CHAPTER 3

UV-VISIBLE AND PL SPECTROSCOPY OF ZnO NANORODS AND NANOTUBES

3.1 Introduction

The energy gap ($E_g$) is an important feature of semiconductors which determines their applications in optoelectronics [1]. This wide band gap can be altered if the particle size of the system lies in the nanometric region. The large band gap coupled with its large excitonic binding energy has made it a potential candidate in light emitting diodes and LASERS in ultraviolet region [1, 2]. In order to use ZnO nanorods and nanotubes in an optoelectronic device, the performance of the device has to be adjusted by controlling their optical properties. Therefore fundamental knowledge about the ZnO nanorods and nanotubes is crucial for their applications in nanodevices. Many studies have shown that the band gap of ZnO nanorods and nanotubes depend on their diameter [3, 4]. Optical absorption edge at the ultraviolet end of the UV-Visible spectrum gives more insight into the band gap enlargement of nanorods and nanotubes due to quantum confinement [5, 6].

In the current renaissance of research related to ZnO, more attention is focused on the material’s near-band-edge optical properties for the development of improved ultraviolet emitters and detectors [1, 7]. While comparing the photoluminescence spectra of bulk ZnO and ZnO nanorods and nanotubes, one encounters a profound difference in the form of a wide below-band-gap-emission band, characteristic of one dimensional nanostructures of ZnO. Generally, ZnO exhibits two kinds of emissions: one is in the ultraviolet region corresponding to near band edge emission and the other in the visible region corresponding to deep level emissions with a peak in the range from 410 to 730nm.
The visible emission is usually considered to be related to various intrinsic defects produced during ZnO preparation and post treatment. Normally these defects are located at the surface of the ZnO nanostructures. The defects could affect the position of the band edge-emission as well as the shape of the luminescence spectrum. There have been several reports with strong UV and weak defect emissions in ZnO nanostructures and in some cases only defect emission is observed or the UV emission is much weaker when compared to the defect emission [5-9]. The intensity ratio of UV emission to visible emission ($I_{UV}/I_{VIS}$) is usually employed as an important criterion to indirectly evaluate the quality of ZnO. Due to the unique optical properties, the absorption and emission spectroscopy of ZnO nanorods and nanotubes become an important topic.

### 3.2 UV-Visible spectroscopy

When a beam of light propagates through a sample which has the ability to interact with the electromagnetic radiation, part of the radiation is absorbed by the sample and rest of it is transmitted through the sample. In UV-Visible spectroscopy, light is used to populate the unoccupied electronic states of the sample and the transitions between the valence and conduction bands. The basic principle for this type of spectroscopy is to irradiate the sample with a continuous spectrum of light with intensity ($I_0$) in the ultraviolet and visible region. The absorption of light ($I$) depends on the absorption coefficient ($\alpha$), thickness of the sample ($t$), and wavelength ($\lambda$).

$$\frac{I}{I_0} = e^{-\alpha t} \quad \text{..........................................................} \quad (1)$$

When a molecule absorbs energy an electron is promoted from the Highest Occupied Molecular Orbital (HOMO) to Lowest Unoccupied Molecular Orbital (LUMO). It must
be noted that occupied molecular orbital with the lowest energy are the $\sigma$ orbitals, then at a slightly higher energy are the $\pi$ orbitals and non-bonding orbitals (those with unshared pair of electrons) at still a higher energy [10]. The highest energy orbitals belong to $\pi^*$ and $\sigma^*$ i.e. the unoccupied or as otherwise known as the anti bonding orbitals [10]. Figure 3.1 represents the electronic energy levels and corresponding transitions in UV-Visible spectroscopy. The schematic representation of UV-Visible spectrometer is shown in figure 3.2.

Fig 3.1 Electronic energy levels and transitions

UV-Visible absorption spectroscopy measures the percentage of radiation that is absorbed at each wavelength. Typically this is done by scanning the wavelength range and recording the absorbance. UV-Visible reflectance spectroscopy is ideal for characterising optical and electronic properties of many different materials such as films, filters, pigments. In many studies, the energy band gap studies of the materials have been reported using absorption spectra [11-13]. Due to low scattering in solid films, it is easy to extract the $E_g$ values from their absorption spectra knowing their thickness. However,
in colloidal samples, the scattering effect is enhanced since more superficial area is exposed to the light beam. This problem can be solved by studying the reflection spectra.

Fig 3.2 Block diagram of double beam UV-VIS spectrophotometer

In this study the UV-VIS measurements were made by a T 90 + PG equipment UK Spectrophotometer in the wavelength range of 190-900 nm. For the UV-visible absorption measurement, the as-grown ZnO samples were ultrasonically dispersed in distilled water before examination, using distilled water as the reference.

3.2.1 Band gap determination

Measurement of optical absorption spectrum in band gap semiconductors bears importance both theoretical as well as practical aspects [14]. Near to band gap absorption of photons, absorption coefficient $\alpha$ steeply increases with increasing the photon energy. The spectral absorption coefficient has been evaluated as

$$\alpha = \frac{4\pi k}{\lambda}$$  

(2)
Where \( k \) is the spectral extinction coefficient and \( \lambda \) is the wavelength of the absorbed photon. The optical band gap (\( E_g \)) of the sample can be estimated from the expression for transition

\[
\alpha E = A(E - E_g)^n 
\]

(3)

Where \( E = \frac{hc}{\lambda} \) is the photon energy, \( A \) is a constant, \( n \) is an index which assumes the values \( n=1/2 \) for allowed direct transition, \( n=3/2 \) for direct forbidden transition, \( n=2 \) for allowed indirect transition and \( n=3 \) for indirect forbidden transition. The value of the optical band gap is obtained by plotting \( (\alpha E)^{1/n} \) versus \( E \) in the high absorption range or near the band edge (\( E_g \)). The extrapolation of the straight line down to \( \alpha E=0 \) gives the photon energy value \( E = E_g \). In principle, there should be no absorption below the band edge and at the band edge it should steeply increase when the photon energy approaches to \( E_g \). But in practice, just below \( E_g \), \( \alpha \) starts increasing slowly with increasing photon energy. Urbach proposed an exponentially varying \( \alpha \), where \( \alpha = \alpha_0 \exp \left( \frac{E}{E_0} \right) \) with \( \alpha_0 \) is a constant and \( E_0 \) is an empirical parameter. Any defect or disorder in the system gives rise to localised energy levels within the band gap or discrete states. This is the band tailing effect.

### 3.2.2 Band gap energy of ZnO nanorods and nanotubes

The band gap energy of ZnO nanorods and nanotubes can be determined using the UV - Visible reflectance spectra as shown in figure 3.3.
Fig 3.3 Reflection spectra of ZnO nanorods and nanotubes

This spectrum resolves the excitonic or interband (valence-conduction band) transition of ZnO and allows us to calculate the band gap energy using Tauc relation [15]. According to Tauc relation, the absorption coefficient, $\alpha$, for direct band gap material is

$$
\alpha \nu = A(h\nu - E_g)^n
$$

Where $E_g$ is the energy gap, $h\nu$ is the energy of photon, $A$ is a constant and $n$ is an index which assumes the values depending on the nature of the electronic transition responsible for the reflection. For ZnO, $n=1/2$ which is responsible to the allowed direct transition. The absorption coefficient, $\alpha$, is directly proportional to

$$
\ln\left[\frac{(R_{max}-R_{min})}{(R-R_{min})}\right] \frac{1}{n}
$$

where $R_{max}$, $R_{min}$ are the maximum and minimum values of reflectance, $R$ is the reflectance at a given photon energy, $h\nu$.

Graphs between $[h\nu\ln\{(R_{max}-R_{min})/(R-R_{min})\}]^{1/n}$ vs $h\nu$ have been plotted as in figure 3.4.
Fig 3.4 Band gap determination of ZnO nanorods and nanotubes

The extrapolation of straight line to $(\alpha h \nu)^{1/n} = 0$ gives the value of energy band gap. The band gap energy obtained from reflectance spectra are $3.43 \pm 0.0003$ eV and $3.47 \pm 0.0002$ eV for ZnO nanorods and nanotubes, respectively. The experimental results show that the band gap energy increases with increasing the surface to volume ratio or the reduction of the diameter.

The band gap increases along with the decrease of the radius due to the radial confinement. XRD analysis shows that the ZnO nanorods and nanotubes grow along $z$ direction or [0001] direction. Almost all 1D ZnO nanostructures are growing along [0001] direction with six facet $[1\overline{0}10]$ surfaces with low surface energy. To gain an insight into the band-gap widening effect in ZnO nanorods and nanotubes, first briefly discuss the electronic structure of ZnO$[1\overline{0}10]$ surface [16]. The valence and conduction
bands near the Fermi level are primarily of Zn–O bond-orbital (mainly O 2p states) and antibond-orbital (mainly Zn 4s states) character, respectively. The conduction band possesses a delocalized distribution in the x-y plane and a large dispersion along z direction due to the radial confinement [14]. Also the energy of the conduction band increases substantially due to the radial confinement of ZnO nanorods and nanotubes. Conversely, the surface state in the valence band can be easily confined in the x-y plane and has weak dispersion along z. The p-like dangling bond states of oxygen atoms at the surface interact with each other, resulting in the dispersion of the corresponding energy levels. Thus, the p-like orbitals which are responsible for the quantum confinement effect, separate the energy levels hence an increase in the band gap [14].

Figure 3.5 presents the optical absorption spectrum of ZnO nanorods and nanotubes at room temperature. The UV-visible spectrum shows a strong exciton absorption peak at 366 nm and 362 nm for ZnO nanorods and nanotubes, respectively and blue shifted relative to the bulk exciton absorption (380 nm) [17] as a result of the quantum size effect. According to the quantum confinement theory [18], the electrons in the conduction band and holes in the valance band are confined spatially by the potential barrier of the surface. Because of the confinement of electrons and holes, the optical transition energy from the valence top to the conduction bottom increases and the absorption maximum shifts to the shorter wavelength region. The stronger exciton effect is an important character of quantum confinement in nanosemiconductors, in which the electrons, holes and excitons have limited space to move and their motion is possible for definite values of energies. Thus, their energy spectrum is quantized.
Fig 3.5 Absorption spectra of ZnO nanorods and nanotubes

As a result, the continuum of states in conduction and valence bands are broken down into discrete states with an energy spacing relative to band edges which is approximately inversely proportional to the square of the particle size and reduced mass [19]. The highest occupied valence band and the lowest unoccupied conduction band are shifted to more negative and positive values respectively resulting in the widening of band gap, which leads to the effective band gap larger than its bulk value. Thus, there will be a blue shift in the absorption spectra with reduction in crystallite size as observed in the present case (chapter 2). The highly confined carriers in the nanotubes enhance the coupling interaction with each other, thus the excitons bounded becomes very stronger. This is the reason why the absorption peak of ZnO nanotubes has a slight blue shift compared with that of nanorods. This is in very good agreement with the previously reported results [20].
3.3 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is a useful technique for the study and characterisation of materials and dynamical processes occurring in materials, specifically the optical properties of the materials. This technique involves measuring the energy distribution of emitted photons after optical excitation. This energy distribution is then analysed in order to determine the properties of material, including defect species, defect concentrations, possible stimulated emission etc. It is widely recognized as a useful tool for characterising the quality of semiconductor materials as well as for elucidating the physics which may accompany radiative recombination. PL is useful in quantifying (1) optical emission efficiencies, (2) composition of the material (alloy composition), (3) impurity content, and (4) layer thickness (i.e. quantum well thickness) etc.

PL measurement is a kind of powerful and nondestructive technique, through we can obtain a variety of material parameters, which will be introduced respectively as follows:

(1) Band gap determination

It is well known that the radiative transition between the band gap in semiconductors is the most important one. So the PL measurement not only helps us determine the band gap of a semiconductor especially for a new compound semiconductor, but also guides us to accomplish the band gap engineering, which is particularly significant for prompting the practical applications of a semiconductor in the industry.

(2) Impurity levels and defect detection

Usually, there are always some native defects and impurities in even pure semiconductors, which will form some localized defect levels between the band gap. These defect levels certainly participate in the radiative transitions. The PL energy associated with these
levels can be used to identify specific defects, and the PL intensity can be used to provide relative information concerning their concentration.

(3) Recombination mechanisms

It is well known that the "recombination" include both radiative and non-radiative processes due to the existence of the surface and defect levels in the band gap. The PL intensity depends on the power of photo excitation and temperature, which is determined by the dominant recombination process. Thus, analyzing power/temperature/time dependent PL spectra will definitely help us understand the underlying physics of the recombination mechanism.

(4) Material quality

The emission process in a material shows an obvious evidence of the existence of the defects. It is clear that these defects are harmful for device performance. PL measurement will help us to judge the optical quality of the material is good or not.

The schematic representation of PL spectrometer is illustrated in figure 3.6. When light of sufficient energy is illuminating in a material, photons are absorbed and excitations are created. These excited carriers relax and emit a photon. Then PL spectrum can be collected and analyzed. However, only the energy of photons is equal to or higher than the band gap, the absorption can happen in materials. Therefore, we have to choose different excitation source to do the measurements according to different material with different electronic band structure.
Fig 3.6 Schematic representation of PL spectrometer

The PL peak positions reveal transition energies and the PL intensity implicates the relative rates of radiative and non-radiative recombination. We also can change other external parameters during the PL measurement, such as temperature, excitation power and applied external perturbation such as magnetic field and/or electrical field and/or pressure, which can help us further understand the electronic states and bands.

In this study the PL spectroscopy measurements were performed at room temperature under a 325 nm UV fluorescent light excitation using a LS 45, Perkin Elmer Fluorescence Spectrometer with a Xe lamp. The emission wavelengths are obtained with an accuracy of 1 nm.

3.3.1 PL Spectra of ZnO nanorods and nanotubes

The room temperature photoluminescence (PL) spectra of ZnO nanorods and nanotubes are shown in figure 3.7. The spectrum of as prepared nanorods and nanotubes mainly consists of a strong UV emission peak and relatively weak defect emission peak. The UV emission peak of ZnO nanorods centered at 390 nm (3.16 eV) with FWHM of 11 nm and that of nanotubes is located at 381 nm (3.25 eV) with FWHM of 14 nm. There is a difference between the UV excitonic emission of the nanorods and the nanotubes. The
wall thickness of the ZnO nanotubes is thinner than the section diameter of the nanorods, which confines the exciton movement in the wall of the ZnO nanotubes. Due to this high quantum confinement effect, the UV emission of nanotubes shifts more towards the higher energy than the nanorods. The typical emission peak in UV region can be assigned as a near band edge emission (NBE) of ZnO, originating from the direct exciton recombination [21]. The emission peaks at 417 nm (2.96 eV), 446 nm (2.78 eV), 483 nm (2.58 eV) and 526 nm (2.38 eV) in the violet, blue and green regions are the defect related emissions observed in ZnO nanorods and nanotubes. These deep-level emissions are related to a radiative transition from donors \([\text{Zinc interstitial (Zn}_i\text{), Oxygen vacancy (V}_o\text{)}]\) to acceptors \([\text{Zinc vacancy (V}_\text{zn}\text{), oxygen interstitial (O}_i\text{)}]\) [8]. The competition of radiative transitions from donors to acceptors and from free exciton and/or donor bound exciton to valence band determines the photoluminescence spectrum of ZnO.

Fig 3.7 PL spectra of ZnO nanorods and nanotubes
3.3.2 UV emission

The UV near band edge emission at room temperature is associated with the free exciton recombination. The excitonic effects in the ZnO nanorods and nanotubes are enhanced since electrons and holes are forced to be closer together. The relative size between the exciton radius and the diameter of rods and tubes are used to gauge the importance of size confinement effects. For ZnO crystal, the binding energy and radius of the ground state exciton are given by [22]

\[ E_{ex} = -\frac{m_r^*}{m_0 \varepsilon_r^2} R_y \approx 60 \text{meV} \]  \hspace{1cm} (5)

\[ a_{ex} = \frac{m_r^*}{m_0 \varepsilon_r} a_0 \approx 5 \text{nm} \]  \hspace{1cm} (6)

Where \( R_y \) is the Rydberg energy, \( a_0 \) is the Bohr radius, \( m_o \) is the electron rest mass and \( m_r^* \) is the reduced mass.

\[ m_r^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*} \]  \hspace{1cm} (7)

Where \( m_e^* = 0.28 m_0 \), \( m_h^* = 0.55 m_0 \) and \( m_r^* = 0.19 m_0 \).

When the Coulomb energy is much larger than the confinement energy, the regime is called weak confinement and the particle size is much larger than Bohr radius [19]. The transition energy for the UV near-band edge emission peak at 390 nm for ZnO nanorod is 3.16 eV and at 381 nm for ZnO nanotube is 3.25 eV. The free exciton emission peak of ZnO nanotube has a blue shift to that in the ZnO nanorods which indicates the enhancement of quantum confinement effects in the nanotube with its small diameter and hollow interior. As nanorods transformed into nanotubes, the energy of UV luminescence is shifted from 3.16 eV (390 nm) to 3.25eV (381 nm). The shift of band gap energy is...
related to the morphology. Hence the energy of UV emission known as near band edge emission is increased from 3.16 to 3.25 eV. The UV emission is shifted from 3.16 to 3.25 eV by the shift of optical band gap from 3.41 to 3.47 eV and it clearly indicates that the origin of UV emission is the near band edge emission. A blue shift of UV emission is observed with the transformation of nanorods into nanotubes which are attributed to quantum size effects.

3.3.3 Defect emission

Room temperature PL spectra of ZnO exhibit a number of different peaks in the visible region, which can be attributed to the defect emission. Different calculations of the native defect levels in ZnO [23] and emission lines at 405, 420, 446, 485, 510, 544, 583, 640 and 700 nm have been reported [24]. The mechanism of deep level emission has not been clearly delineated. Wu et al. [25] attributed the violet, green and yellow emissions to the radiative recombination of delocalized electrons close to the conduction band with deeply trapped holes in $V_{zn}^-$, $V_o^+$ and $O_i^-$ centers respectively, while blue peak is recently observed in thin films and nanostructures due to zinc interstitials. However, the origin of the green emission is the most controversial one. The green emission is commonly referred to a deep-level or a trap-state emission. Vanheusden [26] proposed that the green emission is the recombination of $V_o$ electrons with photo excited holes in the valence band. Reynolds et al. [27] suggested that the green luminescence is a phonon assisted transition between two shallow donors and a deep acceptor. Lin et al. [28] assigned the green luminescence to an electron transition from the bottom of the conduction band to the anti site defect $O_{zn}$ level. Xu et al. [29] suggested that the green
emission come from the donor levels \( Z_{ni} \) to acceptor levels \( V_{zn} \). Generally, green emission peak is observed in oxygen deficient ZnO samples.

In the ZnO growth, there are several intrinsic defects such as Zinc interstitials (\( Z_{ni} \)), Oxygen vacancies (\( V_{o} \)), zinc vacancies (\( V_{zn} \)), oxygen interstitials (\( O_{i} \)) and oxygen antisite (\( O_{zn} \)). However, zinc interstitials (\( Z_{ni} \)) and oxygen vacancies (\( V_{o} \)) are the dominant defects in undoped ZnO. In ZnO, oxygen has tightly bound 2p electrons and Zn has tightly bound 3d electrons, which sense the nuclear attraction efficiently. The first principal calculation found that the Zn3d electrons strongly interact with the O2p electron in ZnO [30]. Since the center energy of the visible emission is smaller than the band gap energy of ZnO, the visible emission cannot be ascribed to the direct recombination of a conduction electron in the Zn3d band and a hole in the O2p valence band. Therefore the defect emission must be related to the localized levels in the band gap.

In the present study four emission peaks are located at 417, 446, 483 and 526 nm. The violet emission centered at 417 nm (2.96 eV) corresponds to the electron transition from the level of interstitial Zn to the valence band [31]. The energy interval from the level of interstitial Zn to the valence band is exactly consistent with the energy of the violet emission observed in our experiment. The luminescence peaks at 446 and 483 nm are responsible to blue emission, originated from the electron transition from the shallow donor level (ionized oxygen vacancies/zinc interstitials) to the top of the valence band [32]. Oxygen vacancies can produce two defect donor levels and the shallow donor level locates below the conduction band about 0.3 to 0.5 eV. The energy interval from the shallow donor level to the top of the valance band is about 2.8 eV, which is consistent with the photon energy of the blue emission observed in this study.
In ZnO nanorods and nanotubes a weak green emission is observed at 526 nm (2.38 eV). A characteristic green emission peak of ZnO has been observed at 2.4 eV [25]. The green emission in ZnO is commonly referred to the radiative recombination of photo-generated holes in the valance band with electrons occupying the oxygen vacancies [26]. However the donor level Z_{ni} and acceptor level V_{zn} of hydrothermally grown ZnO nanostructures are located nearly at 0.5 and 3.06 eV below the conduction band edge, respectively [23]. Therefore the calculated energy of green emission in the present study is more reliable with the argument that this emission is ascribed to the electron-hole recombination of transitions from the donor levels Z_{ni} to acceptor levels V_{zn}. As per the above observation it concludes that the prepared ZnO nanorods and nanotubes have potential application in the violet-blue emission region.

3.3.4 Temperature dependence of UV and visible emission

Figure 3.8 and 3.9 shows the PL spectra of ZnO nanorods and nanotubes annealed at different temperatures, respectively. The intensity of UV emission is found to decrease with increasing the annealing temperature. As temperature increases large number of singly and doubly ionized oxygen vacancies are produced on the surface of nanorods and nanotubes and the radiative emission via these surface states quench the band edge emission appreciably. Figure 3.8 and 3.9 also shows that the position of UV emission is shifted towards the lower energy side, which results from the formation of defect related shallow binding excitons in the samples during high temperature annealing. The intensity ratio of UV to visible emission (I_{UV}/I_{VIS}) is strongly dependent on the annealing temperature. At room temperature, the intensity ratio of UV to visible emission (green) is 2.17 for nanotubes and 2.39 for nanorods. It is observed that ZnO nanorods have
excellent optical quality compared to ZnO nanotubes because nanotubes possess plentiful defects owing to their large surface to volume ratio.

Fig 3.8 PL spectra of ZnO nanorods annealed at different temperatures

Fig 3.9 PL spectra of ZnO nanotubes annealed at different temperatures
3.3.5 Weak confinement regime (R>>\textsubscript{a_{ex}})

The dimension of nanorods and nanotubes are found to be larger than the exciton Bohr radius, therefore consider these as semiconductor quantum rods/tubes and propose an approximation to estimate the transition energy of that in the weak confinement regime [19]. On solving the Schrödinger equation, we get the energies of possible related optical transitions as

\[ E_n = E_g - E_{\text{exc}} + \frac{\hbar^2 \pi^2 n^2}{2MR^2} \] \hspace{1cm} (8)

The third term in equation (8) is determined by the ground states of the quantized energy levels above the conduction band and below the valence band. Where M is the total mass of the electron-hole pair or exciton, R is the position of center of mass and n is the quantum number. The second term in equation (8) is related to the binding energy of the exciton in the nanorods/nanotubes, which is modified from the bulk by size confinement effects.

\[ M = m_e^* + m_h^* \]

The energy of (n+1)\textsuperscript{th} optical transition is,

\[ E_{n+1} = E_g - E_{\text{exc}} + \frac{\hbar^2 \pi^2 (n+1)^2}{2MR^2} \] \hspace{1cm} (9)

\[ E_{n+1} - E_n = \alpha(n + 1/2) \] \hspace{1cm} (10)

Where \[ \alpha = \frac{\hbar^2}{4MR^2} \] \hspace{1cm} (11)

For ZnO nanorod of average diameter R= 34 nm,

\[ \alpha = \frac{\hbar^2}{8m_oR^2} = 3.08 \times 10^{-4} \text{ eV} \]
Where the rest mass of electron is, \( m_0 = 9.1 \times 10^{-31} \)

When \( n=1 \), the energy of first optical transition is

\[
E_1 = E_g - E_{exc} + \frac{\alpha}{2} = 3.31\text{eV}
\]

Where the bulk band gap energy of ZnO is 3.37 eV and the exciton binding energy is 60 meV. Assume that the emission peak at 390 nm (3.16 eV) for nanorods results from the transition from a higher energy level corresponding to quantum number \( n \) to the lowest one corresponding to \( n=1 \). The transition energy from \( n \) to 1 for nanorods is

\[
E_n - E_1 = \frac{\alpha}{2} (n^2 - 1)
\]

\[
\frac{\alpha}{2} (n^2 - 1) = 3.16\text{eV}
\]

\( \alpha = 3.08 \times 10^{-4} \text{eV} \) and \( n = 143 \)

For ZnO nanotube of average diameter \( R = 21 \text{ nm} \), the emission peak at 381 nm (3.25 eV) results from the transition from a higher energy level \( n \) to the lowest \( n = 1 \)

\[
\frac{\alpha}{2} (n^2 - 1) = 3.25\text{eV},
\]

\( \alpha = 8.077 \times 10^{-4} \text{eV} \) and \( n = 88 \)

Similarly for other emission peaks of ZnO nanorods and nanotubes, transitions are identified based on this model and is shown in figure 3.10.
Fig 3.10 energy level diagram showing the transitions corresponding to the observed peaks in the emission spectrum of ZnO nanorods and nanotubes.

The energy level diagram shows that the excitons are more confined in ZnO nanotubes rather than nanorods.

3.4 Conclusions

In this chapter the absorption and emission properties of ZnO nanorods and nanotubes are thoroughly investigated by UV-visible and photoluminescence spectroscopy. The band gap energy calculated from UV-reflectance spectra are 3.43 eV and 3.47 eV for ZnO nanorods and nanotubes, respectively. As ZnO nanorods transformed into nanotubes, the band gap energy start to increase. The higher band gap energy of ZnO nanotubes indicates the quantum confinement effect is dominant in
nanotubes rather than nanorods due to its large surface to volume ratio. The absorption peaks of nanorods and nanotubes have a blue shift compared with that of the bulk. The observation has been attributed to that of the changing morphologies which strongly influence the absorption properties. Both nanorods and nanotubes demonstrate strong UV-emission at 390 nm and 381 nm, respectively and weak defect emissions in the visible region. The strong $I_{UV}/I_{VIS}$ ratio shows that both nanorods and nanotubes have good optical quality. Visible emission indicates that the as prepared ZnO nanorods and nanotubes are potential material in the violet-blue region. The different emission peaks related to transitions from different excited state energy levels of exciton to ground state by modeling it in weak confinement regime using Schrödinger equation. The energy level diagram gives the insight that excitons are more confined in ZnO nanotubes rather than ZnO nanorods.

3.5 References


5. Lili Wu, Youshi Wu, Wei Lu, Preparation of ZnO nanorods and optical characterizations, Physica E 28 (2005) 76.


