Chapter IV

Studies on Pure (undoped) ZnO thin films

4.1 Introduction

ZnO possess good transparency in the visible wavelength, is a strategic material for various photonic applications. Not only it finds application in various photonic associated technologies but because of its piezoelectric nature, it can be used effectively as a sensor in various MEMS related devices. In this work, the crystal structure, morphology and emission characteristics of ZnO nanostructured films synthesized by the sol-gel spin coating technique on glass substrate were investigated. The ZnO nanostructured films exhibit high crystalline quality. They show a strong UV excitonic emission at 383 nm (3.25 eV).

4.2 Experimental techniques used in the preparation of ZnO thin films

ZnO nanocrystalline thin films were synthesized by preparing the starting sol of suitable consistency. The precursor solution was prepared by mixing 2.1949 g of zinc acetate dihydrate (Zn(CH₃COO)₂.2H₂O) and a few drops of diethanolamine in ethanol. The prepared solution was stirred continuously for one hour at 50°C and one day aging was given before using it as a starting sol in spin-coating process. The glass substrates used for coating purposes were first cleaned in a mixed solution of HCl and HNO₃ and again rinsed in distilled water and ethanol for several times. The glass substrates were further dried and a thin uniform ZnO film was deposited by a spin coater rotated with a maximum speed of 3000 rpm for 30 s. Preparation of samples using the first process of annealing is explained as follows. Each layer of ZnO film was spin coated on the substrate which was followed by drying at 200°C in air for 1 min and cooling down to room temperature. The above said spinning and drying process was continued successively for eight more times. Finally, all the prepared samples were post-annealed at 350, 450 and 550°C in ambient atmosphere for an hour and allowed to cool slowly.
Fig 4.1 Flow chart of sol–gel technique for ZnO thin films.
### 4.3 Characterizations

The crystal structure of samples were examined by x-ray diffractometer (XRD-XPERT-PRO) in the angle (2θ) range of 20-80° using CuKα radiation of wavelength 0.15405 nm. Field emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM- JEOL 2010) were used for morphological observations of the ZnO. The SEM images of the sol–gel derived films were taken by using FESEM-JEOL-6460F. Energy dispersive spectroscopy (EDX) was also conducted in the same chamber. Optical transmission spectra of ZnO films were obtained using UV-VIS spectrophotometer (JASCO V 570) in the wavelength region of 350-850 nm. The photoluminescence spectra was taken to study the luminescent behaviour of the films using photoluminescence spectrometer (Varian Cary Eclipse- EL08083851) in which a Xenon lamp was used as the light source and the films were excited with a wavelength of 280 nm. All the spectra were obtained by keeping the samples in ambient atmosphere. Magnetization measurements were performed using a vibrating sample magnetometer (VSM- Lakeshore-7404).

### 4.4. Results and discussion

#### 4.4.1 Structural properties of the crystalline ZnO thin film

The crystal structure and orientation of the ZnO thin film of the as prepared and annealed samples at 350, 450 and 550°C were investigated using X-ray diffraction (XRD) patterns. The X-ray diffraction patterns for the crystalline ZnO thin films are shown in Fig 4.2 which indicates that the films are of polycrystalline in nature and exhibit single phase hexagonal wurtzite structure. It is clearly seen from the figure that the crystallinity of ZnO films increases with the increase in annealing temperature.

Three peaks appear on the XRD pattern for the as-deposited film. As seen in Fig 4.2(a), the as prepared ZnO thin film has (101) as the preferred orientation while the other orientations like (100) and (002) are also seen comparatively with lesser intensities. However, most of the ZnO thin films which grow with wurtzite structure have (002) preferential orientation. The annealing temperature plays an important role on the
surface reactions and species mobility. In Fig 4.2 (b & c), it is seen that the ZnO films have (002) planes as the preferred orientation and other intense peaks correspond to the orientations of (100) and (101) planes.

**Fig 4.2(a-d) XRD patterns of ZnO thin films. (a) as-prepared, annealed (b) at 350°C (c) at 450°C (d) at 550°C**

Again, some low intensity peaks corresponding to the orientations (102), (110) and (103) are also present. It is observed that in Fig 4.2d which corresponds to the XRD pattern of the ZnO thin film annealed at 550°C, the prominent peak of (100) orientation plane and peaks of other orientations also appear. Thus it could be stated that annealing causes increase in intensity and reorientation of planes and a similar behaviour is also reported by others [Yakuphanoglu *et al.*, 2007]. An analytical method [Ilican *et al.*, 2007] was used to calculate the lattice constants ‘a’ and ‘c’ for the spin coated ZnO thin
films. The values of lattice constants ‘a’ and ‘c’ for the as prepared and annealed films at various temperatures are calculated using equation [3.2] and the calculated values are given in Table 4.1. Comparing with the lattice constants for hexagonal ZnO crystal given in JCPDS (36-1451) standard data file $a = 3.2498 \text{ Å}$ and $c = 5.2066 \text{ Å}$, it is seen that the calculated values are in good agreement with the standard values for ZnO wurtzite structure.

**Table 4.1: Lattice constant values of ZnO thin films.**

<table>
<thead>
<tr>
<th>Lattice Parameter</th>
<th>Standard value (Å)</th>
<th>As prepared (Å)</th>
<th>At 350°C (Å)</th>
<th>At 450°C (Å)</th>
<th>At 550°C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.2498</td>
<td>3.2536</td>
<td>3.2508</td>
<td>3.2543</td>
<td>3.2525</td>
</tr>
<tr>
<td>c</td>
<td>5.2066</td>
<td>5.2233</td>
<td>5.2089</td>
<td>5.2111</td>
<td>5.2097</td>
</tr>
</tbody>
</table>

The relative percentage error for the observed and JCPDS standard d–value [36-1451] for all the films is calculated using the formula [3.5] and given in Table 4.2.
Chapter IV

Studies on Pure (undoped) ZnO thin films
The size of crystallites is calculated using the well-known Scherrer’s formula as given in equation [3.4]. The grain size varies from 9 to 72 nm. The grain size values of all the films are given in Table 4.3. The grain size of the as-prepared ZnO thin film is very small compared to the annealed films. The grain size increases as the annealing temperature increases which is well supported in literature [Krunsks et al., 2006]. The variation of the grain size of ZnO crystallites with annealing temperature is given in Table 4.3.

The texture coefficient (TC) represents the texture of the particular plane, deviation of which from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation was obtained from the different texture coefficient $TC_{(hkl)}$ defined by the relation [3.3] and the calculated values are given in Table 4.4.

**Table 4.4: Texture coefficient of ZnO thin films**

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>Without Annealing</th>
<th>350°C</th>
<th>450°C</th>
<th>550°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I/I_o$</td>
<td>$TC_{hkl}$</td>
<td>$I/I_o$</td>
<td>$TC_{hkl}$</td>
</tr>
<tr>
<td>(100)</td>
<td>77.25</td>
<td>0.8447</td>
<td>45.55</td>
<td>0.6345</td>
</tr>
<tr>
<td>(002)</td>
<td>97.12</td>
<td>1.0619</td>
<td>100</td>
<td>1.3931</td>
</tr>
<tr>
<td>(101)</td>
<td>100</td>
<td>1.0934</td>
<td>69.80</td>
<td>0.9724</td>
</tr>
</tbody>
</table>

Fig 4.3 shows the FESEM micrographs of as-prepared and ZnO nanocrystalline thin films calcined at 350, 450, 550°C for 1h, respectively. It is observed that film annealed at 450°C shows good homogeneity of grains of hexagonal shape well dispersed on the surface of the film. The morphology of sample annealed at 450°C is better
compared with the other films. So, for the further work all the samples are annealed at 450ºC.

**Fig 4.3 (a)** SEM micrograph of ZnO thin film of as prepared
Chapter IV

Studies on Pure (undoped) ZnO thin films

Fig 4.3 (b) SEM micrograph of ZnO thin film calcined at 350°C

Fig 4.3 (c) SEM micrograph of ZnO thin film calcined at 450°C
4.4.2 Optical properties

The transmittance spectra of ZnO thin films, taken in the wavelength range of 350 to 850 nm are shown in Fig 4.4. The films are highly transparent in the visible range of the electromagnetic spectrum with an average transmittance value up to 80 %. The ZnO film annealed at 450°C shows a high transmittance whereas the film becomes hazy and the transmittance is dropped drastically low for the ZnO film annealed at 550°C [Mingsong Wang et al., 2008].
The absorption coefficient $\alpha$ of ZnO films was determined from transmittance measurements. Since envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient $\alpha$ of the film in this region was calculated using the expression [3.6]. Thickness of the film was measured using digital micrometer (Mitutoyo, Japan). The thicknesses of the films were approximately 962,844,811 and 934 nm for the as prepared and annealed at 350,450 and 550$^\circ$C respectively. The calculated absorption coefficients values are used to determine the optical energy band gap of the prepared ZnO thin films. Fig 4.5 (a-d) shows the plot of $(\alpha h\nu)^2$ versus $h\nu$, where $\alpha$ is the optical absorption coefficient and $h\nu$ is the energy of the incident photon. Assuming a direct transition between valence and conduction bands, the energy band-gap ($E_g$) was determined by the expression [3.10]. The deduced optical energy band-gap, $E_g$ 2.75, 3.00, 3.13 and 2.50 eV for as prepared, annealed at 350,450 and 550$^\circ$C film respectively. These values are slightly smaller than the bulk value of 3.37eV [Krasimira Shtereva et al., 2009] and is in good agreement with previously reported results of ZnO thin films.
Fig 4.5 Plots of absorption against photon energy for ZnO thin films.

4.4.3 Photoluminescence studies of ZnO thin films

Photoluminescence measurements were used to evaluate the optical and crystalline quality of the ZnO layers deposited at different annealing temperatures. The excitation spectra shown in Fig 4.6 were obtained for the maximum emission wavelength indicated in Fig 4.7. All spectra show a peak around 383 nm (3.24 eV) resulting due to electron transfer from valence band (V_B) to conduction band (C_B) that could be the origin of any emission.
There are two emission peaks for the as prepared film namely the defect peak which is of lower intensity compared with the strong near band edge (NBE) emission peak. The defect peak of as-prepared film has disappeared with the increase in annealing temperature, indicating the better crystalline quality of the samples deposited at higher temperatures. PL intensity increases as the annealing temperature increases till 450°C. PL intensity decreases for the ZnO thin film annealed at 550°C as the film became hazy which is true for the transmission spectra also.

Fig 4.6 Photoluminescence excitation spectra for pure ZnO
Changes in relative intensities of the dominant peaks are observed. The intensity of the peak at 383 nm decreases with the annealing temperature. Strong near band edge (NBE) emission dominates for all samples in the PL spectra taken at room temperature. Though the emission energy of the PL spectra does not change with increasing annealing temperature (Fig. 4.7), the PL intensity varies with annealing temperature.

4.5 Physical properties of ZnO having different number of layers

4.5.1 Structural properties

The ZnO thin films were characterized by XRD to confirm the crystalline phase of the films. Fig 4.8 (a-e) shows the representative XRD pattern of ZnO thin films synthesized at 450°C, film revealing wurtzite phase of ZnO. The sharp XRD peaks imply good crystallinity. All deposited ZnO films showed crystalline nature whereas with increase in the number of layers, crystalline nature of the deposited ZnO films became more defined and
progressively more intense and sharp for films with up to eight layered depositions. For the ten layered film, peaks were well defined and sharp but slight reduction in intensity were observed. X-ray diffraction (XRD) revealed a strong influence of thickness on film surface topography. X-ray diffraction based structural characterization shows that the ZnO films have grown predominantly along the c-axis (002) direction where the angular position of the (002) peak varies slightly with increasing film thickness [Mukes Kapilashrami et al., 2010]. As the thickness of the film increased, the crystalline nature of the film improved, which is also in agreement with the literature [Linhua Xu et al., 2011].

The values of lattice constants ‘a’ and ‘c’ for various layers calculated using equation [3.2] and the calculated values are given in Table 4.5. Comparing with the lattice constants for hexagonal ZnO crystal given in JCPDS standard data file $a = 3.2498 \text{Å}$ and $c = 5.2066 \text{Å}$, it is seen that the calculated values are in good agreement with the standard values for ZnO wurtzite structure.

**Table.4.5: Lattice constants of ZnO thin films.**

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>2 layers</th>
<th>4 layers</th>
<th>6 layers</th>
<th>8 layers</th>
<th>10 layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.24197</td>
<td>3.25955</td>
<td>3.25981</td>
<td>3.25430</td>
<td>3.24716</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.20150</td>
<td>5.21898</td>
<td>5.21990</td>
<td>5.21110</td>
<td>5.20734</td>
</tr>
</tbody>
</table>
Fig 4.8 (a-e) XRD spectra of ZnO thin film of 2,4,6,8 and 10 layers annealed at 450°C.

The particular plane and information concerning the preferential crystallite orientation were determined from the texture coefficient $T_C(\text{hkl})$ using equation [3.3] is given in the Table 4.6. The particle size (D) of the films with various layers was calculated by the Debye–Scherrer formula [3.4] using raw data from XRD patterns. The crystalline size was calculated by the Debye–Scherrer formula along the dominant peaks (100), (002) and (101) is given in Table 4.7.
The surface morphology and micrographs of the ZnO thin films grown on glass substrate with different layers were observed by FESEM. Fig. 4.9 (a-e) shows the surface morphology of films with 2, 4, 6, 8 and 10 layers. The surface morphologies of all the thin film samples are distinct. The surface morphology of the thin film grown up to 8 layers were more densely packed with some pits on it, while that grown with 10 layers slight agglomeration [Mondal et al., 2008] appeared.

![FESEM image of ZnO with 2 layers.](image)
Chapter IV

Studies on Pure (undoped) ZnO thin films

Fig 4.9(b) FESEM image of ZnO with 4 layers.

Fig 4.9(c) FESEM image of ZnO with 6 layers.
Chapter IV

Studies on Pure (undoped) ZnO thin films

Fig 4.9(d) FESEM image of ZnO with 8 layers.

Fig 4.9(e) FESEM image of ZnO with 10 layers.
Fig 4.10 TEM image of ZnO thin film with 8 layers and calcined at 450°C

Transmission electron microscopy (TEM) was employed to observe the microstructure of pure ZnO thin films with 8 layers annealed at 450°C (Fig-4.10). ZnO powders obtained by scraping the coated film were dispersed in ethanol and a few drops of the suspension were placed on carbon-coated copper grid which acted as the specimen holder for taking TEM image. The image was recorded with a JEOL-2010 microscope operated at 200 kV using a low-background Gatan double tilt holder. The TEM image confirms the nanocrystalline nature of pure ZnO films having particles of around 10 nm in dimension based on the scale given in the micrograph.
4.5.2 XPS Analysis

To find the stoichiometry of ZnO films, quantitative analysis should be carried out using the XPS analysis of Zn 2p$_{3/2}$ and O 1s energy lines respectively, it is shown in Fig 4.11(a) and Fig 4.11(b). In the present study, the observed Zn 2p$_{3/2}$ peak located at 1022.58, 1024.16, 1023.61, 1024.16 and 1022.47 eV for the 2, 4, 6, 8 and 10 layers respectively, which is nearly the same as the standard value of 1021.8 eV. Also O 1s peak positions are observed at 531.02, 529.96, 530.78, 531.05 and 531.12 eV for the 2, 4, 6, 8 and 10 layers respectively. It is very close to the standard value of 530.05 eV. The important observation is that the XPS peak intensities increase with the increasing thickness of the ZnO films. Observation of these Zn 2p$_{3/2}$ and O 1s peaks confirm the
presence of these elements in the ZnO film studied here. The stoichiometry was found out from this peak, which gives the presence of Zn : O as 1.02 : 0.98.

**Fig 4.11(b)** XPS close scan spectra (O 1s) of ZnO films with different thicknesses
(a) 2 layer, (b) 4 layer, (c) 6 layer, (d) 8 layer and (e) 10 layer

**4.5.3 Optical properties**

**Fig 4.12** Optical transmission spectra of the ZnO multilayer thin films.
Fig 4.13 Variation of $(\alpha h\nu)^2$ of the ZnO (a)2 layer (b)4 layer (c)6 layer (d) 8 layer (e)10 layer multilayer thin films as a function of photon energy ($h\nu$)

Figure 4.12 shows the optical transmission spectra of the ZnO thin films with various layers measured at room temperature using UV-Vis-NIR spectrometer. All the
films show 60-80% transmission in the visible region except for 10 layers. The band-gap energy ($E_g$) of the multilayer thin film was calculated from the plot of $(\alpha h\nu)^2$ versus $h\nu$, where $\alpha$ is the optical absorption coefficient and $h\nu$ is the energy of the incident photon. Assuming a direct transition between valence and conduction bands, the energy band gap ($E_g$) was determined by from the expression [3.8]. $E_g$ is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. The absorption coefficient $\alpha$ of ZnO films was determined from transmittance measurements. Since envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient $\alpha$ of the film in this region was calculated using the expression [3.6].

Figure 4.13 shows $(\alpha h\nu)^2$ plots of the ZnO thin films as a function of photon energy. The band-gap energies, obtained using the Fig 4.13, of the multilayer thin films are 2.97, 3.03, 3.06, 3.13 and 3.03 eV for the ZnO thin films with 2,4,6,8 and 10 layers respectively. The band-gap energies obtained in this study for pure ZnO are lower than the bulk ZnO value of 3.37 eV. By increasing the number of layers of ZnO, the effective band-gap energy of the multilayer thin films increased in this study as reported by the literature [Bin-Zhong Dong et al., 2007].

4.5.4 Photoluminescence

The PL spectra in Fig 4.14 of the ZnO films exhibited UV emission peak around 383 nm, green-yellow luminescence at 496 nm. The first peak (near band edge-NBE) due to UV emissions is attributed to band-to-band transitions, excitonic emissions, and donor-acceptor pair transitions. The green-yellow band at around 496 nm is due to the deep level emissions (DLE) in green region, which is attributed to oxygen vacancies, zinc interstitials or zinc vacancies [Haiping Tang et al., 2008]. These two peaks are the most commonly found luminescent peaks in all the ZnO samples. In addition to these peaks one shoulder peak near the NBE, two shoulder peaks near DLE also appear. The intensities of the excitonic emissions and defects emissions decreases with increase the number of the layers and the shoulder peaks disappear for 8 and 10 layers. When the ZnO film is relatively thin, its structural disorder is relatively large and some interstitial Zn
atoms exist, which possibly lead to the blue emission. With the increase of film thickness, the structural disorder decreases and the density of Zn interstitial defect is reduced. As a result, the intensity of blue emission is also decreased.

![Graph showing photoluminescence spectra of ZnO thin films](image)

**Fig 4.14** Room-temperature photoluminescence spectra of the samples.

### 4.5.5 Magnetic properties

![Graph showing magnetic hysteresis loops](image)

**Fig 4.15** Magnetic hysteresis loops of Pure ZnO thin films of various thicknesses at room temperature.
The samples prepared were handled carefully to avoid any possible magnetic contamination. The undoped ZnO films prepared were examined at room temperature (RT) in the range of the magnetic field 0–17.5 kOe using a Vibrating Sample Magnetometer and showed non ferromagnetic behavior, confirming that there is no extrinsic magnetic impurity contamination during the procedure of preparation. presents the magnetization (M) vs magnetic field (H) of pure ZnO thin films with various thicknesses. Hysteresis curves are obtained at room temperature, showing all pure samples have non ferromagnetic characteristic property. A typical diamagnetic behaviour has been observed in the bare ZnO samples. The diamagnetic behaviour of pure ZnO is due to the unpaired electrons of its d orbital, which is responsible for the absence of a permanent magnetic moment.

4.6 Effect of different process of annealing

In addition to the above annealing process, physical properties through hybrid annealing also studied. In the process of hybrid annealing, each layer of film was preheated using a microwave oven by supplying a power of 900 W for 1 min after each spin coating. The above process is repeated again for eight more times after bringing down the substrate to room temperature. As a final step, all the samples were post-annealed in the microwave oven at a power of 900 W for 30 min and subsequently in open air at 450°C for 30 min which is termed as hybrid annealing. The annealed samples were brought down to room temperature in a natural manner. The sample prepared in the normal and hybrid annealing processes were given the names A and B respectively.

4.6.1 Structural properties

X-ray diffraction patterns of the samples A and B are shown in Fig 4.16 Both the films show a diffraction peak at 31.86° which corresponds to the reflection of the (100) plane of the wurtzite structure of ZnO material.
Fig 4.16 X-ray diffraction patterns of the samples A (a) and B(b)

Sample A shows polycrystalline behaviour exhibiting wurtzite structure and all the observed XRD peaks are identified with their corresponding planes in the recorded range. This film showed a strong orientation along the c-axis corresponding to the (002) plane and other planes such as (100), (101), (102), (110), (103) and (112) were also present. Sample B have an intense peak at 34.86° corresponding to (100) plane and another peak of lesser intensity corresponding to (200) plane. Comparing the intensities of the characteristic peaks of samples A and B, the peak intensity of sample due to hybrid annealing is higher than normal annealing process. The characteristic peaks are higher in intensity and narrower in spectral width, indicating that the films have good crystalline behaviour. No peaks corresponding to impurities are detected, showing that the final products purely consist of ZnO [Zhu Jian-yu et al., 2009].

The crystallite size of the ZnO films was calculated using Scherrer’s formula [3.4] [Nanda Shakti et al., 2010]. Table 4.8 gives the crystallite size along prominent diffraction planes for films A and B. It is found that the size of the grains in samples from hybrid annealing is greater than from normal annealing process.
Table 4.8: Crystallite size along prominent diffraction planes for ZnO thin films.

<table>
<thead>
<tr>
<th>Type of Annealing</th>
<th>(hkl)</th>
<th>$2\theta$ (degrees)</th>
<th>$\beta$ (FWHM)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open air</td>
<td>(100)</td>
<td>31.8602</td>
<td>0.30900</td>
<td>27</td>
</tr>
<tr>
<td>Hybrid</td>
<td>(100)</td>
<td>31.8642</td>
<td>0.23550</td>
<td>35</td>
</tr>
</tbody>
</table>

The morphology of the samples is observed using FESEM pictures taken for samples A and B as shown in Fig. 4.17. It is observed that the crystallites found in sample A is uniform and regular shape. The morphology of sample B is hazy and the crystallites are not clearly seen. Energy dispersion spectrum of sample gives the atomic contents of ZnO thin film corresponding to sample A and B (Fig. 4.18)

**Fig 4.17** SEM picture of ZnO layers grown on glass substrates (a) sample A and b) sample B
Studies on Pure (undoped) ZnO thin films

4.6.2 Optical properties

In order to investigate the optical properties of thin films, the absorbance was measured as a function of wavelength in the range of 350-850 nm as shown in Figure 4.19(a). The expression for absorption coefficient $\alpha$ is given by equation [3.6]. The fundamental absorption, which corresponds to the transition from valence band to conduction band, can be used to determine the optical band-gap ($E_g$) by the equation [3.8].

As ZnO is a direct transition material, the values of direct band-gap energy ($E_g$) obtained from the linear portion of the curve by extrapolation to zero of $(\alpha h\nu)^2$ to the energy(E) intercept. Fig.4.19b shows the optical band-gap curve obtained from $(\alpha h\nu)^2$ vs. $(h\nu)$ for the transmittance spectra of samples A and B. Band-gap values are 3.13 and 3.34 eV for open air annealing and hybrid annealing respectively.
Chapter IV

Studies on Pure (undoped) ZnO thin films

Fig 4.19(a) Absorption spectra of the spin coated thin film with different annealing processes

Figure 4.19(b) \((ahv)^2\) vs. \((hv)\) plot based on the transmittance spectra

Fig.4.20 shows the photoluminiscence spectra of sample A (curve a) and B (curve b) taken at room temperature. Two peaks are seen for both the samples. A sharp UV band-edge emission centered at 383 nm and green bands centered at 525 nm are seen for sample A.
Fig 4.20 PL spectra of ZnO thin films annealed in open air and in hybrid annealing processes

The PL signal at 383 nm is a typical ZnO near-band-edge (NBE) ultraviolet (UV) emission, which indicates a direct recombination of excitons through an exciton-exciton collision process [Jianguo Lu et al., 2010, Yaoming Li et al., 2010] and the green transition at 525 nm referred to a deep-level emission is usually attributed to the presence of the ionized oxygen vacancy on the surface. This results from the recombination of a photo-generated hole with a single ionized charged state of the defect in ZnO [Kenanakis et al., 2007, de Moura et al., 2010]. A broad blue band centred at 407 nm and shoulder peak at 489 nm are present for sample B. The NBE emission of sample A shifts towards red in comparison with sample B which might be ascribed to the size effect [Wang et al., 2003] which is supported from the different particle size of samples A and B calculated using XRD results.
4.7 Summary

Highly transparent ZnO thin films were successfully prepared by the spin coating technique on glass substrate. The impact of annealing on structural, optical and photoluminescence properties was systematically studied. XRD studies indicate that the crystallinity is enhanced on annealing and the average crystalline grain size also increases with annealing. The magnitude of the optical band gap determined from optical result is in agreement with the reported works. The photoluminescence spectra of ZnO thin films exhibit a strong UV excitonic peak.

Consequently, it was seen that the effect of annealing makes a significant change on the structural and optical properties of ZnO spin coated thin films. A high optical quality of the deposited ZnO films would potentially allow their application for UV light emission. From the above results, it may be concluded that the ZnO thin films could be annealed at 450°C is of good quality and it could be used for application purposes.

From the XRD patterns of undoped ZnO thin films with various thickness, where all samples show similar diffraction peak positions. No peaks were observed as phases of impurities, indicating high purity of the ZnO thin film obtained by the sol-gel technique. The experimental results showed that both the ultraviolet emission in PL spectrum and the magnetic properties are evidently influenced by the thickness of the film. The presence of sharp UV emission line as well as the LO-phonon lines indicates that these films have good crystalline quality. Higher thickness drastically changes the photoluminescence of spectra and shoulder peak disappears.

Based on the structural and optical studies carried out by varying the number of layers of ZnO film, it was found out that eight layer film shows high crystalline quality with the prominent (002) peak which is the characteristic peak for the c-axis oriented wurtzite ZnO structure. Again the morphology of the eight layer sample showed hexagonal shaped grows reflecting the basic unit cell structure. Hence, further
preparation of doped ZnO films was carried out with eight layer thickness annealed at 450°C in open air.

The effects of different kinds of annealing on the structural and optical properties were investigated. The XRD results show that the ZnO thin films annealed in open air is polycrystalline in nature having lesser crystallinity compared with the sample prepared using hybrid annealing. Photoluminescence studies show that the intensity of NBE emission in sample B is lesser than that of sample A. Enhancement of NBE emission is clearly observed in sample A which was annealed in open air environment. The increase in intensity of NBE emission during open air annealing might be due to the presence of excess oxygen compared to the hybrid annealing process. Thus there is a significant difference in the structural and optical properties of ZnO thin films which were undergone different types of annealing processes. Further work was continued with open air annealing.
References


