

EFFECT OF QUANTUM CONFINEMENT, SURFACE STATES AND EXCITONIC
ENERGY LEVELS ON PHOTOLUMINESCENCE OF ZINC OXIDE
NANOSTRUCTURES

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To my parents, teachers,
wife, brothers, sisters and friends

ACKNOWLEDGEMENT

Universiti Teknologi Malaysia has given me great experiences and opportunities from various aspects. I would like to thank all those who supported me to finish the compulsory master dissertation.

Special thanks are to Associate Prof. Dr. Sib Krishna Ghoshal, my supervisor for his support, guidance, tolerance and humility in sharing his knowledge and precious time to discuss my thesis.

I wish to thank my parents for raising me as I am now, my wife for her love and patience, my brothers, sisters and friends for all their encouragement.

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ABSTRACT

Nanostructuring of semiconductors is a novel means of developing new electronic and optoelectronic devices. The discovery of room-temperature visible photoluminescence (PL) from ZnO nanostructures has stimulated much interest in these particular kinds of nanoclusters and in small semiconductor particles. The possibility of tuning the optical response of ZnO nanomaterials by modifying their size has become one of the most challenging aspects of recent semiconductor research. It is established that quantum confinement (QC) can modify the energy gap that results visible luminescence as experimentally observed. Despite numerous proposed models, experiments and simulations to explain the luminescence, the mechanism of visible PL is far from being understood. The QC alone cannot interpret the essential features of the PL. The porous ZnO NWs and nanocrystalline with passivated surface has received extensive attention. Optical gain, observed in ZnO-NWs has given further impulse to this research. We develop a phenomenological model by combining the effects of surface states and QC. The size and shape dependent band gap and photoluminescence (PL) intensity for nanowires (NWs) with diameter ranging from 1.0 to 6.0 nm are calculated. By controlling a set of fitting parameters it is possible to tune the PL peak and intensity. It is found that the gap decreases for increasing NWs size. So both QC and surface effects in addition to exciton effects determine the optical and electronic properties of ZnO NWs. Visible luminescence is due to radiative recombination of electrons and holes in the quantum confined nanostructures. The role of surface states, exciton and QC effects on the gap energy and room temperature PL is understood. The results are in conformity with other model calculations and experimental observations. Our model can be extended to study the light emission from other nanostructures and may contribute towards the development of ZnO based optoelectronics.

ABSTRAK

Penstrukturan nano semikonduktor ialah cara baharu dalam membangunkan peralatan elektronik dan optoelektronik. Penemuan foto pendarcahaya (PL) nampak pada suhu bilik daripada struktur nano ZnO telah menimbulkan minat terhadap jenis-jenis gugusan nano dan zarah semikonduktor kecil tertentu. Kemungkinan bagi pelarasan tindak balas optik bahan-bahan nano ZnO dengan mengubah suai saiz bahan-bahan tersebut telah menjadi salah satu aspek yang paling mencabar dalam penyelidikan semikonduktor akhir-akhir ini. Kurungan kuantum (QC) terbukti berupaya mengubah suai jurang tenaga yang menghasilkan pendarcahaya nampak seperti yang dilihat melalui eksperimen. Meskipun pelbagai model, eksperimen dan simulasi yang dicadangkan untuk menerangkan mengenai pendarcahaya, mekanisme PL nampak masih belum difahami. QC sendiri tidak dapat mentafsir sifat-sifat PL. ZnO NWs berliang dan hablur nano dengan permukaan pasif telah menarik perhatian ramai. Gandaan optik, seperti yang diperhatikan pada ZnO-NWS telah memberikan lagi galakan kepada kajian ini. Kami membangunkan model fenomenologi dengan menggabungkan kesan keadaan permukaan dan QC. Saiz dan bentuk bersandar sela jalur dan intensiti PL bagi wayar nano (NWs) dengan diameter antara 1.0 hingga 6.0 nm telah dihitung. Dengan mengawal set parameter yang sesuai, pelarasan puncak dan intensiti PL boleh dilakukan. Sela didapati menurun dengan peningkatan saiz NWs. Selain daripada kesan eksiton, kedua-dua kesan permukaan dan QC juga menentukan sifat-sifat optik dan elektronik ZnO NWS. Pendarcahaya nampak adalah hasil daripada proses penggabungan semula sinaran elektron dan lubang dalam kuantum nano terbatas. Peranan keadaan permukaan, eksiton dan kesan QC pada sela tenaga dan suhu bilik PL telah difahami. Keputusan adalah selaras dengan pengiraan model dan pemerhatian eksperimen lain. Model kami boleh dilanjutkan untuk mengkaji pancaran cahaya daripada struktur nano lain dan boleh menyumbang ke arah pembangunan optoelektronik berasaskan ZnO.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Developing high quality direct band gap light emitting Zinc Oxide (ZnO) nanostructures for optoelectronic applications is a never-ending quest. In this chapter we discuss some properties of bulk as well as nanostructured ZnO to explain the process of photoluminescence (PL). The objectives, problem statement, significance, methodology and thesis structure are also included.

ZnO is a direct band gap, II-VI semiconductor compound with numerous uses in various fields because of its excellent optical, electronic and chemical properties. The wurtzite structure of ZnO with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm provides wide band gap and high excitonic binding energy suitable for optoelectronic devices. It is also characterized with a high breakdown voltage, high power operation, lower electronic noise, good ability to sustain large electric field and high temperature. Its direct band gap implies a higher probability of radiative recombination which is a two body process and hence more efficient than the three body process in indirect band gap materials. ZnO has been studied and characterized since 1935 or even earlier (Özgür *et.al*, 2005). Recently, much attention is attracted within the scientific community and renewed interest is generated due to the development of accurate growth technologies for the fabrication of high quality

single crystal and epitaxial layers. This allows the realization of ZnO-based electronic and optoelectronic devices (Coleman and Jagadish, 2006).

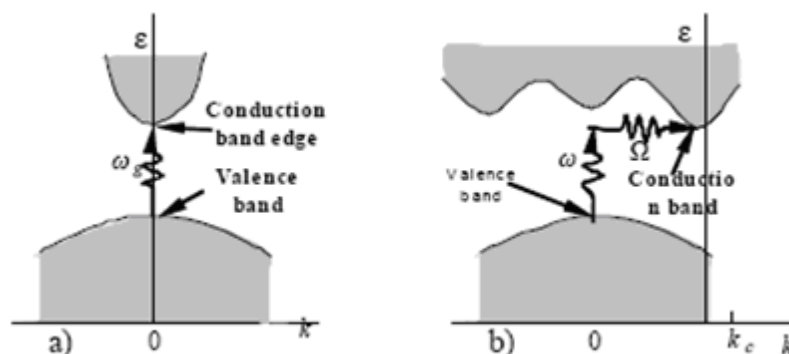


Fig. 1.0 Schematic representation of transition in (a) direct and (b) indirect band gap semiconductor.

Figure 1.0 shows the band to band transition in momentum space in the Brillouin zone for direct and indirect band gap materials. In indirect band gap SCs, a mismatch in momentum space between the electron and hole states make the transition phonon mediated. To conserve momentum, excitation and relaxation between the conduction band and valence band extremes require the assistance of a crystal lattice vibration. Radiative recombination of excited charge carriers is therefore a three body process and as a result, it is much less efficient than the analogous two body recombination in a direct band gap semiconductors. The low probability of radiative recombination in indirect band gap favors non-radiative decay processes, excited electrons generally lose energy as heat and not by emitting photons.

ZnO possess remarkable optoelectronic properties such as three exciton resonances due to spin-orbit coupling in the crystal field with a large oscillator strength and is a very attractive functional inorganic semiconductive material for optoelectronic and electronic applications (Irimpan *et al*, 2008, Yuan *et al.*, 2011). The direct band gap of 3.37 eV at room temperature, large exciton binding energy of 60 meV, availability of fairly high-quality bulk single crystals and high transparency ($> 80\%$) in the visible wavelength region make them viable for sundry applications. ZnO has several fundamental advantages over its chief competitor, GaN: (i) its free exciton is bound with energy 60 meV, much higher than that of GaN (21–25 meV);

(ii) it has a native substrate; (iii) wet chemical processing is possible and (iv) it is more resistant to radiation damage.

At ambient pressure and temperature ZnO crystallizes exist in wurtzite (B4) structure as shown in Fig. 1.1 (Özgür et al., 2005). This hexagonal lattice belongs to the space group $P6_3mc$, where two interconnecting sub-lattices of zinc (Zn^{2+}) and oxygen (O^{2-}) ions are arranged in such a way that each Zn^{2+} is surrounded by a tetrahedra of O^{2-} , and vice-versa. This tetrahedral coordination gives rise to polar symmetry along the hexagonal axis, the polarity is responsible for a number of the properties of ZnO, including its piezoelectricity and spontaneous polarization, and is a key factor in crystal growth, etching and defect generation. In single crystal wurtzite structure, 4 atoms per unit cell give rise to 12 phonon modes. These modes are important for understanding the thermal, electrical and optical properties of the crystal (Coleman and Jagadish, 2006).

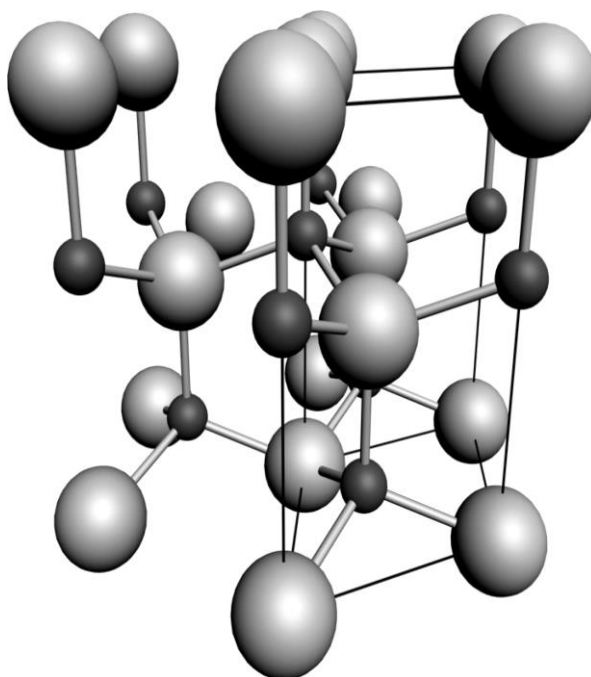


Figure 1.1: The unit cell of hexagonal wurtzite structure of ZnO. Large white spheres are oxygen and smaller black spheres are Zn atoms (Adapted from Coleman and Jagadish, 2006).

Researches on the optoelectronic materials involving the development of high and direct band gap material reveal that ZnO is a very promising candidate in this purpose because of its direct high energy band gap of 3.3 eV and large exciton binding energy of 60 meV at room temperature (Kar *et al.*, 2006; Zhu *et al.*, 2008; Al-Suleiman *et al.*, 2009). ZnO is one of the most important functional oxide semiconductors because of its unique properties and potential applications in manifold fields, such as transparent electronics, ultra-violet light (UV) emitter, surface acoustic wave (SAW) devices and spin electronics (Fan and Lu, 2006). ZnO is already widely used and is a key element in many industrial manufacturing processes including paints, cosmetics, pharmaceuticals, plastics, batteries, electrical equipment, rubber, soap, textiles, floor coverings to cite a few. Moreover, the radiation hardness of ZnO to MeV proton irradiation makes it an ideal candidate for space applications (Coleman and Jagadish, 2006).

ZnO doped with transition metals shows great potential for spintronic applications. It has also been suggested that ZnO exhibits sensitivity to various gas species, namely ethanol (C₂H₅OH), acetylene (C₂H₂), and carbon monoxide (CO), which makes it suitable for sensing applications. Furthermore, its piezoelectric property (originating from its non-centrosymmetric structure) makes it suitable for electromechanical sensor or actuator applications. Besides, ZnO is biocompatible which makes it suitable for biomedical applications. Last but not the least, ZnO is a chemically stable and environmentally friendly material. Consequently, there is considerable interest in studying ZnO in the form of powders, single crystals, thin films and nanostructures (Aleksandra and Yu, 2006).

ZnO has the additional advantage of being easy to grow and possessing the richest known family of nanostructures (Willander *et al.*, 2010). Our main interest is to examine the light emission from ZnO nanostructures. It is therefore customary to introduce the essential features of such nanostructures.

1.2 ZnO Nanostructures

Studies of scientific research and publications reveal that when matter is composed of only a few atoms (nanometric dimension) new physical and chemical properties begin to emerge in the behaviour of the material. This observation providing an impetus to the study of nanoparticles has become a very active field of research. Lately, a variety of techniques are used for creating nanostructures with varying degree of quality, speed and cost.

Since 1960 synthesis of ZnO thin films has been an active field because of their applications as sensors, transducers and catalysts. Size reduction causes the emergence of novel electrical, mechanical, chemical and optical properties which are largely believed to be the result of surface and quantum confinement effects (Zhong, 2006). Nanoscale zinc oxide structures are attractive due to its exceptional optoelectronic (Samantha *et al.*, 2009), piezo-electric (Kong and Wang 2003) and magnetic properties (Garcia *et al.*, 2007; Xu *et al.*, 2009). These are very much useful in optoelectronic, nano-electronic and spintronic device fabrications (Wang 2007; Iqbal *et al.*, 2009).

Different methods for the preparation of varieties of ZnO nanostructures are reported and their optical properties are investigated (Haranath *et al.*, 2009). These nanostructures with various shapes such as nanowires (quantum wires), nanoparticles (quantum dots), nanofilms (quantum films), nanobelts, nanorings, nanotubes, nanodonuts and nanopropellers, serve as ideal systems for studying transport mechanisms in low-dimensional systems. This renders immense benefit for understanding the fundamental phenomena in low-dimensional systems and also for developing new generation nanodevices with high performance and efficiency (Ozgur *et al.*, 2005). Figures 1.2 to 1.9 display the structures and morphologies of different ZnO nanostructures grown and characterized by various methods in recent years.

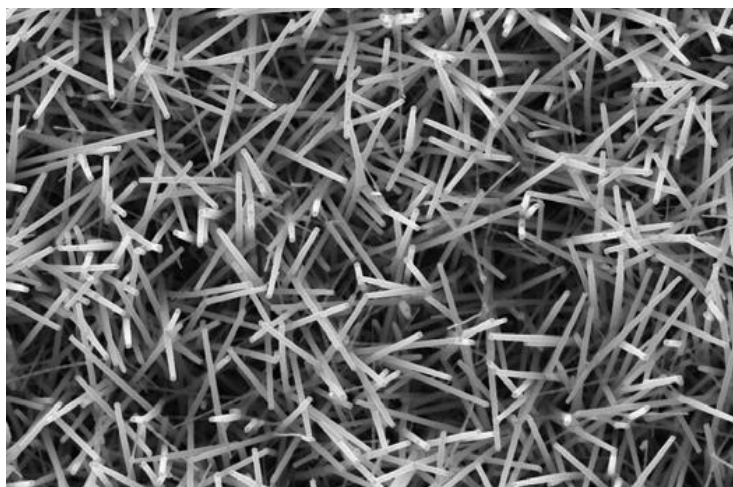


Figure 1.2. ZnO nanorods grown using gold as a catalyst (Adapted from Zhong, 2004).

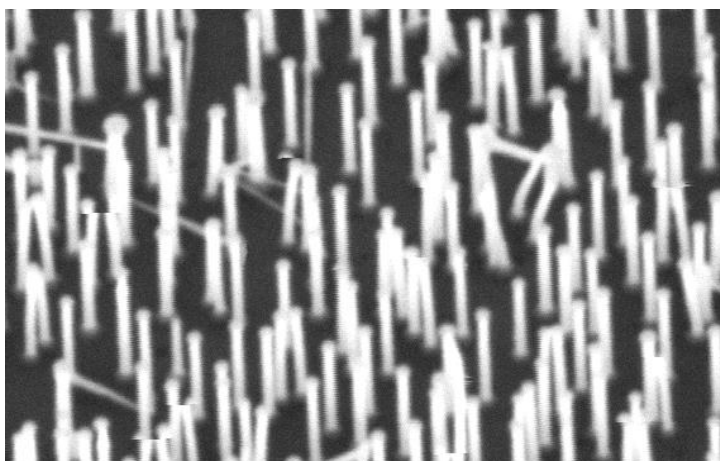


Figure 1.3. Aligned ZnO nanorods/nanowires epitaxially grown on ZnO substrate using Sn as a catalyst (Taken from Gao *et al.*, 2003).

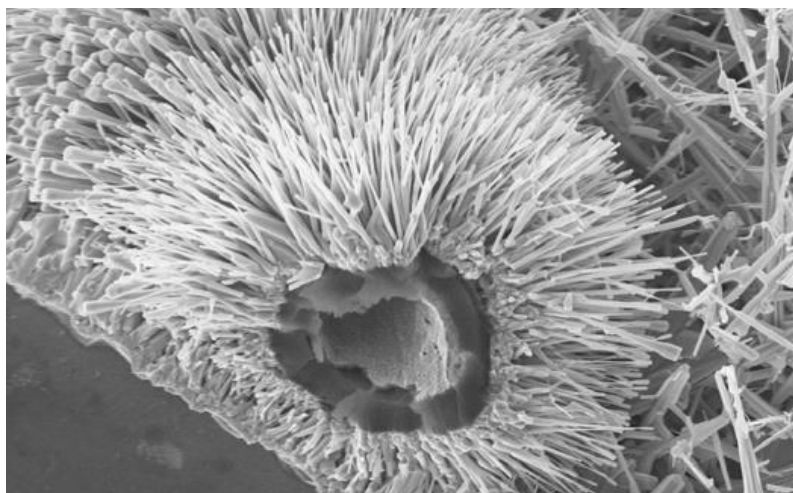


Figure 1.4. ZnO nanowires and nanonails grown following the cylindrical shape of a substrate (Adapted from Zhong, 2004).



Figure 1.5. TEM image of the as-synthesized ZnO nanobelts, showing uniform morphology (Adapted from Pan *et al.*, 2001).



Figure 1.6. SEM image of comb-like cantilever arrays of ZnO (Adapted from Wang *et al.*, 2003).



Figure 1.7. Seamless single-crystal nanorings of ZnO (Adapted from Kong *et al.*, 2004).

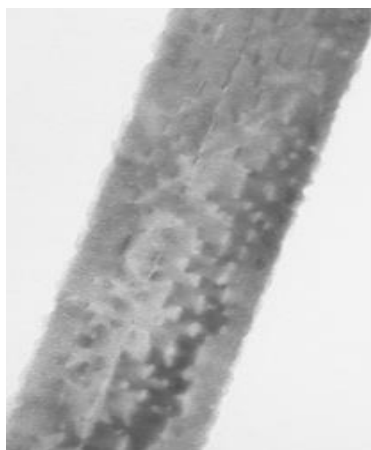


Figure 1.8. Bright-field and dark-field TEM images of ZnO nanobelts doped with Mn (Adapted from Ronning *et al.*, 2004).

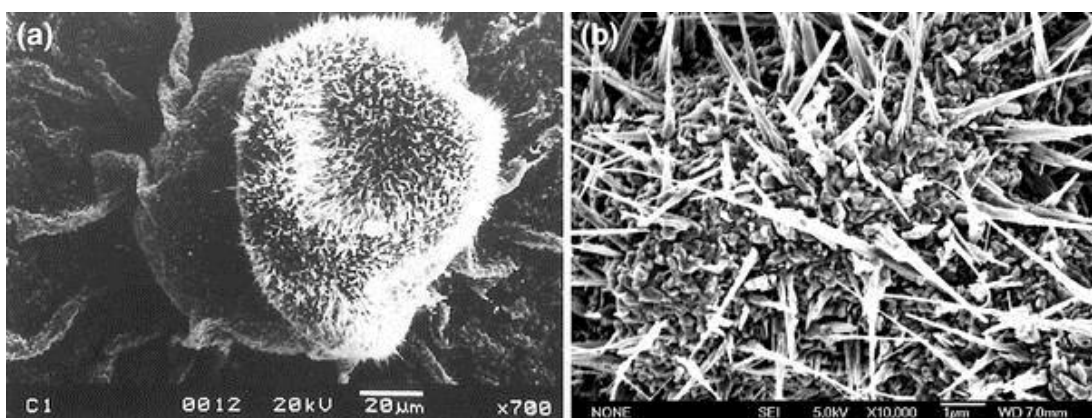


Figure 1.9. FESEM images of ZnO nanoparticles.(Adopted from Panda *et al.*,2009)

ZnO-based nanostructures, including nanowire arrays hold a host of opportunities for flat screen displays, field emission sources, gas, chemical and biological sensors and as UV light emitters and switches. Epitaxial layers and single crystals are important for the development of optoelectronic (blue and ultraviolet light emitters and detectors), piezoelectric and spintronic devices. They also holds much promise as a semi-conducting transparent thin film, which again are significant for solar cells, gas sensors, displays and wavelength selective applications. Existing technologies are being revolutionized with ZnO nanoparticles, which have led to the development of improved sunscreens, paints and coatings to name just a few (Özgür *et al.*, 2005).

In order to characterize the physical and optical properties, charge transport, etc., the detail knowledge on the density of states is very crucial. The density of states (DOS) depend on the dimensionality of the system and the energy versus the corresponding wave vector dispersion relation for the system at hand. Figure 1.10 schematically shows the modifications in the DOS as a function of dimension. Transformation from a 3-D bulk system to a 2-D thin film changes the DOS from a continuous parabolic dependence to a step like dependence. This is due to the quantization of carrier motion in the confined direction. Consequently, the optical absorption edge is shifted to higher energy with respect to the bulk and above the absorption edge the spectrum is stepped rather than smooth. It is the DOS that decides the coupling between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) to modify the oscillator strengths. The light emission in the visible range so called PL is indeed the manifestations of these DOS combined with surface states originate from the defects. It is important to discuss at this stage the origin of PL.

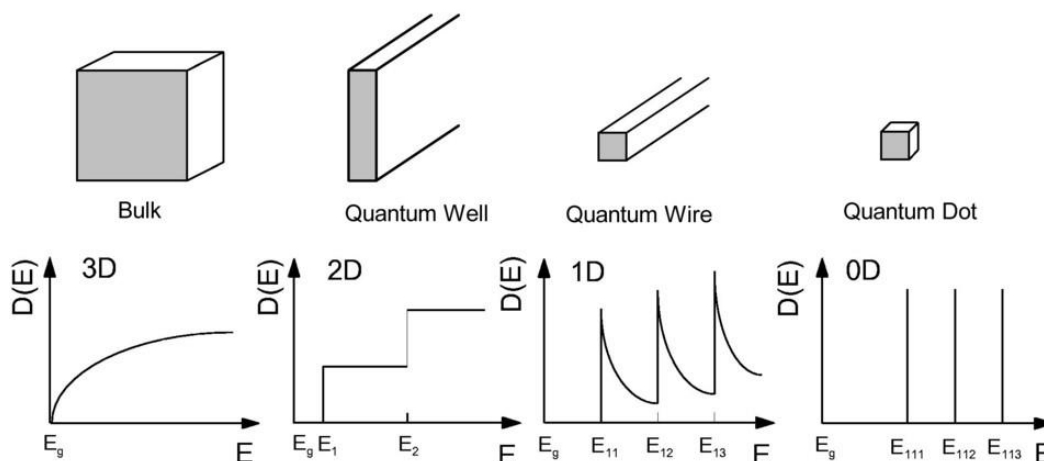


Figure 1.10. Density of states for various geometries of semiconductor materials : Bulk (3D), Quantum Well (2D), Quantum Wire (a 1D structure), and Quantum Dot (0D) (Scholz, 2009).

1.2.1 Photoluminescence

The study on the mechanism of room temperature visible PL is very important in optoelectronics especially in band gap engineering. This is because the optical devices such as detectors, lasers, sensors, optical switches and others need PL as prerequisite for their operation.

Electrons are excited across the band gap, from the valence band (HOMO) to the conduction band (LUMO) upon providing an appropriate energy greater than the band gap of the material. These excited electrons must decay back to the valence band by radiative or non-radiative thermal process. Non-radiative process is predominant routes to de-excitation when the electron-phonon coupling is strong. Phonon coupling provides quasi continuous states which electrons can occupy successively to de-excite to the ground state. In the absence of strong phonon coupling, the electrons have to make a radiative transition that often correspond to energies close to the visible region of the electromagnetic spectrum. This

phenomenon is known as PL. PL occurs in nanocrystals in a variety of ways via the recombination of electron-hole by involving the electronic states at the band edge, surface, defect and other trap states. States on doped impurity atoms in materials exhibit PL at different energies for the same un-doped impurity atoms (Rao *et al.*, 2004). Figure 1.11 shows the typical band structure of ZnO for nanocrystallites and single crystal calculated from the luminescence data in which the presence of wide band gap is evident. Figure 1.12 describes the PL processes involved in ZnO via direct recombination across the band gap and the deep states recombination involving oxygen defects.

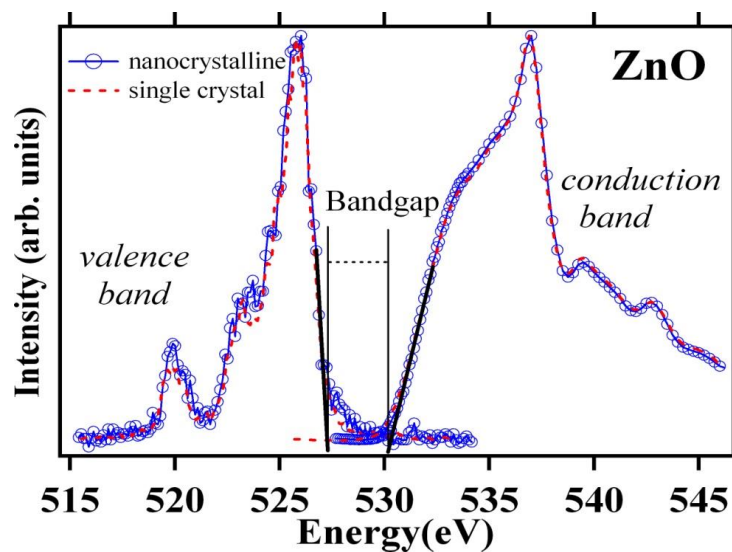


Figure 1.11: Band structures of ZnO nanocrystallite and single crystal (Adopted from Dong *et al.*, 2004)

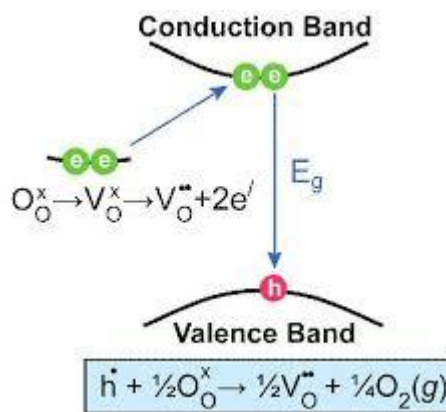


Figure 1.12: PL processes in ZnO (Adopted from Walsh *et al.*, 2011)

Electrons can de-excite radiatively by a transition from the bottom of the conduction band to the top of valence band. In the absence of any significant trap states, the energy absorbed by the system to create an electron-hole pair must be equal to the energy emitted, when the electron and the hole recombine without loss of any energy prior to the emission. The presence of un-quenched dangling orbitals at the surface or any defect states in the bulk, provide traps for the excited electrons and the holes for their preferable recombination. These orbitals possess energies in the band gap regions. Therefore, an electron excited to the conduction band can transfer itself non-radiatively to one of these surface or defect states before making radiative transition to a lower energy states. Likewise, a hole excited in the valence band can move in to the defect states depending upon the donor/acceptor character of the defect states. The net result of such non-radiative transfers of electrons and holes to lower energy states preceding to radiative recombination is that the emission occurs at energies much lower than the band gap energy of the nanocrystals in contrast to the band edge recombination considered earlier. This is often referred to as the red-shifted emission in nanocrystals.

Lately, several attempts are made to identify the origin of photoluminescence in ZnO nanostructures especially motivated by appreciable qualities in energy conversion and energy storage/harvesting (Sheng *et al.*, 2010). The large exciton binding energy paves way for an intensive near band edge

excitonic emission at room temperature and even higher temperature because this is 2.4 times larger than that of room temperature thermal energy ($K_B T = 25$ meV). Therefore, laser operation based on excitonic transition as opposed to electron-hole plasma is expected (Ozgur and Morkoc, 2006). Figure 1.13 displays the PL spectra of n-type bulk ZnO in which the peaks in the visible and Uv region are evident.

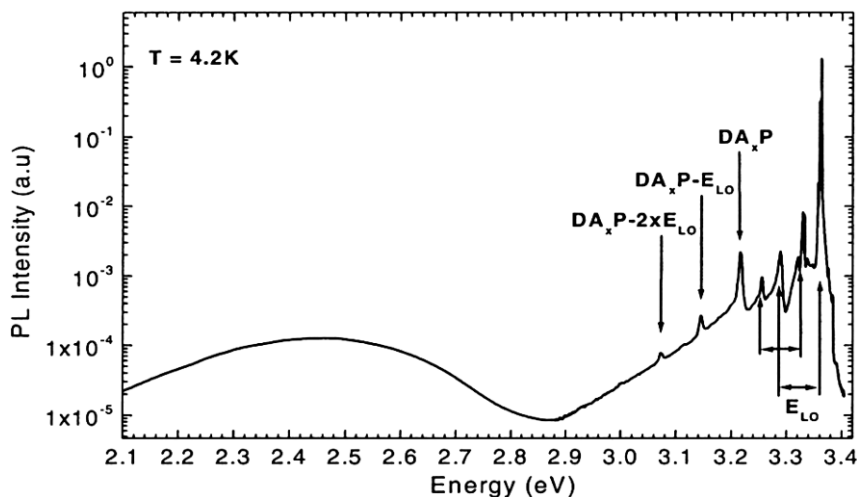


Figure 1.13: Photoluminescence spectra of n-type bulk ZnO (HeCd excitation) showing excitonic, donor acceptor pair and green-band emission. The longitudinal optical phonons with the corresponding phonon replicas are indicated on the figure (Adapted from Coleman and Jagadish, 2006)

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 450 to 730 nm. Out of the different reported emission peaks, the origin of the green emission is the most controversial. It is known that visible luminescence is mainly due to defects which are related to deep level emissions, such as Zn interstitials and oxygen vacancies. It is believed that the oxygen vacancies are responsible for the green luminescence in ZnO. Stoichiometric zinc oxide is an insulator that crystallizes with the wurtzite structure to form transparent needle-shaped crystals. It is virtually impossible to prepare really pure crystals of ZnO. It always ends up with voids and interstitial defects. When these crystals are heated, they tend to lose oxygen. For these reasons, ZnO shows *n*-type semiconducting properties (never *p*-type) with many defects, such as lack of oxygen and the excess of zinc. Oxygen vacancies occur

in three different charge states: the neutral oxygen vacancy (V_o^0), the singly ionized oxygen vacancy (V_o^*) and the doubly ionized oxygen vacancy (V_o^{**}) of which only V_o^* can act as the so-called luminescent center. The nanoparticles size dependent PL spectra of ZnO are shown in Figure 1.14.

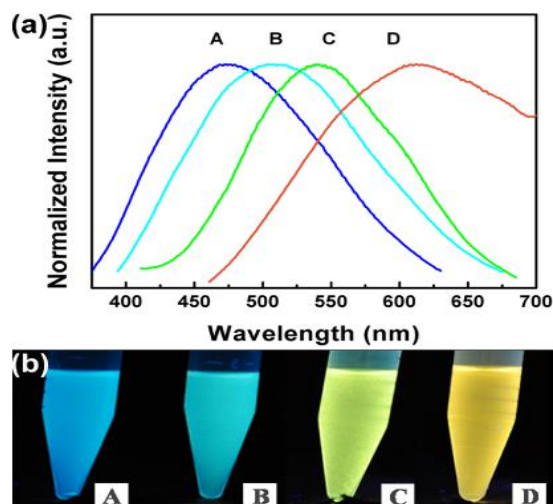


Figure 1.14: (a) PL spectra of ZnO nanoparticles for 4 different samples A-D with increasing particles sizes and (b) the visible colour of ZnO nanoparticles samples A–D under 365 nm UV light excitation. (Adopted from Lv *et al.*,2013)

In contrast to the UV spectra, visible fluorescence spectra of ZnO nanoparticles are sensitive to the preparation procedure and therefore, to environmental conditions. The concept of surface fluorescence-centers seems to be more realistic for nanoparticles. Researches indicate that the surface passivation via surfactant and polymer capping is an effective method to enhance the UV emission and quench the defect-related visible PL from nanosized ZnO. The effects of the method of preparation and surface passivation itself is an indication that the green emission is due to surface states. Despite extensive studies on PL no consensus in the literature still exists on the positions of the PL peaks of ZnO nanostructures and thin films or on their origin. Since the center energy of the green peak is *smaller* than the bandgap 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. The green emission must be related to the *localized* level in bandgap. The UV emission band is assigned to a direct *bandgap* transition. The UV emission

show shifts from 3.5 to 3 eV by the shift of optical bandgap from 4 to 3.5 eV and it clearly indicates that the origin of UV emission is the near band edge emission.

Figure 1.14 illustrates the room temperature PL spectra in the entire visible region of 400-700 nm under two different excitation wavelengths (300 and 320 nm) for monodispersed nanoparticles of ZnO prepared in double distilled water via chemical technique. The maximum emission is evidenced under the excitation of 320 nm in which the emission intensity is increased by 7 times compared to that of 300 nm excitation. The spectra reveal an intense band centered at ~ 558 nm (green) and a weak band at ~ 410 nm under the excitation wavelength of 320 nm. The broad visible PL band is reported earlier in bulk ZnO as well as in ZnO quantum dots.

It is demonstrated that the visible emission from nanocrystalline ZnO particles is due to a transition of a photo-generated electron from the conduction band to a deeply trapped hole. In ZnO nanoparticles along-with the visible green emission, UV excitonic emission is also reported. For efficient visible emission a step must be involved in which the photo-generated hole is trapped efficiently somewhere in the particle. The rate of this hole trapping must be much faster than the radiative recombination rate of the exciton emission. Because of the large surface-to-volume ratio in nanoparticles, efficient and fast trapping of photo-generated holes at surface sites are expected. A probable candidate for the trapping of holes are O^{2-} ions at the surface. Trapping of a photo-generated hole at the surface often agrees with the size-dependence of the emission intensities. The rate for a surface trapping process increases as the particle size decreases since the surface-to-volume ratio increases and thus the green emission is observed in all samples with reduced particle size (1-5 nm).

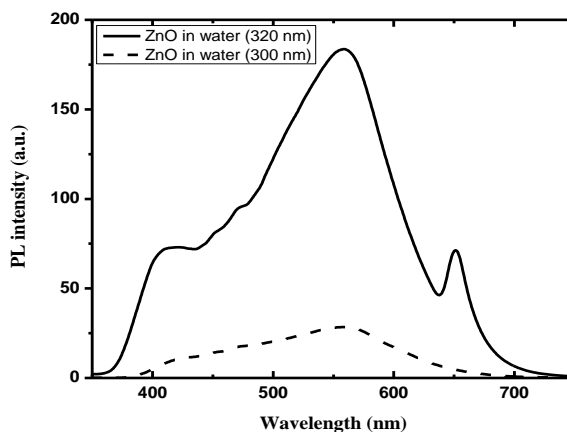


Figure 1.15 Photoluminescence (PL) spectra of ZnO nano-particles dispersed in double distilled water under 300 and 320 nm UV excitation wavelengths (Adapted from Kumbhakar *et al.*, 2008)

The effects of preparation methods and surface passivation itself is an indication that the green emission is due to surface states. For the uncapped ZnO nanoparticles, there exist abundant surface defects, the valence band hole can be trapped by the surface defects and then tunnels back into oxygen vacancies containing one electron to form V_o^{**} recombination center. The recombination of a shallowly trapped electron with a deeply trapped hole in a V_o^{**} center causes visible emission. The green emission is commonly referred to a deep-level or a trap-state emission attributed to the singly ionized oxygen vacancy and the emission results from the radiative recombination of photo-generated hole with an electron occupying the oxygen vacancy. ZnO is an *n*-type semiconductor and it means that most defects are Zn interstitials and oxygen vacancies. As particle size increases, a red shift of UV luminescence was observed from 3.5 to 3 eV because the optical energy gap decreases from 4 to 3.5 eV. The visible luminescence in the range of 420–530 nm (2.9–2.4 eV) is mainly due to surface defect states. The UV luminescence center is not related to visible luminescence center.

Raman spectroscopy is widely used to study the optical phonon spectrum modification in ZnO nanostructures as compared to bulk crystals. This presents a powerful tool for identifying specific materials in complex structures and for extracting useful information on properties of nanoscale objects. This provides the signatures of the vibrational modes of structures through inelastic scattering of

monochromatic excitation in the routine range of 200 to 4000 cm^{-1} . Structural vibrations are either infrared (IR) and/or Raman active. Therefore, Raman technique is mainly used to complement the IR measurements. Understanding the phonon spectrum change in wurtzite ZnO nanostructures is important because the optical phonons affect the light emission and absorption. The interpretation of the phonon peaks in the Raman spectrum from ZnO nanostructures continues to be the subject of debates. Several possible mechanisms for the peak position shifts, such as optical phonon confinement by the quantum dot boundaries, phonon localization on defects (oxygen deficiency, zinc excess, surface impurities, etc.) and laser-induced heating are responsible. Accurate interpretation of the Raman spectra from ZnO nanostructures is important for assessment of the material quality and nanostructure optimization for the proposed optoelectronic applications.

Wurtzite structure belongs to the space group C_{6v}^4 with two formulae units per primitive cell, where all atoms occupy C_{3v} sites. The Raman active zone-center optical phonons predicted by the group theory are $A_1+2E_2+E_1$. The phonons of A_1 and E_1 symmetry are *polar* phonons and, hence, exhibit different frequencies for the transverse optical (TO) and longitudinal optical (LO) phonons. In wurtzite ZnO crystals, the *non-polar* phonon modes with symmetry E_2 have two frequencies, E_2 (high) is associated with oxygen atoms and E_2 (low) is associated with Zn sublattice. The described phonon modes are reported in the Raman scattering spectra of bulk ZnO. Surface plasmons, excited by the interaction between light and electron plasma waves at the metal surface attracted intense scientific interest due to its applications in enhancement of the weak physical process, such as the absorption of light in molecules and Raman scattering intensities. Recently, SPs mediated emission in ZnO nanostructures has also been proven as an effective way to improve the quantum efficiency of light emitting materials and light emission diodes.

In most cases for ZnO nanostructures a large number of carriers are trapped by defects or impurities inside luminescence centers, resulting in a low efficiency of the light emission. Hence, to obtain highly efficient ultraviolet emission from the near band edge is one of most important issues for photonic applications of ZnO. The absence of a center of symmetry in its wurtzite structure, along with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties.

1.2.2 Electrical Properties

The electrical properties of ZnO are difficult to quantify due to large variance of the quality of samples available. The background carrier concentration varies a lot according to the quality of the layers but is usually $\sim 10^{16} \text{ cm}^{-3}$. The largest reported n-type doping is $\sim 10^{20} \text{ electrons cm}^{-3}$ and largest reported p-type doping is $\sim 10^{19} \text{ holes cm}^{-3}$. However, such high levels of p-conductivity are questionable and have not been experimentally verified (Look, 2006). The effective mass for electron and hole in ZnO are $0.24 m_0$, and $0.59 m_0$, respectively. The corresponding electron Hall mobility at 300K for low n-type conductivity is $\mu = 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and for low p-type conductivity is $5\text{--}50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Pearson et al., 2005).

1.2.3 Optical Properties

Optical properties of ZnO are heavily influenced by the energy band structure and lattice dynamics. Meyer et al., 2004 provided a comprehensive review on the optical properties and the influence of excitonic recombinations in bulk n-type ZnO. They introduced an inclusive treatment and analysis of the excitonic spectra of ZnO and assigned many defect related spectral features as well as donor–acceptor pair (DAP) emission. A presence of a broad defect related green band extending from 1.9 - 2.8 eV is a common optical feature of ZnO. The origin of this luminescence is far from being understood and has been attributed to a variety of different impurities and defects. Figure 1.16 shows a typical room temperature photoluminescence spectra of n-type ZnO nanowire film the low temperature (4.2 K) spectra is displayed in Figure 1.13. The excitonic DAP and extended green band emission are clearly seen. The phonon replicas produced from the longitudinal optical phonons (LO).

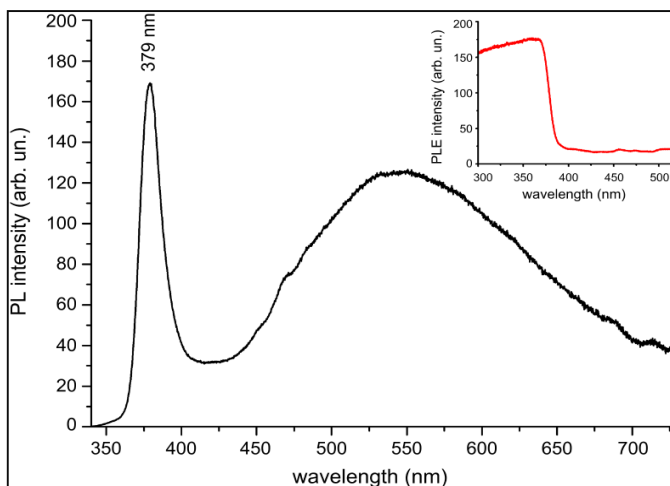


Figure 1.16 Room temperature photoluminescence spectra of *n*-type ZnO nanowire film. The photoluminescence excitation is shown in the inset (Adopted from Aga Jr. and Mu,2010)

Intensive researches are performed for fundamental understanding in the optical properties of ZnO. A number of detailed studies are dedicated to determine the refractive index and dielectric constants of ZnO (Yoshikawa *et al.*, 1997; Sun and Kwok, 1999; Ashkenov *et al.*, 2003). The measurements are all carried out using spectroscopic ellipsometry. The refractive index dispersion for both $E_{\perp c}$ and $E_{\parallel c}$ as measured and calculated by Yoshikawa and Adachi (Yoshikawa *et al.*, 1997) is shown in Figure 1.17. The refractive index of wurtzite ZnO is commonly given as $n_{\omega} = 2.008$ and $n_e = 2.029$ (Pearson *et al.*, 2005).

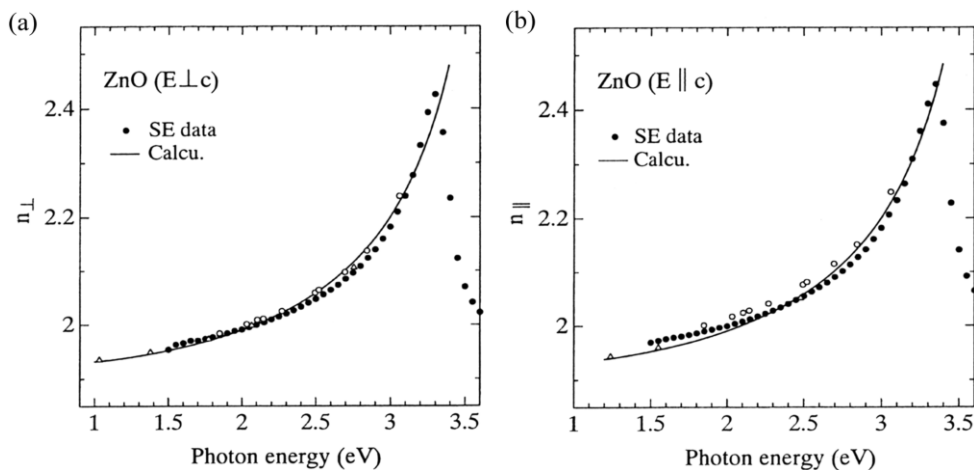


Figure 1.17: Refractive index dispersion of ZnO for $E \perp c$ and $E \parallel c$ along with the fundamental absorption edge. The solid circles represent the spectroscopic ellipsometry data and the solid line is calculated one (Adapted from H. Yoshikawa and S. Adachi, 1997).

1.3 Problem Statement

Intrinsic optical properties of ZnO need to be studied intensively using model and simulation for implementing photonic devices. Much experimental data exist but theoretical model and simulation are lacking. No comprehensive model exist that include the effect of quantum confinement, surface state and oxygen defects to explain the PL results accurately. Previous experimental studies attributed photoluminescence mechanism are due to quantum confinement and surface effects. It is, therefore, necessary to understand the effect of size and structure, as well as defect content in order to obtain an enhanced device performance. The strong emissions peaks are usually ascribed to band-to-band transition. Besides, the defect related emissions intensity shows increment with decreasing nanowire or nanoparticle diameter. The size and shape dependent PL response is far from being understood. The explanations of blue shift in the PL spectra and the enhancement of band gap with decreasing size of ZnO in different morphology are needed. The role played by the exciton in modifying the PL spectral features is not clearly understood.

1.3 Research Objectives

1. To develop a phenomenological model by combining the effects of quantum confinement, surface states and excitonic energy levels.
2. To determine the ZnO nanostructures size and shape dependent photoluminescence spectra.
3. To understand the mechanism of photoluminescence of ZnO nanostructures and compare our model result with experiment.

1.5 Significance of the Study

The fundamental understanding of photoluminescence mechanism due to quantum confinement, exciton states and surface defects in ZnO will contribute towards the development of optoelectronic devices particularly solar cells. Our model results will better explain the experimental data because PL is now used as a standard characterization technique to demonstrate the nanocrystalline nature of these samples. Studying PL and understanding its origin may be useful for various photonic applications. A comprehensive model and corresponding simulation has the ability to bridge the gap between theory and experiment. This model can further be extended for temperature and field dependent studies. The electroluminescence is also worth to look at using our model with modifications.

1.6 Research Method

We develop a model to describe the mechanism of light emission from ZnO nanostructures and fit our model to explain the experimental observation. The model includes the following:

1. Effective mass Approximation (EMA) and
2. Quantum confinement
3. Surface-recombination approximation
4. Excitonic states

We derive an analytical expression for size dependent energy band gap and PL intensity. Matlab Software is used to numerically calculate the PL spectra and band gap energy.

1.7 Organisation of the Dissertation

This chapter discusses the brief background, objectives, significance and the problem statement. Chapter 2 provides the detailed literature review on optical properties of ZnO nanostructures. Chapter 3 renders the methodology of our research, the model that we derived. The results and discussions are presented in Chapter 4 where the simulation on the model is performed. Finally, Chapter 5 concludes our results and show the future possibility of extending our model.

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