Chapter 5
Doped nanostructured zinc oxide thin films synthesized by SILAR and CBD

5.1 Introduction

ZnO electrical conductivity is mainly due to the zinc excess at interstitial positions [1] Non-stoichiometric films had excellent electrical and optical properties but they are not stable at higher temperatures. However, doped ZnO films can be made to have very stable electrical and optical properties.

The performance of the DSSC will improve if the electrical conductivity of the electrode is high. The mesoporous ZnO electrodes used in DSSC are very much different compared with their compact analogues because the inherent conductivity of the film is low and the small size of the individual colloidal particles does not support a built-in electrical field [2]. Doping or introducing impurity atoms into semiconducting materials is the primary method for controlling the properties of the semiconductors, such as band gap, electrical conductivity etc.

In the present study, doped ZnO films of nanoflower and nanorod morphologies were synthesized using SILAR and CBD techniques. Aluminium and magnesium doped ZnO films were grown using SILAR method. Aluminium and selenium doped ZnO films were prepared using CBD method. Structural, morphological, optical, electrical properties and porosity of the films were studied. Because of doping, enhancements of properties such as better conductivity, transmittance and size improvements have been achieved.

5.2 Doped zinc oxide films

5.2.1 Experimental

5.2.1a Aluminium doped zinc oxide films with nanoflower morphology by SILAR

Aluminium doped ZnO films were deposited by SILAR technique [3-8] onto soda lime glass substrates using 100 ml of 0.1 M cationic precursor of zinc kept at room temperature while distilled water kept at 368K served as the anionic
precursor. Zinc sulfate (ZnSO₄·7H₂O) was used as the zinc source and aluminium sulfate (Al₂(SO₄)₃·6H₂O) was used as the aluminum doping source.

The cationic precursor was prepared by adding ammonia droplets (25%) in 100 ml of 0.1 M zinc sulfate solution. The pH value of the reaction solution was 11.5. 5 ml of 10 mM aluminium sulfate was added to this solution and thoroughly stirred using a magnetic stirrer. Distilled water maintained at room temperature was used to rinse the substrate immediately after each of the adsorption and reaction processes. Immersion time in cationic and anionic solution was optimized to 2 s and the optimized immersion time for rinsing the substrates was 5 s. 300 deposition cycles were carried out until films with a desired thickness was obtained. The experimental set up of SILAR is shown in Fig. 2.1.

The as-deposited films were washed in distilled water and dried in hot air before characterization and the films were named as DSZO-A.

5.2.1b Magnesium doped zinc oxide films with nanoflower morphology by SILAR

Magnesium doped ZnO films were synthesized using SILAR technique [3-8]. The soda lime glass substrates were pre-cleaned using distilled water and chromic acid before the deposition of the films. Reagents of zinc acetate (Zn(CH₃COO)₂·2H₂O) and lithium hydroxide (LiOH) were used to prepare the cationic precursor. The transparent complex solution was obtained when 100 ml of 0.1 M zinc acetate and 50 ml of 2 M lithium hydroxide were used. 5 ml of 10 mM magnesium acetate (C₄H₆MgO₄·4H₂O) was added into the solution, which was used as the magnesium-doping source.

The pH value of the solution was about 10.7. 100 ml of the complex solution of cations and distilled water for intermediate rinsing was kept at room temperature while the beaker with distilled water as anionic precursor was kept at 368K during deposition. Immersion time in cationic and anionic solution was optimized to 2 s. The optimized immersion time for rinsing the substrates was 5 s. 350 deposition cycles were repeated until a desired thickness was obtained. After
the film deposition, the substrates were washed in distilled water and dried in hot air before characterization. As-synthesized films were named as DSZO-B.

5.2.1c Aluminium doped zinc oxide films with nanorod morphology by CBD

In this CBD process, 80 ml of aqueous 0.15 M zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O) solution and 2 ml of 3.5 M monoethanolamine (C$_2$H$_7$NO) were mixed slowly with vigorous magnetic stirring to give an optically transparent reaction mixture. To this solution mixture, 5 ml of 10 mM aluminum sulfate (Al$_2$(SO$_4$)$_3$·6H$_2$O) was added as the aluminum doping source. Ammonia (25%) was added drop-wise to make the final pH of the mixture to 11. The glass substrates were placed inclined in the reaction mixture, which was kept at 353K in a water bath for 2 hour, and then allowed to stand at ambient temperature for 3 hour. Film was named as DCZO-A. The experimental set up is shown in Fig. 2.2.

5.2.1d Selenium doped zinc oxide films with nanorod morphology by CBD

Selenium doped ZnO thin films here were synthesized by chemical bath deposition (CBD). Prior to film deposition, the glass substrate was cleaned with chromic acid and distilled water. Film deposition was carried out by immersing the soda lime glass substrate in 80 ml of 0.15 M of aqueous solution of zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O) and 4 ml of 7.4 M triethanolamine (C$_6$H$_{15}$NO$_3$) in a 100 ml glass beaker. 50 mg of Sodium selenite (Na$_2$SeO$_3$) was added into reaction mixture as the selenium doping source. The pH of the reaction solution was raised to 11 by adding ammonia (25%) solution. Glass substrate was immersed in the middle of the solution at an angle. The solution was maintained at 363K for 3 hour using a thermostatically controlled water bath. The film was named as DCZO-B.

5.2.2 Result and discussion

(i) Thickness of the films

The thickness of ZnO films was determined both by taking the cross-sectional SEM micrograph (not shown) of the films and by gravimetric method. The film thickness was computed by gravimetric method using Eq. (2.21). The estimated average value of thickness is depicted in Table 5.1. Thickness of all the doped ZnO
films is found to be slightly increased from than that of the undoped films prepared under the same conditions.

(ii) Structural analysis

According to Bragg’s equation, if there is a crystal lattice expansion in the ZnO crystal then the diffraction peak will shift to a lower angle, on the other hand the contraction of crystal lattice results in the shift of diffraction peak to a higher angle. For ions with smaller ionic radius than zinc, there is possibility of substitution or placing into the interstitial site [8-11]. If an ion of greater ionic radius substitutes Zn$^{2+}$ in ZnO structure (which is possible if there is no charge mismatch and if ionic radii are not very dissimilar) then the XRD peaks will shift towards the lower angles because of increase in ‘d’ spacing due to substitution of lattice site by ion of higher radius [12, 13]. For smaller ionic radii like Al, Mg, Se ions settlement in interstices of ZnO become dominant instead of substitution of Zn$^{2+}$ [1]. Ideally, when smaller ions go into interstitial sites, they impel the surrounding atoms because their size is greater than interstitial sites. This impelling by interstitial atoms will stretch the lattice resulting in increase in the interplanar distance. Based on this understanding, interstitial diffusion of smaller ions in to ZnO lattice will still cause the XRD peak to shift towards the lower angles due to increased ‘d’ spacing [10, 11, 14, 15]. Hence, shifting of the diffraction angle of the diffraction peak in the XRD patterns of the doped ZnO film can be attributed either to the substitution Zn$^{2+}$ by the dopant or the placing the dopant in the interstices of ZnO.

Fig. 5.1(a-d) shows the XRD patterns of all the doped DSZO-A, DSZO-B, DCZO-A and DCZO-B ZnO films. Fig. 5.1(a) and Fig. 5.1(c) show the XRD patterns of the aluminium doped films DSZO-A and DCZO-A. The observed XRD patterns are found to match with the JCPDS File No. 80-0074. Both the films are found to be polycrystalline in nature, possessing hexagonal wurtzite structure. No phase corresponding to aluminium or other aluminium compound is detected in the XRD patterns. It is seen from the XRD patterns that both the films exhibited a strong orientation along c-axis (002) perpendicular to the substrate surface. This is in comparison with the XRD patterns of the undoped films prepared under similar
experimental conditions shown in Fig. 3.1 in Chapter 3 (SZO-A film) and that shown in Fig. 4.7 in Chapter 4 (CZO-D film).

The positions of the observed diffraction peaks of Al doped ZnO, slightly shift to the lower diffraction angles in the case both the films as reported [16, 17] but the intensity of (002) peak becomes more intense. This shifting may be due to the incorporated Al of smaller ionic radii (0.053 nm) than that of Zn$^{2+}$ (0.074 nm) and the subsequent increase in the compressive stress [16]. In the present investigation, for both the films the peak (100) in XRD patterns does not appear most likely due to texturization of the films along (002) direction. Similar results for the aluminium doped ZnO films have been reported by many researchers [18-20].

![XRD patterns of as-grown (DSZO-A, DSZO-B, DCZO-A and DCZO-B) ZnO films](image)

Fig. 5.1 XRD patterns of as-grown (DSZO-A, DSZO-B, DCZO-A and DCZO-B) ZnO films

Fig. 5.1(b) shows XRD patterns of Mg-doped ZnO thin film DSZO-B. The XRD patterns indicate that the doped film is polycrystalline ZnO with the hexagonal wurtzite structure (JCPDS File No. 36-1451) as that of undoped film SZO-F shown in Fig. 3.16 in Chapter 3. The ‘Mg’ doped ZnO thin film DSZO-B is showing (002) preferred dominant orientation. No phase corresponding to magnesium or other magnesium compound like magnesium oxide is detected in the XRD patterns. Shift in the positions of the observed diffraction peaks is not noticed in the XRD patterns.
of the doped ZnO films. The substitution of 'Mg' did not cause marked changes in the diffraction patterns as expected from the similar four coordination ionic radii [20] of Zn$^{2+}$ (0.074 nm) and Mg$^{2+}$ (0.072 nm).

Fig. 5.1(d) shows XRD patterns of Se-doped ZnO thin film DCZO-B. The XRD patterns indicate that the doped film is polycrystalline ZnO with the hexagonal wurtzite structure (JCPDS File No. 36-1451) as that of undoped film CZO-F shown in Fig. 4.10 in Chapter 4. The 'Se' doped ZnO thin film DCZO-B is showing dominant orientation along (100), (002) and (101) directions. It can be noted that the intensity of the peak corresponding to the reflection from (002) plane is comparatively increased while that from other planes are decreased from than that of the undoped films. No phase corresponding to selenium or other selenium compound is detected in the XRD patterns. Shift in the positions of the observed diffraction peaks to the lower angel is noticed in the XRD patterns of the doped ZnO films as mark of placing the selenium ions into the interstices of ZnO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Grain size (nm)</th>
<th>Dislocation density ($10^{15}$ lines/m)</th>
<th>Microstrain</th>
<th>Transmittance (%) at 600 nm</th>
<th>Band gap (eV)</th>
<th>Refractive index at 600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSZO-A</td>
<td>4650</td>
<td>11.40</td>
<td>7.68</td>
<td>0.0045</td>
<td>78.85</td>
<td>3.47</td>
<td>1.84</td>
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<td>DSZO-B</td>
<td>2750</td>
<td>25.92</td>
<td>1.48</td>
<td>0.0048</td>
<td>81.91</td>
<td>3.23</td>
<td>1.77</td>
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<tr>
<td>DCZO-A</td>
<td>1300</td>
<td>42.37</td>
<td>0.55</td>
<td>0.0028</td>
<td>86.75</td>
<td>3.26</td>
<td>1.62</td>
</tr>
<tr>
<td>DCZO-B</td>
<td>1050</td>
<td>37.64</td>
<td>0.71</td>
<td>0.0033</td>
<td>82.73</td>
<td>3.30</td>
<td>1.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Grain size (nm)</th>
<th>Dislocation density ($10^{15}$ lines/m)</th>
<th>Microstrain</th>
<th>Transmittance (%) at 600 nm</th>
<th>Band gap (eV)</th>
<th>Refractive index at 600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZO-A</td>
<td>4610</td>
<td>18.66</td>
<td>2.87</td>
<td>0.00049</td>
<td>82.22</td>
<td>3.23</td>
<td>1.76</td>
</tr>
<tr>
<td>SZO-F</td>
<td>2600</td>
<td>25.12</td>
<td>1.58</td>
<td>0.00046</td>
<td>76.98</td>
<td>3.17</td>
<td>1.88</td>
</tr>
<tr>
<td>CZO-D</td>
<td>1250</td>
<td>43.88</td>
<td>0.51</td>
<td>0.00026</td>
<td>70.72</td>
<td>3.08</td>
<td>2.02</td>
</tr>
<tr>
<td>CZO-F</td>
<td>980</td>
<td>31.65</td>
<td>0.99</td>
<td>0.00039</td>
<td>73.53</td>
<td>3.73</td>
<td>1.96</td>
</tr>
</tbody>
</table>
The grains or particles of the films are comprised of small crystallites. The mean crystallite sizes of all the doped ZnO films computed by the Debye-Scherrer’s equation given by Eq. (2.3) are given in Table 5.1. The crystallite size of the films DSZO-A and DCZO-A doped with aluminium is decreased while that of the films DSZO-B and DCZO-B doped with magnesium and selenium respectively is increased from than that of crystallite size of undoped films as depicted in Tables 5.1 and 5.2.

Dislocation is an imperfection in a crystal. The defects in the ZnO films was quantified by computing the dislocation density (δ) using Williamson Smallman relation [21] given by Eq. (2.19) and is given in Table 5.1. Dislocation density obtained for the films doped with aluminium is slightly increased whereas it decreased for the other two films. All the values indicate the presence of minimum defects in the doped films.

Microstrain in the nanocrystals of ZnO films was computed by using the tangent formula given by Eq. (2.16) and is depicted in Table 5.1 [22]. Strain developed in all of the doped ZnO films is increased by one order than that of the undoped ZnO films. The strain formed may be correlated to the lattice misfit, lattice expansion or contraction, which in turn depends upon the deposition conditions and the dopants used [23].

(iii) Morphological analysis

Figs. 5.2 and 5.3 illustrate the SEM images of the doped ZnO films. Morphology of the doped DSZO-A film has changed into flower with sharp petals from the cauliflower morphology of the undoped film SZO-A, which is shown in Fig. 3.3 of Section 3.2.1b(ii) of Chapter 3. New pores are evolved in the doped films. Morphology of film DSZO-B and that of undoped film shown in Fig. 3.16 in Section 3.2.3b(iii) of Chapter 3 is identical except that of the improved substrate coverage. Films are clustered and hierarchically structured, hence introduces pores in the doped films. Both the CBD doped ZnO films exhibit a different morphology even though they are still nanorods. The spindled nanorods of DCZO-A turned into exact hexagonal rods and the substrate coverage is increased. Hence, voids in the film are reduced and as a result, pores in the doped film are increased.
In DCZO-B films, the hexagonal nanorods are covered with a fibrous net as can be seen in the magnified images and mostly it may be formed by the selenium
particles. The presence of these selenium particles in the film might have given brownish red color to the film when viewed directly. The fibrous net and voids between the rods introduced new pores in the films. All the doped films offer very high specific surface area and can be expected to hold dyes for sensitization of the films to be used as photoanodes in DSSC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSZO-A</td>
<td>Zn</td>
<td>46.87</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>49.76</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>3.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSZO-B</td>
<td>Zn</td>
<td>44.37</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>53.68</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>1.95</td>
</tr>
</tbody>
</table>

The compositional purity of all the doped ZnO nanostructured films has been confirmed by EDAX analyses. The corresponding EDAX measurements shown in Table 5.3 reveals the atomic ratio of the involving elements, which indicate that the films contain mainly Zn, O, and the dopant, no significant signal from other elements being detected.

### (iv) Optical analysis

Fig. 5.4 depicts the optical transmittance and reflectance spectra of as-grown DSZO-A, DSZO-B, DCZO-A and DCZO-B ZnO films. More significantly, it can be observed that doping enhances the optical transmittance of all the ZnO films except the DSZO-A film. Transmittance of the doped films lies in the 75-85% range in the entire visible region. DCZO-A film exhibits high transmittance. Moreover spectra shows a steady nature in the entire visible region. Films show 8-12% reflectance in the 400-800 nm wavelength range. It was reported that an decrease of the average roughness promotes a increase in transmittance [24]. The high value of
transmittance of the doped ZnO films indicate that surface roughness of the film has decreased on doping.

Fig. 5.4 Optical (a) Transmittance and (b) reflectance spectra of as-grown (DSZO-A, DSZO-B, DCZO-A and DCZO-B) ZnO films

The variation of refractive index and extinction coefficient with wavelength of as-synthesized doped DSZO-A, DSZO-B, DCZO-A and DCZO-B ZnO films is shown in Fig. 5.5. Refractive index of the films lies in the 1.60-1.85 range in the visible region of the spectrum. The refractive index of film does not depend on average roughness [24]. The low refractive values indicate the high porosity of the doped films [25, 26].
From the measured optical absorbance data, the value of optical absorption coefficient, \( \alpha \) was determined by using the Beer–Lambert law [27]. The optical energy band gap of the films were determined by plotting \((\alpha h \nu)^2\) against photon energy \((h \nu)\) as shown in Fig. 5.6. As can be seen \((\alpha h \nu)^2\) varies linearly with \(h \nu\) above the optical band gap energy of the ZnO films. Accordingly, the energy band gap is obtained by extrapolating the straight-line portion of the curve to the \(h \nu\)-axis.

Fig. 5.5 The variation of (a) refractive index and (b) extinction coefficient of as-synthesized (DSZO-A, DSZO-B, DCZO-A and DCZO-B) ZnO films with wavelength

Fig. 5.6 The \((\alpha h \nu)^2\) vs \(h \nu\) plot of as-synthesized (DSZO-A, DSZO-B, DCZO-A and DCZO-B) ZnO films
The optical band gap energy of the films is depicted in Table 5.1. Band gap energy of the doped films varies in the range 3.23-3.47 eV, which are larger than that of the pure ZnO films. The increase of the optical energy gap of the doped ZnO films can be attributed to the Burstein–Moss effect, which is related to a high carrier concentration [28]. The obtained values of band gap agree with the reported values [29]. The increase in the optical band gap confirms that doping has increased the carrier concentration in the films than that of undoped films. The band gap energy of all the doped films has increased from than that of the undoped films as depicted in Tables 5.1 and 5.2.

Porosity of the doped films was determined by water saturation and water evaporation imbibition methods using Eq. (2.30) and the values obtained are tabulated in Table 5.4. Porosity was further determined from optical method using refractive index of the films by Eq. (2.31) [30]. The porosity obtained from optical method and the average porosity obtained from the imbibition methods are plotted in Fig. 5.7. As depicted in the Table 5.3, the doped films possess high porosity and indicate that films possess large number of pores. The doped ZnO films with high porosity possess high specific surface area and hence adsorb more dye molecules. This enhances light harvesting and is an essential property of a film electrode of DSSC [31, 32].

Fig. 5.7 Porosity of the as-synthesized (DSZO-A, DSZO-B, DCZO-A and DCZO-B) ZnO films by optical and imbibition methods

Porosity of the doped films was determined by water saturation and water evaporation imbibition methods using Eq. (2.30) and the values obtained are tabulated in Table 5.4. Porosity was further determined from optical method using refractive index of the films by Eq. (2.31) [30]. The porosity obtained from optical method and the average porosity obtained from the imbibition methods are plotted in Fig. 5.7. As depicted in the Table 5.3, the doped films possess high porosity and indicate that films possess large number of pores. The doped ZnO films with high porosity possess high specific surface area and hence adsorb more dye molecules. This enhances light harvesting and is an essential property of a film electrode of DSSC [31, 32].
Table 5.4 Morphology and porosity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Porosity (%) by water saturation method-I</th>
<th>Porosity (%) by water evaporation method-II</th>
<th>Average Porosity (%) (from imbibition methods I and II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSZO-A</td>
<td>Nanoflowers</td>
<td>42.45</td>
<td>40.82</td>
<td>41.64</td>
</tr>
<tr>
<td>DSZO-B</td>
<td>Nanoflowers</td>
<td>37.30</td>
<td>42.50</td>
<td>39.90</td>
</tr>
<tr>
<td>DCZO-A</td>
<td>Nanorods</td>
<td>49.10</td>
<td>46.80</td>
<td>47.95</td>
</tr>
<tr>
<td>DCZO-B</td>
<td>Nanorods</td>
<td>46.80</td>
<td>40.950</td>
<td>43.88</td>
</tr>
</tbody>
</table>

(v) Electrical properties

Electrical behavior of the doped films was studied. All the films exhibited n-type conductivity, which was determined by hot-probe method. The order of electrical resistivity of doped films is depicted in Table 5.5. The electrical resistivity of the doped films is decreased by two/three order of magnitude from than that of the undoped counterparts as illustrated in Table 5.5.

Two processes control the doping of Al and Mg in ZnO films namely: substitutional and interstitial. All the dopants used in this study are possessing ionic radius less than that of the zinc ion.

When ZnO is doped with Al, the carrier concentration was found to increase with doping concentration. At higher doping concentration, a tendency towards saturation was observed [7, 33]. The ionic radii of Zn$^{2+}$ and Al$^{3+}$ are 72 pm and 53 pm. Saturation of electrical conductivity was expected because of substitutional doping of Al$^{3+}$ at Zn$^{2+}$ site creating one extra free carrier. An aluminium atom replacing a zinc atom in a ZnO crystal produces only one free electron. While an aluminium atom occupying an interstitial position might produce up to three electrons. The process of doping by which an aluminium atom occupies in a ZnO crystal depends on many factors such as aluminium concentration, deposition temperature, method of deposition, etc. [1]. In the present study, doping using SILAR/CBD might have promoted interstitial doping since there is much decrease in the electrical resistivity of the samples DSZO-A and DCZO-A as depicted in Table 5.4.
Table 5.4 Electrical resistivity of doped and undoped ZnO films

<table>
<thead>
<tr>
<th>Doped ZnO film</th>
<th>Resistivity (Ωcm)</th>
<th>Undoped ZnO film</th>
<th>Resistivity (Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSZO-A</td>
<td>10⁻¹</td>
<td>SZO-A</td>
<td>10²</td>
</tr>
<tr>
<td>DSZO-B</td>
<td>10⁻²</td>
<td>SZO-F</td>
<td>10⁻³</td>
</tr>
<tr>
<td>DCZO-A</td>
<td>10⁻⁻²</td>
<td>CZO-D</td>
<td>10⁰</td>
</tr>
<tr>
<td>DCZO-B</td>
<td>10⁻¹</td>
<td>CZO-F</td>
<td>10⁻²</td>
</tr>
</tbody>
</table>

The resistivity of the ZnO thin films may increase with Mg doping. It is because the valences of Zn²⁺ and Mg²⁺ are the same, and the substitution of Mg²⁺ for Zn should not generate carriers of ZnO. However, there are reports stating that heat decreased the sheet resistance of Mg doped ZnO [34]. The XRD analysis confirmed that there was no shift in the position of the diffraction peaks of the doped ZnO films and hence resistivity increase due to lattice distortion can be ruled out. In addition, there were no diffraction peaks of magnesium oxide (MgO), which will have increase the resistivity of ZnO in the XRD patterns of doped ZnO. For pure ZnO, electrical conductivity is mainly due to the zinc excess at interstitial positions [1]. For Mg with similar ionic radius, ions settlement in interstices of ZnO becomes dominant instead of substitution of Zn²⁺. Hence, the resistivity decrease of one order of magnitude as depicted in Table 5.3 may be due to the occupying of Mg²⁺ at the interstitial positions in ZnO and the deposition temperature 368K at which the film was synthesized using SILAR.

Doping using SILAR/CBD might have promoted interstitial doping of Se atoms since there is three order of decrease in magnitude in the electrical resistivity of the sample DCZO-B as depicted in Table 5.4.

5.2.3 Conclusion

Doped ZnO films of nanoflower and nanorod morphologies were synthesized using SILAR and CBD techniques. Aluminium and magnesium doped ZnO films were grown using SILAR method. Aluminium and selenium doped ZnO films were prepared using CBD method. Structural, morphological, optical and electrical properties and porosity of the films were studied.
All the doped ZnO films were oriented more preferentially along the (002) direction. The thickness of all the doped ZnO films is found to be slightly increased from than that of the undoped films prepared under the same conditions. All the films are polycrystalline with hexagonal wurtzite structure. The grain size of the films increased for magnesium and selenium dopants where as the grain size decreased for aluminium dopant. Values of dislocation density in the films indicate the presence of minimum defects in the doped films. Strain developed in all of the doped ZnO films is increased by one order than that of the undoped ZnO films.

Doped SILAR ZnO films exhibit nanoflower morphology whereas the CBD ZnO films are comprised of nanorods, which offer very high internal surface area. Transmittance of the doped films became higher and lies in the 75-85% range in the entire visible region. Refractive index of the films lies in the 1.60-1.85 range in the visible region of the spectrum. Band gap energy of the doped films varies in the range 3.23-3.47 eV, which are larger than that of the pure ZnO films. The doped films possess high porosity and indicate that films possess large number of pores. The electrical resistivity of the doped films was decreased by two/three order of magnitude from than that of the undoped films.

Because of doping, enhancements of properties such as better conductivity, transmittance and size improvements have been achieved. i.e. Doping has enhanced the required properties of the ZnO thin film electrodes, which are very much demanded by DSSC.
References