................................... 130
    4.3A.4 Electrical Resistivity ............................................................................. 131
    4.3A.5 Optical Properties .................................................................................. 133
  Section (B)
  4.3B Effect of Thickness variation on properties of B:ZnO Thin Films 135
    4.3B.1 X-ray diffraction Studies ................................................................. 135
    4.3B.2 Surface Morphology ............................................................................. 137
    4.3B.3 AFM studies .......................................................................................... 138
    4.3B.4 Electrical Properties ............................................................................. 139
    4.3B.5 Hall Effect Measurements ................................................................. 140
    4.3B.6 Optical Absorption Studies ............................................................... 141
    4.3B.7 Photoluminescence Spectra ............................................................... 143
References ................................................................................................................. 145
Chapter Four  
Synthesis of Boron doped ZnO thin films & its characterization
4.1 Introduction

In the previous chapter intrinsic ZnO thin films were synthesized at different core temperature and substrate temperature. The growth, morphology, structure, electrical and optical properties of the films were studied and results were reported. The major benefits of this technique are precise control of parameters and its ability to deposit vapors on a large surface area with a high uniformity of thickness. The commercialization potential is enhanced by the low deposition temperature. The previous chapter provides fundamental knowledge required for fruitful structural, electrical and optical characterization of undoped ZnO thin films with newly fabricated novel spray CVD technique. However, literature survey [1-5] shows that ZnO becomes unstable and its resistivity increases in ambient condition due to the chemisorptions of oxygen \([O_2(g) + 2e^- \leftrightarrow O_2^-(ad)]\) at the surface. The use of intrinsic ZnO is limited due to its high or moderate resistivity coupled with poor dc conductivity. Therefore it is planned to fabricate doped polycrystalline ZnO films. In literature it is found that group VII or group III metal ions such as indium [6], aluminum [7], gallium [8], copper (Cu), cadmium (Cd) etc. were doped to enhance the structural, optical and electrical properties of ZnO. Doping is particularly done to get high transparent, good stability and high conductivity ZnO films. Considerable attention has been devoted to study the effect of different dopants on the properties of ZnO. However, it is seen that very few reports were available on synthesis of Boron doped ZnO \([B:ZnO]\) thin films. Furthermore, \(B^{3+}\) ions are readily incorporated into the ZnO lattices by substitution, because the ionic radius of \(B^{3+}\) (0.23 Å) is smaller than that of \(Zn^{2+}\) (0.74 Å). This chapter focused on the synthesis of B: ZnO thin films by using newly fabricated spray CVD technique at low substrates temperature. The structural morphological, optical, electrical characterization of B:ZnO thin films were carried out for all samples and results were explain at length.

4.2. Experimental Details of B: ZnO thin films

The conventional physical techniques can synthesize transparent and conducting thin films however; they are not comfortably use for commercial applications at the industrial level because of high cost and smaller area. On the other hand, chemical deposition techniques are relatively cost effective and can be easily scaled up for industrial applications. Among various chemical methods
employed so far to deposit B: ZnO thin films, the conventional spray pyrolysis are a high temperature process and at low substrate temperature the films exhibits low crystallinity or sometimes amorphous. In view of this aspect B: ZnO films were synthesized by new technique which is based on principals of combination of chemical vapor deposition and spray pyrolysis at relatively low substrate temperature. The details of different steps involved in the synthesis process of growth mechanism have been discussed previous chapter.

4.2.1 Film Synthesis

The glass micro slides supplied by Blue Star (75mm × 25mm × 1.35mm) have been used as the substrates. The substrates were cleaned by the procedure explained in Section 3.3B.1 of Chapter Three. The analytical grade Zinc Acetate [Zn(CH₃COO)₂, 2H₂O] (Thomas Baker) and Boric acid [(H₃BO₃) S. D. Fine-Chem] were used as precursor's. Methanol is used as solvent throughout the length of experiment and act as a reagent. We optimized the preparative conditions of ZnO thin film, to get good quality films using spray CVD technique. The molarities of the solution was fixed at 0.075 M and volume of the spray solution, at 200 ml. Substrate were kept at 220°C and core temperature 330°C. For synthesis of B: ZnO thin films, initially, the spraying solution was prepared by mixing appropriate volumes of (0.075M) non-aqueous solution of zinc acetate and Boric acid in methanol to obtain appropriate doping percentage. The total solution of 200 ml is sprayed. To synthesize the optimum Boron doping concentration in ZnO lattice matrix, the range of 0.2 to 1 at% (in steps of 0.2) have been selected while all other previously optimized preparative parameters [spray rate (6ml min⁻¹), nozzle to substrate distance (40 cm) and carrier gas pressure (10 LPM)] were kept constant. Throughout the experimentation, both the substrate and core temperature were controlled using electronic temperature controllers. Hazardous gases evolved during the thermal decomposition were expelled out. In the first stage of work, effects of doping concentration variation of Boron were studied by keeping reaction chamber (core temperature) and substrate temperature constant at 330°C & 220°C respectively. In the second stage of investigation the effect of ZnO film thickness variation were studied by spraying different volumes of spraying solution (100ml to 500ml at a step of 100ml) for optimized parameters.
4.2.2 Characterization Techniques

The X-ray diffraction studies of as-prepared boron doped ZnO thin films were carried out using a X-ray diffractometer (German make Bruker axis D-8 Advance Model) with Cu Kα radiation having wavelength 1.5406 Å. Film thickness was measured by using AMBIOS-XP-1 surface profilometer. Surface morphology of the Boron doped ZnO thin films; grain size and distribution of grains were examined by a JEOL JSM-6360 scanning electron microscope (SEM). The surface morphologies were also observed at room temperature by atomic force microscopy (AFM, Digital Instrument, nanoscope III) under contact mode. AFM images were collected in contact mode on a molecular imaging system using a silicon nitride cantilever. The heights, roots mean square (RMS) surface roughness, and surface area was calculated using digital instruments software. Optical absorption (normal incidence) measurements of the films were carried out at room temperature in the spectral range of 350–850 nm using a UV-VIS spectrophotometer (Shimatzu 1800 model). To measure the electrical resistivity of the B: ZnO thin films contact was made by colloidal silver paste. The electrical resistivity was measured by home made two-probe resistivity unit.

4.3 Results and Discussion

Sprayed droplets of non-aqueous solution of zinc acetate, when enters in the reaction chamber then pyrolytic decomposition of solution takes place. These decomposed particles are pushed upward and deposited on substrate which is placed at the top of reaction chamber. The films deposited were mirror smooth, uniform and well adherent to the substrate and are found to be stable under typical environmental condition.

Section (A)

4.3A. Effect of concentration variation on properties B: ZnO thin films

4.3A.1 X- Ray Diffraction Studies

The effect of boron doping on the properties of the Boron doped ZnO films has been analyzed as a function of the doping concentration. Change in structural aspects with doping concentration is explained at length. Fig. 4.1 shows the key role played by variation in doping concentration of boron on the structural properties of
ZnO thin films. XRD patterns of undoped ZnO and boron doped (B: ZnO) films, exhibits the domination of (002) diffraction peak at 34.4°. The dominant peak arises from diffraction of (002) planes of ZnO grains oriented with c-axes perpendicular to the substrate. Similar structural patterns were also observed by others researchers [11, 20]. Along with the dominant peak some weak peaks were also observed. The diffraction planes (100) and (101) have little impact on the structure however, (102), (110), (103), (200) and (112) peaks are minor. The observed peaks are well match with the standard polycrystalline wurzite structure planes of ZnO. The d values are in good agreement with those reported in the PDF for ZnO (JCPDS card no. 80-0075) a = 3.24982and c = 5.20661 Å) and are reported in Table 4.1.

![XRD Spectra of B: ZnO thin films](image)

**Fig. 4.1 XRD Spectra of B: ZnO thin films**

The results imply that the crystallinity and degree of orientation of the B: ZnO films were closely associated to the B doping concentration. No additional peaks of ZnO phases and/or the traces of either boron oxide were observed. This indicates that the B⁺³ are substituted at Zn⁺² sites without changing the ZnO structure. In B: ZnO films, the introduction of boron atoms on substitution or interstitial sites may promote meaningful changes in films lattice parameters and
increase impurity defects at the grain boundaries. At this point, it is also interesting to verify the influences of the doping level on the crystalline parameters. The crystallite size (D) in the films has been calculated according to the Scherrer equation. The effect of crystallite size induced broadening and strain induced broadening [27] in the full width at half maximum (FWHM) of XRD peak can be studied using Williamson–Hall plot [4.1]:

\[
\beta \cos(\theta) = \frac{k\lambda}{D} + 2\eta \sin\theta \\
\text{(4.1)}
\]

where \( \beta \) is the line broadening solely due to small crystallite size, \( k \) is constant whose value depends on particle size, and usually taken as one, \( \theta \) is Bragg’s angle, \( \lambda \) is wavelength of incident X-ray beam, for Cu target it is 0.15406 nm and \( \eta \) is the lattice strain.

![Fig. 4.2 Variation of \( \beta \cos(\theta) \) vs \( \sin(\theta) \)](image)

A typical plot for 0.8 at% doping is as shown in Fig. 4.2. In thin films, strains originate mainly due to a mismatch between the polycrystalline films and the amorphous substrate and/or differences in coefficients of thermal expansion of the films and the substrate. The strain in the films can be calculated from slope of the plot and the actual particle size in the films can be estimated from the y-intercept of the plot. The size of the particles corrected for strain effects is shown in Table 4.1. It shows that the increase of the boron content decreases the grain size. The smaller average grain size causes to reduce surface roughness and, as a consequence, less-textured films with lower light-scattering properties. Here we assume that, the incorporation of Boron atoms into the lattice matrix of zinc oxide reduces the surface mobility of the growing film which causes the lateral expansion
of grains resulting into smaller grains. We observed that boron incorporation reduces the grain size and, as a consequence, more grain boundaries are present inside a unitary area. These phenomena are responsible of the increasing of the tensile stress with increasing the doping level.

Fig. 4.3 Variation of tensile stress with Boron doping concentration

For hexagonal crystals, the stress(s) in the plane of the films can be calculated using the biaxial strain model [28]

$$\sigma = -453.6 \frac{c_f - c_b}{c_b} \quad \text{.......................... (4.2)}$$

where $c_b = 5.209 \text{ Å}$ is the c-axis lattice constant of bulk ZnO and $c_f$ the c-axis lattice constant calculated from the XRD data. The estimated values of stress in the films grown at different doping concentrations are listed in Table 4.1. Fig. 4.3 shows variation of tensile stress with doping concentration. The lattice constant ‘c’ of ZnO films is shorter than the bulk ZnO; all the films exhibit tensile stress. The value of the bi-axial stress is positive indicating that the films are under tensile stress. Also, stress is found to increase with increase in doping concentration. The increase in tensile stress induces porosity as is observed in surface morphology.

The lattice constants ‘a’ and ‘c’ were calculated by using the following equation 4.3. They are mentioned in table 4.1 and match with JCPDS card 80-0075.

$$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad \text{.......................... (4.3)}$$

From Table 4.1 it is observed that, crystallite size values obtained from Willson-
Hall method come out to be more than those derived from Scherrer equation. This is due to the fact that the Scherrer equation does not take into account the effect of lattice strain and instrumental factors on peak broadening.

Table 4.1 Structural parameters of the doped and undoped zinc oxide films

<table>
<thead>
<tr>
<th>Doping Concentration (at%)</th>
<th>Particle Size (nm)</th>
<th>a=b (Å)</th>
<th>c (Å)</th>
<th>Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Debye-Scherrer</td>
<td>WH plot</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>28</td>
<td>40</td>
<td>3.253</td>
<td>5.211</td>
</tr>
<tr>
<td>0.2</td>
<td>26</td>
<td>38</td>
<td>3.252</td>
<td>5.2039</td>
</tr>
<tr>
<td>0.4</td>
<td>25</td>
<td>37</td>
<td>3.25</td>
<td>5.2037</td>
</tr>
<tr>
<td>0.6</td>
<td>24</td>
<td>30</td>
<td>3.249</td>
<td>5.2032</td>
</tr>
<tr>
<td>0.8</td>
<td>23</td>
<td>21</td>
<td>3.248</td>
<td>5.2031</td>
</tr>
<tr>
<td>1.0</td>
<td>22</td>
<td>20</td>
<td>3.247</td>
<td>5.2028</td>
</tr>
</tbody>
</table>

The deformation of any individual grain within a thin film is strongly influenced by its neighbouring grains. These grains induce residual strain within this individual grains. Thus the residual strain induced by Boron doping within the grains of ZnO matrix phase, not only restrict the grain growth of former but also produce residual strains which results into broadening of diffraction.

4.3A.2 Surface morphology

Fig. 4.4 FESEM images of undoped and B: ZnO thin film.
Fig. 4.4 shows the surface morphologies of undoped & B: ZnO thin films. It shows striking dependence on the concentration of dopant ions with transition of shapes from triangular columnar pyramids of undoped ZnO into cluster of islands, nanospheres, and finally into petal shaped morphology. In the synthesis of ZnO nanocrystals, introduction of Boron leads to dramatic shape evolution in addition to the compositional variation in the films. With increasing boron content the pyramidal shapes of the grains deteriorate and the size of these grains decreases. At higher doping level, smaller average grain size produces reduction in a surface roughness.

4.3A.3 AFM studies

**Fig. 4.5 (2D) Surface Topography for of B: ZnO thin films**

**Figure 4.6 (3D) Surface Topography of B: ZnO thin films**
Fig. 4.5 and 4.6 shows 2D and 3D surface topography of Boron doped ZnO thin films for varying concentration of Boron. From the images it is seen that all the film surfaces are well covered with the uniformly distributed spherical grains of varying sizes. It is evidently seen that addition of Boron changes the topography of films from clusters into well defined spherical grains which are correlated with FESEM morphology. In Fig. 4.6, the 3D micrographs revealed that Boron doping reduces roughness of thin film indicating very smooth surface at 0.8at%.

The thickness and surface roughness is also recorded using XP-1 surface profiler and is as shown in Fig. 4.7. It is observed that increase in doping concentration causes increase in thickness of thin films. The smaller ionic radii of boron may increase ionic bonding between Boron and Oxygen as compared to the ionic bonding between Zinc and Oxygen. This strong bonding between Boron and Oxygen reduces the rate of evaporation resulting in to increase in thickness of thin film.

### 4.3A.4 Electrical Resistivity

As observed from Fig. 4.8, the linear relationship between logarithmic of resistivity and inverse of temperature with a negative of slope indicates the following well known Arrhenius law,

\[
\rho = \rho_0 \exp\left(-\frac{E_a}{kT}\right) \quad \text{......................................................... (4.4)}
\]

where \( \rho_0 \) is the constant of material, \( E_a \) is the activation energy, \( T \) is the absolute temperature and \( k \) is the Boltzmann constant. Fig. 4.8 shows Arrhenius plot of \( \ln(\rho) \) versus \( 1000/T \) for B: ZnO thin films synthesized by spray CVD technique. The plot shows two clear conduction regions one at low temperature and other at high
temperature. It also shows decrease in resistivity with increase temperature indicating semiconducting behavior of the deposits. At higher temperature the adsorbed oxygen molecules are desorbed [20, 21, and 22] from the surface of thin film, hence potential barrier at grain boundaries decreases which causes the electrons to cross grain boundaries. It also affects to increase donor densities due to thermal excitation.

![Arrhenius Plot for B: ZnO thin films](image)

**Fig. 4.8 Arrhenius Plot for B: ZnO thin films**

**Table 4.2 Activation Energy of B: ZnO thin films**

<table>
<thead>
<tr>
<th>Doping concentration (at. wt. %)</th>
<th>Low temp region 60°C-150°C (eV)</th>
<th>High temp region 150°C-300°C (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
<td>0.63</td>
</tr>
<tr>
<td>0.2</td>
<td>0.033</td>
<td>0.20</td>
</tr>
<tr>
<td>0.4</td>
<td>0.049</td>
<td>0.33</td>
</tr>
<tr>
<td>0.6</td>
<td>0.054</td>
<td>0.38</td>
</tr>
<tr>
<td>0.8</td>
<td>0.09</td>
<td>0.15</td>
</tr>
<tr>
<td>1.0</td>
<td>0.07</td>
<td>0.21</td>
</tr>
</tbody>
</table>
The activation energy in two temperature zone can be calculated by using equation (4.4) and is mentioned in Table 4.2. In the low temperature region of conduction, the decrease in resistivity may be due to the increase in mobility of charge carriers, hence small thermal energies are quite sufficient to activate these charge carriers to take part in conduction process. In high temperature region, the conduction is attributed to the intrinsic defects caused by the thermal fluctuations. The high value of activation energy is mainly determined by the intrinsic defects and hence is called as intrinsic conduction [7].

4.3A.5 Optical Properties

![Optical transmittance of B: ZnO thin films with wavelength.](image)

Fig. 4.9 Optical transmittance of B: ZnO thin films with wavelength.

The optical transmission of the Boron doped ZnO thin films synthesized by spray CVD system on corning glass substrates were measured by using UV spectrophotometer in the wavelength range 360nm to 1000nm and is as shown in Fig. 4.9. It shows variation of spectral transmittance with wavelength for concentration variation in the range 0 to 0.8 at% (in steps of 0.2 at %). The maximum visible average transmission was found to be 90% for 0.8at% Boron doping in ZnO thin films. It shows that increasing doping concentration, results into increased transmittance of thin films. As observed for undoped ZnO thin films, the transmittance curves with variation of Boron doping concentration also show interference fringe pattern between the wave fronts generated at the two interfaces.
(air and substrate). The pattern defines sinusoidal behavior of the curves. This revealed the smooth reflecting surfaces of the film and there was not much scattering/absorption loss at the surface suggests uniform distribution atom. In transparent metal oxides, metal to oxygen ratio decides the percentage of transmittance. A metal rich film usually exhibits less transparency. In the present case increase in transparency may be attributed to reduction in oxygen deficiency with boron contain.

The optical absorption of the film is also studied in the same wavelength range as above. The spectra (not shown) reveal that the deposited film has low absorbance in the visible and near infrared regions while the absorbance is high in the UV region. It indicates that the absorbance is high for photons of energy greater than the band gap while beyond the gap edge the absorbance is very small and the transmittance is high.

![Graph showing variation of \((\alpha h\nu)^2\) vs \(h\nu\) for undoped and B: ZnO films.](image)

**Fig. 4.10 Variation of \((\alpha h\nu)^2\) vs \(h\nu\) for undoped and B: ZnO films.**

The recorded optical absorption data was further used to evaluate the band gap energy. Fig. 4.10 reveals the variation of band gap of synthesized ZnO thin films by spray CVD technique with respect to incident photon energy \(h\nu\). The optical band gap of the films can be calculated by using equation (3.20). Fig.4.10 shows the relationship between \((\alpha h\nu)^2\) with \(h\nu\). The \(E_g\) value can be obtained by extrapolating linear portion of the graph to the energy axis. Boron doping results blue shift in
optical band gap from 3.25eV of undoped ZnO to 3.30 eV for optimized doping concentration of 0.8at%. Similar blue shift phenomenon of optical band gap was also observed by B. J. Lokhande et al [20] in B doped ZnO thin films deposited by spray pyrolysis technique.

The deteriorated crystallinity by addition of Boron may cause the blue shift in optical band gap. The decreased grain size by Boron doping in ZnO films deposited at low temperature is believed to be the main reason for the blue shift of optical band gap. Above results, force to conclude that at 0.8 at wt. % doping of boron shows minimum resistivity with maximum transmission. This gives good figure of merit for the transparent conductors.

Section (B)

Effect of Thickness variation on Different properties of B: ZnO thin films

Previous section deals with optimization of doping concentration of Boron in ZnO thin films in order to achieve transparent and low resistive (good quality) films. The present section deals with synthesis of Boron doped ZnO thin films for thickness variation. These films were obtained by varying solution quantity from 100ml to 500ml at a step of 100ml. The films were deposited by keeping all other preparative parameters constant. The optimized boron doping concentration (0.8 at %) was used for this study.

4.3B.1 X ray diffraction Studies

Fig. 4.11 exhibits XRD spectrum of thickness varied B: ZnO thin films. It reveals the effect of thickness on structural properties of B: ZnO thin films. The registered X-ray spectra well fit with hexagonal wurtzite structure [23]. No any new, additional reflection peaks and/or the traces of either B or Zn metals have been observed. This indicates that the B⁺³ ions are substituted at Zn⁺² sites without changing ZnO structure. In general all range of thickness variation prepared by this technique indicates polycrystalline nature. However, the (002) peak intensity increased with increasing thickness of thin film. This increase in (002) peak intensity meant that the film quality was improved with increasing thickness of thin film. The preferred growth of film was expressed in terms of texture coefficient and defined by Barrette and Massalski. The texture coefficient was calculated by using the formula of
Barrette and Massalski. It was found that texture coefficient increases with increase in thickness which indicates random orientation of crystallites. The textured growth phenomenon was similar with others [11, 20, and 17] due to survival of the fastest growth direction model suggested by Van Der Drift model.

Fig. 4.11 XRD patterns of B: ZnO thin films at various thicknesses

Table 4.3 Structural parameters of B: ZnO thin films for varying thickness

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>Grain size (nm)</th>
<th>Dislocation Density (m)²</th>
<th>Texture Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>232</td>
<td>20</td>
<td>2.5 x10¹⁵</td>
<td>0.9372</td>
</tr>
<tr>
<td>182</td>
<td>102</td>
<td>23</td>
<td>1.9 x10¹⁵</td>
<td>1.181</td>
</tr>
<tr>
<td>261</td>
<td>90</td>
<td>27</td>
<td>1.4 x10¹⁵</td>
<td>1.5287</td>
</tr>
<tr>
<td>381</td>
<td>66</td>
<td>28</td>
<td>1.3 x10¹⁵</td>
<td>2.014</td>
</tr>
<tr>
<td>486</td>
<td>40</td>
<td>30</td>
<td>1.1 x10¹⁵</td>
<td>2.231</td>
</tr>
</tbody>
</table>
Furthermore, the intensity of the (002) peak was increased while the full width half maximum decreased with increasing film thickness, indicating the crystallinity and grain size were enhanced with the film thickness. The mean crystallite size of the film was estimated by using standard Scherrer formula. The calculated values are tabulated in Table 4.3. From the table it is seen that grain size increases with increase in film thickness. The increase thickness may provide the possible increase in growth in third dimension and this result in increase in crystallite size. The improvement in crystallinity is due to increased ability of adatoms to move towards stable sites in the lattice with increase in thickness.

4.3B.2 Surface Morphology:

Fig. 4.12 shows FESEM micrographs of B: ZnO thin films with variation of film thickness. The very small size and uniform nanospheres were observed at 102 nm film thickness (Fig. 4.12a). With increase in thickness of films, (Fig. 4.12b to c) the nanospherical morphology transforms into microspheres with the size become larger. The observed larger particles are bunch of nanospheres. As compared with nanospheres, microspheres have smooth morphology. Fig.4.12d shows that some microspheres are broken and the core/shell structures can be observed. It indicates that the shells of some microspheres collapse into pieces. It shows the bowl-like microsphere which has a core inside with tightly aggregated nanoparticles. Finally for maximum 486nm thickness core shell morphology transforms into nanoflowers.
4.3B.3 AFM studies

![AFM images](image1)

Fig. 4.13 AFM (2D) micrographs of B: ZnO thin films with thickness variation

![AFM images](image2)

Fig. 4.14 AFM (3D) micrographs of B: ZnO thin films for varying thickness

![Graph](image3)

Fig. 4.15 Variation of thickness and roughness with solution quantity

To support the discussion on the optimization of growth conditions the AFM studies were carried out. The 2D and 3D micrographs of B: ZnO thin films for varying thickness of thin films are shown Fig. 4.13 & Fig. 4.14. Both the micrographs supported the observation made from FESEM investigations. That is that the spherical grains whose diameter goes on increasing with increase in thickness of thin films. 3D micrographs show increase in smoothness with increase thickness of...
film. The typically perfect smooth films are form at 486nm thickness and it can be seen from the figure 4.14(d). The behavior of variation of thickness & roughness is shown in following Fig. 4.15. It seen that roughness decreases with increase in solution volume and it attends minimum value when 500ml solution is sprayed to deposit the films. However, film thickness increases with solution quantity as expected.

4.3B.4 Electrical Properties

![Arrhenius plot for thickness varied B: ZnO thin films.](image)

The electrical resistivity measurement by two-point probe method was carried out within temperature range of 300–500K. Arrhenius plot of ln(ρ) against 1000/T (Fig.4.16) indicates the semiconducting nature of thin films. It is seen that there are two distinct conduction regions. It shows decrease in resistivity with increase in thickness of thin films. It may be due to improvement in crystallinity with increases in thickness of thin films. The resistivity studies show that all films exhibits two conduction regions at different temperatures. At high temperature
significant change in activation energies is observed. However activation energies at low temperature are slightly decreased with increase in thickness. In the low temperature region, the increase in conductivity is due to change in the mobility of charge carrier, which depends on the defects concentration. In this region activation energy decreases because a small thermal energies quite sufficient for the activation of charge carriers to take part in the conduction process. In high temperature region, the activation energy is higher than that of low temperature region. In this region the electrical conductivity is mainly determined by the intrinsic defects and hence is called as intrinsic conduction.

4.3B.5 Hall Effect Measurements

The electrical properties, measurements revealed thickness dependent behavior. Van der Pauw resistivity and Hall effect measurements are used to measure the electrical parameters; such as the sheet resistance ($R_s$), resistivity ($\rho$), carrier concentration ($n$), and mobility($\mu$) as the function of thickness of the Boron doped ZnO films at room temperature.

**Table 4.4 Hall Effect Measurements for all samples.**

<table>
<thead>
<tr>
<th>Sample (nm)</th>
<th>Sheet Resistance (KΩ)/cm²</th>
<th>Resistivity x10⁻² (Ω.cm)</th>
<th>conductivity (Ω.cm)⁻¹</th>
<th>Carrier Conc. X 10¹⁹ (cm⁻³)</th>
<th>mobility [cm²/V.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>4.5</td>
<td>4.7</td>
<td>21</td>
<td>4.2</td>
<td>3.2</td>
</tr>
<tr>
<td>182</td>
<td>1.6</td>
<td>3.9</td>
<td>34</td>
<td>5.9</td>
<td>3.6</td>
</tr>
<tr>
<td>261</td>
<td>0.9</td>
<td>2.3</td>
<td>42</td>
<td>8.5</td>
<td>3</td>
</tr>
<tr>
<td>381</td>
<td>0.5</td>
<td>1.9</td>
<td>52</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>486</td>
<td>0.15</td>
<td>7.7</td>
<td>129</td>
<td>15</td>
<td>6</td>
</tr>
</tbody>
</table>

From Table 4.4 it is observed that, both the sheet resistance and resistivity are found to decrease with increasing quantity of spraying solution i.e. thickness. Hall mobility and the carrier concentration increases resulting in decrease in resistivity. This improvement of electrical properties of the films can be explained in terms of enhancement of crystallization of Boron doped ZnO and their larger grain sizes as observed from the XRD and SEM results. From the Hall Effect measurements, it was observed that the Boron doped ZnO films exhibit n-type conductivity. The moderate value of resistivity may be attributed to nanocrystalline...
or grain boundary discontinuities presence of surface states and more roughness of B: ZnO thin film.

### 4.3B.6 Optical Absorption Studies

![Transmittance Spectra of Thickness Varied B: ZnO thin films](image)

**Fig. 4.17 Transmittance Spectra of Thickness Varied B: ZnO thin films**

The optical transmission of thickness varied B: ZnO thin films synthesized by spray CVD system on corning glass substrates is as shown in Fig. 4.17. The transmission spectra's show interference patterns with sharp fall of the transmission at the band edge, which is an indication of good homogeneity of the films occurring when the film surface is reflecting without much scattering or absorption in the bulk of the film. The average transmittance decreases with increase in thickness of thin film. The films were transparent and uniform to the naked eyes. This is evident from the transmittance curves. Maximum transmittance obtained in present investigation is 91% at 550 nm for the sample with thickness of 102 nm. However with variation in thickness from 103nm to 486nm, the transmittance varied from 91% to 80% in visible region. The absorption spectra of thickness varied B: ZnO thin films were measured within the same wavelength range. It indicates the absorbance is nearly equal to zero for 102nm and 186nm thickness and slightly increases with increase in thickness of thin film. From the transmittance and absorbance spectra the corresponding reflectance values can be calculated by using equation (3.4). From the reflectance spectra 'R' the refractive index ‘n’ and extinction coefficient ‘k’ can be calculated by using equation (3.9) and
(3.10). The variation of refractive index and extinction coefficient is as shown in Fig. 4.18 and Fig. 4.19 respectively. The extinction coefficient is nearly equal to zero indicating very low absorbance. The refractive index increases with increase in film thickness. Generally, the optical band gap ($E_g$) and absorption coefficient $\alpha$ could be evaluated from transmittance or absorbance spectra. There are several reports on this method [24-26].

Fig. 4.18 Variation of R. I. with wavelength for B: ZnO thin films

Fig. 4.19 Variation of extinction coefficient for B: ZnO thin films

Considering the material as a direct band gap semi-conductor and by using equation (3.3) the band gap is determined by locating the intercept of $(\alpha h\nu)^2$ vs. $h\nu$ on energy axis. Fig. 4.20 shows the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for thickness varied Boron
doped ZnO thin films synthesized by spray CVD technique. It has been observed that the plot is linear over a wide range of photon energies indicating a direct type of transitions.

![Graph showing the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for ZnO films with different film thicknesses.](image)

**Fig. 4.20 The plot of $(\alpha h\nu)^2$ vs. $h\nu$ for B:ZnO films with different film thicknesses.**

The intercepts (extrapolations) of these plots (straight lines) on the energy axis reflect the energy gap value was found to decrease with the increase of the film thickness (Fig. 4.20). The decrease of direct band gap with the increase of thickness can be attributed to an increase of particle size, decrease of strain and increase of lattice constant [17]. The optical band gaps vary between 3.36 eV to 3.27 eV. It reveals minimum optical band gap value for the film with maximum thickness i.e. 486nm indicating better crystallinity. These observed values of optical band gap are in good agreement with the previously reports by others [19, 20].

**4.3B.7. Photoluminescence Spectra:**

Room temperature photoluminescence spectra of Boron doped ZnO thin films as a function of thickness of thin films is as shown in Fig. 4.21. It shows that the PL characteristics of B doped ZnO thin films strongly dependent on thickness variation of thin films. It shows very intense UV emission peak located at 385nm along with a weak blue emission band located at 475nm. The intensity of UV emission band goes on increasing with increasing thickness on the other hand intensity of blue emission
band remains unchanged. The UV peak is usually considered as the characteristic emission of ZnO. It is attributed to the band edge emission or the exciton transition. The amplification of the UV emission indicates that the crystalline defects in the ZnO film have changed after B doping. Strong UV emission depends on microcrystalline structure indicating enhanced crystallinity with increased thickness of thin films.

Figure 4.21 Photoluminescence Spectra for B: ZnO thin film

PL results are confirmed with XRD spectra and FESEM micrograph results. The blue emission might come from the intrinsic defects or B impurity. In intrinsic ZnO, according to literature review the donor as well as acceptor defects are present. Zn interstitial (Zn$_i$) and oxygen vacancy (V$_O$) are main donor defects while Zn vacancy (V$_{Zn}$) and oxygen interstitial (O$_i$) are main acceptor defects in intrinsic ZnO. However, it is observed that the energy interval from the level of interstitial Zn (Zn$_i$) to zinc vacancy (V$_{Zn}$) is 2·62eV (473nm). Hence the blue transition centered at 475nm corresponds to the transition of electron from the level of interstitial zinc to the zinc vacancy.
References

23. JCPDS-ICDD card no. PDF#800075