Chapter 3

CHARACTERIZATION OF DEFECTS IN ZnO NANOCRYSTALS
3.1 Introduction

In the recent decades zinc oxide (ZnO) has been studied with renewed interest due to their fascinating applications in optics, electronics and photonics [1, 2]. ZnO is a direct band gap semiconductor that crystallizes in wurtzite structure. The lack of centre of symmetry in ZnO makes it suitable for piezoelectric and mechanical actuator applications. ZnO has a wide band gap of 3.3 eV that is suitable for short wavelength opto-electronic applications. The high excitonic binding energy (60 meV) ensures efficient excitonic emission at room temperature. Due to having these distinguished properties, ZnO has found wide range of applications in light emitting diodes (LED), photo-detectors, sensors, solar cells, lasers, and acoustic wave filters [3-6].

In addition to a UV excitonic emission, ZnO generally exhibits luminescence in the visible region of different wavelength ranges. These luminescence effects have been assigned to electronic transitions involving the conduction band, the valence band and various intrinsic or extrinsic defect levels lying within the band gap. Some of the unwanted properties of bulk ZnO such as weak excitonic emission can be eliminated in nanocrystalline ZnO while keeping the large excitonic binding energy intact. This facilitates high yield luminescence from ZnO nanostructures even at room temperature [7]. However, nanocrystalline materials exhibit extraordinary properties as grain boundary related phenomena effectively manifest themselves as the grain sizes are reduced to nanometric regime. A variety of structural defects, especially vacancies and their clusters may exist in the grain boundaries of nanostructured ZnO. These defects influence the electronic and opto-electronic properties of a semiconductor material. Hence, proper identification of these defects and knowledge on their evolution are required to understand how defects control properties of a semiconductor. These defects are created in semiconductors during the growth where it is governed by growth kinetics and thermodynamics. The intrinsic defects commonly found in ZnO are zinc
interstitials (Zn), zinc vacancies (VZn), oxygen interstitials (Oi), oxygen vacancies (VO), oxygen antisites (O_{zn}) and zinc antisites (ZnO). The energy levels of all these intrinsic defects had been calculated by Sun using the full-potential LMTO method [8]. All these defects can also have various charge states. A detailed description about these defects has been reported by Kohan et al. [9].

The defects in ZnO can be characterized by various experimental methods such as photoluminescence (PL), cathodoluminescence (CL), positron annihilation spectroscopy (PAS), x-ray diffraction (XRD), deep level transient spectroscopy (DLTS) etc. The photoluminescence spectra of nanocrystalline ZnO, typically display emission bands in the UV and visible regions (green [10-14], blue [15] and violet [16]). The violet PL band in ZnO is not frequently seen and its defect emission mechanism is not fully understood. Positron annihilation spectroscopy is an efficient and non-destructive technique for investigating neutral or negatively charged vacancy type defects in semiconductors [17]. Positrons in nanocrystals diffuse through the grains and are annihilated in the grain boundaries. These positrons get trapped preferentially in Zn vacancies and their lifetime in these defect sites is longer whereas the area-normalized Doppler broadened annihilation line is narrower in comparison with those in the bulk.

In the present chapter of the thesis, the results of x-ray diffraction, photoluminescence and positron annihilation (both lifetime and Doppler broadening) studies on nanocrystalline ZnO having sizes 19 to 39 nm are presented. The samples were prepared by an equilibrium wet chemistry method and the wurtzite structure of the ZnO nanocrystals was confirmed by x-ray diffraction analysis. A violet (~ 434 nm) luminescence was observed in all the samples, the intensity of the emission was found to be particle size dependent. The violet emission has been argued to be due to electronic transitions from the zinc interstitial defect level to the valence band. Since it is difficult to characterize interstitials experimentally, indirect
information on their dynamics can be obtained by studying the dynamics of vacancies for which PAS is an excellent technique. An attempt has been made to correlate the results of PL measurements with those obtained by PAS in the light of evolution and quenching of zinc interstitials and vacancies.

3.2 Experimental details

Calculated amount of zinc chloride (AR grade, E. Merck, Germany) was dissolved in 200 ml of Milli-Q water. 0.5M NaOH was added to the solution drop wise under vigorous stirring. The pH of the resulting solution was adjusted to 9. A dense white precipitate was obtained which was separated and washed with Milli-Q water repeatedly to obtain a neutral pH. This precipitate was divided into five equal parts and heat treated at 200, 400, 600, 800 and 1000 °C to prepare samples of different sizes. XRD of all the samples were carried out using a Bruker D8 Advance diffractometer working with Cu Kα radiation (λ =1.54056 Å). The XRD lines were identified with JCPDS standard data files of ZnO. PL spectra were recorded by a Perkin-Elmer LS-55 luminescence spectrometer at an excitation wavelength of 345 nm. Positron annihilation lifetime measurements were carried out using a fast-fast coincidence system consisting of two 1 inch tapered off BaF₂ scintillators coupled to XP 2020Q photo multiplier tubes. The prompt time resolution of the system using a ⁶⁰Co source with ²²Na gate was 298 ps. The lifetime spectra were deconvoluted using the code PATFIT 88 [18]. A total source correction of 10% had been deducted while analyzing the spectra. The Doppler broadening measurements had been performed with an HPGe detector with an energy resolution of 1.8 keV at 662 keV.

3.3 Results and Discussion

3.3.1 XRD analysis

Figure 3.1 shows X-ray diffractograms of the samples heat treated at different temperatures. A comparison of the 2θ values of the observed diffraction peaks with that reported for bulk
ZnO in the standard JCPDS files indicates the formation of single-phase ZnO. It is also observed that the peaks tend to become sharper with increasing heat-treatment temperature indicating grain growth and improvement in the crystallinity of ZnO nanocrystals. The lattice parameters of prepared samples have been estimated from (101) and (100) peak by using the following equation.

\[
\frac{1}{d_{hkl}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)
\]  

(3.1)

where \( a \) and \( c \) are lattice parameters, \( h, k, \) and \( l \) are Miller indices and \( d_{hkl} \) is interplanar spacing. Interplanar spacing \( d_{hkl} \) were calculated by equation \( 2d \sin \theta = n \lambda \). The calculated lattice parameters are shown in table 3.1 that are very close to wurtzite phase of bulk ZnO ( \( a = 3.25 \) \( \text{Å} \) and \( c = 5.21 \) \( \text{Å} \)). The average crystallite sizes calculated from the Debye-Scherrer equation using the full width at half maximum (FWHM) of the most intense diffraction line (101) profile were 19, 24, 29, 34 and 39 nm for the corresponding heat treatment temperatures of 200, 400, 600, 800, and 1000 °C respectively. The average grain sizes have increased systematically with heat treatment temperature, depicting a good controllability over size variation of the nanocrystals.

<table>
<thead>
<tr>
<th>Samples annealing temperature (°C)</th>
<th>Lattice parameter a (Å)</th>
<th>Lattice parameter c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3.253</td>
<td>5.194</td>
</tr>
<tr>
<td>400</td>
<td>3.248</td>
<td>5.237</td>
</tr>
<tr>
<td>600</td>
<td>3.249</td>
<td>5.199</td>
</tr>
<tr>
<td>800</td>
<td>3.2494</td>
<td>5.193</td>
</tr>
<tr>
<td>1000</td>
<td>3.2492</td>
<td>5.209</td>
</tr>
</tbody>
</table>
3.3.2 Photoluminescence

The room temperature photoluminescence spectra of ZnO nanocrystals are shown in Figure 3.2. For all the samples, two distinct emission features can easily be discerned; one centered around 386 nm (3.21 eV) and the other at 434 nm (2.86 eV). The fluorescence at 386 nm corresponds to the characteristic band edge emission. The violet luminescence (434 nm) observed in the present case has been assigned to electronic transitions from the Zn\textsubscript{i} level to the valence band [14]. The energy level corresponding to Zn interstitials lies just below the conduction band and it can trap photo-excited electrons followed by their radiative recombination with holes in the valence band. The energy difference (2.9 eV) between the level corresponding to Zn interstitials and the top of the valence band as calculated theoretically is in good agreement with the observed energy (2.86 eV) of violet emission in ZnO nanocrystals observed in the present case [15]. For the sample heat treated at 200 °C, the
emission at 434 nm dominates and appears as the main peak. A constant decline in the relative intensity of the violet emission (434 nm) has been observed in the samples prepared by heat treatment of the precursor at higher temperatures whereas intensity of the excitonic emission (386 nm) goes up with the increase of heat treatment temperature. This suggests a reduction of the defect (zinc interstitials) concentration in the samples heat treated at higher temperature. The interstitials are highly mobile at higher temperature and are likely to recombine with the zinc vacancies dominantly present in the grain boundaries of the nanocrystals.

![Figure 3.2: Variation of PL intensities with heat treatment temperatures.](image)

### 3.3.2.1 Photoluminescence quantum efficiency (PLQE)

PL efficiency of all the nanocrystals were found to be remarkably high though no capping agent was used. A maximum PLQE of 11% was obtained for the 19 nm ZnO nanocrystals obtained by heat treatment of the precursor at 200 °C. The PLQE was determined by comparing the wavelength-integrated intensity of the ZnO nanocrystals with that of a standard quinine sulphate using the following equation [19].
where, $Q$ is the PLQE of nanocrystals, $Q_R$ is the PLQE of the reference (quinine sulphate); $I$ and $I_R$ are the integrated intensities, $A$ and $A_R$ are the absorbance at 350 nm and $\eta$ and $\eta_R$ are the refractive indices of the nanocrystals and the reference respectively.

Figure 3.3(a) shows the variation of PLQE of the ZnO nanocrystals with heat treatment temperatures. The PLQE of samples has been found to decrease with increased particle size. The major contribution to the exceptionally high value of PLQE for the 19 nm ZnO comes from the defect emission (434 nm). With increase in the heat treatment temperature, the defect concentration in the sample gets reduced and consequently, the PLQE of the samples of larger size decreases and attains a value of 4.5% for the 34 nm sized ZnO nanocrystals.

In order to look into the individual contribution of the defect and excitonic emission to the overall PL efficiency, each of the as-obtained PL spectra was deconvoluted into two
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Figure 3.3: Variation of (a) PLQE with increased temperature and (b) excitonic PLQE with heat treatment temperature.

Gaussian functions. The wavelength-integrated intensity, i.e., area under the curve, for each of the excitonic and defect luminescence was calculated. On increasing the heat treatment temperature from 200 °C to 400 °C corresponding to particle size increase from 19 nm to 24 nm, efficiency of the excitonic luminescence shoots up remarkably from the initial value as shown in Figure 3.3(b). But further increase in heat treatment temperature has virtually no effect on the PL efficiency of the excitonic emission. With increasing heat treatment temperature, the decrease in defect concentration should have strengthened the excitonic luminescence and a rise in PLQE of the excitonic emission should have been observed. This is not observed in the present case, which is possibly due to strong electron-phonon coupling, the strength of which increases with increasing particle size [20]. The enhanced electron-phonon coupling in larger size particles would cause the photo-excited electrons to follow a non-radiative deactivation path through lattice vibrations. Thus, a delicate interplay between
two opposing factors, (i) the decrease of defect concentration with increasing heat treatment temperature and (ii) stronger electron-phonon coupling with increasing particle size, could be responsible for the unchanged PLQE of the excitonic luminescence in the temperature range 400-800 °C.

3.3.3 Positron annihilation studies

3.3.3.1 Doppler broadening studies

The Doppler broadening of the annihilation radiation (DBAR) reflects momentum distribution of the annihilating electrons. The contribution from conduction electrons is located in the central part of the Doppler broadened annihilation line profile whereas core electrons contribute to the wing area. The S-parameter obtained from the annihilation profile gives overall defect concentration in a sample. The S-parameter is defined as the number of counts integrated under a central segment spreading over ± 800 eV around the 511 keV annihilation line divided by the counts under the full spectrum. In negatively charged or neutral open volume defects, positrons are trapped which results in localization of their wave functions. The wave function of a localized positron decreases rapidly with distance from the trap center. Consequently, the overlap of the wave functions of the localized positron and core electron is reduced as opposed to outer-shell valence electrons, which are much less susceptible to the reduction to the overlap because they are at larger distance from the nucleus. Hence the probability of annihilation of trapped positrons with core electrons is reduced by a larger magnitude than that with valence electrons. Because of significantly low momentum of the valence electrons, the momentum distribution of annihilating electrons shifts to smaller values and hence Doppler broadening of the annihilation line decreases. Therefore, the curve of a defect-rich sample becomes higher and narrower compared with that of a defect-free sample, when both curves are normalized to equal area. As a result of
this, S-parameter of a defect-rich sample becomes higher compared with that of a defect-free sample.

![Figure 3.4: Variation of S-parameter with heat treatment temperatures.](image)

S-parameter of the sample heat treated at 200 °C was found to be 0.489. A sharp drop in S-parameter has been observed for the sample heat treated at 400 °C, followed by its gradual decrease in the samples, which are heat treated at higher temperatures as shown in Figure 3.4. This variation of the S-parameter with the increase of heat treatment temperature is a clear indication of the reduction of overall defect concentration in the samples of larger crystallite sizes, which were prepared by heat treatment of the precursors at higher temperatures.

3.3.3.2 Positron annihilation lifetime studies

The lifetime of positrons in a sample depends on the density of electrons at the annihilation site. In a sample with vacancy or void, the average electron density is less at the defect site and lifetime of positrons is more than that in a defect free sample. In a nanocrystalline material with grain size smaller than the positron diffusion length (100-200 nm in a solid), the mechanism of positron annihilation is qualitatively different from that in bulk crystals. Grain boundaries being rich in defects, act as strong trapping centers for positrons and all positrons

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get trapped in the vicinity of grain boundaries. Thus, positron lifetime spectra of nanocrystalline materials generally do not have any contribution from the electrons residing inside the grains and provide information regarding the annihilation at grain boundaries only.

The positron lifetime spectra of the ZnO nanocrystals were deconvoluted with three lifetime components, $\tau_1$, $\tau_2$ and $\tau_3$ with relative intensities $I_1$, $I_2$ and $I_3$ respectively, to obtain the best fit. The shortest lifetime $\tau_1$ corresponds to positron annihilation at structural defects in the grain boundaries. Chen et al. have reported that in ZnO, zinc vacancy ($V_{zn}$) is the dominant defect which is sensed by positrons, as they appear in negative and neutral charge states [21]. Also, theoretical calculations have shown that the formation energy of zinc vacancy is lower at grain boundaries than that in the bulk [22]. Other vacancy type defects found in ZnO are oxygen vacancies ($V_O$), but since positron binding energy to $V_O$ is only 0.04 eV, which is much lower than that of $V_{zn}$ (0.39 eV), $V_O$ is essentially invisible to positrons [21, 23]. So, $\tau_1$
gives information on $V_{2a}$ clusters present at grain boundaries. The intermediate lifetime $\tau_2$ has been assigned to trapping of positrons in nano-voids at the intersection of three or more grain boundaries (e.g. triple junction) and the longer lifetime $\tau_3$ is attributed to the pick-off annihilation of ortho-positronium formed in the intercrystalline regions characterized by a large free volume. However, the variation of $\tau_3$ with the heat treatment temperature has not been discussed here owing to its very low intensity. Figure 3.5 shows the variation of mean-lifetime ($\tau_m$) of positrons annihilating in the sample with heat treatment temperature. $\tau_m$ has been calculated as

$$\tau_m = \frac{\tau_1 I_1 + \tau_2 I_2 + \tau_3 I_3}{I_1 + I_2 + I_3} \quad (3.3)$$

Like the Doppler broadened S-parameter, $\tau_m$ also gives overall defect (vacancy) concentration in a sample. A gradual decrease in $\tau_m$ has been noticed with increasing grain size. The decrease in the value of $\tau_m$ is a clear indication of the reduction of overall defect concentration in the samples of higher crystallite size thereby further confirming the DBAR results.
To have a closer look at the defect dynamics, the variation of individual lifetimes and the corresponding intensities with the heat treatment temperature should be inspected. Figure 3.6 illustrates the variation of the deconvoluted lifetimes $\tau_1$ and $\tau_2$ with heat treatment temperature of the precursor.

$\tau_1$ is seen to decrease from $239 \pm 4$ ps to $160 \pm 5$ ps as the heat treatment temperature is increased from 200 to 1000 °C. The reported value of lifetime in a monovacancy in ZnO is $\sim 237$ ps whereas the lifetime of positrons in defect-free ZnO is $\sim 158$ ps [21, 24]. For the sample heat treated at 200 °C, $\tau_1$ is close to the lifetime of positrons in a monovacancy, which indicates that almost all the positrons annihilate in the zinc vacancy sites. Photoluminescence results have shown that the sample prepared by heat treatment of the precursor at 200 °C contains a large number of zinc interstitials. Hence it is expected that the sample contain a large number of zinc vacancies also.

For the samples heat treated at 400 °C and above, the decrease of $\tau_1$ to a value lower than the lifetime of positrons in a monovacancy, can be explained by assuming that positrons not only annihilate at the structural defects ($V_{zn}$) in the grain boundaries, but also with free electrons in defect-free regions. The lifetime $\tau_1$ in that case will be the weighted average of lifetime $\tau_D$ at the defect sites and the lifetime $\tau_B$ corresponding to annihilation in defect-free sites. If $n_D$ and $n_B$ are the fractions of positrons getting annihilated at the defect sites and at the defect-free sites respectively, the observed lifetime $\tau_1$ is given by

$$\tau_1 = n_D \tau_D + n_B \tau_B$$

(3.4)

The concentration of zinc vacancy at the grain boundaries of these samples decreases because some of them recombine with highly mobile zinc interstitials. As a result, a fraction of positrons may escape through one or more grain boundaries without being trapped and annihilate with free electrons present well within adjacent grains. This causes a decrease in the fraction $n_D$, whereas the fraction $n_B$ increases and according to Eq. (3), values of $\tau_1$
decrease. Finally at 1000 °C, when almost all the vacancies have annealed out, the value of $\tau_1$ becomes equal to 160 ps, which is the characteristic lifetime of positrons annihilating with free electrons. $\tau_2$ is seen (Figure 3.6) to decrease steadily with the heat treatment temperature implying reduction of the size of triple junctions at higher temperature due to grain growth.

Table 3.2 Trapping rates and experimental and calculated values of $\tau_1$

<table>
<thead>
<tr>
<th>Heat treatment temperature (°C)</th>
<th>$k_1$ (ns$^{-1}$)</th>
<th>$k_2$ (ns$^{-1}$)</th>
<th>$\tau_1$ (experimentally obtained values) (ps)</th>
<th>$\tau_1^{\text{cal}}$ (calculated values) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>35</td>
<td>17</td>
<td>220 ± 4</td>
<td>220</td>
</tr>
<tr>
<td>600</td>
<td>14</td>
<td>8</td>
<td>203 ± 4</td>
<td>204</td>
</tr>
<tr>
<td>800</td>
<td>5</td>
<td>2</td>
<td>180 ± 4</td>
<td>181</td>
</tr>
</tbody>
</table>

To verify the above-mentioned hypothesis, a three state trapping model analysis has been carried out with the lifetime data. The trapping rates in the two types of defect sites have been calculated with the deconvoluted lifetime parameters. These trapping rates are used to calculate the shortest lifetime ($\tau_1^{\text{cal}}$) in the samples prepared at different temperatures, which are compared with the corresponding experimentally obtained values of $\tau_1$. Assuming that the shortest lifetime $\tau_1$ is an admixture of positron lifetimes $\tau_{D1}$ in monovacancies and $\tau_B$, whereas $\tau_2$ (which is equal to $\tau_{D2}$ in the present trapping model) is the correctly resolved lifetime component, the trapping rates in both the defects were calculated using the following equations,

$$k_1 = \frac{\tau_1 (\lambda_B - I_1 \lambda_{D2}) - I_1}{\tau_{D1} - \tau_1} \quad (3.5)$$

and

$$k_2 = \frac{I_2}{I_1} (\lambda_B - \lambda_{D2} + k_1) \quad (3.6)$$

where the annihilation rates $\lambda_B = \tau_B^{-1}$ and $\lambda_{D2} = \tau_2^{-1}$. The lifetime $\tau_B$ is taken as 158 ps and $\tau_{D1}$ as 237 ps. The values of trapping rates $k_1$ and $k_2$ are listed in table 3.2. From the two calculated trapping rates, $\tau_1^{\text{cal}}$ is obtained as

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\[ \tau_{1}^{\text{cal}} = \frac{1 + \left( \frac{\lambda_{1}}{\lambda_{\text{m}}} \right)}{\lambda_{2} + \left( \frac{\lambda_{2} - \lambda_{1} + k_{1}}{\lambda_{\text{m}} + k_{1}} \right)} \] (3.7)

Table 3.2 also shows a comparison between the experimental \( \tau_{1} \) and \( \tau_{1}^{\text{cal}} \) values of the samples prepared at 400, 600 and 800 °C. An excellent match between the two values has been obtained which supports the assumption of a mixed state for the lifetime \( \tau_{1} \).

Figure 3.7 shows the variation of I₁ and I₂ with heat treatment temperature. I₁ does not truly reflect the behavior of the \( V_{zn} \) concentration, as contribution from the free annihilation events is also included in it and moreover its variation is dependent on the variation of I₂. On the other hand, I₂ shows the percentage of positrons annihilated at the triple junctions. An increase in I₂ is seen when the heat treatment temperature was increased from 200 to 400 °C. This increase has most probably taken place due to transformation of large voids present in the intercrystalline regions into smaller voids like triple junctions. Similar kind of
transformation has also been observed by Qin et al. [25]. Above 400 °C, I$_2$ tends to decrease indicating a decrease in the concentration of triple junction, which most likely is due to grain growth.

At this juncture, it may be concluded that the results obtained from the PL and the PAS studies are well correlated. Zinc interstitials are formed and trapped in the nanocrystals during sample preparation, as indicated by the presence of violet band in the PL spectra. With increasing heat treatment temperature, a rapid decrease in the concentration of zinc interstitials is observed, as evident from the decreasing intensity of the violet band. On the other hand, from the PAS studies, we observe a considerable fall in the S-parameter and the mean lifetime ($\tau_m$) values with increasing heat treatment temperatures, which confirms the rapid quenching of zinc vacancies with zinc interstitials.

3.4 Conclusions

In conclusion, nanocrystalline ZnO with sizes varying from 19-39 nm was prepared via a wet chemical route. XRD results confirmed the formation of single-phase wurtzite structure. A strong violet luminescence was observed in the PL spectra and it was assigned to the radiative electronic transitions from the zinc interstitial defect level to the valence band. The intensity of the luminescent peak was seen to diminish with increasing heat treatment temperature, which is ascribed to decrease in zinc interstitial concentration in the samples heat treated at higher temperatures. A high overall photoluminescence quantum efficiency (~11%) has been obtained in the sample heat treated at 200 °C. The overall PLQE decreases with increasing grain size, which is due to decrease in the defect concentration with increasing heat treatment temperature. A decrease in the concentration of zinc vacancies with increasing heat treatment temperature was observed by positron annihilation spectroscopy. The reduction of concentrations of both zinc interstitials and vacancies with heat treatment temperature strongly suggests their recombination at higher temperature. A three state
trapping model analysis was performed with the lifetime parameters, which gave an excellent agreement between the calculated and experimentally observed shortest lifetime $\tau_1$. 
References:


