CHAPTER 4

GROWTH AND CHARACTERIZATION OF PURE ZnO NANOROD THIN FILMS

4.1 INTRODUCTION

Over the past several years, ZnO nanorod (NR) and nanowire arrays were widely studied for their excellent potential applications in manufacturing electronic, optoelectronic, electrochemical and electromechanical devices, like solar cells, ultraviolet (UV) lasers, piezo-nanogenerators, light-emitting diodes, and field emission transistors (Xu et al. 2008). Consequently, it is crucial to synthesize well-aligned ZnO NRs for accomplishing the above stated applications. Until now, 1-D ZnO nanostructures such as nanorods, nanowires, nanotubes, nanobelts, nanonails, and nanocombs are widely studied by many researchers owing to their fabulous electrical, optical, magnetic, mechanical and photochemical properties. In addition, aligned one-dimensional nanostructured arrays have ideal geometrical structures to deliver a direct pathway for charge transport along with high junction area which are useful for photovoltaic applications (Tak et al. 2009). Particularly, to modulate the physical properties by changing the aspect ratio of nanorods, vertically aligned 1-D ZnO NRs would offer exclusive opportunity among all the nanostructures (Gayen et al. 2010). Therefore, it is a prerequisite requirement for controlled growth of nanostructures in terms of size, shape, orientation and also to formulate desired ZnO architectures, a large amount of intensive research has been conducted. However, for the fabrication of compound semiconductors from aqueous solution, chemical bath deposition (CBD) is considered as one of the most useful solution techniques having some advantages of low growth temperature and low fabrication cost (Cao et al. 2008). Hence, the present work followed a two-step CBD
technique for the growth of vertically aligned ZnO NRs for its reliability and simplicity.

It is important to obtain ZnO NRs with uniform size and shape for many applications. Accordingly, to control the morphology and for achieving a high aspect ratio (length/width) ZnO NRs, it is essential to vary three important growth parameters such as precursor concentration, growth temperature and growth time.

This chapter mainly deals with the growth process of vertically aligned ZnO NR thin films by tailoring the growth parameters for controllable aspect ratio on ZnO NRs using a two-step CBD method utilizing various characterization tools.

**4.2 EXPERIMENTAL METHOD FOR GROWING PURE ZnO NR THIN FILMS**

**4.2.1 ZnO seed layer**

Pre-coating of the substrate with ZnO seed nanoparticles is important for providing appropriate conditions for heterogeneous nucleation and crystal growth which can also reduce the nucleation energy barrier and the lattice mismatch effectively (Li et al. 2011). Further, to grow NRs, to control the morphology, texture and even orientation, pre-depositing the substrates using ZnO seed nanocrystals is an effective method (Zhao et al. 2006). Thus, introduction of pre-seeding with ZnO nanoparticles play an important role on the growth of ZnO NRs which can be achieved through spin coating, dip coating or sputtering processes. Among them, sol-gel spin coating method has been chosen to accomplish ZnO seed layer.

**4.2.2 Preparation of ZnO seed layer**

Vertically aligned ZnO NR thin films have been synthesized by the two-step chemical method (Yang et al. 2009). At first, a thin layer of ZnO seed layer of thickness 70 nm has been prepared by sol-gel spin coating technique. 0.1 M concentration of zinc acetate dihydrate \([\text{(CH}_3\text{COO)}_2\text{Zn}._2\text{H}_2\text{O)}\] was initially dissolved in ethanol and then diethanolamine was added dropwise to stabilize the solution. The resultant solution kept at a temperature of 50 °C was thoroughly
mixed for 1 h using a magnetic stirrer to turn into a homogeneous, clear and transparent precursor solution. After allowing to age for a day, the precursor sol was coated onto glass substrates at a spinning rate of 3000 rpm for 30 s using a spin coater. After each coating, the coated wet films were dried at 200 °C for 2 min on a hot plate to vaporize the solvent and to remove organic residuals. The procedure from spin coating to drying process was repeated several times to obtain a layer of dense and uniformly distributed ZnO nanoparticles on the glass substrate. Then the ZnO seed layer coated substrate was post annealed at 400 °C for 1 h to increase the crystallinity of ZnO seed layer. A schematic representation of sol-gel spin coating method and the ZnO seed nanoparticles coated glass substrate are shown in figure 4.1 and 4.2 respectively.

![Figure 4.1 Schematic representation of sol-gel spin coating method](image1)

![Figure 4.2 Schematic illustration of ZnO seed nanoparticles coated glass substrate](image2)
4.2.3 Growth of ZnO NR thin films

ZnO NRs were prepared by suspending the ZnO seed layer coated substrate upside-down in a closed glass beaker containing 150 ml of aqueous solution consisting of an equal molar amount of zinc acetate dihydrate and hexamethylenetetramine \([C_6H_{12}N_4]\). The growth solution prepared at various concentrations (20, 40, 60 and 80 mM) was placed in an oven at various temperatures (30, 50, 70 and 90 °C) and at various the growth times (1, 3, 5 and 9 h) by varying any one of the growth parameter at a time. Finally, the substrate was removed from the solution, rinsed with deionized water and dried in air. A schematic illustration of the growth process of ZnO NR thin film is presented in figure 4.3. To select the optimum growth condition, for each growth parameter, four ZnO NR thin films were prepared amounting to a total of 12 films for the three growth parameters.

![Schematic illustration of growth process of ZnO NR thin film](image)

**Figure 4.3** Schematic illustration of growth process of ZnO NR thin film
4.3 CHARACTERIZATION TECHNIQUES

In order to select the growth parameters for obtaining ZnO NRs with high aspect ratio, the prepared films were systematically analyzed using different characterization tools. Surface morphological studies were performed by FEI Quanta FEG 200, a high resolution scanning electron microscope (HRSEM) attached with energy dispersive X-ray (EDX) analyzer. Structural studies have been carried out using Schimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation recorded in the range 10-90°. The detailed nanostructural properties were analyzed using JEOL JEM 2100, a high resolution transmission electron microscope (HRTEM). Fourier transform infrared spectroscopy (FTIR) analysis was carried out using IR prestige-21 Shimadzu Fourier transform infrared spectrometer. The ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were recorded using JASCO-670 UV/VIS/NIR spectrometer. Room temperature photoluminescence (PL) analysis was performed using a Fluoromax-4 spectrophotometer. The current to voltage (I-V) measurements were carried out using the automated testing device by National Instruments (NI PXI-1044).

4.4 MORPHOLOGICAL STUDIES

In this section, surface morphologies of seed layer and ZnO NR thin films grown under various precursor concentrations, growth temperatures and growth time are studied using HRSEM images taken at 30,000, 40,000, 50,000 and 70,000 x magnifications.

4.4.1 Morphological studies of ZnO seed layer

Figure 4.4 shows the top view HRSEM image (70,000 x) of ZnO seed layer deposited film on glass substrate. The image depicts the presence of a large number of spherically shaped ZnO seed nanoparticles having an average diameter of 37 nm. It is observed that the nanoparticles are uniform in dimension with well-defined boundaries.
4.4.2 Influence of precursor concentration

To study the influence of precursor concentration on the morphology and aspect ratio of ZnO NRs, the precursor concentration has been varied as 20, 40, 60 and 80 mM by keeping the growth temperature (90 °C) and time (3 h) constant. Figure 4.5 shows the top and cross-sectional view HRSEM images of ZnO NR thin films for various precursor concentrations. The top-view image (70,000 x) of all concentrations clearly shows the hexagonal shaped ZnO NRs. Again, the HRSEM images demonstrate that the diameter and length of the ZnO NRs are greatly influenced by the precursor concentration. The average diameter of the ZnO NRs progressively increases from 60 to 1350 ±10 nm with increase in precursor concentration from 20 to 80 mM, whereas, the average length becomes longer from 2.3 to 3.5 ±0.1 μm till 40 mM and further becomes shorter for higher concentration. The increase in diameter of ZnO NRs might be due to the excess amount of Zn(OH)$_2$ produced by the precursor solution for higher concentration which causes an increase of growth rate during the synthesis process.
Figure 4.5 Top and the corresponding cross-sectional view HRSEM images of ZnO nanorods grown at different precursor concentrations with constant growth temperature (90 °C) and time (3 h)
As these are endothermic processes hindering the growth of ZnO NRs, formation of thicker and shorter NRs is attained at higher precursor concentration (Li et al. 2010). Thus, the result discloses that the size of the ZnO NRs depends strongly on Zn$^{2+}$ concentration (Polsongkram et al. 2008).

Figure 4.6 (a) shows a plot of variation of average diameter and length of the ZnO NRs for different precursor concentrations. It is observed that average diameter of the ZnO NRs increased gradually but the length shows unsystematic behavior with respect to precursor concentration. However, both diameter and length of the ZnO NRs are closely associated with the precursor concentration. Variation of aspect ratio as a function of different precursor concentration is shown in figure 4.6 (b). It is seen that the calculated aspect ratios are found to reduce with the increase in precursor concentration from 20 to 80 mM and lower precursor concentration (20 mM) produced higher aspect ratio ZnO NRs. Hence for the rest of the work the lowest precursor concentration (20 mM) has been chosen for its yield to produce high aspect ratio ZnO NRs.

**Figure 4.6** (a) Average diameter, length versus concentration and (b) aspect ratio versus precursor concentration of ZnO NRs

### 4.4.3 Influence of growth temperature

Temperature plays an important role for attaining hexagonal shaped ZnO NRs having high aspect ratio (Xu et al. 2008).
Figure 4.7 Top and the corresponding cross-sectional view HRSEM images of ZnO nanorods grown at various temperatures with constant precursor concentration (20 mM) and growth time (3 h)
In order to find the influence of growth temperature on the morphology of ZnO NRs, growth temperatures has been varied as 30, 50, 70 and 90 °C by keeping the selected precursor concentration, 20 mM and growth time, 3 h.

Figure 4.7 illustrates top and cross-sectional view HRSEM pictures of ZnO NRs grown at different temperatures. For the film grown at 30 °C, it is seen that there is no remarkable change in the length of ZnO NRs and the morphology seems to be same as the seed layer coated thin film. However, notable change in length of NRs is observed when the growth temperature increases from 50 to 90 °C. The average diameter of the ZnO NRs varied from 30 to 90 ±10 nm while the average length rapidly progressed from 0.9 to 2.3 ± 0.1 μm as the growth temperature increased from 30 to 50 °C. The presence of many residual organics seen on film grown at 50 °C might be due to the decomposed zinc acetate not being completely washed away (Chen et al. 2006). By further enhancing the growth temperature from 70 to 90 °C, the length of the nanorods becomes longer having high aspect ratio. This result demonstrates that the length of the ZnO NRs strongly depends on growth temperature. However, lower temperature (30 °C) does not promote the lengthwise growth of the ZnO NRs.

![Graphs showing variation](image)

**Figure 4.8** Variation of (a) average diameter and length; (b) aspect ratio for various growth temperatures

Figure 4.8 (a) illustrates a plot of variation of average diameter and length at various growth temperatures. It is seen that there is no much change in average
diameter whereas the length of the ZnO NRs is found to increase with the growth temperature. Thus, longer length achieved at higher temperatures implies that maximum growth rate is possible at higher temperature. The aspect ratio of ZnO NRs grown at different temperatures is depicted in figure 4.8 (b). Obviously, high growth temperature (90 °C) yields high aspect ratio ZnO NRs. Based on HRSEM images, the growth temperature has been selected as 90 °C as it yields high aspect ratio ZnO NRs.

4.4.4 Influence of growth time

In order to find the influence of growth time on the morphology of ZnO NRs, growth time was varied as 1, 3, 5 and 9 h by keeping the selected precursor concentration (20 mM) and temperature (90 °C) as constant. To control the growth of ZnO NRs, the time immersed in growth solution is an additional important parameter (Li et al. 2010). Figure 4.9 shows the top and cross-sectional view HRSEM photographs of ZnO NR thin films with various growth times. The obtained average diameter and length of the ZnO NRs vary from 60 to 80 ±10 nm and 1.5 to 2.3 ±0.1 μm respectively, with increasing growth time from 1 to 9 h. When the growth time is extended from 1 to 3 h, the average diameter and length of the ZnO NRs are found to increase. However, further increasing the growth time from 3 to 9 h, the average diameter slightly increases while the average length shows no appreciable change. The result reveals that continuous and steady growth of ZnO NRs seems to be completed around 3 h and then the system would be in dissolution-precipitation equilibrium (Li et al. 2010). A similar result has been observed by Yuan et al (2011), who reported that the growth of the ZnO NRs should be slow after 2.5 h. This might be due to the reduction in concentration of Zn\textsuperscript{2+} ions in the chemical bath (Baruah et al. 2009).
Figure 4.9 Top view and cross-sectional view HRSEM images at various growth times with constant precursor concentration (20 mM) and temperature (90 °C)
Figure 4.10 *Plots of variation of (a) average diameter and length (b) aspect ratio for different growth times*

Figure 4.10 (a) displays the plot of variation of average diameter and length under various growth times. It is seen that, the average diameter of the ZnO nanorods is slightly enhanced with growth time while the length does not show much change when the time is greater than 3 h. Figure 4.10 (b) represents the corresponding aspect ratio of ZnO NRs for various growth time. It is noticed that, 3 h growth time shows the highest aspect ratio (35) but the longer growth duration results in reduced aspect ratio of ZnO NRs. Based on the results, the optimum growth time is taken as 3 h for all further growth of ZnO NRs.

4.4.5 Summary of morphological studies

ZnO NRs were grown using CBD method for various precursor concentrations, growth temperatures and growth times. Based on the morphological results it has been found out that 20 mM, 90 °C and 3 h are the most conducive growth parameters to produce the high aspect ratio ZnO NRs. Therefore, ZnO NRs grown with the above selected growth parameters were further examined for the structural, optical and electrical characterization studies.
4.5 ELEMENTAL COMPOSITION OF PURE ZnO NR THIN FILM

The elemental composition of ZnO NR thin film was carried out using energy dispersive X-ray spectrum (EDX) analyzer attached with HRSEM instrument to find the purity of the prepared film. EDX spectrum (figure 4.11) detected the presence of Zn, O along with Ca signal arising from the substrate and Au peak appering due to the gold sputtering of the sample for performing HRSEM analysis. Presence of no other elements indicates that the prepared sample is exhibiting pure ZnO phase.

![EDX analysis of pure ZnO NR thin film](image)

**Figure 4.11 EDX analysis of pure ZnO NR thin film**

4.6 STRUCTURAL STUDIES

In this section, structural properties of ZnO seed layer and pure ZnO NR thin films are discussed. To identify the phases and structural parameters, XRD analysis was performed in the range of 10 to 90° in steps of 0.1° at a scanning speed of 3°/min for all the films. The observed reflections were verified using JCPDS files.

4.6.1 XRD pattern of ZnO seed layer

XRD pattern of ZnO seed layer film is shown in figure 4.12. All the diffraction peaks are well indexed to hexagonal crystal phase of ZnO (JCPDS card no.79-0205).
4.6.2 XRD studies of pure ZnO NR thin film

A strong and dominant diffraction peak appears at 34.4° corresponding to (002) plane which indicates the existence of preferential orientation along the c-axis direction. XRD pattern exhibits a hump in the 2θ value ranging from 20 to 30° that might originate from the glass substrate. There are some other minor diffraction peaks located at 31.8°, 36.3° and 63.0° to relate with (100), (101) and (103) reflecting planes respectively. The calculated average crystallite size present in ZnO seed layer film is around 20 nm.
XRD pattern of ZnO NR thin film grown under the optimum growth parameters of 20 mM concentration at 90 °C for 3 h is depicted in figure 4.13. All the diffraction peaks correspond to the hexagonal crystal phase of ZnO with the lattice constant a=3.237 Å and c=5.164 Å that are agreeable with JCPDS card no.79-0205. It clearly shows a sharp and dominant diffraction peak located at 34.7° to relate with the (002) plane implying that the c-axis orientation is highly preferred for ZnO NRs. Among all the diffraction peaks, (002) plane shows higher intensity than other planes indicating the good crystalline nature of the prepared film. Some other weak diffraction peaks are also recorded at 2θ values, 31.7°, 36.1°, 47.8°, 63.1°, 68.2° and 72.8° corresponding to (100), (101), (102), (103), (112) and (004) planes respectively. No other impurity peaks are detected from the XRD pattern to display the purity of ZnO phase.

4.6.3 HRTEM analysis of ZnO NR thin film

![HRTEM images of ZnO nanorods at different magnifications and their corresponding SAED pattern](image)

**Figure 4.14** (a-c) HRTEM images of ZnO nanorods at different magnifications and (d) their corresponding SAED pattern
To investigate the nanostructure of the ZnO NRs, HRTEM images were taken in the dimension ranging from 200 to 21 nm. Figure 4.14 (a-d) represents low and high resolution HRTEM images of ZnO NRs which clearly depicts the rod-like structure of ZnO NRs. Figure 4.14 (c) shows the image of a single crystalline individual ZnO nanorod having a diameter of ~50 nm and the corresponding selected area electron diffraction (SAED) pattern given in figure 4.14 (d), clearly shows the sharp diffraction spots demonstrating the single crystal nature of the ZnO nanorod.

4.6.4 FTIR analysis of ZnO NR thin film

To investigate the surface composition of ZnO NR thin film, FTIR analysis was recorded in the wavenumber range of 400 to 4000 cm\(^{-1}\) and the spectra is shown in figure 4.15. The strong and broad absorption band appearing at 3433 cm\(^{-1}\) is due to the O-H stretching vibrations of hydroxyl groups. The peaks positioned between 2300 and 2900 cm\(^{-1}\) are assigned to C-H stretching vibration mode of the alkane groups (Krishnan et al. 2009). The two bands observed at 1591 and 1421 cm\(^{-1}\) are assigned to the asymmetric and symmetric stretching vibrations of carboxyl groups (-COOH). The peaks located at 1184 and 1024 cm\(^{-1}\) correspond to the deformation mode and the stretching vibration of C-O respectively. The peak

![FTIR analysis of pure ZnO NR thin film](image)

**Figure 4.15** FTIR analysis of pure ZnO NR thin film
at 422 cm\(^{-1}\) is due to the Zn-O stretching vibrations of ZnO NR thin film. Thus, FTIR analysis confirms the presence of ZnO compound in the thin film.

### 4.7 OPTICAL STUDIES OF PURE ZnO NR THIN FILM

In this section, UV-visible absorption, transmission and PL–emission spectral studies of pure ZnO NR thin film is discussed in detail.

#### 4.7.1 UV-visible analysis of ZnO NR thin film

![Optical transmittance spectra and Tauc's plot](image)

**Figure 4.16** (a) Optical transmittance spectra and (b) Tauc’s plot of \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) of pure ZnO NR thin film

It is important to study the optical properties of ZnO NRs for suitable opto-electronic applications. Figure 4.16 (a) depicts the optical transmission spectrum of pure ZnO NR thin film recorded in the wave length range of 300 to 1200 nm. It is observed that the prepared film is transparent and the average transmittance is larger than 80% in the visible region. The optical energy band gap value is evaluated from the transmission spectra and figure 4.16 (b) displays the Tauc’s plot of \((\alpha h\nu)^2\) versus \((h\nu)\). The determined optical energy band gap value is found to be 3.24 eV which is slightly lower than that of bulk ZnO (3.37 eV).

#### 4.7.2 Photoluminescence study of pure ZnO NR thin film

Room temperature photoluminescence (PL) spectrum of pure ZnO NR thin film with an excitation wavelength of 350 nm is represented in figure 4.17. The PL spectrum consists of two emission peaks of which the first one is UV emission
corresponding to a near-band-edge emission (NBE) due to the recombination of free excitons (Hu et al. 2010). The other one is a visible emission accepted as deep-level emission (DLE) closely related with several crystal structure defects such as zinc vacancies, oxygen vacancies, interstitial zinc or interstitial oxygen (Rahman et al. 2012). Again, the PL spectrum clearly exhibits the strong and sharp NBE emission peak centered at 380 nm along with the broad and weak deep-level yellow emission band positioned around 574 nm to be attributed to the interstitial oxygen (Li et al. 2004). Thus, the dominant NBE emission over the suppressed deep–level visible emission reveals that the obtained ZnO NR thin film is having good crystal quality and demonstrating excellent optical property (Wahab et al. 2007).

![Photoluminescence spectrum of pure ZnO NR thin film](image)

**Figure 4.17 Photoluminescence spectrum of pure ZnO NR thin film**

4.8 ELECTRICAL STUDIES

In order to study the electrical resistivity of ZnO NR thin film, silver contacts were made on the film to carry out current-voltage (I-V) measurements for both dark and light illumination conditions with an applied voltage varying from -10 to +10 V.

Figure 4.18 illustrates I-V plots of pure ZnO NR thin film under dark and light illumination which are linear indicating ohmic behavior, an essential feature
for many electronic devices (Zhou et. al 2008). The obtained resistivity values are 2.86 x10\(^{-2}\) and 5.43 x10\(^{-3}\) Ω cm for dark and light illuminations respectively that shows a decrease in resistivity on illumination due to the creation of electron-hole pairs by UV radiation (Illican et al. 2008).

Figure 4.18 I-V characteristics of pure ZnO NR thin film under dark and light illumination

### 4.9 CONCLUSIONS

For achieving controlled morphology, ZnO NRs were grown on glass substrate by varying the precursor concentration, growth temperature and time. The morphological studies reveal that the low precursor concentration (20 mM), high growth temperature (90° C) and short growth time (3 h) produce thinner, longer and high aspect ratio vertically aligned ZnO NRs. Therefore, these values are chosen as the best parameters for further growth of doped (chapter 5) and surface modified core/shell-type ZnO NR thin films (chapter 6 and 7). XRD result reveals that the ZnO NRs have the hexagonal crystal phase with the preferential c-axis growth direction. HRTEM analysis confirms the single crystalline nature of ZnO nanorod having the diameter of ~50 nm. FTIR analysis infers the presence of Zn-O stretching mode at 454 cm\(^{-1}\). Optical studies reveal that the prepared film has good optical transparency and the determined energy band gap is found to be 3.24 eV.
The fine optical quality of ZnO NR thin film is evident from the PL spectrum. I-V measurements demonstrate that the pure ZnO NR thin film has lower resistivity value under illumination compared to dark condition.