Chapter 4
Synthesis and characterization of nanostructured zinc oxide thin films- Chemical bath deposition method

4.1 Introduction
ZnO is a versatile functional material that has a diverse group of growth morphologies. CBD involves deposition of semiconductor thin films on substrates that are kept in the aqueous solutions [1-3]. This method seems to be more suitable for synthesizing ZnO nanorod electrodes with a high specific surface area. It has been reported that when ZnO nanorods were applied in dye-sensitized solar cells, measured electron transport time in these systems was found to be much faster than in comparable mesoporous ZnO films [4-6]. Together with the high internal surface area and good electrical conductivity, CBD ZnO films offer excellent visible light transmittance. DSSCs has shown that the light harvesting efficiency of film electrodes is influenced by its crystallinity, particle size, surface area, dye affinity, and film porosity [7].

In the present study, nanostructured polycrystalline ZnO films with morphologies of nanoflowers, nanorods, nanoflakes, microspheres and microdisc were grown on unseeded soda lime glass substrates directly using CBD method. Analytical grade zinc sulfate and zinc nitrate were used as the zinc precursors while ammonia, monoethanolamine, diethanolamine, triethanolamine, hydrazine hydrate, ethylenediamine, hexamine and trisodium citrate were used alone and together as complex agents to synthesize the different ZnO nanostructured films. Structural, morphological, optical, textural, and electrical properties of the films were studied. The results bring out the ZnO films’ potential for DSSC applications.

4.2 Zinc oxide films with nanoflower morphology
4.2.1 Experimental
4.2.1a Synthesis using zinc sulfate and ammonia
ZnO thin films have been synthesized through CBD technique [8-18] on soda lime glass substrates. The experimental set up is shown in Fig. 2.2. Analytical grade zinc sulfate (Zn(SO₄)₂.7H₂O) and ammonia were employed as reactants without further purification. Initially, 100 ml of 0.15 M zinc sulfate solution was prepared.
Subsequently, ammonia (25%) solution was added drop-wise into the prepared solution of zinc sulfate under stirring. Addition of ammonia was continued until the pH value of the reactive solution became 10.5. The solution became milky first and then turned transparent with the increase of the pH on the addition of ammonia. The mixture was further stirred for 10 minutes to yield a homogenous solution. Immediately after the solution preparation, the glass substrate was placed in the beaker containing the reaction solution (slightly inclined from vertical to prevent particles, which might form in the solution from settling on the downward-facing side of the substrate – the side chosen for characterization).

The beaker containing the reaction solution and the substrate was kept in the water bath at 363K for 30 minutes. After being cooled to the room temperature, the substrates with thin films were taken out of the beaker, washed with distilled water and dried in hot air. The films were named as CZO-A.

4.2.1b Synthesis using zinc sulfate and triethanolamine
ZnO films were prepared by CBD method. The soda lime glass substrates were placed in 80 ml of 0.15 M of zinc sulfate (Zn(SO₄)₂·7H₂O) and 3.7 M of triethanolamine (C₆H₁₅NO₃) solutions taken in a 100 ml glass container. The solution temperature was maintained at 353K using a thermostatically controlled water bath for 1 hour. Finally, the prepared films were thoroughly washed by distilled water and dried by blowing hot air before characterization. The films were name as CZO-B.

4.2.1c Synthesis using zinc nitrate, TEA and ammonia at room temperature
Zinc nitrate (Zn(NO₃)₂·6H₂O) and triethanolamine (C₆H₁₅NO₃) were used as received. ZnO films were synthesized by CBD method. Soda lime glass was used as a substrate. 0.2 M zinc nitrate solution was prepared in distilled water and 3 ml of 7.4 M triethanolamine was added to the solution to induce the formation of ZnO. The solution became clouded shortly after the addition of triethanolamine. Ammonia (25%) solution was added drop-wise to this solution to increase the pH of the solution. The solution became milky first and then became transparent with the increase of the pH on the addition of ammonia. Glass substrate was immersed in the
middle of the solution at an angle, and the solution was kept at room temperature for 48 hours with no stirring. The substrates with thin films were taken out of the beaker, washed with distilled water and dried in air. The films were named as CZO-C.

4.2.2 Results 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 4.1.

(ii) Structural analysis

Fig. 4.1 show the XRD patterns of ZnO samples CZO-A, CZO-B and CZO-C. XRD patterns show peaks which correspond to (100), (002), (101), (102), (110), (103) and (200) crystal planes of hexagonal wurtzite structure of ZnO (JCPDS File No. 36-1451). The intensity or sharpness of the diffraction peaks indicates the high crystallinity of the as-grown samples. No characteristic peak of other phases or impurities was observed.

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

Fig. 4.1 XRD patterns of as-grown (CZO-A, CZO-B and CZO-C) ZnO films
The CZO-C film, which was synthesized at room temperature, is highly crystalline compared to the other films as per the XRD patterns of the films. The grains or particles of the films are comprised of small crystallites. The mean crystallite sizes of all the ZnO films fabricated are given in Table 4.1 and were determined using the FWHM of the (100), (002) and (101) peaks by the Scherrer’s equation given by Eq. (2.3). The crystallite size of all the films is found to be nearly 32 nm.

<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>CZO-A</td>
<td>950</td>
<td>32.43</td>
<td>0.95</td>
<td>0.00033</td>
<td>58.62</td>
<td>3.00</td>
<td>2.22</td>
</tr>
<tr>
<td>CZO-B</td>
<td>1100</td>
<td>31.75</td>
<td>0.99</td>
<td>0.00040</td>
<td>47.60</td>
<td>3.04</td>
<td>2.32</td>
</tr>
<tr>
<td>CZO-C</td>
<td>1550</td>
<td>31.07</td>
<td>1.03</td>
<td>0.00040</td>
<td>62.86</td>
<td>3.05</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Significant properties, such as resistivity, for example, are influenced by the presence of defects, strains in the structure and the stresses acting in the thin film. Stresses and strains are usually present in thin films. The defects in the ZnO films was quantified by computing the dislocation density ($\delta$) using Williamson Smallman relation [19] given by Eq. (2.19) and is given in Table 4.1. Dislocation density obtained for the films is low, which indicates the presence of minimum defects. Microstrain in the nanocrystals of ZnO films was computed by using the tangent formula given by Eq. (2.16) and is depicted in Table 4.1 [20]. Microstrain developed in as-grown ZnO films is almost negligible. The microstrain may be developed in the polycrystalline ZnO thin films due to the predominant recrystallization process. The strain formed may also be correlated to the lattice misfit, which in turn depends upon the deposition conditions [21].

(iii) Morphological analysis

The morphology of a material dictates its electro-optic properties, porosity etc. Differently magnified SEM images of the films CZO-A, CZO-B and CZO-C are illustrated in Fig. 4.2. All the films exhibit nanoflower morphology. The petals of CZO-A and CZO-B are comprised of hexagonal rods whereas CZO-C possesses petals
of lotus flower. The flower shaped nanostructures are uniformly distributed on the substrate surface in the case of CZO-A and CZO-C films while CZO-B exhibits a sparse surface morphology. Due to this mesoporous structure, all films can yield high specific surface area.

![Fig. 4.2 SEM images of as-grown (CZO-A, CZO-B and CZO-C) ZnO films](image)

It can be observed from the SEM images of the CZO-C films that certain clusters were formed through the aggregation of the 'lotus' flowers, which yielded a hierarchical structure to this ZnO films. Investigations showed better efficiency of electrolyte diffusion or penetration and high dye loading in such aggregated and structured films [22, 23]. The compositional purity of the all the ZnO films has been confirmed by energy dispersive X-ray analyses (EDAX).
(iv) Optical analysis

The optical transmittance and reflectance spectra the CZO-A, CZO-B and CZO-C films are shown in Fig. 4.3(a, b). Films show 55-65% transmission in the entire visible region of the spectrum. The reduction in transmittance of the films may be due to the internal scattering due to the rough surface of the films. Film CZO-C exhibit comparatively more transmittance from the other two films. To realize the light-scattering effect in a film, the reflectance of the film can be utilized [24, 25]. In the entire visible region the reflectance of the films, lie in the 17-20% range as shown in Fig. 4.3(b).

The optical energy band gap of the ZnO films was determined by plotting \((a \nu)^2\) against photon energy \(\nu\) as shown in Fig. 4.4. As can be seen \((a \nu)^2\) varies linearly with \(\nu\) above the optical band gap energy of the ZnO films. Accordingly, the energy band gap was obtained by extrapolating the straight-line portion of the curve to the \(\nu\)-axis. The optical band gap energy of the films is depicted in Table 4.1. Films possess nearly same optical band gap though they were prepared from different chemical baths.
The films with high refractive index, has excellent light-scattering characteristics, which is required for effective light harvesting [7]. The variation of refractive index and extinction coefficient of the films with wavelength is shown in Fig. 4.5.
Films exhibit refractive index in the range 2.15 to 2.35 in the visible region of the spectrum. Film CZO-B has comparatively high refractive index while CZO-C possesses the least value among the three films. In the NIR region of the spectrum, the value of refractive index of the films appears to decrease. Extinction coefficient of all the films shows a linear increase with increase in wavelength in the visible region.

<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>CZO-A</td>
<td>Nanoflowers</td>
<td>32.44</td>
<td>34.35</td>
<td>33.40</td>
</tr>
<tr>
<td>CZO-B</td>
<td>Nanoflowers</td>
<td>29.23</td>
<td>27.96</td>
<td>28.59</td>
</tr>
<tr>
<td>CZO-C</td>
<td>Nanoflowers</td>
<td>39.25</td>
<td>43.40</td>
<td>41.32</td>
</tr>
</tbody>
</table>

Porous film electrode used in DSSC helps to enhance its efficiency. Porosity of the CZO-A, CZO-B and CZO-C films was determined from optical method using refractive index of the films by Eq. (2.31) [26]. Porosity was further experimentally determined by water saturation and water evaporation imbibition methods using Eq. (2.30) and the values are depicted in Table 4.2.
The porosity obtained from optical method and the average porosity obtained from the imbibition methods are plotted in Fig. 4.6. Values obtained from both the methods are nearly agreeing. Values of porosity of the films depicted in Table 4.2, give evidence of pores present in the films. Hence, the synthesized films would be capable of adsorbing more dye molecules on sensitization to act as photoanode in DSSC.

**(v) Electrical studies**

Films exhibited n-type conductivity, which was determined by hot-probe method. The resistivity of thin film coating is a measure of how strongly it opposes the flow of electrons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZO-A</td>
<td>$10^1$</td>
</tr>
<tr>
<td>CZO-B</td>
<td>$10^2$</td>
</tr>
<tr>
<td>CZO-C</td>
<td>$10^1$</td>
</tr>
</tbody>
</table>

The electrical resistivity of the ZnO films was examined and the value of resistivity of the films determined is given in Table 4.3. Films CZO-A and CZO-C has lower resistivity compared to CZO-B films.

**4.2.3 Conclusion**

Various nanostructured polycrystalline ZnO films with nanoflower morphology were synthesized on unseeded soda lime glass substrates using CBD technique. ZnO films were prepared from different baths comprising of zinc sulfate-ammonia, zinc sulfate-triethanolamine and zinc nitrate-TEA-ammonia at temperature 90°C, 80°C and at room temperature respectively. Films were highly crystalline having hexagonal wurtzite structure. The crystallite size of the films is ~32 nm. The low dislocation density indicates the presence of minimum defects in the films and the microstrain in the films is negligible. All the ZnO films exhibit nanoflower morphology, which offer high specific surface area. Films show 55-65% transmission in the entire visible region of the spectrum. ZnO films possess nearly same optical band gap though they were prepared from different chemical baths.
Films exhibit refractive index in the range 2.15 to 2.35 in the visible region of the spectrum and have high porosity. The excellent crystallinity, porous nature with high specific surface area, good optical and electrical properties makes the films potential candidates in DSSC applications.

4.3 Zinc oxide films with nanorod morphology

4.3.1 Synthesis using zinc nitrate and different complex agents

4.3.1a Experimental

(i) Using monoethanolamine

In this deposition process, 80 ml of aqueous 0.15 M zinc nitrate (Zn(NO₃)₂·6H₂O) solution and 2 ml of 3.5 M monoethanolamine (C₂H₇NO) were mixed slowly with vigorous magnetic stirring to give an optically transparent reaction mixture. 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 h, and then allowed to stand at ambient temperature for 1.5 hour. Film was named as CZO-D.

(ii) Using diethanolamine

In the synthesis process, 0.15 M of zinc nitrate (Zn(NO₃)₂·6H₂O) was dissolved in 80 ml of distilled water followed by the addition of 3 ml 3.5 M diethanolamine (C₄H₁₁NO₂). Then, ammonia solution (25%) was used to make the pH of the solution 10.8. CBD ZnO nanorod fabrication was carried out on cleaned soda lime glass substrates by suspending the substrates in the solution. The growth temperature and time were set at 353K and 2 hour. The film was named as CZO-E.

(iii) Using triethanolamine

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(NO₃)₂·6H₂O) and 4 ml of 7.4 M triethanolamine (C₆H₁₅NO₃) in a 100 ml glass beaker. 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 CZO-F.

**(iv) Using ethylenediamine**

A solution of 0.15 M zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O) in 100 ml distilled water was stirred at room-temperature for 10 minutes. 2 ml of 3.5 M ethylenediamine (C$_2$H$_4$(NH$_2$)$_2$) was added drop-wise to this solution and thoroughly mixed for 15 minutes using a magnetic stirrer. This reaction solution was then adjusted to the desired pH by adding an aqueous solution of NH$_4$OH droplets. The pH of the mixed aqueous solution was raised to 11. The final solution was heated to 363K on a hot plate. During heating, the solution was not stirred. When the aqueous solution reached 363K, a soda lime glass substrate was dipped into it for 2.5 hour. This growth time was used to ensure sufficient thickness of the ZnO films. After keeping the substrate in aqueous solution for the desired time, the sample was washed several times in distilled water and dried with blowing hot air. The ZnO nanostructured film obtained was named as CZO-G.

**(v) Using hydrazine hydrate**

ZnO thin films were grown on soda-lime glass substrates by the CBD technique. Before the deposition, the glass substrates were cleaned in chromic acid then in distilled water and subsequently dried in flowing hot air. The CBD bath contained 80 ml of 0.15 M zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O) and 2 ml of 3.7 M hydrazine hydrate (N$_2$H$_4$.H$_2$O). The solution pH was raised to 10.8 using ammonia (25%) solution. The glass substrates were inserted at an angle into the chemical bath. During CBD, the solution was maintained at a temperature of 353K, while the bath was kept unstirred. The reaction time was kept fixed and lasted for 1.5 hour. After completion of film deposition, the glass substrates were taken out of the solution. The films were rinsed with distilled water to remove white loose adherent powder precipitates. Films were dried by blowing hot air. Then the deposited films were examined and named as CZO-H.
(vi) Using hydrazine hydrate and monoethanolamine

The CBD bath contained 80 ml of 0.15 M zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O), 3 ml of 3.7 M hydrazine hydrate (N$_2$H$_4$.H$_2$O) and 2 ml of 3.5 M monoethanolamine (C$_2$H$_7$NO). The reaction solutions were mixed slowly with vigorous magnetic stirring to give an optically transparent reaction mixture. The solution pH was raised to 11 by adding ammonia (25%) droplets. The glass substrates were inserted at an angle into the chemical bath. During CBD, the solution was maintained at a temperature of 363K, while the bath was kept unstirred. After film deposition, substrates with film was removed, rinsed in distilled water and dried in hot air. Film was named as CZO-I.

(vii) Using hydrazine hydrate and diethanolamine

In this process, the aqueous solutions of 85 ml 0.15 M zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O), 3 ml of 3.7 M hydrazine hydrate (N$_2$H$_4$.H$_2$O) and 2 ml of 3.5 M diethanolamine (C$_4$H$_{11}$NO$_2$) were first prepared respectively and mixed together. Ammonia (25%) droplets were added to adjust the pH of the growth solution to 11. The pre-cleaned soda lime glass substrates were immersed into the aqueous solution and tilted against the wall of beaker. Then the beaker was put into the water bath and kept in it for 2 hour time at 363K. After the film growth, the substrate was removed from the solution, rinsed with distilled water and then dried at room temperature. Film was named as CZO-J.

4.3.1b Results 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 estimated average value of thickness is depicted in Table 4.3.

(ii) Structural analysis

Fig. 4.7 shows the X-ray diffraction patterns of the as-grown CZO-D, CZO-E, CZO-F and CZO-G ZnO thin films. Fig. 4.8 shows the X-ray diffraction patterns of the as-grown CZO-H, CZO-I and CZO-J ZnO thin films. The XRD patterns of all the films show peaks which correspond to (100), (002), (101), (102), (110), (103) and (200) crystal planes of hexagonal wurtzite ZnO (JCPDS File No. 36-1451). No
characteristic peaks from other impurities are detected. The sharp and high intensity diffraction peaks indicates high crystallinity of the as-grown samples.

CZO-D, CZO-F, CZO-I and CZO-J films exhibit very high intensity diffraction peaks compared to the other films. CZO-D and CZO-F films were prepared by using complex agents monoethanolamine and triethanolamine respectively. CZO-I and CZO-J films were prepared by using combination complex agents hydrazine hydrate-monoethanolamine and hydrazine hydrate-triethanolamine respectively. In the XRD patterns of CZO-D film, the (002) peak is dominant, and its intensity is much higher than that of other peaks which reveals the preferential growth of orientation along c-axis. The other ZnO films were dominating with (100), (002) and (101) crystal plane oriented crystallites.
Fig. 4.8 XRD patterns of the as-grown (CZO-H, CZO-I and CZO-J) ZnO thin films

Table 4.4 Structural and optical parameters of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Grain size (nm)</th>
<th>Dislocation density ((10^{15} \text{ 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>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-E</td>
<td>1050</td>
<td>32.08</td>
<td>0.97</td>
<td>0.00033</td>
<td>55.58</td>
<td>3.64</td>
<td>2.26</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>
<tr>
<td>CZO-G</td>
<td>1300</td>
<td>33.21</td>
<td>0.90</td>
<td>0.00037</td>
<td>66.82</td>
<td>3.69</td>
<td>2.09</td>
</tr>
<tr>
<td>CZO-H</td>
<td>1100</td>
<td>27.39</td>
<td>1.33</td>
<td>0.00046</td>
<td>71.25</td>
<td>3.78</td>
<td>2.01</td>
</tr>
<tr>
<td>CZO-I</td>
<td>1550</td>
<td>36.84</td>
<td>0.73</td>
<td>0.00034</td>
<td>65.00</td>
<td>3.17</td>
<td>2.12</td>
</tr>
<tr>
<td>CZO-J</td>
<td>1150</td>
<td>33.08</td>
<td>0.91</td>
<td>0.00037</td>
<td>71.60</td>
<td>3.88</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Each complexing agent used to synthesize the films has slightly affected both the diffraction peak positions of XRD patterns and full-width at half maximum (FWHM) obtained from the ZnO films. In addition, there is variation of FWHM with respect to the crystal planes of all as-grown films.
Using Scherrer’s formula given by Eq. (2.3), the crystallite size was calculated according to the broadening of the highest intensity peaks corresponding to the (1 0 1), (002) and (101) diffraction planes. The mean crystallite sizes of all the ZnO films fabricated are given in Table 4.4. The crystallite size of the films varies from 27 nm to 44 nm. During crystallization the degree of microstrain and disorder of the material depends on the initial choice of organic solvent and deposition temperature in film preparation [27]. The defects in the ZnO films was quantified by computing the dislocation density (δ) using Williamson Smallman relation [19, 28] given by Eq. (2.19) and is given in Table 4.4. Dislocation density obtained is low, which indicates the presence of minimum defects in the films.

Microstrain in the nanocrystals of ZnO films was determined by using the tangent formula given by Eq. (2.16) and is depicted in Table 4.4 [20]. Strain developed in all of ZnO the films is almost negligible. The lowered microstrain may reflect a lower degree of disorder in thin films [27].

(iii) Morphological analysis

Figs. 4.9, 4.10, 4.11 and 4.12 illustrate the SEM images of CZO-D, CZO-E, CZO-F, CZO-G, CZO-H, CZO-I and CZO-J films. It is observed that the CZO-E, CZO-F and CZO-J films, which were synthesized on bare glass substrate, are not vertically aligned nanorods but consisted of assorted nanorods. Most of the nanorods are aligned parallel to the substrate surface.

In the case of CZO-E and CZO-F, it may be noted that the coverage on the substrate surface is not uniform. It can be noted that CZO-E, CZO-F and CZO-J were synthesized by using diethanolamine, triethanolamine and hydrazine hydrate-triethanolamine complex agents. It can be noted that presence of diethanolamine or triethanolamine in the chemical bath alone or in combination created nanorods, which are aligned parallel to the substrate surface. It can be noted from the SEM images of CZO-D and CZO-E depicted in Fig. 4.9 that the nanorods of this films are tapered at the ends.
A close observation of the SEM images of the film CZO-F indicates that the nanorods are grown on a thin layer of film initially developed on the substrate.
Whereas the packed nanorods of CZO-G are appeared to be grown from a large number of nucleation sites developed on the substrate and hence are aligned vertically to the substrate surface.

SEM images of CZO-H and CZO-I also illustrate the formation of purely hexagonal nanorods, which are aligned vertically to the substrates. One can clearly observe a distinct change in surface morphology of CZO-D, CZO-G, CZO-H and CZO-I ZnO nanorod-films deposited on glass substrate using complex agents monoethanolamine, ethylenediamine, hydrazine hydrate, and hydrazine hydrate-monoethanolamine. Most of the nanorods are vertically aligned to the glass substrates in all these cases.
SEM images depicted in Figs. 4.11 and 4.12 of the films CZO-I and CZO-J indicates that purely hexagonal shaped nanorods were obtained when hydrazine hydrate was used in combination with either monoethanolamine or triethanolamine. The nanorod morphology of the ZnO films incorporates nano-meso-micro pores of irregular shapes in the films and are thereby comprised of a very large specific surface area. This makes the films potential candidates in the DSSC applications. The EDAX spectra indicate (not shown here) that the films contain mainly Zn and O and no significant signal from other elements being detected. The compositional purity of all the ZnO nanostructured film has been thus confirmed.

(iv) Optical analysis

The optical transmittance and reflectance spectra of as-grown CZO-D, CZO-E, CZO-F, CZO-G, CZO-H, CZO-I and CZO-J films are shown in Fig. 4.13.

Fig. 4.13 The optical transmittance and reflectance spectra of the as-grown (CZO-D, CZO-E, CZO-F, CZO-G, CZO-H, CZO-I and CZO-J) ZnO thin films
Transmittance in the range 55-70% can be observed for all the ZnO films in the entire visible region. The lowest transmission is noted in the case film CZO-E, which was grown using the complexing agent diethanolamine. It can be observed that the absorption edge is blue shifted with respect to the complexing agents used to synthesize the ZnO films. The absorption edge of films CZO-D and CZO-I, prepared in the presence of monoethanolamine in the chemical bath, was not shifted compared to the other films. To understand the light-scattering effect in a film, the reflectance of the film can be utilized [24, 25]. Films exhibit 12-20% reflectance in the same region. This reflectance will enhance light harvesting due to the internal light scattering, which is an essential property of a DSSC electrode [29, 30].

The optical energy band gap ($E_g$) of the films were determined by plotting $(\alpha h \nu)^2$ against photon energy ($h \nu$) [31]. In Fig. 4.14, $(\alpha h \nu)^2$ versus $h \nu$ plots of the films are shown. As can be seen $(\alpha h \nu)^2$ varies linearly with $h \nu$ above the optical band gap energy of the ZnO films. The energy band gap is obtained by extrapolating the straight-line portion of the curve to the $h \nu$-axis. The optical band gap energy ($E_g$) of the films is depicted in Table 4.4. Band gap energy of the films varies in the range 3.08-3.88 eV. The $E_g$ values obtained were in agreement with the reports [32, 33].

Fig. 4.14 The $(\alpha h \nu)^2$ vs $h \nu$ plot of as-synthesized (CZO-D, CZO-E, CZO-F, CZO-G, CZO-H, CZO-I and CZO-J) ZnO thin films
Nanoporosity can blue shift the absorption edge, leading to the variation observed for material with pronounced nanocrystallinity [34]. The optical band gap values obtained indicate that the energy gap is enlarged with respect to the respective complexing agents used to synthesize the films. The obtained ZnO thin film material is of polycrystalline nature with crystallite of a size (between 27 and 44 nm) that, from a general point of view, should not result in any noticeable quantum confinement. Nevertheless, blue shift of the fundamental absorption edge in comparison with the corresponding bulk materials can be observed. This effect can be attributed to the material porosity, which is a typical feature of chemical bath deposition technique. The blue shift is caused by quantum confinement in pores [34]. The blue shift of absorption edge or increase in the optical energy gap can also be attributed to the increase of carrier concentrations, known as Burstein–Moss effect [35]. The variation in carrier concentration in the prepared ZnO films may be aroused with respect to the deposition conditions and the complexing agents present in the chemical bath.

Fig. 4.15 shows the variation of extinction coefficient of as-grown ZnO films. In the visible region, extinction coefficient of the films increases with increase in wavelength. It can be noted that variation of extinction coefficient of the films, CZO-E and CZO-F synthesized using diethanolamine and triethanolamine respectively, is
different from that of the other films. Extinction coefficient of the film CZO-D is higher than the other films.

Excellent light-scattering characteristics, which are required for effective light harvesting in DSSC can be noticed in the case of films with high refractive index [7]. Variation of refractive index of the films is depicted in Fig. 4.16. All the films, except that of CZO-F, exhibit high refractive index value, which lies in the range 2.00-2.25 in the entire visible region. It is interesting to note that the value of refractive index of the CZO-F film decreases with respect to the increase in the wavelength in the visible region sharply as shown in Fig. 4.16. For other films, there is a gradual decrease of refractive index in the visible region.

The porous ZnO electrode plays a vital role in determining the performance of DSSC. Porosity of the ZnO films was determined from optical method using refractive of the films by Eq. (2.31) [26]. Porosity was further determined by water saturation and water evaporation imbibition methods using Eq. (2.30) and the values obtained are depicted in Table 4.5.
### Table 4.5 Morphology and porosity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Porosity (%) by optical method</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>CZO-D</td>
<td>Nanorods</td>
<td>28.68</td>
<td>25.34</td>
<td>27.80</td>
<td>26.57</td>
</tr>
<tr>
<td>CZO-E</td>
<td>Nanorods</td>
<td>18.58</td>
<td>21.35</td>
<td>23.00</td>
<td>22.18</td>
</tr>
<tr>
<td>CZO-F</td>
<td>Nanorods</td>
<td>33.47</td>
<td>30.50</td>
<td>36.50</td>
<td>33.50</td>
</tr>
<tr>
<td>CZO-G</td>
<td>Nanorods</td>
<td>25.34</td>
<td>22.32</td>
<td>28.45</td>
<td>25.39</td>
</tr>
<tr>
<td>CZO-H</td>
<td>Nanorods</td>
<td>29.52</td>
<td>26.20</td>
<td>30.25</td>
<td>28.23</td>
</tr>
<tr>
<td>CZO-I</td>
<td>Nanorods</td>
<td>22.76</td>
<td>24.25</td>
<td>22.60</td>
<td>23.43</td>
</tr>
<tr>
<td>CZO-J</td>
<td>Nanorods</td>
<td>30.23</td>
<td>27.30</td>
<td>32.80</td>
<td>30.05</td>
</tr>
</tbody>
</table>

Analysis of porosity of the films from Table 4.5 and the SEM images of the respective mesoporous ZnO films confirmed that they possess enough pores to hold the dye molecules. This enhances light harvesting and is an essential property of a film electrode of DSSC [26, 29]. Material porosity inherent to CBD method can be used to fine-tune the material band gap with the help of suitable complexing agents towards the required values, paving promising ways for solar cell applications.

**(v) Electrical studies**

Electrical behavior of the films was studied. For the ZnO films, Ohmic conduction was observed to be the dominant mechanism. Films exhibited n-type conductivity, which was determined by hot-probe method. n-type conductivity in ZnO is due to the oxygen vacancies and interstitial zinc atoms, both acts as donors, which are present in the films. The order of electrical resistivity of the films determined was depicted in Table 4.6 and the values lie in the range $10^{-1} - 10^{2} \, \Omega \text{cm}$. It can be observed that the electrical resistivity of films varies with respect to the bath conditions and the various complexing agents used in the chemical bath.

The lowest resistivity obtained was for the CZO-G, CZO-H, CZO-I and CZO-J films which exhibited higher optical band gap due to blue shift as mentioned earlier.
Table 4.6 Electrical resistivity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Complexing agent</th>
<th>Resistivity (Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZO-D</td>
<td>Monoethanolamine</td>
<td>10^0</td>
</tr>
<tr>
<td>CZO-E</td>
<td>Diethanolamine</td>
<td>10^2</td>
</tr>
<tr>
<td>CZO-F</td>
<td>Triethanolamine</td>
<td>10^2</td>
</tr>
<tr>
<td>CZO-G</td>
<td>Ethylenediamine</td>
<td>10^-1</td>
</tr>
<tr>
<td>CZO-H</td>
<td>Hydrazine hydrate</td>
<td>10^-1</td>
</tr>
<tr>
<td>CZO-I</td>
<td>Hydrazine hydrate-Monoethanolamine</td>
<td>10^-1</td>
</tr>
<tr>
<td>CZO-J</td>
<td>Hydrazine hydrate-triethanolamine</td>
<td>10^-1</td>
</tr>
</tbody>
</table>

4.3.1c Conclusion

Nanostructured polycrystalline ZnO films with nanorod morphology deposited on unseeded soda lime glass substrates using the CBD deposition technique. Various films were prepared by using zinc nitrate and complexing agents monoethanolamine, triethanolamine, diethanolamine, ethylenediamine, hydrazine hydrate, hydrazine hydrate-monoethanolamine and hydrazine hydrate-diethanolamine. The sharp and high intensity diffraction peaks indicates high crystallinity of the films. The crystallite size of the various films varies in the range 27-44 nm. The low value of microstrain reflects the low degree of disorder in thin films. Films possess assorted and vertically aligned nanorod morphology. The nanorod morphology of the ZnO films incorporates nano-meso-micro pores of irregular shapes in the films and are there by comprised of a very large specific surface area. Band gap energy of the films varies in the range 3.08-3.88 eV. All the films, except that of CZO-F, exhibit high refractive index value, which lies in the range 2.00-2.25 in the entire visible region. Films have reasonably high porosity. The order of electrical resistivity of the films lies in the range 10^-1 - 10^2 Ωcm. The films with excellent characteristics can be used as working photoelectrodes in DSSC.
4.4. Zinc oxide films with nanosheet/nanoflake morphology

4.4.1 Synthesis using zinc sulfate

4.4.1a Experimental

(i) Using ammonia

In the CBD process, 20 ml of 0.01 M zinc sulfate (Zn(SO$_4$)$_2$.$7$H$_2$O) were first prepared. Ammonia (25%) droplets were added under stirring to adjust the pH of the growth solution to 10.3. The transparent solution obtained was taken in a test tube and heated in a water bath kept at 368K for 10 minutes. The heated reaction solution was filtered using an ordinary filter paper. The filtered clean hot solution was poured over the pre-cleaned glass substrate kept inclined in another test tube gradually. The test tube containing the solution and the substrate was put into the water bath and kept in it for 3 hour under 368K. After the film growth, the substrate was removed, rinsed with distilled water and then dried blowing hot air. The film sample was named as CZO-K.

(ii) Using hexamine and trisodium citrate

In this process, the aqueous solutions of 20 ml of 0.05 M zinc sulfate (Zn(SO$_4$)$_2$.7H$_2$O), 20 ml of 0.1 M hexamine (C$_6$H$_{12}$N$_4$) and 3 ml of 0.01 M trisodium citrate (Na$_3$C$_6$H$_5$O$_7$) were first prepared respectively and mixed together. The pH of the growth solution was 9. The experimental procedure was continued as in 4.4.1a(i). Heating was stopped after 3 hour duration and the test tube containing the substrate was kept for 1 hour in the water bath. Then the substrate was removed, rinsed with distilled water and dried blowing hot air. The film sample was named as CZO-L.

4.4.2 Results 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 as mentioned in section 4.2.2(i) and the estimated average value of thickness is depicted in Table 4.8.
(ii) Structural analysis

Fig. 4.17 shows the XRD patterns of the CZO-K and CZO-L ZnO films. XRD patterns show peaks which correspond to (100), (002), (101), (102), (110), (103), (200), (112) and (210) crystal planes of hexagonal ZnO (JCPDS File no. 36-1451). The high intensity of the diffraction peaks demonstrates good crystallinity of the films. Characteristic peaks corresponding to other phases or impurities, such as zinc hydroxide, basic reactants etc., were not observed in the XRD patterns of any of the films. This indicated the formation of pure ZnO films.

The mean crystallite sizes of all the ZnO films fabricated are given in Table 4.7 and were determined using the FWHM of the high intensity peaks corresponding to the crystal planes (100), (002) and (101) by the Debye-Scherrer’s equation given by Eq. (2.3). The crystallite size of CZO-K and that of CZO-L is approximately the same.

![XRD patterns of the as-grown (CZO-K and CZO-L) ZnO films](image)

**Fig. 4.17 XRD patterns of the as-grown (CZO-K and CZO-L) ZnO films**

**Table 4.7 Structural and optical parameters of ZnO films**

<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>CZO-K</td>
<td>1150</td>
<td>30.54</td>
<td>1.07</td>
<td>0.00041</td>
<td>79.42</td>
<td>3.66</td>
<td>1.83</td>
</tr>
<tr>
<td>CZO-L</td>
<td>1350</td>
<td>29.81</td>
<td>1.12</td>
<td>0.00042</td>
<td>82.39</td>
<td>3.88</td>
<td>1.75</td>
</tr>
</tbody>
</table>
The defects in the ZnO films was quantified by computing the dislocation density (δ) using Williamson Smallman relation [28] given by Eq. (2.19) and is given in Table 4.7. Dislocation density obtained for the films is low, which indicates the presence of minimum defects. Microstrain in the nanocrystals of ZnO films was computed by using the tangent formula given by Eq. (2.16) and is depicted in Table 4.7 [32]. Microstrain developed in all of the ZnO films is almost negligible.

(iii) Morphological analysis

Differently magnified SEM micrographs of CZO-K and CZO-L are shown in Fig. 4.18. SEM images of CZO-K exhibits a profile of irregular shaped planar nanosheets and all of these nanosheets show similar morphologies and dispersed homogenously on the substrates. SEM images of the film CZO-L showed fibrous surface morphology with interconnected flakes forming micro pores. The pores having diameter about 0.5–1 μm and flakes with average thickness ~10 nm are clearly visible on the film surface. Such novel morphology, leading to large surface area, finds applications in DSSC.

![SEM images of the as-grown (CZO-K and CZO-L) ZnO films](image)

The compositional purity of all the ZnO nanostructured film has been confirmed by EDAX analyses.
(iv) Optical analysis

Fig. 4.19 shows the optical transmittance and reflectance (inset) spectra of the as-grown CZO-K and CZO-L ZnO films. It is observed that the optical transmittance is above 75% and 80% in the visible region of the spectrum for CZO-K and CZO-L films respectively. Reflectance of the films lies in the range 8-12% in the visible region.

The optical behavior of a material is determined by its optical constants, i.e., the optical energy band gap, the extinction coefficient and the refractive index of the material. Fig. 4.20(a, b) depicts the variation of optical constants refractive index and extinction coefficient of the films. Refractive index of the film lies in the 1.75-1.90 range in the visible region.

Extinction coefficient indicates the amount of absorption loss when light transmits through the material. As shown in Fig. 4.20(b), extinction coefficient of the films increases with increase in wavelength in the visible region.
Fig. 4.20 Variation of (a) refractive index and (b) extinction coefficient of the as-grown (CZO-K and CZO-L) ZnO films

The $(\alpha h\nu)^2$ vs $h\nu$ plot of CZO-K and CZO-L ZnO films is shown in Fig. 4.21. The optical band gap values determined is depicted in Table 4.7.

Fig. 4.21 The $(\alpha h\nu)^2$ vs $h\nu$ plot of as-synthesized (CZO-K and CZO-L) ZnO films
The optical band gap values obtained indicate that the energy gap is blue shifted in the case of both the films. The polycrystalline ZnO thin films are with crystallites of size ~30 nm. From a general point of view, it should not result in any noticeable quantum confinement effect. Therefore, this effect can be attributed to the material porosity, which is a typical feature of chemical bath deposition technique. The blue shift is caused by quantum confinement in pores [34].

### Table 4.8 Morphology and porosity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Porosity (%) by optical method</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>CZO-K</td>
<td>Nanosheets</td>
<td>8.60</td>
<td>10.50</td>
<td>9.55</td>
<td>8.60</td>
</tr>
<tr>
<td>CZO-L</td>
<td>Nanoflakes</td>
<td>38.40</td>
<td>39.45</td>
<td>38.92</td>
<td>38.40</td>
</tr>
</tbody>
</table>

Porosity by optical and imbibition methods of the as-grown CZO-K and CZO-L ZnO films are tabulated in Table 4.8. Porosity of the film CZO-K is low and that of the film CZO-L is high. CZO-L offers very high surface area due this high porosity and is a potential candidate for DSSC applications.

**(v) Electrical studies**

The electrical behavior of the films was studied by determining the electrical resistivity of the CZO-K and CZO-L ZnO films. The electrical conductivity of ZnO thin film is generated by defects such as zinc excess at the interstitial position and oxygen vacancies. The electrical resistivity was determined and the values are tabulated in Table 4.9.

### Table 4.9 Electrical resistivity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity ($\Omega$cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZO-K</td>
<td>$10^3$</td>
</tr>
<tr>
<td>CZO-L</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>

It can be noted that resistivity of the ZnO films are moderately high. This may be due to the mesoporous structure of the films.
4.4.3 Conclusion

Nanostructured ZnO films with nanosheets/nanoflake morphology were synthesized on unseeded soda lime glass substrates using the CBD deposition technique. ZnO films were prepared from zinc sulfate-ammonia and zinc sulfate-hexamine-trisodium citrate chemical baths. The ZnO thin films are polycrystalline with ~30 nm crystallite size. Films possess minimum defects and microstrain developed is negligible. CZO-K exhibits a profile of irregular shaped planar nanosheets while CZO-L showed fibrous surface morphology with interconnected flakes forming micro pores. Optical transmittance of the ZnO films is between 75% and 80% and refractive index lies in the 1.75-1.90 range in the visible region. The optical band gap of the films is 3.66 and 3.88 eV. Porosity the film CZO-K is low and that of the film CZO-L is high. Resistivity of the ZnO films is moderately high. The excellent film characteristics find applications in DSSC.

4.5. Zinc oxide films with microsphere/microdisc morphology

4.5.1 Synthesis using zinc nitrate

4.5.1a Experimental

(i) Using hexamine and trisodium citrate

ZnO thin films were grown on soda-lime glass substrates by the CBD technique. Before the deposition, the glass substrates were cleaned in chromic acid then in distilled water and subsequently dried in flowing hot air. The CBD bath contained 75 ml of 0.15 M zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O), 5 ml of 0.1 M hexamine (C$_6$H$_{12}$N$_4$) and 5 ml of 0.05 M trisodium citrate (Na$_3$C$_6$H$_5$O$_7$). The solution pH was kept at 9. The glass substrates were inserted at an angle into the chemical bath. During CBD, the solution was maintained at a temperature of 363K, while the bath was kept unstirred. The reaction time was kept fixed for 3 hour. After completion of film deposition, the glass substrates were taken out of the solution. The films were rinsed with distilled water to remove white loose adherent powder precipitates and were dried in hot air. Then the deposited films were examined and named as CZO-M.
(ii) Using triethanolamine and trisodium citrate

The CBD bath contained 75 ml of 0.15 M zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O), 5 ml of 7.4 M triethanolamine (C$_6$H$_{15}$NO$_3$) and 5 ml of 0.05 M trisodium citrate (Na$_3$C$_6$H$_5$O$_7$). The solution pH was kept at 9.3. The glass substrates were inserted at an angle into the chemical bath. During CBD, the solution was maintained at a temperature of 90$^\circ$C, while the bath was kept unstirred. The reaction time was kept fixed for 3 hours. After completion of film deposition, the films were rinsed with distilled water and dried by blowing hot air. Then the deposited films were named as CZO-N.

4.5.2 Results 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 and the estimated average value of thickness is depicted in Table 4.10.

(ii) Structural analysis

The XRD patterns of the CZO-M and CZO-N ZnO films are shown in Fig. 4.22.

Fig. 4.22 XRD patterns of as-grown (CZO-M and CZO-N) ZnO films
XRD patterns show peaks which correspond to (100), (002), (101), (102), (110), (103), and (200) crystal planes of hexagonal ZnO (JCPDS File no. 36-1451). The high intensity diffraction peaks indicates high crystallinity of the as-grown samples. CZO-M is highly crystalline than the CZO-N films. No characteristic peak of other chemical compounds or impurities was observed.

Table 4.10 Structural and optical parameters of ZnO films

<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>CZO-M</td>
<td>1450</td>
<td>28.93</td>
<td>1.19</td>
<td>0.00043</td>
<td>62.40</td>
<td>3.53</td>
<td>2.16</td>
</tr>
<tr>
<td>CZO-N</td>
<td>1250</td>
<td>27.64</td>
<td>1.30</td>
<td>0.00045</td>
<td>63.05</td>
<td>3.88</td>
<td>2.15</td>
</tr>
</tbody>
</table>

The mean crystallite sizes of all the ZnO films fabricated are given in Table 4.10 and were determined using the FWHM of the high intensity peaks corresponding to the crystal planes (100), (002) and (101) by the Debye-Scherrer’s equation given by Eq. (2.3). The crystallite size of CZO-M and that of CZO-N film is approximately the same.

The defects in the ZnO films was quantified by computing the dislocation density ($\delta$) using Williamson Smallman relation [28] given by Eq. (2.19) and is given in Table 4.10. Dislocation density obtained for the films is low, which indicates the presence of minimum defects. Microstrain in the nanocrystals of ZnO films was computed by using the tangent formula given by Eq. (2.16) and is depicted in Table 4.7 [32]. Microstrain developed in all of the ZnO films is insignificant.

(iii) Morphological analysis

Fig. 4.23 illustrates the SEM images of CZO-M and CZO-N ZnO films. Morphology of both the films is less common. Morphology of CZO-M is micro-spheres whereas that of CZO-N is a mixture of microspheres and microdiscs. Evolution of this type morphology may be due to the use of trisodium citrate or more specifically due to the presence of citrate ions in the chemical bath [37]. This peculiar morphology offers high surface area and large number of meso-micro pores to attach the dye molecules when these films are sensitized to act as photoanode in DSSC.
The EDAX analyses revealed that the as-grown ZnO films are composed of ‘Zn’ and ‘O’ elements only.

**(iv) Optical analysis**

The optical transmittance and reflectance (inset) spectra of the CZO-M and CZO-L films are shown in Fig. 4.24. Films show 50-60% transmittance and 5-20% reflectance in the visible region. This indicates that the film surface is rough and the film promotes internal scattering. Both these are the properties demanded by the thin film electrodes which are used in DSSC.

Fig. 4.25(a, b) illustrates the variation of refractive index and extinction coefficient of as-grown CZO-M and CZO-N ZnO films with wavelength. In the visible region of the spectrum, refractive index of the films lies in the range 2.00-2.25. The films with high refractive index, has excellent light-scattering characteristics, which is required for effective light harvesting [7]. The extinction coefficient of the films slightly increases with respect to the increase in wavelength in the visible region.
Fig. 4.24 The optical transmittance and reflectance (inset) spectra of as-grown (CZO-M and CZO-N) ZnO films

Fig. 4.25 Variation of (a) refractive index and (b) extinction coefficient of as-grown (CZO-M and CZO-N) ZnO films with wavelength
The optical energy band gap of the ZnO films was determined by plotting \((\alpha hv)^2\) against photon energy \((hv)\) as shown in Fig. 4.26. The energy band gap was obtained by extrapolating the straight-line portion of the curve to the \(hv\)-axis. The optical band gap energy of the films is depicted in Table 4.10. Films possess high optical band gap. The blue shift may be caused by quantum confinement in pores and not due to the crystallite size effect [34]. Hence, it is clear that material porosity inherent to CBD method can be used to fine-tune the band gap with the help of suitable complexing agents towards the required values, paving promising ways for solar cell applications.

Porosity of the ZnO films was determined from optical method using refractive of the films by Eq. (2.31) [26] and by further determined by water saturation and water evaporation imbibition methods using Eq. (2.30) and the values obtained are depicted in Table 4.5. Analysis of porosity of the films from Table 4.11 and the SEM images of the respective mesoporous ZnO films confirmed that they possess enough pores to hold the dye molecules. This enhances light harvesting and is an essential property of a film electrode of DSSC [29, 36].

Fig. 4.26 The \((\alpha hv)^2\) vs \(hv\) plot of as-synthesized (CZO-M and CZO-N) ZnO films
Table 4.11 Morphology and porosity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Porosity (%) by optical method</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>CZO-M</td>
<td>Microspheres</td>
<td>21.45</td>
<td>23.55</td>
<td>25.34</td>
<td>24.44</td>
</tr>
<tr>
<td>CZO-N</td>
<td>Microdiscs</td>
<td>20.74</td>
<td>17.49</td>
<td>21.23</td>
<td>19.66</td>
</tr>
</tbody>
</table>

(v) Electrical studies

Electrical behavior of the films was studied. Both the ZnO films exhibited n-type conductivity, which was determined by hot-probe method.

Table 4.12 Electrical resistivity of ZnO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZO-M</td>
<td>$10^2$</td>
</tr>
<tr>
<td>CZO-N</td>
<td>$10^1$</td>
</tr>
</tbody>
</table>

The electrical resistivity of the ZnO films was examined and the value of resistivity of the films determined is given in Table 4.12. CZO-N films have low resistivity compared to the other film.

4.5.3 Conclusion

Nanostructured ZnO films with microsphere/microdisc morphology were synthesized on unseeded soda lime glass substrates using the CBD deposition technique. Films were synthesized using zinc nitrate, trisodium citrate and hexamine. Films were further prepared by replacing hexamine with triethanolamine also. Films were polycrystalline with crystallite size ~27 nm. Minimum dislocation density and negligible microstrain were noticed. Morphology of CZO-M is micro-spheres whereas that of CZO-N is a mixture of microspheres and microdiscs and offers high surface area and large number of meso-micro pores. Films exhibit 50-60% transmittance and 5-20% reflectance in the visible region. In the visible region of the spectrum, refractive index of the films lies in the range 2.00-2.25. The quantum confinement in pores (not due to the crystallite size effect) increased the optical band gap of the films. Value of porosity of the films indicates the presence of pores. Films show a resistivity in the order $10^1$-$10^2$ Ωcm. The films possess the essential property of an electrode of DSSC.
References