Chapter 5

ZINC OXIDE NANOSTRUCTURES

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5. Introduction

ZnO is a semiconducting material having direct wide band gap of 3.37 eV and high excitonic binding energy of 60 meV at room temperature. These features make it a promising material for transparant electronics, solar cells and other optoelectronic devices [1-3]. Growth of ZnO nanostructures such as one-dimensional rods, wires, tubes etc., has received increasing attention for its specific properties and for the fabrication of nanoscale devices. Many different techniques were employed for the growth of nanostructures; these include vapour-liquid-solid (VLS) epitaxy [4], chemical vapour deposition (CVD) [5], pulse laser deposition (PLD) [6], thermal decomposition [7], hydrothermal synthesis [8], etc.

In our study we used two simplest processes for ZnO nanorods preparation; they are thermal decomposition of Zinc acetate dihydrate in air and the hydrothermal process. The thermal decomposition of Zinc acetate dihydrate (ZAD) in air at 300°C is a simple, cost effective and rapid synthesis method for fabricating ZnO nanorods in crystal form. The hydrothermal method is also a simple and cost effective process for the growth of ZnO nanorods. It has low growth temperature below 100°C, catalyst free process and is suited for the uniform growth of ZnO nanorods over large area of the substrates. The structural and optical properties of the nanorods prepared by hydrothermal process shows strong dependence on conditions such as seed layer crystallinity, choice and concentration of surfactant used and reaction time for growth. Ma et al. [9] had reported the effect of annealing substrates on the density of ZnO nanorods array. Wu et al. [10] had studied the effect of addition of NaOH on the diameter of ZnO nanorods grown by hydrothermal method. Liu et al. [11] had synthesized ZnO nanorods on sputtered ZnO seed layer. N.Shakti et. al.[7] have compared photoluminescence of ZnO film and nanowire.

We have prepared ZnO nanorods array on ZnO seed coated p-type Si substrate by hydrothermal process. XRD of the film showed c-axis orientation. Average diameter of the rods was ~200 nm and length was ~1µm. The nanorods array showed UV- emission at room temperature. The I-V curve of the array showed rectifying behavior.
The ZnO nanorod crystals were prepared from thermal decomposition of Zinc acetate dihydrate. Undoped, Al and Li doped nanorods were prepared. XRD of the nanorods showed highly crystalline wurtzite phase. SEM and TEM of nanorods gave diameter of ~50 nm to 100 nm. While length was greater than 2 µm. Both Al and Li doped nanorods showed blue emission at room temperature. Further doping concentration of Li was varied in ZnO nanorod which showed a optimum doping concentration of 7.5 % for a green emission band. Also the nanorod morphology showed dependence on doping concentration. 10 % Li doped samples had deviation from rod shaped morphology to particle shaped morphology.

5.1 Synthesis of ZnO nanorods array by hydrothermal process

In this work we have synthesized ZnO nanorods on sol-gel prepared ZnO seed layer over p-Si substrate. The structural properties of the nanorods were studied by X-ray diffraction (XRD). The nanorods showed c-axis orientation perpendicular to the substrate. The surface morphology of the nanowires was studied by Scanning electron microscopy (SEM) and Field emission scanning electron microscopy (FESEM). The surface of the ZnO film showed vertical ZnO nanorods with hexagonal crosssection. The diameter of the nanorods was of the order of 200 nm. The optical properties of the samples were studied by UV-Vis spectrophotometer and spectrofluorophotometer. The reflectance of the nanorod showed an absorption edge at the band gap of ZnO. The photoluminescence of nanorods showed UV emission at room temperature. The intensity of emission showed dependence on nanorod diameter. The current-voltage characteristics of ZnO nanorod films showed rectifying behaviour.

5.1.1 Experimental method

The ZnO thin films were deposited on the Si substrate by a sol-gel method [12] which served as the seed layers for the growth of nanorods. For sol preparation, 1gm of zinc acetate dihydrate [Zn (CH₃COO)₂·2H₂O] was dissolved in 10 ml of boiling isopropanol at 84°C on the magnetic stirrer. The solution became milky white. The turbid solution
was cleared by adding 5-6 drops of diethanolamine (DEA). The resulting solution was aged for 2hrs to make a homogeneous stable colloidal solution.

For the film preparation, a p-type Si wafer was mounted on the spin coater (SCU 2005 Apex Inst.Co.). With a 5ml dropper, 6-7 drops of the sol was coated on the wafer while it was spinning at the rate of 3000 rpm for 20sec. The wet film was dried at 100ºC for 10 min and subsequently annealed at two different annealing temperatures of 400 ºC and 600 ºC for 1 hr. This process was repeated 8 times to form multilayer ZnO films.

ZnO nanorods were grown by hydrothermal method. The aqueous solution was prepared by dissolving 50mM zinc nitrate hexahydrate \( \text{[Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O]} \) and 50mM hexamethylenetetramine (HMTA) \( \text{[C}_6\text{H}_{12}\text{N}_4] \) in a beaker covered with a Petri dish. The molar ratio was 1:1. The solution was preheated to a constant temperature of 75ºC in a water bath. For the growth of ZnO nanorods samples were immersed at the bottom of the beaker by keeping film side up at a constant temperature of 75ºC for 4hours and was stirred mechanically. The substrates were then rinsed with deionised water for several times and were dried at 60ºC for 1 hour to remove any residual salts and organic materials.

The structural properties of ZnO nanorods films were studied by X-ray diffraction (XRD) (Panalytical Xpert pro) using Cu K\(_\alpha\) radiation \( \lambda = 1.54060 \) Å. The surface morphology of the ZnO nanorods was observed by Scanning electron microscopy (SEM) (JSM-6390 PC-SEM, JEOL/EO) and Field emission scanning electron microscopy (FESEM) (JEOL). The reflectance spectrum of the ZnO nanorod was measured using UV–Vis spectrophotometer (HR 4000 Ocean Optics). The Photoluminescence properties were studied by using Fluorescence spectrophotometer (Hitachi). The electrical properties of the films were measured using 2400 Keithley Source meter.
5.1.2 Structural properties

From figure 5.1 we observe that the peak position in the XRD spectrum of nanorods corresponds to the hexagonal wurtzite ZnO with lattice constants $a = 0.325$ nm and $c = 0.521$ nm as given in JCPDS card no. 75-0956.

Fig5.1. XRD of ZnO nanorod films annealed at 400°C and 600°C.
The ZnO nanorod samples annealed at 400ºC and 600ºC are polycrystalline with preferred orientation along c-axis perpendicular to the substrate surface. The degree of c-axis orientation is defined by expression

\[ P = \frac{I(002)}{\sum I(hkl)} \]  

Where P is the degree of crystal orientation along the (002) direction, \( I(002) \) is the intensity of the (002) diffraction peak and \( I(hkl) \) is the intensity of all diffraction peaks. Using this expression the degree of crystal orientation along different diffraction planes is calculated and plotted in figures 5.2(a) and 5.2(b) which shows that the nanorods have preferential growth along c-axis for both the annealing temperatures.

Fig 5.2(a) Degree of crystal orientation of various planes of ZnO nanorod film annealed at 400ºC
Fig 5.2(b) Degree of crystal orientation of various planes of ZnO nanorod film annealed at 600°C.
Figures 5.3a, 5.3b show the FESEM micrographs (top view) of ZnO nanorods by hydrothermal process at annealing temperatures 400°C.
It is observed that the nanorods are uniformly distributed over the ZnO film. The average diameter of the nanorods ~ 200 nm having hexagonal cross section. Figure 5.3c shows the edge view of the ZnO nanorod arrays over film annealed at 400°C.

*Fig 5.3(c) SEM image of ZnO nanorods array over ZnO film annealed at 400°C (edge view).*
The average length of the nanorods is ~ 1 µm. Figure 5.4a, 5.4b shows the top view of the nanorod arrays at annealing temperature 600°C.

Fig. 5.4(a,b). FESEM image of ZnO nanorod film annealed at 600°C.
The micrograph shows that nanorods are smaller in diameter (about 20 nm) than samples annealed at 400°C. This may be due to the inversion of the substrate during stirring in the solution phase reaction.

5.1.3 Optical properties

Figure 5.5 is the reflectance of the ZnO nanorod film annealed at 400°C and 600°C.

![Graph showing reflectance of ZnO nanorod films](image)

Fig. 5.5 Reflectance of ZnO nanorod films annealed at 400°C and 600°C

We find that the reflectance of the ZnO nanorod film annealed at 600°C is greater in the wavelength range 320-386 nm as compared to film annealed at 400°C. The nanorod film annealed at 600°C shows absorption edge at 376.9 nm while the film annealed at 400°C shows absorption edge at 376.4 nm.

Using the relation,

\[
\frac{h\nu (eV)}{\lambda (\mu m)} = 1.24
\]

(5.2)
The Optical band gap of the ZnO nanorod films annealed at 400°C and 600°C was found to be 3.294 eV and 3.289 eV respectively.

The Photoluminescence properties of the ZnO nanorod films annealed at 400°C and 600°C were studied using Fluorescence spectrophotometer. The PL spectrum in figure 5.6 indicates that the films annealed at 400°C and 600 °C show strong UV emission at 386.4 nm and 388.3 nm respectively.

Fig. 5.6 Room temperature photoluminescence spectrum of ZnO nanorod films annealed at 400°C and 600°C.
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The origin of UV emission in ZnO is due to the recombination of electron–hole pair in free excitons. The UV emission peak intensity decreases for film annealed at 600°C. This may be due to decrease in density of excitons as a result of thermal ionization and formation of free electron and free hole which in turn decreases the intensity of UV emission.

Figure 5.6 also shows a weak blue-green emission band (~ 475-525 nm) for nanorod films annealed at 400°C and 600°C. This blue-green emission in ZnO may be due to defect related emission (O or Zn vacancy). For film annealed at 600°C the weak blue-green emission is relatively less intense than for film annealed at 400°C, this is attributed to the increase in crystallinity of the film with increase in annealing temperature, which in turn leads to the decrease in the concentration of structural defects in the crystal, thereby decreasing the defect related emission.

As, ZnO films are prepared at the atmospheric pressure, the oxygen vacancies density in these films are very low and hence we observe almost negligible green band in the PL spectrum as shown in figure 5.6.
5.1.4 Electrical properties

Figure 5.7 shows the current-voltage characteristics of ZnO nanorod films annealed at 400 °C and 600 °C.

![Graph of current-voltage characteristic]

*Fig. 5.7 Current-Voltage Characteristics of ZnO nanorod films annealed at 400°C and 600°C.*

From figure we observe that ZnO nanorod film annealed at 400 °C shows more rectifying behaviour than that annealed at 600 °C. The rectifying behaviour may arise due to the contact resistance developed at the interface of the nanorod film and silver paste that was used to make electric contact to the film. The more rectifying behaviour of film annealed at 400 °C is due to large quantity of nanorods growth at its surface compared to that annealed at 600 °C as seen in FESEM image.
5.2 Synthesis and characterization of Al, Li doped ZnO nanorod crystals by thermal decomposition of Zinc acetate dihydrate

In this study we have used simple, cost effective and rapid synthesis method for fabricating ZnO nanorod crystals via thermal decomposition of Zinc acetate dihydrate in air at 300°C. Lithium hydroxide monohydrate and Aluminium isopropoxide were used as precursors for synthesizing Li and Al doped ZnO nanorods respectively. The structural property of doped and undoped ZnO nanorods was studied by X-ray diffraction (XRD). The samples showed polycrystalline nature. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) was used to identify the nanostructured morphology of the samples. Photoluminescence studies of ZnO nanorods showed ultra violet (UV) emission.

5.2.1 Experimental method

Zinc acetate dihydrate was used as the precursor for the synthesis of ZnO nanorods. Aluminium isopropoxide C\textsubscript{9}H\textsubscript{21}AlO\textsubscript{3} and Lithium hydroxide monohydrate LiOH.H\textsubscript{2}O were used as the precursors for the synthesis of Al doped and Li doped ZnO nanorods respectively. In the synthesis process 2 grams of Zinc acetate dihydrate was mixed with 0.1 gram of dopant precursor in a Quartz crucible and was covered with the Quartz lid. The crucible was heated from room temperature to 300°C in the furnace for 12 hours to produce Al and Li doped ZnO nanorods in the powder form. The structural properties of the samples were studied with X-ray diffraction (XRD) (Panalytical Xpert Pro) using Cu K\textsubscript{α} radiation (\(\lambda = 1.54059\) Å). Surface morphology of the samples was studied using Scanning electron microscope (SEM) (Jeol; JSM-6390LV) and Transmission electron microscope (TEM) (Jeol JSM). The Photoluminescence (PL) of ZnO nanorods was recorded at room temperature using spectrofluorophotometer (Hitachi).
5.2.2 Structural properties

Figure 5.8 shows the X-ray diffraction (XRD) spectrum of undoped, Al doped and Li doped ZnO nanowires grown at 300°C for 12 hours.

*Fig. 5.8 XRD spectrum of undoped, Al doped and Li doped ZnO nanorods.*
The peak positions in the undoped ZnO spectrum matches with that of wurtzite ZnO with lattice constants of $a = 0.325$ nm and $c = 0.521$ nm from JCPDS card no. 75-0956 and no other peaks (impurity) are visible. The high intensity of the peaks in XRD pattern indicates that both doped and undoped nanorods are highly crystalline. The Li doped ZnO nanorod show some orientation in (101) direction as compared to undoped and Al doped ZnO nanorods. The XRD pattern of the Li and Al doped ZnO nanorods shows a slight shift of the (101) peak towards the higher angle side with reference to undoped ZnO indicating a small decrease in the lattice spacing for Li and Al doped ZnO nanorods. It is known generally that dopants can be substituted or inserted, depending on the doping ions size. Yamamoto et al. [12] have shown theoretically that most of the doping ions which are larger in size than Zn ions replace the Zn ions and smaller dopant ions are inserted between Zn ion and O ion. Since the ionic radius of the dopants $\text{Al}^{3+}$ and $\text{Li}^{+}$ is smaller than $\text{Zn}^{2+}$, it can be inferred that the $\text{Al}^{3+}$ and $\text{Li}^{+}$ have possibly been inserted between Zn ion and O ion in host matrix in the present study. The intensity of the (100),(002),(101) peaks in Al and Li doped nanorods in the XRD pattern shows a small decrease compared to undoped nanorod, which can be attributed to the reduction in crystallinity of nanorod by lattice deformation due to doping. Further the difference in intensity reduction between Al and Li doped nanorods may be due to the difference in the ionic radius of the two ions.

The morphology of the grown undoped, Al doped and Li doped ZnO nanorods were examined with Scanning electron microscope (SEM) and Transmission electron microscope (TEM). Figures 5.9, 5.10 and 5.11 show the SEM and TEM micrographs of undoped, Al doped and Li doped ZnO nanorods respectively.
Fig. 5.9 SEM images (a), (b) & TEM image (c) of ZnO nanorods with selected area electron diffraction (SAED) (d).
Fig. 5.10 SEM image (a) & TEM image (b) of Al doped ZnO nanorods.
From the SEM image in figures 5.9 (a,b), 5.10 (a) & 5.11(b) it is observed that both undoped and doped ZnO nanorods show flower like growth having uniform length and diameter. The average diameter of the undoped ZnO nanorod is about 50 nm having
average length of 1.5 µm. From the TEM images in figures 5.9 (c), 5.10 (b) & 5.11(b) the aspect ratio of the nanorods was found to be ~20, 12 and 15 for undoped, Al doped and Li doped ZnO nanorods respectively. A selected area electron diffraction (SAED) pattern was recorded under TEM in proper recording conditions such as beam divergence and proper exposure time. Several regions were examined before the exposure of SAED pattern. In all areas, only limited rings were observed. SAED pattern of undoped ZnO nanorod is shown in figure 5.9 (d). The diffused contrast over the Debye ring is presumably being due to combined effect of several ZnO nanorod boundaries. Since the SAED gives the information about the orientation of crystallographic planes in a selected area, it would be appropriate to visualize that these are local area textured nanorods, as observed under TEM. The electron diffraction pattern of figure 5.9 (d) demonstrates three important planes of hexagonal structure (100, 101, 202) in the form of continuous rings in the reciprocal space with interplaner spacing of 0.28, 0.25 and 0.12 nm respectively. It may be noticed from XRD and SAED pattern that not all the planes as observed in XRD spectrum, Figure 5.8 are observable in the selected area electron diffraction. This is because XRD is a representative of entire area of the sample while the electron diffraction is from the selected area of the nanorod.

5.2.3 Optical properties

The room temperature photoluminescence (PL) of undoped, Al and Li doped ZnO nanorods were recorded with a fluorescence spectrophotometer using Xe lamp with an excitation wavelength of 315 nm. Figure 5.12 shows the photoluminescence spectrum of undoped, Al and Li doped ZnO nanorods.
The PL spectrum shows that all the samples show strong violet emission in the wavelength range (400-410 nm). Blue emission is also observed in the wavelength range (450-470 nm). This band has higher intensity for Al doped ZnO nanorod compared to undoped and Li doped nanorods. The blue band emission of ZnO films has been also reported using cathodoluminescence [13]. A weak green band (510-580 nm) is also observed for all the nanorod samples. The green band emission corresponds to singly ionized oxygen vacancy in ZnO and results from the recombination of a photogenerated hole with the singly ionized charge state of this defect[14]. The weak green emission indicates very low concentrations of oxygen vacancy in both undoped and doped ZnO nanorods synthesized by thermal decomposition of Zinc acetate dehydrate. The increased PL emission intensity (450 – 470 nm) of the Al doped ZnO nanorods as compared to undoped ZnO may be attributed to the increase in number of electrons occupying the deep donor level on the account of doping [15]. As compared to Li$^+$, Al$^{3+}$ has greater charge density which strongly effects the crystal field in host ZnO leading to greater emission intensity.
5.3 Effect of Li doping in ZnO nanorod crystals prepared by thermal decomposition of Zinc acetate dihydrate

In this study we have prepared Li doped ZnO nanorods by thermal decomposition of Zinc acetate dihydrate in air. The Li doping in ZnO nanorods were done at four different weight % viz. 2.5, 5, 7.5 & 10. The XRD of the sample doped at 10 weight % showed a peak of low intensity Zincite phase. Scanning electron microscopy (SEM) was used to study the surface morphology of nanorod samples which showed rod like structures. Transmission electron microscopy was used to identify the inside structure of individual nanorod. The photoluminescence of Li doped nanorods showed blue emission. Moreover at 7.5 Weight % doped Li, the photoluminescence spectrum showed a new green band emission which disappears for 10 Weight % doped sample.

5.3.1 Experimental method

Zinc acetate dihydrate was used as the precursor for the synthesis of ZnO nanorods. Lithium hydroxide monohydrate LiOH.H\textsubscript{2}O was used as the precursors for Li doping. In the synthesis process Zinc acetate dihydrate was mixed with dopant precursor in a Quartz crucible and was covered with the Quartz lid. The crucible was heated from room temperature to 300° C in the furnace for 12 hours to produce Li doped ZnO nanorods in the powder form. Five different samples of undoped, 2.5 %, 5%, 7.5% and 10 % Li doped samples were prepared. The structural properties of the samples were studied with X-ray diffraction (XRD) (Bruker) using Cu K\textsubscript{a} radiation (\(\lambda = 1.54059\) Å). Surface morphology of the samples was studied using Scanning electron microscope (SEM) (Jeol; JSM-6390LV) and Transmission electron microscope (TEM) (Jeol JSM). The Photoluminescence (PL) of ZnO nanorods was recorded at room temperature using spectrofluorophotometer (Hitachi).
5.3.2 Structural property

Figure 5.13 shows the X-ray diffraction (XRD) spectrum of undoped and Li doped ZnO nanorods grown at 300°C for 12 hours. The peak positions in the undoped ZnO spectrum matches with that of wurtzite ZnO with lattice constants of $a = 0.325$ nm and $c = 0.521$ nm from JCPDS card no. 75-0956. The high intensity of the peaks in XRD pattern indicates that nanorods are highly crystalline.

![XRD spectrum of Li doped ZnO nanorods with different doping concentrations.](image)

*Fig. 5.13 XRD of Li doped ZnO nanorods with different doping concentrations.*
It has been shown that most of the doping ions which are larger in size than Zn ions replaces the Zn ions and smaller dopant ions are inserted between Zn ion and O ion. Since the ionic radius of Li$^+$ is smaller than Zn$^{2+}$, it can be inferred that Li$^+$ have possibly been inserted between Zn ion and O ion in host matrix in the present study. The XRD of the sample doped at 10 weight % showed a peak of low intensity Zincite phase of ZnO in addition to its Wurtzite phase as confirmed by JCPDS data. The morphology of the grown Li doped ZnO nanorods were examined with Scanning electron microscope (SEM) and Transmission electron microscope (TEM). Figures 5.14 shows the SEM micrographs of Li doped ZnO nanorods.

**Fig. 5.14 SEM of Li doped ZnO nanorods with different doping concentrations.**
Figures 5.14 shows the SEM images of Li doped ZnO nanorods at different doping concentrations. From the micrographs we observe that Li doped ZnO has rod shaped morphology. At 2.5% Li doping concentration, the average diameter of nanorods is ~ 50 nm and length ~ 0.5 µm. In 5% doped samples we see that the nanorods are thinner and have grown 2-3 together. In 7.5 % doped sample the nanorods have about same diameter as of 5 % doped sample but here the individual nanorods have grown separately. As the doping concentration of Li is increased to 10%, we observe that the rod shaped morphology of the sample starts disappearing.

Figures 5.15 shows the TEM images of undoped ZnO nanorods. The cluster of undoped ZnO nanorods is shown in figure 5.15 (a). The corresponding Selected area electron diffraction pattern is shown in figure 5.15 (b). Clearly the pattern shows polycrystalline nature due to overlapping of of nanorods. Figure 5.15 (c) shows the single nanorod with diameter ~ 70 nm. Figure 5.15 (d) shows the corresponding electron diffraction which shows diffraction spots from single plane and in background diffuse ring indicates amorphous system.

Figure 5.15 (e-f) shows the bright field and dark field zone image of single nanorod w.r.t. just lower bright spot from center in figure 5.15 (d). The nonuniform darkness in the image shows the structural defect in single nanorod.

Figure 5.15 (g) shows the high resolution TEM image of single nanorod , clearly showing the stacked planes of the crystal lattice. From the figure lattice spacing is found to be ~ 0.266 nm.
Fig. 5.15 (a-d) TEM images of 0% doped ZnO nanorods.
Fig. 5.15 (e,f) bright field & dark field images of single 0% doped ZnO nanorod.

Fig. 5.15 (g) showing HR TEM image of single undoped ZnO nanorod.
Fig. 5.16 (a) TEM image of 2.5% Li doped ZnO nanorods, (b) showing single 2.5 % Li doped ZnO nanorod.
Fig. 5.17 (a) TEM image of 5% Li doped ZnO nanorods, (b) showing single 5% Li doped ZnO nanorod (c) Selected area diffraction of that nanorod.
Fig. 5.18 (a) TEM image of 7.5% Li doped ZnO nanorods, (b) showing single 7.5 % Li doped ZnO nanorod (c) Selected area diffraction of that nanorod.
Fig. 5.19 (a) TEM image of 10% Li doped ZnO nanorods, (b) showing single 10% Li doped ZnO nanorod (c) Selected area diffraction of that nanorod.
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Figure 5.16 (a) shows the TEM image of 2.5% Li doped ZnO nanorods cluster. The image shows that the nanorods may be much thicker than the average diameter of the cluster. Figure 5.16 (b) shows the image single Li doped ZnO nanorod with diameter ~ 80 nm. Figure 5.17 (a) shows the TEM image of 5% Li doped ZnO nanorods cluster. We observe that the nanorods have relatively smaller length, however the diameter of the nanorod from figure 5.17 (b), remains almost same. Figure 5.17 (b) shows the selected area electron diffraction of the nanorod, the sharp concentric rings represent nanocrystalline morphology. In figure 5.18 (a), 7.5% Li doped ZnO nanorods are there in cluster and the diameter of the single nanorod is about 100nm. In figure 5.18 (c) the bright spots in the parallel plane indicates the local single crystallinity. Figure 5.19 (a) shows the cluster of 10% Li doped ZnO nanorods. The diameter of the single nanorod in figure 5.19 (b) is ~70 nm. The selected area electron diffraction pattern, figure 5.19 (b) indicates structural defect in nanorods, due to overlapping circular diffraction spots. Thus we observe that as the Li doping concentration has been increased the morphology of the nanorods degrades. At 10% doping concentration the average length of the nanorods has decreased which has some relation with the appearance of Zincite peak in XRD at 10% of Li doping.

5.3.3 Photoluminescence of Li doped ZnO nanorods

The PL spectrum in figure 5.20 shows that all the samples show strong violet-blue emission in the wavelength range (400-410 nm). This is verified by the photographs, figure 5.21 of the emission from Li doped ZnO nanorod samples for various doping concentrations taken in the sample chamber of the Fluorescence spectrophotometer. We observe that as the doping concentration increases a new peak in green band (510-580 nm) starts to rise attains maximum for ZnO nanorods doped with 7.5% Li and again falls for doping concentration of 10%. The green band emission corresponds to singly ionized oxygen vacancy in ZnO and results from the recombination of a photo generated hole with the singly ionized charge state of this defect. A recent study in ZnO nanomaterials has shown that green emission is originated by oxygen vacancy brought by Li$^+$ incorporation into ZnO [16]. This fact clears about the origin of green band in PL spectrum. From the figure 5.20 we can thus say that 7.5% Li doping is the optimum doping concentration for observing green emission. However, in figure 5.21 green
colour is not seen in the emission photograph which may be due to strong blue background.

![Normalized photoluminescence curves of Li doped ZnO nanorods at different doping concentration.](image)

*Fig. 5.20 Normalized photoluminescence curves of Li doped ZnO nanorods at different doping concentration.*
Fig. 5.21 Blue light emission from Li doped ZnO nanorods at various doping concentration.
5.4 Conclusions

ZnO nanorods were grown on sol-gel prepared ZnO seed layer over p-type Si substrate by hydrothermal process. Undoped, Al doped and Li doped ZnO nanorods were synthesized in the powder form using thermal decomposition of Zinc acetate dihydrate. The structural properties of the nanorods were studied by X-ray diffraction (XRD). The nanorods array showed c-axis orientation perpendicular to the substrate. The surface morphology of the nanorods was studied by Scanning electron microscopy (SEM) and Field emission microscopy (FESEM). The surface of the ZnO film showed vertical ZnO nanorods arrays with hexagonal crossection. The optical properties of the samples were studied by UV-Vis spectrophotometer and fluorescence spectrophotometer. The reflectance of the nanorod array showed a absorption edge at the band gap of ZnO. The photoluminescence of nanorods array showed UV emission at room temperature. The intensity of emission showed dependence on nanorod diameter. The current-voltage characteristics showed rectifying behaviour. Further of Li and Al doped ZnO nanorods synthesized by thermal decomposition, the SEM and TEM image revealed the aspect ratio of the nanorods are 12-20. The photoluminescence of the nanorods showed blue emission 400-420 nm. This strong blue emission of undoped, Al and Li doped ZnO nanorod makes it potential candidate for the fabrication of blue lasers and related optoelectronic devices. Li was doped at five different concentrations in ZnO nanorods synthesized by thermal decomposition. The TEM image revealed the diameter of the nanorods are ~50 nm. The SAED images of nanorods showed nanocrystalline morphology. The PL spectrum revealed strong blue emission and optimum Li doping concentration fore green emission was found to be 7.5%. It is also concluded that the ZnO film prepared by sol-gel process emit in UV region while the nanorod crystals emit in blue region.
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References


