Facile synthesis of flat crystal ZnO thin films by solution growth method: A micro-structural investigation

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Abstract Flat crystal ZnO thin films were prepared by chemical bath deposition technique onto glass substrates. XRD patterns of the films deposited at about 80 °C and annealed at 200 °C for 1 h in oxygen environment revealed the existence of polycrystalline hexagonal wurtzite phase with c-axis orientation of crystallites in the films. The crystallite size and lattice strain from X-ray line broadening profile were evaluated using the Scherrer method and Williamson–Hall method. Structural parameters such as dislocation density, stacking faults probability, lattice constants, lattice stress, unit cell volume, internal parameter, texture and number of crystallites per unit area have also been calculated. Surface morphology of the films was analyzed by scanning electron microscopy and atomic force microscopy. Photoluminescence spectrum at room temperature exhibited two luminescence centers, one is for UV emission (near band edge emission) located at 3.18 eV and another is for deep level emission located at 2.56 eV.

1. Introduction

Zinc oxide (ZnO), often known as II–VI semiconductor in material science, is an important and promising material with many typical properties such as wurtzite structure, transparency in the visible range, direct wide band gap, resistivity of semiconductor (usually in the range of $10^{-3}$–$10^{5}$ Ω cm), electrochemical stability, and absence of toxicity [1]. Since ZnO has a relatively large direct band gap of $\sim$3.3 eV at room temperature, pure ZnO is colorless and transparent. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain
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large electric fields, lower electronic noise and high-temperature and high-power operation. ZnO is one of the most fascinating materials for the fabrication of next generation optoelectronic devices [2,3]. It has a number of potential applications in the fabrication of gas sensors, photo detectors [4], antibacterial agent [5], light emitting diodes [6], ultraviolet (UV) sensors [7], thin film transistors [8] and solar cells [9].

The deposition of thin films of ZnO has been demonstrated by a number of techniques such as pulsed laser deposition [10,11], metal organic chemical vapor deposition (MOCVD) [12], thermal CVD [13], spray-pyrosynthesis [14], sol-gel [15,16], radio frequency sputtering [17,18], electrodeposition, [19–22] chemical bath deposition (CBD) [23] etc. Among them, preparation of ZnO thin films by the CBD method [24–27] has attracted special interest during last few years. The simplicity of the method, requirement of inexpensive equipments, low cost of the process and low deposition temperatures, altogether boosted up a large area of scientific and industrial applications. The method allows controlling the growth factors by varying the solution pH, temperature and bath concentration with ease [28].

There are a number of studies for CBD grown ZnO films which inter alia include morphologies of: rod, sphere, and nano stars; however, very few reports are available for flat crystals [29,30]. The presence of imperfections in the crystal can bring about significant changes in the properties of nanostructures. The imperfections include: dislocations, stacking faults probability, and lattice distortion which leads to formation of strained crystals and have been a very important topic for investigations.

In this study we aim at synthesizing ZnO flat crystals and evaluating micro structural parameters such as crystallite size, micro-strain, dislocation density, stacking faults probability, lattice stress, lattice constants, unit cell volume, number of crystallites etc. including morphological and optical characteristics of ZnO thin film, ZnO capped with 2-mercaptopethanol (ME) and ZnO capped with ME and annealed at 200 °C. In addition, we also carried out a comparative study of mean crystal size and lattice strain by employing the Scherrer plot, modified form of the Williamson–Hall (W–H) method, namely uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy-density model (UDEDM) and the size–strain plot (SSP) method.

2. Experimental details

2.1. Materials used

The commercial microscopic glass slides (1.45 × 75 × 25 mm3) were used as a substrate for the CBD of ZnO thin films. Before deposition, the substrates were boiled for 2 h in chromic acid, cleaned with single distilled water (SD), deionized water (DI), degreased with acetone, ultrasonically cleaned by DI and finally dried in air.

2.2. Preparation and optimization of chemical bath

All the chemicals used were of analytical reagent grade. Aqueous solutions of 0.20 M zinc acetate dihydrate [Zn(CH3COO)2·2H2O], 0.13 M trisodium citrate (TSC) as a complexing agent, 1.0 mL triethanolamine (TEA), 1.0 mL of 0.1 M 2-mercaptopethanol (ME) as a capping agent and 1.0 M NaOH were used to prepare ZnO thin film. TEA was added to ensure uniformity of the film. First 10 mL zinc acetate solution and 10 mL trisodium citrate solution were placed in a 100 mL beaker and the solution was stirred for 25–30 min to get a clear and homogenous solution. Thereafter, 1 mL of TEA was added. To obtain uniform and adherent film, optimized condition of ME was found to be 1.0 mL of 0.1 M solution. Deionized water was added to make the volume up to 50 mL and then the solution was made alkaline with 1.0 M NaOH and pH of the bath was maintained at ≈10. The deposition temperature varied from 50 to 90 °C with optimized temperature of 80 °C. Similarly, the deposition time varied from 1 to 2 h with optimized time of 75 min. The mixture was poured into a beaker and heated to 80 °C by keeping the beaker in a thermostated water bath. The glass substrates were then placed vertically inside this beaker. The time of introduction of substrate in deposition bath was very important. The substrates were placed in a heated deposition bath at the point of onset of visible turbidity [31]. After deposition, the substrates were removed, washed in running tap water, rinsed in DI to remove soluble impurities and then dried in air. The sample was annealed at 200 °C for 1 h in oxygen atmosphere.

Three different samples were used and their related micro-structural parameters and morphological and optical properties have been investigated in this work. For instance, Sample-1 refers to as-synthesized uncapped ZnO thin film, Sample-2 refers to as-synthesized ZnO thin film capped with ME and Sample-3 corresponds to ZnO thin film capped with ME and annealed at 200 °C for 1 h in oxygen atmosphere.

2.3. Characterization techniques

X-ray diffraction (XRD) patterns were recorded to characterize the phase and structure of the thin films using a Bruker D8 advance X-ray diffractometer with CuKa radiation (40 kV and 40 mA) for 20 values over 20–80°. Optical absorption data were obtained with a Cary Bio 50 Varian UV–Vis. Spectrophotometer. The photoluminescence measurements were performed on a Perkin–Elmer LS55 luminescence spectrophotometer. Morphological studies were carried out by VEGA II LSU SEM and NSE (Nanoscope-E), AFM with Contact mode.

3. Results and discussion

3.1. XRD analysis

In recent years, XRD profile analysis has been developed to reveal micro-structural details such as, microstrain, crystallite size, dislocation density, etc. XRD patterns of all the samples are shown Fig. 1. All the diffraction peaks could be indexed to phase pure wurtzite type ZnO [32–34]. The diffraction planes and respective d-spacing values are tabulated in Table 1, which showed good agreement with standard values [35]. No extra diffraction peaks corresponding to Zn, Zn(OH)2 or other ZnO phases are detected indicating that the pure single phase ZnO nanoparticles are crystalline in nature. The peaks intensity is strong with narrow full width at half maximum (FWHM) confirming that the sample is of high quality. In addition, the prominent peak (002) indicated preferential
c-axis orientation of the crystals [36]. The c-axis orientation has also been reported for ZnO nanoparticles deposited as thin films on glass substrate by microwave-assisted chemical bath deposition (MACBD) [37], pulsed laser deposition (PLD) [38], spray pyrolysis technique [39], successive ionic layer adsorption and reaction (SILAR) method [40], chemical vapor deposition (CVD) [41] and the sol-gel process [42]. Recently, the c-axis orientation of ZnO thin films has also been reported for different substrates (other than glass) like p-type GaN, sapphire, ITO glass and quartz substrate [43], Si substrate [44], and PET (polyethylene terephthalate) substrate [45]. Higher intensity of (002) diffraction peak (Fig. 1) showed that the CBD grown ZnO is better aligned along (002) direction. In the ZnO crystal, the surface energy density of the (002) orientation is the lowest. Grains with the lowest surface energy become larger as the thin film grows and growth orientation develops at the crystallographic direction of the lowest surface energy [46].

3.1.1. Crystallite size and strain

The broadening of lines in the X-ray diffraction pattern arises due to both instrumental- and sample-related factors. Therefore, it is customary to first correct for instrument-related broadening. The residual broadening is then attributed to sample-related factors. Sample-related factors include broadening due to crystallite size and strain. The instrumental corrected line broadening of each diffraction peak is calculated through the relation:

$$\beta_{\text{hkl}} = \left[ \left( \beta_{\text{hkl}} \right)_{\text{measured}}^2 - \left( \beta_{\text{hkl}} \right)_{\text{instrumental}}^2 \right]^{1/2}$$

(1)

where $\beta_{\text{instrumental}}$ is the broadening due to instrumental contribution.

3.1.1.1. Scherrer method. The average crystallite size of the ZnO thin films ($D$, in nm) was estimated using Scherrer’s equation [47].

$$D = 0.94 / \beta \cos \theta$$

(2)

where, $\lambda$ is the X-ray wavelength for CuK\(\alpha\) (1.54056 Å), $\beta$ is the full width in radians at the FWHM of the diffraction line and $\theta$ is the diffraction angle. Two approaches have been used to evaluate average crystallite size: firstly, directly taking average of the crystallite sizes obtained for three main peaks and secondly from the linear fit to the data plotted between $1/\beta_{\text{hkl}}$ and $\cos\theta_{\text{hkl}}$. Results are summarized in Table 2.

3.1.1.2. Williamson–Hall methods. To decouple size and strain related broadening we carried out Williamson–Hall analysis [49]. The value of $\beta\cos\theta_{\text{hkl}}$ plotted against $4\sin\theta_{\text{hkl}}$ and crystalline size and strain ($\epsilon$) was extracted from the intercept and slope of the linear fit, respectively [Table 2]. Eq.(5) shows the isotropic nature of the crystals and represents the UDM, where strain is assumed to be uniform in all crystallographic directions.

$$\beta_{\text{hkl}} \cos \theta = \left( \frac{k \lambda}{D} \right) + \left( 4\epsilon \sin \theta \right)$$

(5)

In the USDM [50], uniform deformation stress ($\sigma$) can be represented as $\sigma = E_{\text{hkl}} \epsilon_{\text{hkl}}$, where $E_{\text{hkl}}$ is the modulus of elasticity or Young’s modulus. This relation is known as Hooke’s law. By assuming small strain in ZnO flat crystals Hooke’s law can be applied here. The value of $\sigma$ is extracted from the slope of the graph plotted between $\beta_{\text{hkl}} \cos \theta$ and $4\sin\theta / E_{\text{hkl}}$, represented in Eq. (6). Results are summarized in Table 2. In the USDM, the W–H equation is simply modified by replacing the value of $\epsilon$ in second term of Eq. (5), we have:

$$\beta_{\text{hkl}} \cos \theta = \left( \frac{k \lambda}{D} \right) + \left( 4\sigma \sin \theta / E_{\text{hkl}} \right)$$

(6)

Table 1 Average grain size and d-spacing of ZnO thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2(\theta)</th>
<th>hkl</th>
<th>d-spacing (Å)</th>
<th>Observed</th>
<th>Standard [35]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample-1</td>
<td>31.78</td>
<td>100</td>
<td>2.813</td>
<td></td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>34.45</td>
<td>002</td>
<td>2.601</td>
<td></td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>36.30</td>
<td>101</td>
<td>2.472</td>
<td></td>
<td>2.47</td>
</tr>
<tr>
<td>Sample-2</td>
<td>31.83</td>
<td>100</td>
<td>2.809</td>
<td></td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>34.47</td>
<td>002</td>
<td>2.599</td>
<td></td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>36.32</td>
<td>101</td>
<td>2.472</td>
<td></td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>47.68</td>
<td>102</td>
<td>1.905</td>
<td></td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>56.67</td>
<td>110</td>
<td>1.622</td>
<td></td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>62.82</td>
<td>103</td>
<td>1.478</td>
<td></td>
<td>1.47</td>
</tr>
<tr>
<td>Sample-3</td>
<td>31.85</td>
<td>100</td>
<td>2.807</td>
<td></td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>34.50</td>
<td>002</td>
<td>2.597</td>
<td></td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>36.34</td>
<td>101</td>
<td>2.470</td>
<td></td>
<td>2.47</td>
</tr>
</tbody>
</table>

Figure 1 Xrd patterns of ZnO thin films, sample 1- ZnO film, sample 2- ZnO capped with ME, sample 3- ZnO capped with ME and annealed at 200°C.
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Table 2: Geometrical parameters of flat crystal ZnO.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Scherrer eq and plot</th>
<th>Stokes and Wilson method</th>
<th>Williamson–Hall method</th>
<th>Size–strain plot (SSP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D (nm)</td>
<td>z no unit x 10^-3</td>
<td>D (nm)</td>
<td>z no unit x 10^-3</td>
</tr>
<tr>
<td>Sample-1</td>
<td>35.7</td>
<td>32.9</td>
<td>3.77</td>
<td>52.3</td>
</tr>
<tr>
<td>Sample-2</td>
<td>33.3</td>
<td>32.5</td>
<td>3.79</td>
<td>52.7</td>
</tr>
<tr>
<td>Sample-3</td>
<td>34.8</td>
<td>32.3</td>
<td>3.51</td>
<td>52.7</td>
</tr>
</tbody>
</table>

Young’s modulus $E_{hkl}$ is related to their elastic compliances $S_{ij}$ as [51]

$$E_{hkl} = \frac{1}{S_{11} \left( \beta_{hkl} \cos \theta \right)^2 + S_{33} \left( \frac{\beta_{hkl} \cos \theta}{2} \right)^2 + (2S_{13} + S_{44}) \left( \beta_{hkl} \cos \theta \right)^2}$$

(7)

Where $'a'$ and $'c'$ are lattice constants and $S_{11}, S_{13}, S_{33}$ and $S_{44}$ are elastic compliances of ZnO with values of $7.858 \times 10^{-12}$, $-2.206 \times 10^{-12}$, $6.940 \times 10^{-12}$ and $23.57 \times 10^{-12}$, respectively [52].

The UDEDM was also employed to determine strain energy density ($u$) and deformation stress of the crystal. In Eq. (5), isotropic nature of the crystals has been assumed: but UDEDM as well as USDM are based on the anisotropic nature of the crystallite. Young’s modulus and $\varepsilon_{hkl}$ are related to strain energy density through the following relation $\varepsilon_{hkl} = (2u/E_{hkl})^{1/2}$ [50]. Now substituting the value of $\varepsilon_{hkl}$ in Eq. (5), we get:

$$\beta_{hkl} \cos \theta = \left( \frac{k^2}{D} \right) + \left( 4 \sin \theta \left( \frac{2u}{E_{hkl}} \right)^{1/2} \right)$$

(8)

A plot of $\beta_{hkl} \cos \theta$ vs. $4\sin \theta \left( 2/E_{hkl} \right)^{1/2}$ was used to calculate the value of $'a'$ and crystallite size from the slope and intercept of linear fit, respectively.

3.1.1.3. Size–strain plot. In the case, W–H plot does not exhibit a marked anisotropy in line broadening profile, a better evaluation of size–strain parameters can be made by considering an average SSP [50]. This method gives more weight to data from reflection at low and mid-angles compared to those obtained from high angles where precision is often lower.

$$\left( d_{hkl} \beta_{hkl} \cos \theta \right)^2 = \frac{k^2}{D} \left( d_{hkl} \beta_{hkl} \cos \theta \right)^2 + \left( \frac{\varepsilon}{2} \right)^2$$

(9)

The plot is drawn between $(d_{hkl} \beta_{hkl} \cos \theta)^2$ and $(d_{hkl} \beta_{hkl} \cos \theta)^2$ for all diffraction peaks of ZnO nanocrystals corresponding to the wurtzite hexagonal phase from $2\theta = 20^\circ$ to $2\theta = 80^\circ$.

By the linear fit of the data, crystallite size and strain were extracted from the slope and intercept respectively [Table 2]. All the results obtained from the Scherrer method, W–H models (UDM, USDM, and UDEDM) and SSP analyses are summarized in Table 2.

Crystallite size calculated by the Scherrer method has lower value compared to the W–H method. This difference corresponds to the role of strain in X-ray peak broadening, which can affect the estimation of crystallite size. Thus while considering crystallite size, strain must be taken into account as in the W–H method.

On the other hand, although various modified forms of the W–H method e.g. UDM, USDM, UDEDM consider different natures of crystallite, no considerable difference could be observed in strain. The strain value estimated by the SSP method, on the other hand, was several folds higher than that obtained from the W–H method. This difference can be attributed to more contributions of lower angles in the SSP method.

3.1.2. The dislocation density ($\delta$)

Dislocation is a crystallographic defect or irregularity within a crystal structure which can strongly affect many properties of
the materials. Crystalline solids exhibit a periodic crystal structure with the atoms or molecules on repeating fixed distance positions and this can be determined by the unit cell parameters. The regular patterns are interrupted by dislocations or crystallographic defects. The dislocation density ($\delta$) has been evaluated using expression [53]:

$$\delta = 15\beta \cos \theta / 4aD \text{ lines/m}^2$$

(10)

where all the symbols have their usual meanings. Data indicated that dislocation density was higher for Sample-3 [Table 3] depicting that the concentration of crystal imperfections is higher.

3.1.3. Stacking faults probability ($x$)

The stacking faults probability ($x$) is the fraction of layers undergoing stacking sequence faults in a given crystal and hence one fault is expected to be found in $1/x$ layer. The presence of stacking faults gives rise to a shift in the peak positions of different reflections with respect to ideal position of fault-free sample. The relation between stacking faults probability ($x$) with peak shift $A$ (2$\theta$) is given by [54]:

$$x = \left[ \frac{2\pi^2}{45\sqrt{3}} \tan \frac{\Delta(2\theta)}{\tan \theta_{020}} \right]$$

(11)

The XRD peak shifting as compared to strain-free ZnO film is tabulated in Table 4 and the calculated values of stacking faults are shown in Table 3. Data showed that Sample-3 exhibits maximum probability of stacking faults among all three samples.

3.1.4. Lattice constants

For hexagonal wurtzite structure of ZnO, lattice constants, $a$ and $c$ of the unit cell can be obtained according to the relation [44]:

$$a_{hkl} = \frac{2}{3} \left( h^2 + hk + k^2 \right)^{1/2} + \frac{f}{c^2}$$

(12)

where $d$ is the interplanar spacing of the atomic planes. For the bulk ZnO the reported values of the lattice constants are $a = b = 3.249$ Å and $c = 5.205$ Å [55]. The lattice parameters $a$, $b$ and $c$ of the films are calculated and given in Table 3. The films with $c$ values greater than that of the bulk value have a negative or extensive stress whereas those with lower values have a positive or compressive stress. In our study, all the samples exhibited lower $c$ values than the value of bulk ZnO to reveal that ZnO crystallites for all the samples are under the state of compressive stress. Another evidence of compressive stress in the films is evident from Table 4. The diffraction angles of (002) peak of all samples are larger than 34.40 of the bulk ZnO to imply that the ZnO films are subjected to a compressive stress in c-axis direction. Less deviation of lattice constants in sample-1 and larger deviation in sample-3 with reference to the standard value indicate higher compressive stress in sample-3 [Table 3].

3.1.5. Lattice stress

The lattice stress $\sigma_l$ of the films has been calculated (Table 3) using the expression [55]:

$$\sigma_l = 2.33 \times 10^{11} \times \frac{C_b - C_f}{C_b}$$

(13)

where $C_b$ and $C_f$ are the lattice constant of the bulk ZnO and ZnO films, respectively. Intrinsic stress in ZnO film has its origin in the imperfection (i.e. defects and impurities) of the crystallites during growth. Several growth parameters may contribute to the intrinsic stress. In the present study, intrinsic stress is compressive in nature. As discussed above, Sample 3 has higher stress [Table 3] revealing that after annealing at 200°C, the degree of crystal imperfections in ZnO crystallites increased.

It therefore appears that post-deposition thermal annealing may introduce new defects in the material to bring about an increase in crystal imperfection as could be observed for Sample-3. This is in agreement with the literature and similar effect of annealing on ZnO was also reported earlier [57,58].

3.1.6. Unit cell volume ($V$)

Unit cell volume for hexagonal ZnO thin films has been calculated using [58]:

$$V = \frac{\sqrt{3}}{2} a^2 c$$

(14)

where $a$ and $c$ are the lattice constants for ZnO nanocrystalline film. Table 5 lists the calculated values of unit cell volume for all the samples. It is apparent that that the Sample-3 has the smallest unit cell volume as compared to the standard. It is a consequence of higher stress in Sample-3 which resulted in reduction in unit cell volume.

3.1.7. Internal parameter ($u'$) and bond length

The internal parameter $u'$ is defined as the length of bond parallel to the $c$-axis (anion–cation bond length or the nearest-neighbor distance) divided by the $c$ lattice parameter and has been evaluated using the relation [60] given below.

$$u' = \left( \frac{1}{3} \right) \left( \frac{a^2}{c^2} \right) + \frac{1}{4}$$

(15)

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Different structural parameters for ZnO thin films.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Lattice constant $a = b$ (Å)</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Sample-1</td>
<td>3.248</td>
</tr>
<tr>
<td>Sample-2</td>
<td>3.244</td>
</tr>
<tr>
<td>Sample-3</td>
<td>3.242</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Comparison of 2$\theta$ values for 002 planes with standard value for ZnO thin films.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>2$\theta$ values for 002 plane</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Sample-1</td>
<td>34.45</td>
</tr>
<tr>
<td>Sample-2</td>
<td>34.47</td>
</tr>
<tr>
<td>Sample-3</td>
<td>34.50</td>
</tr>
</tbody>
</table>
The values of \( u' \) are tabulated in Table 5. The bond length in \( c \)-direction has been calculated as \( u_0 \) and for other three by 
\[
\left[ \frac{a^2}{3} + \left( 1/2 - u' \right)^2 c^2 \right]^{1/2}
\]
for the Wurtzite crystal structure [61]. The values are summarized in Table 5, where \( a \) and \( c \) are the lattice constants for ZnO nanocrystals.

### 3.1.8. Number of crystallites (\( N_c \))

Using the particle size ‘\( D \)’ and film thickness ‘\( t \)’, number of crystallites ‘\( N_c \)’, can be estimated using the relation [62]:

\[
N_c = \frac{t}{D^3} \text{ /unit area}
\]  
(16)

### 3.1.9. Relative intensity of XRD peak

Texture is the distribution of crystallographic orientation of a polycrystalline material. According to the literature, the relative intensity of (002) plane can characterize the degree of texture of ZnO based thin film with its \( c \)-axis perpendicular to substrate. The preferred orientation of (002) plane can be

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative XRD intensity for (002) plane</th>
<th>Number of crystallites ( N_c \times 10^{15} \text{ m}^{-2} )</th>
<th>Density in g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample-1</td>
<td>0.8108</td>
<td>12.8</td>
<td>5.659</td>
</tr>
<tr>
<td>Sample-2</td>
<td>0.6325</td>
<td>17.6</td>
<td>5.679</td>
</tr>
<tr>
<td>Sample-3</td>
<td>0.9180</td>
<td>15.7</td>
<td>5.691</td>
</tr>
</tbody>
</table>

The values are summarized in Table 5, where \( a \) and \( c \) are the lattice constants for ZnO nanocrystals.

![Figure 2](image_url)  
**Figure 2** SEM images of (a) sample-1, (b,c) sample-2, (d–g) sample-3 and AFM images (h–j) of sample 3.
estimated using following relation [63]. For Sample-3 high relative intensity revealed the good textured film [Fig. 1 and Table 6].

\[ i_{(002)} = \frac{I_{(002)}}{I_{(100)} + I_{(002)} + I_{(101)}} \]  

(17)

where \( I_{(100)}, I_{(002)}, \) and \( I_{(101)} \) are the peak intensities of diffraction planes (100), (002) and (101) respectively.

3.1.10. Determination of density of the film

Density of the hexagonal ZnO films was calculated using the following relation [64] and values are tabulated in Table 6 for all the samples.

\[ \rho = \frac{1.6609 \times M \times n}{a^2 c \sqrt{3/4}} \]  

(18)

where \( M \) is the molecular weight of substance and \( n \) is the number of formula units in the unit cell \((n = 2 \text{ for ZnO})\), \( a \) and \( c \) are the lattice constants of the unit cell.

3.2. Morphological characterization

The presence of citrate ions in the deposition bath can lead to the formation of flat crystal [29,65]. Fig. 2 demonstrates a typical nanoscale vision of SEM and AFM images of CBD grown flat crystal ZnO film capped with ME and annealed at 200°C (Sample-3). SEM images displayed that ZnO crystals are embedded on the substrates with voids. Fig. 2d and h displays flat crystals consisting of smaller crystallites, size comparable to XRD results. In addition, AFM pictures confirmed the presence of flat structured ZnO crystals in the samples. AFM images, in particular, confirmed the layer by layer growth of ZnO flat crystals.

3.3. Optical characterization

3.3.1. Absorption spectra

Optical absorbance spectra of ZnO thin film capped with ME (sample-2) were recorded in the wavelength ranged from 300 to 800 nm (Fig. 3a). The direct-band gap estimated from the plot of \((\alpha h \nu)^2\) vs photon energy \((h \nu)\) is shown in Fig. 3b. Linear part of the curve was extrapolated to the \(h \nu\)-axis. The point of intersection gives band gap \((E_g)\). The estimated band gap energy is 3.32 eV, which is in good agreement with the band gap of bulk ZnO (3.3 eV). No blue shift in absorption edge was observed and hence no quantum size effect can be marked. It is due to the relatively small effective masses for ZnO \((m_e = 0.26, m_h = 0.59)\); that quantum size effects are expected to occur for particles sizes up to 8 nm [66,67] and in our samples particle size is quite large to show quantum size effect.

3.3.2. Photoluminescence

Photoluminescence spectra of ZnO thin films at room temperature are presented in Fig. 4. PL spectra of all the samples are in the wavelength range 350–550 nm with excitation wavelength of 320 nm. The photoluminescence spectra exhibited two luminescence centers. One is for the UV emission at 390.2 nm (3.18 eV) corresponding to the near band edge tran-
sition of a wide band gap of ZnO, namely the recombination of excitons through an exciton-exciton collision process. Another luminescence center is for blue-green emission at 484.7 nm (2.56 eV) and is called the deep level (DL) emission. This is approximately closer to the values reported by Singh et al. [68]. The deep level visible emissions are due to the radial recombination of a photogenerated hole with an electron that belongs to the native defects in the surface and sub-surface lattice of ZnO crystal. Behera et al. [64] reported that several defect related recombination centers such as Zn vacancy ($V_{Zn}$), O vacancy ($V_O$), interstitial Zn ($Zn_i$), interstitial O ($O_i$), Zn antisite ($ZnO$) and oxygen antisites defect $O_{Zn}$ (oxygen at zinc site) were responsible for luminescence process of ZnO in the visible region of the electromagnetic spectrum. $V_{Zn}$ and $O_{Zn}$ are acceptor type defects and common in oxygen-rich condition. In our preparative condition of ZnO, oxygen was rich and furthermore ZnO thin film was annealed in oxygen environment. The transition between the conduction band (or a
shallow donor) and \(V_{\text{zn}}\) acceptor level that would give rise to luminescence around 2.5 eV is in good agreement with the observed energy transition in our samples. Wang et al. [69] also reported that emission energy of 2.56 eV corresponds to the \(V_{\text{zn}}\) and oxygen antisites defect \(O_{\text{zn}}\). The ratio of the UV peak intensity to the DL peak intensity (\(I_{\text{UV}}/I_{\text{DL}}\)) is the main identifying feature of high-quality ZnO. The \(I_{\text{UV}}/I_{\text{DL}}\) ratio of samples-1, 2 and 3 was found to be 5.84, 3.98 and 3.39, respectively indicating that sample-3 has the least value of \(I_{\text{UV}}/I_{\text{DL}}\) ratio and hence higher defect concentration, which is also revealed from XRD data [Table 3]. The intensity ratio (\(I_{\text{UV}}/I_{\text{DL}}\)) decreased with post-deposition thermal annealing, which is merely due to increase in the concentration of \(V_{\text{zn}}\) and \(O_{\text{zn}}\) defects within the ZnO crystals in O-rich condition.

4. Conclusions

Flat structured ZnO thin films could be successfully synthesized by the CBD method. AFM analysis showed the layer by layer growth of flat crystals on the surface. XRD patterns of all the samples showed that ZnO possessed the polycrystalline hexagonal wurtzite structure with the preferred (002) orientation of crystals. Moreover, crystallite size and strain analysis by the Scherrer, W–H and SSP methods suggested significant contribution of strain in X-ray line broadening. Thus strain related broadening must be decoupled for the estimation of crystallite size. XRD spectra have also been used to calculate different crystallographic imperfections such as dislocation density, microstrain, stacking faults probability and unit cell parameters. The blue–green emission energy centered at 2.56 eV in PL spectra was due to the transition between conduction band and \(V_{\text{zn}}\) acceptor level. The \(I_{\text{UV}}/I_{\text{DL}}\) ratio depicts that \(V_{\text{zn}}\) and \(O_{\text{zn}}\) defects’ concentration was high in air-annealed ZnO film.

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References

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