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**STUDIES OF THE ROLE OF DEFECTS ON THE
CHARACTERISTICS EMISSION PROPERTIES OF THE
ZINC OXIDE**

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2010

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List of Symbols and Acronyms

List of Symbols and Acronyms

A	peak value of the raman spectrum
x_c	wavenumber of the raman peak
Υ	halfwidth full maximum
a	describes the shape of the profile.
Υ_a	halfwidth at half maximum
Υ_b	half width at the half maximum
E_b	binding energy
h	peak height
M	lorentzian gaussian mixing
E_o	Peak/peak energy position
a_o	asymmetry index
H	Hamiltonian of the system
g	ground state
H_g	Hamiltonian of the system in ground state
e	excited state
H_e	Hamiltonian of the system in excited state
H'	coupling between the primary oscillators and bath modes with a coupling strength of cn_j
P_j	momentum of the j th nuclear mode of the primary oscillators
q_j	coordinate of the j th nuclear mode of the primary oscillators
m_j	mass of the j th nuclear mode of the primary oscillators
w_j	angular frequency of the j th nuclear mode of the primary oscillators
$\hbar\omega_{eg}$	energy difference in the two level system

List of Symbols and Acronyms

d_j	displacement of the j th nuclear mode in the electronic excited state
p_n	momentum of the j th nuclear mode of the bath oscillators
Q_n	coordinate of the j th nuclear mode of the bath oscillators
m_n	mass of the j th nuclear mode of the bath oscillators
ω_n	angular frequency of the j th nuclear mode of the bath oscillators
c_{nj}	coupling strength
$C(\omega)$	spectral density
λ	wavelength
ω_{LO}	wavenumber of the LO phonon
Υ	real part of the self energy
Γ	spectral distribution function
d	displacement of the atoms
$g(t)$	spectral response function
C''	spectral density function
β	$1/(k_B T)$ where T is the temperature
S	huang rhys factor
α	absorption coefficient
s	scattering factor
E_g	Energy Bandgap
E_p	phonon energy for indirect transition
n	order of transition
m^*	effective mass
μ	carrier's mobility
m_o	mass of electron

List of Symbols and Acronyms

δ	Dirac function
k_B	Boltzman's constant
$I_p(x)$	modifiex bessel function
R	raman scattering cross section
I_s	light intensity from surface
I_d	light intensity from from the depth of te surface.

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Abstract

ZnO is widely known to have an eminent potential to be applied as an UV laser material, which will play an important role in the laser applications. However, the quality of the UV emission of the ZnO can be easily influenced by the appearance of the green emission. Therefore, it is important to perform an in-depth study on the nature of the green emission.

This work reveals that the subtle differences in the energy of green emissions from ZnO cannot be neglected. The observed green emissions can be identified as two types of individual emissions, high energy and low energy. We first investigated the Quasi-LO phonon vibrational mode of the post-treated ZnO and we observed some variation of the Quasi-LO phonon mode. The variation can be related to specific defects that are strongly related to the observed green emissions.

Using physical analysis and multimode Brownian oscillator (MBO) modeling, we revealed the underlying mechanisms of the variant effects on the green emissions. They are associated with the specific defects and their locations. We studied in depth the influence of the surface band bending effect of ZnO. We determined from X-ray Photoelectron Spectroscopy (XPS) that Type I defects are likely to be oxygen vacancies which are near the surface of ZnO. As the oxygen vacancies are electron donors, they create an electron accumulation layer near the surface that leads the core level and the valence band shifting to higher binding energy. Thus the electronic transition between the oxygen vacancy defect energy state and the downwards band bending region result in the high

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energy green emission. On the other hand, we determined that the ZnO with Type II defects should be oxygen vacancies that reside beneath the surface. This is supported by a consistent relationship between the relative intensity of the low energy green emission and the crystallographic lattice contraction determined by X-ray Diffraction (XRD). This is also supported by the results from Raman Spectroscopy.

The green emission has either structured or structureless features at very low temperatures. The proposed surface band bending mechanism due to the presence of defects can possibly explain the origin of these features. We show that the Type I defects are likely to be associated with the structureless green emission of higher energy while the Type II defects beneath the surface of ZnO will cause a structured green emission of lower energy.

CHAPTER 1:

INTRODUCTION

1.1 Introduction to Zinc Oxide (ZnO)

Zinc Oxide is a II-VI wide bandgap compound semiconductor which has a bandgap energy of around 3.4 eV in the UV region. The crystal structure preferentially stabilizes as a hexagonal structure and could occur in minerals. It is interesting to note that scientific research on ZnO can be dated back as early as the 1930s but such activities soon declined. Recent decades have seen a quantum leap in many novel scientific discoveries and these have become the driving force leading to numerous groundbreaking technologies that are essential to newer state of art applications. A good example would be nanotechnology as the size dependent architecture plays a pivotal role in creating many novel electrical, mechanical, optical and chemical properties. Not limited to nanotechnology, the field of spintronics is a potential replacement for current electronic arena; and ZnO is foreseen as one of the likely candidate. These have opened up enormous new opportunities and revived the research activities in ZnO over the past decade.

1.2 ZnO - Challenges

To date, the most viable potential found in ZnO is its application as a UV laser material. This gives ZnO an important role in the huge market for laser applications such as laser printers, bar-code readers, image scanning, holography, coherent communications and telecommunications. Compared to the past, there

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is a pressing need to search for larger storage space to store information. UV laser has become attractive because it can possibly be used to boost the storage space by many folds in compact discs (CD) as compared to a red laser due to a shorter wavelength.¹ As a result, the optimization of the UV emission is being actively researched. A very important observation found in compromising the quality of the UV emission is the appearance of green emission.² However, the origin of green emission is not well understood, although it is widely known to be related to defects or impurities. There have been many reports pertaining this to date, but until now no conclusive agreement has been reached. Therefore, a good understanding of the origin of green emission is desirable. With this, strategies can then be proposed to effectively suppress green emission while achieving high quality UV emission.

1.3 Analysis Setbacks on the Green Emission Origins

Although Dingle *et. al.* have determined that the origin of the green emission could be due to the presence of copper impurities, it may be one but not the only origin of the green emissions.³ Vanhuesden *et. al.* have otherwise proposed that the origin could be other candidates.⁴ On the other hand, Reynolds *et. al.* did not find any contamination of Cu in their work and suggested that the origin of the green emission could be due to either zinc or oxygen vacancies.⁵ In fact, it was proposed with the support from Electron Paramagnetic Resonance (EPR) results that the origin of the green emission could be due to singly charged oxygen vacancies V_o^+ .⁴ In another study by Garces *et. al.*, it was suggested that this EPR result could have been misinterpreted and could be due to neutral shallow

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donors instead.² In fact, doubly ionized Vo^{++} centers,⁶ zinc vacancies⁷ or interstices⁸ have also been proposed as the origin of the green emissions.

While the experimental data and interpretation could be more convincing with the support of theoretical calculation, the origin of green emission proposed by many others using theoretical approaches are not consistent.^{7,9} For example, the origin of green emission using DFT can be due to either oxygen vacancies or zinc vacancies depending on the methodology of the DFT chosen. It is also noted that DFT has its own intrinsic problems such as the underestimated bandgap which could produce certain errors in the calculation.^{10,11} In addition, computational resources restrict the calculated size of the system of interest which is relatively a mismatch to the real system containing a dilute concentration of defects. This might lead to some errors that are difficult to identify.

1.4 Objectives and Scopes

The green emission observed is in fact made up of a diverse emission spectra with peak emission wavelengths ranging from ~ 510 nm (~ 2.43 eV)⁴ to ~ 550 nm (~ 2.25 eV).¹⁰ The variation may appear deceptively insignificant since after all it is still within the domain of green spectrum and that instrument configuration could also have contributed to these subtleties.¹¹ While it has often been erroneously assumed that the defects formed are homogeneously distributed, it has been noted that the green emission could be due to some specific defects that were particularly confined to the surface.¹² While there are some works which investigate the defects near the surfaces, there is little study

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on the emission from these defects. As ZnO is a wide bandgap semiconductor, the presence of surface band bending is inevitable and therefore, it is important to understand the interactions between the surface band bending, defects and the green emission.

The objective of this thesis, therefore, is to address the following:

- 1) Discriminate the effect of defects at different locations such as the defects (i) near and (ii) beneath the surface respectively [Fig 1.1]. The green emission due to the location of the defects in the materials will be investigated. The defects that are near

Fig 1.1: Schematic Diagram on the study of defects beneath and near the surface.

and beneath the surface will be known as the Type I and II defects respectively. Various advanced characterizations used in our work are able to ascertain the nature of these defects.

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- 2) An in-depth analysis of the interaction between the site dependent defects and the green emission will be conducted. This is addressed in terms of the electronic band structure that involves emission mechanism. This will enable a better understanding of how these factors are responsible for different types of the green emission observed.
- 3) Theoretical analysis of how the site dependent defects could further influence the green emission at ultra-low temperature will be conducted. The proposed mechanism could possibly explain the observed green emission in the literature hence verify our analysis in this study.

CHAPTER 2:

LITERATURE REVIEW

2.1 Structure of ZnO

Zinc Oxide (ZnO) has been a center of attraction in the field of optoelectronics to date. As a hexagonal wurtzite structure (space group- P 63 m c), it has a formula weight of 81.369 with lattice constants of $a = 0.3249858 \pm 6$ nm and $c = 0.5206619 \pm 7$ nm at 298K with a unit cell volume of 0.047622830 ± 9 nm³. Within ZnO, one cation is surrounded by four other anions positioned at the corners of the tetrahedron or vice versa (Fig 2.1). In terms of

Fig 2.1: Crystal Structure of ZnO. Each cation is surrounded by 4 other anion position at the corners of tetrahedron or vice versa.

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tetrahedral coordination, the anion and the cation share a sp^3 share a sp^3 covalent bonding thus ZnO does not have a fully ionic character but an ionicity of partially covalent and ionic.⁶

The structure of ZnO is composed of two interpenetrating hexagonal close packed (HCP) sublattices. In each of the sublattices, there is one type of atom that is displaced from one another along the threefold c-axis by an amount, u (Fig 2.2). The u parameter is defined as the length of the bond parallel to the c axis, in units of c . The wurtzite structure of ZnO often deviates from the ideal arrangement thus changing the c/a ratio and the u parameter.

Fig 2.2: Crystal Structure of ZnO with definition of U parameter. It is defined as the length of the bond parallel to the c -axis, in units of c .

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Nevertheless, the c/a ratio is inversely related which allows the four tetrahedral distances to remain almost constant. This is achieved through a distortion of tetrahedral angles as a result of long range polar interaction.⁶

ZnO has a non inversion symmetry which has crystallographic polarity that determines the direction of the bonds. For example, the (0001) basal plane in the wurtzite structure is different from the (000-1) plane. Normally, it is defined as the positive z direction from the cation (Zn) to anion (O) from the face of O plane to the Zn plane. Therefore the bonds along the c direction connected from the cation (Zn) to anion (O) are referred as Zn polarity and vice versa. This is important because properties such as the growth, etching, defect generation, plasticity, spontaneous polarization and piezoelectricity depend on it.

The lattice parameters of ZnO determined from various experiments are in agreement with the theoretical calculations.⁶ The c/a and u parameters vary in a slightly wider range from 1.593 to 1.6035 and 0.383 to 0.3856 respectively. This deviates from the perfect wurtzite crystal due to lattice stability and ionicity. On the other hand, the presence of free charges maybe responsible for expanding the lattice. This is directly related to the deformation potential of the conduction band minimum and is inversely proportional to the carrier density and bulk modulus.^{6,13}

2.2 Applications of ZnO

Despite the fact that ZnO has one of the simplest crystal structures, it is a very versatile material that can be used for many applications. One of the most constant demands for ZnO is in its applications in the rubber and concrete

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industries. It can be used as an additive to the rubber car tires as it improves the vulcanisation process. Due to the relatively good heat conductivity, ZnO can also be used to dissipate heat resulting from the deformation as the tyres rolls on the ground.¹⁴⁻¹⁵

ZnO has also been used as UV-blocker in cosmetics such as suntan lotions or foundation due to the bandgap in the UV range which can absorb UV rays effectively. It can also be used in energy-saving or heat-protecting windows. For example, coating ZnO on a piece of glass reflects infra-red (IR) rays, allowing the glass panel to either retain the heat in a room or protect the room from heat depending on which side of glass it is coated on. It has high energy radiation stability so it is a good candidate for space application at low cost.¹⁶⁻¹⁸

The current applications of ZnO that are available in the market do not maximize its potential. Current research postulates that ZnO can be fully exploited in the semiconductor industry. The wide bandgap of ZnO is very attractive because of its potential to be applied as a transparent conducting oxide¹⁹ This is appealing as it can replace ITO which is comparatively more expensive and toxic. Furthermore, it can be used in different kinds of optical display panels.²⁰ It can be implemented as the front contact for solar cells avoiding the shadow effect that is associated with metal finger contacts.²¹

ZnO can be applied as a gas sensor because its surface conductivity is sensitive to different types of gases particularly oxidizing gases.²¹ In fact, ZnO has high chemical sensitivity to other volatile and radical gases. Additionally, ZnO can be made into nano-particles easily. The increment of the surface area as a

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function of reducing size implies an increase in the sensitivity of the material. This allows minute amount of gases to be detected.²²

Although ZnO is natively an n-type material and is difficult to make into p-type, it can still be taken advantage of in the application of field effect transistors which do require a p-n junction.²³⁻²⁸ Combined with its transparent nature, the potential of ZnO as a field effect transistor can be fully maximized if it can be made into transparent thin film transistors (TTFT). One of the TTFT's major application is in the organic light emitting diode (OLED) which is gradually becoming important in the field of optoelectronics due to its ultra thin and flexible nature. Such attractive features are highly sought after as they open up opportunities in many potential applications.

ZnO can also be used as light emitting diodes (LED) based on heterojunction architecture. This can be achieved by using the readily available n-type ZnO with a good p-type semiconducting material such as n-ZnO/pGaN or n-ZnO/p-SiC.²⁹ While such application is currently used as demonstrator, it can be implemented in the production line when it meets future industrial standards. There is also a report on ZnO homojunctions which can be used for LED. This can be achieved by building a $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ barrier. The quality of the LED is affected by parameters such as carrier diffusion and recombination efficiency.³⁰⁻³¹

Recently, it has been hypothesized that ZnO exhibits ferromagnetic behaviour.³² For example, it is possible that the magnetization will increase by several orders in the ZnO ferromagnetic nano-rods.²⁹ The current issue is to flip the direction of the magnetisation by applying an external field. If this is possible,

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the nanorods can be used as nanosized read/write heads for magnetic data storage.

In the scientific investigation of ZnO nanostructures, the pointed tips of single crystals or nanorods allow the electric field to be strongly enhanced which is attractive in its potential be used as a field emitter. There are other attractive properties of the nanostructures of ZnO waiting to be harvested. For example, it has been shown that the nanowires of ZnO in array configuration could have potential in making nano-lasers.³³ On the other hand, the clusters of ZnO nanoparticles are also found to emit random laser, a new kind of laser since laser is normally found in a directional coherent manner.³⁴ Assembled ZnO nanostructures could be used in photonic crystals for optoelectronic applications.³⁵

2.3 Origin of the Green Emission in ZnO

2.3.1 Principle of Radiative Emission

It is necessary to explain briefly the mechanism of radiative emission. The radiative emission discussed here can be described as a form of photoluminescence. The mechanism of photoluminescence can be simply described in Fig 2.3.

Initially, a light source with energy greater than the material's bandgap is shone on the material. This allows (1) excitation of the electron from the valence band to the conduction band. During relaxation, the electron has to return to the valence band. The presence of impurities or defect which maybe either a donor or

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acceptor will have an energy state in the band gap. During the relaxation, the electrons might be temporary

Fig 2.3: Mechanism of Photoluminescence.

trapped in these defect states before (2) relaxing to the valence band where it combines with a free hole. This is also known as (A) Lambe-Klick model. On the other hand, the free electrons relaxes and combine with a trapped hole in a deep level acceptor and is known as the (B) Schon-Klasens model.³⁶ During this relaxation, (3) energy is released in the form of photoluminescence or also known as the radiative emission. Normally, such relaxation has energy smaller than the bandgap energy hence the radiative emissions usually have an energy smaller than the bandgap.

Often, the above mentioned mechanism is assumed to be taking place at zero thermal state. At a finite temperature, the atoms in the material are vibrating from their mean position. The vibrational states of the atoms have in fact certain degree of influence on the electronic state of the materials. Such relationship is

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described in the transition between the ground and the excited state by the Franck-Condon Principle. The Franck-Condon Principle can be shown by a configurational coordinates q_i in Fig 2.4. The energy transitions are indicated by the vertical arrows between the ground and excited state. The energy transition begins at the lowest phonon (vibrational) energy level of the electronic states. The largest transition probability (largest wavefunction overlap) occurs when the photon energy is equal to the energy difference between the two electronic states ($E_1 - E_0$) plus four quanta of lattice mode i vibrational energy ($\hbar\Omega_i$). This four phonon transitions are mirrored in the emission when the excited state quickly decays to its zero point lattice level by means of a radiationless process, and from there, transit by photon emission to the ground state. The electronic transition independent of any phonon coupling (zero phonon transition or 0-0 electronic transition) is shown as having a lower wavefunction overlap and therefore a very low transition probability is noticeable.

There are three approximations assumed in the Fig 2.4. Firstly, the lattice vibrational mode is described by a quantum harmonic oscillator implied in the parabolic shape of the potential well of Fig 2.4 and has equal energy spacing between the phonon energy levels. Secondly, only the lowest (zero point) lattice vibration is excited. This is called the low temperature approximation and it means that electronic transitions do not originate from any of the higher phonon levels. Lastly, the interaction between the emission center and the lattice is the same in both the ground and excited state. The harmonic oscillator potential is equal in both states and the approximation is called linear coupling. It is

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presented by two equally parabolic potentials and equally spaced phonon energy levels in both the ground and excited states.

Fig 2.4: Energy diagram of an electronic transition with phonon coupling along the configurational coordinate q_i , a normal mode of the lattice. The upwards arrows represent absorption without phonons and with four phonons. The downwards arrows represent the symmetric process in emission.³⁷

The strength of the zero phonon transition arises in the superposition of all the lattice modes. Each lattice mode m has a characteristic vibrational frequency Ω_m which has an energy difference between phonons $\hbar\Omega_m$. When the transition probabilities for all the modes are summed, the zero phonon transitions always add at the electronic origin ($E_1 - E_0$), while the transitions with phonons contribute at a distribution of energies. Fig 2.5 describes the superposition of transition probabilities of several lattice normal modes. The phonon transition contributions from all lattice modes constitute the phonon

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sideband. This phonon sideband is another term that describes the emission (such as the green emission) with the inclusion of phonon coupling.

Fig 2.5: Representation of three lattice normal modes (i, j, k) and how their intensities combine at the zero-phonon frequency, but are distributed within the phonon side band due to their different characteristic harmonic oscillator frequencies Ω . The frequency separation between the maxima of the absorption and fluorescence phonon sidebands is the phonon contribution to the Stokes's shift.³⁷

2.3.2 Copper Impurities

The origin of the green emission of ZnO was first explained by R. Dingle by associating it with the divalent copper impurities.³ Fig 2.6 shows the green emission as observed at 1.6K. Notice that the broad green emission has various fine structures that are apparent as blunted spikes on the broad curve. A magnified spectrum shows that in the 0-0 electronic transition region, there are two sharp lines separated by ~ 0.1 meV (Fig 2.5). These are two different zero

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phonon lines (ZPL). In Fig 2.7, the intensity ratio of these two zero phonon lines, namely A and B is $\sim 2.25 \pm 0.05$. The intensity ratio remains constant over the range of 1.6 – 20.4 K indicating that they are not dependent on the crystal origin.

Fig 2.6: Broad Green Band Emission.³

R. Dingle explained that the two lines A and B are due to identical electronic processes that took place at similar but separate lines. The ratio of the emission intensity between the lines A and B correspond to the natural abundance of the Cu isotopes. For example the ratio of A/B shares the same values for $\text{Cu}^{63}/\text{Cu}^{65}$. This is supported by other measurement like the Zeeman pattern by applying a magnetic field. The A and B zero phonon lines are split into four symmetrically disposed components.

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Fig 2.7: High-resolution spectra in the region of the A and B no-phonon lines near 2.859 eV.³

By changing the angle dependence of their splitting in the magnetic field, the g -factors can be obtained. They are identical to the result obtained by Electron Paramagnetic Resonance (EPR) studies of a divalent copper ion Cu^{2+} on a zinc lattice site of ZnO .³⁸ These experiments were the basis of the unequivocal identification of the green emission band with characteristic fine structures due to the Cu_{Zn} defect.³

The Cu^{2+} (A^0) is a very deep neutral acceptor with a hole in the 3d shell (electronic configuration $3d^9$, ~ 3.26 eV above valence band). During excitation, the hole is transferred from the d shell thus the configuration becomes a $3d^{10}$ and the hole is transferred to the sp^3 orbital where it becomes relatively loosely bound. Particularly, the $3d^{10}$ electronic configuration belongs to Cu^+ ion (A^-)

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which is ~ 0.4 eV above the valence band. Generally for this emission model, the luminescence process involves transfer of a hole from an orbital encompassing these oxygen atoms to a highly shielded localized level in the 3d shell of the Cu atom (Fig 2.8).

Fig 2.8: Origin of green emission due to the presence of Cu impurities.

Kuhnert and Helbig studied this green phonon sideband (emission).³⁹ The energy separation between the subsequent peaks is ~ 72 meV, close to a LO-phonon mode of the ZnO crystal. The spectral distribution of the GL band can be described in terms of the one dimensional configuration coordinate model. The Huang Rhys factor $S=6.5$ is obtained from the fitting. Alivov found that the green emission had a triplet fine structure instead of the doublet commonly found by others.⁴⁰ This feature could be due to the radiative recombination between the

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acceptor excitons that are localized at the copper atoms and each of the subbands of the ZnO valence band.

Garces *et. al.* suggested the different charge state of copper impurities will produce different green emissions.² For example, it is possible to change the nature of green emission from structureless to structured green emission by annealing the ZnO in air for an hour at 900°C (Fig 2.9).² It is an indication of stable charge state variation of the Cu impurities from Cu^+ to Cu^{2+} . The presence of the structureless emission is due to donor-acceptor pair recombination involving the Cu^+ acceptor and a singly ionized shallow donor impurity. The structured emission observed in their result needs a two-step structured emission process to take place. Initially, an electron is needed to be extracted from the singly ionized copper (Cu^+) to transform into a neutral copper acceptor (Cu^{2+}). Subsequently, an electron from the neighboring oxygen could then transfer to the copper (Cu^+) before the first electron returned.

2.3.3 Oxygen Vacancies

K. Vanheusden *et. al.* proposed that the origin of green emission of ZnO is due to the presence of singly charged oxygen vacancies.⁴ The samples were treated in forming gas ($\text{N}_2: \text{H}_2 = 95:5$) as a function of temperature. Using Electron Paramagnetic Resonance (EPR), it was found to have $g = 1.956$ for their samples. This value is attributed to singly charged oxygen vacancies. This is supported by a coherent relationship between the

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Fig 2.9: Photoluminescence spectra from an undoped ZnO crystal taken (a) in the as-grown state and (b) after a thermal anneal at 900°C in air for 1hr. The data were taken at 5 K with 364 nm excitation.²

concentration of the singly charged oxygen vacancies, electron concentration and the intensity of the green emission shown in Fig 2.10. The green emission is observed in the presence of V_o^+ electrons recombination with the photoexcited holes in the valence band. However, the EPR result was highlighted by Garces *et al.* suggesting that the value could be due to shallow donor instead.²

Leiter *et al.* using optically detected magnetic resonance (ODMR) suggested that the EPR values for oxygen vacancies should be $g_{||} = 1.984$ and $g_{\perp} = 2.205$.⁴¹ They arise from a spin-triplet system ($S = 1$) and the green emission is related to these values instead of $g = 1.956$. In their observation, this green emission is structureless, different from the structured green emission. The structureless green emission is due to a transfer from the shallow donor signal by

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a shunt process or a spin dependent energy-transfer mechanism. Initially, the oxygen vacancy is neutral and diamagnetic, having a

Fig 2.10: Intensity of the (a) green emission peak and (b) free carrier (electron) density for powder B (ZnO: Zn), but masured at 294 K, vs oxidation anneal temperature. Oxidation treatments were done in a flow of pure oxygen for 1hr at a flow of 1L/min. The densities of paramagnetic singly ionized oxygen vacancies (V_o^+) detected with EPR (dark) at 20 and 294 K have been added for comparison.⁴

singlet state with two electrons. Upon excitation, an excited singlet state appears. The relaxation took place causing the electrons to transfer into a triple state ($S = 1$) and the green emission is found when the electron is transferred from the triple state to the ground state $S = 0$ (Fig 2.11). It is found that the presence of shallow donor signal ($g = 1.956$) would quenched the GL band.⁴¹⁻⁴² However this appears to be in contradiction to Vanheusden work because the strong signal $g = 1.956$ appears along with strong green emission signal.

Fig 2.11: Emission Spectrum of undoped ZnO excited with the 325 nm line of an HeCd laser (5K). The inset shows the spin dependent energy transfer mechanism.⁴¹

2.3.4 Zinc Vacancies

Zn vacancies are known to be deep level acceptors.⁴³ It has been shown that ZnO should contain some considerable amount of Zinc vacancies using state of art characterization technique such as the Positron Annihilation Spectroscopy (PAS).⁴⁴⁻⁴⁵ Although the presence of Zn vacancies has been determined, the relationship with the green emission is not clear as it is not well supported in terms of experimental results. Some experimental data suggest that this is possible. For example, Sekiguchi *et. al.* observed that introducing hydrogen plasma to ZnO will reduce the intensity of the green emission which is similar to the passivation of Zn vacancies.⁴⁶ On the other hand, Guo *et. al.* have done a

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room temperature time-integrated and time resolved PL measurement on undoped ZnO thin film to verify this.⁴⁷ During the experiment, the green emission decayed as hyperbolic function t^{-1} (inverse time), and its peak energy was observed to increase nearly logarithmically with increase in excitation intensity, I_{ex} . Both results are in agreement with a donor-deep-acceptor pair (DAP) model which involves the single ionized oxygen and zinc vacancies. Based on Density Functional Theory (DFT), it is also proposed that zinc vacancies may give rise to the green emission and this will be elaborated under DFT section 2.3.7.^{7,48}

2.3.5 Surface Related Emission

Dijken *et. al.* worked on ZnO nanocrystals and proposed a mechanism that would explain the green emission.¹⁰ Initially, a photogenerated hole is trapped at a surface system (probably O₂⁻/O⁻). The surface-trapped hole then tunnel back into the particle where it recombines with an electron in an oxygen vacancy (V_o^+) resulting in the creation of a V_o^{++} center [$V_o^+ + h^+ \rightarrow V_o^{++}$]. The latter is the center of the green emission where the shallowly trapped electron would combine with it [$e^- + V_o^{++} \rightarrow V_o^+ + h\nu$]. Therefore the green emission is due to a recombination of a shallowly trapped electron with a deeply trapped hole such as the V_o^{++} center.

Recently, Li *et. al.* synthesized nanostructures of ZnO. These ZnO nanostructures are found to emit green emission.⁴⁹ However, by coating these ZnO nanostructures with surfactant, the green emission is suppressed. This is a strong indication that the green emission is related to the surface although the emission center of this green emission remains unknown.

2.3.6 Other Concerns

The work of D.C Reynolds *et. al.* suggest a different mechanism. They found that there was no copper contamination of their sample although the structured green emission was observed.⁵ This structured green emission had a doublet features. Using Hall measurement, they found that the two shallow donors that are 30 meV and 60 meV below the conduction band. Therefore, the green emission could be due to the transition from the two shallow donors to a deep level acceptor. However, they did not specify the nature of the acceptors and donors involved.

2.3.7 Density Functional Theory (DFT) Result

The Density Functional Theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functional, i.e functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functional of the electron density. To date, it is among the most popular and versatile methods available in condensed matter physics, computational physics and computational chemistry.

Recently, Kohan *et. al.* make use of the Density Functional Theory to determine the formation energy, electronic structures, atomic geometry of the native point defects in ZnO.⁷ It is found that the Zn and O vacancies are the likely defects found in ZnO. The defect energy of Zn vacancies is less affected by the

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nature of the calculation error hence it is more likely to be responsible for the origin of green emission. DFT has a problem of underestimating the band gap of ZnO. Janotti *et. al.* applied a correction to this problem and found that oxygen vacancies are deep level donors with high formation energy while zinc vacancies have low formation energies under n-type conditions.⁴⁸ Therefore the zinc vacancies is likely to be the origin of the green emission.

On the other hand, Zhang *et. al.* showed that although native defects such as oxygen interstitials or zinc vacancies are shallow acceptors, other donor defects such as oxygen vacancies, zinc interstitials or zinc antisites have low formation enthalpies that could readily act as hole killers.⁹ He identified that oxygen vacancies could be the source of the green emission. Based on the most common schemes under the DFT such as the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA), two major intrinsic problems must be addressed. Firstly, when the DFT based on LDA or GGA is applied onto semiconductor, the results exhibit a substantial underestimation of the electronic bandgap. Secondly, although general computation capabilities nowadays are able to calculated up to ~ 1000 atoms, it still correspond to a very high concentration [$10^{19} - 10^{20} \text{ cm}^{-3}$] for semiconductor standards. This prompts a need to correct the finite size effects present in the supercell calculations especially in case of charge defects or when Moss Burstein type band filling effects occur, for example in the case of shallow electron donors and acceptor.⁵⁰

Although the schemes and corrections are implemented to correct these issues, it is known that these have led in some cases to strongly varying predictions by different theory groups. This happens to the calculation of oxygen

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vacancies in ZnO as shown in Fig 2.12. In Fig 2.12, the theoretical results of the formation energy of V_o were calculated. The formation energy controls the oxygen deficiency in ZnO. As observed from this figure, one would notice that the formation energies are very different from

Fig 2.12: The formation energy ΔH of the O vacancy in ZnO under O-poor/Zn-rich conditions as calculated in recent theoretical works, using different schemes and procedures to account for LDA/GGA deficiencies and supercell finite-size effects. The references are KCMW00⁷, ZWZ01⁹, LKJC01⁵¹, EAK06⁵² (closed symbol: GGA; open symbol: GGA+U), LZ07⁵³, and JW07.^{48,50}

each other. It could be from as low as $\Delta H \approx 1$ eV ($< 10^{19}$ cm⁻³ of V_o) to as high as $\Delta H \approx 4$ eV ($< 10^{10}$ cm⁻³ of V_o).⁵⁰ It is important to note that although Density Functional Theory is a very powerful tool for theoretical calculation to determine the formation energies of defects, further studies have to be carefully made to produce consistent results.

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3.1 Inducing Defects in ZnO

To separate the subtle changes in the visible emission, the specific defects were induced artificially under two different conditions. In the first condition, Type I defects were induced by annealing the as-received ZnO powder (99.5% pure, Analyticals Carlo Erba) in a reducing atmosphere of 3 % H₂ + 97 % Ar from 500°C to 900°C for 24 hours. In the second condition, the Type II defects were generated by annealing in ambient atmosphere. This atmosphere could be considered a mixture of 21 % O₂ + 79 % N₂. Here, both the Type I and Type II defects could be oxygen vacancies but dominate at different locations in the material, e.g. Type I is found near the surface while Type II is found beneath the surface. Different characterization techniques were carried out to determine and verify the assumptions of the above mentioned defects. Simulation data were correlated with the experimental results to obtain a better understanding of the defect origin. Defects are also specifically induced in nanocrystalline ZnO. A method that can avoid possible complications induced by temperature, pressure, and oxygen variation is to reduce the crystal size physically. In this work, the size of ZnO crystals was finely divided by means of the ball-milling technique in tungsten carbide (WC) bowls in a controlled fashion. The balls for the ball milling are also made of tungsten carbide.

This technique can produce a sufficient amount of nanosized particles, thus enabling characterization of subtle changes of the chemical states of the

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materials with X-Ray Photoelectron Spectroscopy (XPS). This is used as a comparison with the core level binding energy shift observed in ZnO with Type I and II defects respectively. In general, most of ZnO nanomaterials are prepared by chemical vapor deposition techniques at $\sim 1200^{\circ}\text{C}$. In order to investigate the effects of size reduction and to provide practical experimental data to the community, similar start conditions of ZnO materials were implemented by annealing the commercial powder at 1200°C for an hour. Subsequently a continuous cycle of 5 mins milling and 3 mins rest-time was programmed to minimize heat accumulation.⁹ In this manner, highly reproducible size reductions could be achieved as a function of milling time.

3.2 Materials Characterizations

Different characterization techniques were carried out to study the materials properties of the prepared samples. They are described as follows:

3.2.1 Raman Spectroscopy

The vibrational modes of the investigated samples were studied using Raman spectroscopy. Raman spectra were measured with a Renishaw 2000 Raman Spectroscope in backscattering geometry at room temperature using a 633 nm laser line with an average power of 15 mW.

The lineshape of the Raman spectrum contains a wealth of information that can be extracted for in-depth analysis. In order to determine the lineshape of the Raman spectra, a non-linear least square minimization of the differences between the observed and calculated profiles was performed. The data collected was processed by removing the baseline and then normalized using the highest

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intensity peak. Subsequently the data was fitted with a Split-Pearson VII function. A Split-Pearson VII function was chosen to be incorporated in this least square scheme as it is robust enough for the asymmetrical lineshape anticipated in the Raman Spectra. The Pearson VII function is given by:

$$f(x) = \frac{A}{[1 + (\frac{x - xc}{\Upsilon})^2 (2^a - 1)]^a} \quad (3-1)$$

Where A is the peak value of the Raman spectrum, xc is the wavenumber of the Raman peak, Υ is the half width full maximum and a describes the shape of the profile. In case of an asymmetrical profile, the Pearson VII function becomes a Split Pearson VII function where

$$f(x) = \frac{A}{[1 + (\frac{x - xc}{\Upsilon_a})^2 (2^m - 1)]^m} \text{ if } x \leq xc \quad (3-2)$$

$$f(x) = \frac{A}{[1 + (\frac{x - xc}{\Upsilon_b})^2 (2^m - 1)]^m} \text{ if } x > xc \quad (3-3)$$

The full width half maximum for the Split Pearson Function is given by:

$$\Gamma = (\Upsilon_a + \Upsilon_b)/2 \quad (3-4)$$

Where Υ_a is the half width at half maximum (HWHM) on the left of the peak position, Υ_b is the HWHM on the right of the peak position.

3.2.2 X-ray Diffraction (XRD)

The crystal structures of the samples were investigated using X-ray Diffraction (XRD). Data was recorded using a Theta/Theta Shimadzu LabX 6000 Diffractometer in a Bragg-Brentano using with a Cu K α radiation operating at 30

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kV, 30 mA, with a divergence slit of 1° , width receiving slit of 0.3 mm and a graphite monochromator. The samples were scanned from 20° to 120° with a sampling pitch of 0.02° and a scanning speed of 1 deg/min. Rietveld analysis was carried out by a Fundamental Parameter procedure as implemented on the TOPAS package to determine the unit cell volume.⁵⁴ The Fundamental Parameters procedure was able to account for the instrumental resolution as a result of imperfect optical alignment that yields various finite divergence of the X-ray source. As a result, such corrections yielded a more accurate result pertaining to the investigated sample. In all cases, a background polynomial, scale factor, cell parameters, zero point correction, sample displacement and preferred orientation were refined in order to obtain an accurate lattice constant. Due to very poor scattering factor of the oxygen, the refinement of the occupancy factor might not yield a meaningful result.⁵⁵ Furthermore, the occupancy factors and thermal parameters had a strong correlation hence, they were kept fixed.

Fig 3.1 below shows a typical plot of Rietveld refinement of the XRD pattern for the as-received ZnO. The black line is the XRD pattern of as-received ZnO. The red line is the calculated XRD pattern that has taken into account the various corrections mentioned above. The blue line is the difference plot, which allows a visual inspection of the quality of the fitting of the calculated pattern relative to the raw pattern. The inset shows the zoomed in pattern. It shows that the calculated pattern matches very well with the experimental data and this is supported by the nearly flat difference plot which indicates a good fit. The quality of the fitting is satisfactorily achieved for the annealed ZnO as well.

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Fig 3.1: A typical plot of As-received ZnO using Rietveld Refinement. The black line is the raw data of as-received ZnO while the red line is the calculated pattern. The blue line is the difference plot which represent the quality of the fitting through visual inspection.

3.2.3 X-ray Photoelectron Spectroscopy (XPS)

The electronic structure of the investigated samples was studied using X-ray Photoelectron Spectroscopy (XPS). This was performed using a VG ESCALAB 220i-XL spectrometer. High intensity x-ray photoelectron spectra were produced using a monochromatized Al K alpha X-ray source ($h\nu = 1486.6$ eV) with a 20 eV pass energy. Core level binding energy was determined by measuring the kinetic energy of the emitted electrons upon x-ray irradiation. A flood gun was used when necessary to reduce surface charging. Close examination indicated an absence of possible differential charging and the results were subsequently calibrated by Adventitious Carbon C 1s peak at 285 eV. High Resolution spectra

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were recorded at 0.1 eV intervals for respective core level binding energies (BE), for example Zn 2p 3/2, Zn 3s and Valence Band (VBM) with extremely good signal to noise ratio. The VBM with respect to the Fermi-level was determined by extrapolating a linear fit to the leading edge of the valence-band photoemission to the background level.⁵⁶

Where peak fittings were necessary, these XPS spectra (in Chapter 8) were fitted using the reported fitting guideline.⁵⁷ The XPS core level line is described by the product of Gaussian and Lorentzian functions of the same width. This product function is given by:

$$f(E_b) = h \left\{ 1 + M \left[\frac{E_b - E_o}{\Upsilon + \alpha_o(E_b - E_o)} \right]^2 \right\}^{-1} \exp \left\{ -(1 - M) \ln 2 \left[\frac{E_b - E_o}{\Upsilon + \alpha_o(E_b - E_o)} \right]^2 \right\} \quad (3-5)$$

Where E_o is the peak position, Υ is the peak width parameter, h is the peak height, α is the asymmetry index and M is the Lorentzian-Gaussian mixing ratio which have to be specified in this product function.

The XPS spectra of the high purity starting material was symmetrically fitted with single peak using this product function, as an asymmetrical peak should be assigned to the interaction of the positive core hole with the conduction electrons in a metal-like conducting system.⁵⁸ In each case, the spectra broadening caused by chemical, structural and electronic fluctuations in the surroundings of the emitting atoms of the peaks was refined.⁵⁹

3.2.4 High Resolution Electron Transmission Microscopy

High-resolution transmission electron microscopy (HRTEM) was used to characterize the atomic structure of the as-prepared materials. The materials

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were slightly dispersed in ethanol and several drops of the suspension were then deposited onto a holey-carbon coated Cu grid for HRTEM characterization which was performed using a Jeol JEM-2010 with 200 KeV accelerating voltage.

3.2.5 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) spectra were determined by an Accent Rapid Photoluminescence Mapping System (RPM 2000) with a He-Cd laser source (325 nm). A constant power of 1.8 mW was maintained to eliminate the possibility of UV to defect emission intensity ratio variation. Emission spectra were collected from the samples in the range of 1.6 eV to 3.1 eV to study the optical properties of different defect states.

3.2 Physical Modelling – Multimode Brownian Oscillator (MBO) Model

The green emission can well be described by the MBO model, a theoretical framework to treat the coupling of nuclear coordinates to optical excitations and electronic relaxation channels in solids. As such, the results extracted from the experiments using a theoretical approach are much more significant than from other empirical method such as the Poisson distribution. In the MBO model, there are dissipation effects that are omnipresent in solids in the form of harmonic oscillator system which can be achieved by coupling the system oscillators linearly to bath modes with a continuous spectrum. There is a two electronic two-level system with some primary nuclear coordinates coupled linearly to it and the harmonic bath. The primary phonons can be those of host medium or pseudo-

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localized modes associate with the guest atoms or molecules.⁶⁰⁻⁶³ The Hamiltonian of the system^{60,64} is given by

$$H = |g\rangle H_g \langle g| + |e\rangle H_e \langle e| + H', \quad (3-6)$$

Where

$$H_g = \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right], \quad (3-7)$$

$$H_e = \hbar \omega_{eg}^0 + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (q_j + d_j)^2 \right], \quad (3-8)$$

And

$$H' = \sum_n \left[\frac{P_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 \left(Q_n - \sum_j \frac{c_{nj} q_j}{m_n \omega_n^2} \right)^2 \right] \quad (3-9)$$

In Eq.(3-6)-(4), P_j (P_n), q_j (Q_n), m_j (m_n) and ω_j (ω_n) are the momentum, coordinate, mass and angular frequency of the j th (n th) nuclear mode of the primary (bath) oscillators, respectively. In Eq. (3-8), d_j is the displacement of the j th nuclear mode in the electronic excited state. The term $\hbar \omega_{eg}^0$ represents the energy difference in the two-level system. H' can be regarded as the coupling between the primary oscillators and bath modes with a coupling strength of c_{nj} . The key parameters of the MBO model are the frequencies of the primary oscillators ω_j , the damping coefficient γ_j that controls the system-bath coupling strength, and the Huang-Rhys factor S_j which reflects the electron-LO phonon coupling strength. Other controlling parameters include the bath temperature T and the 0-0 electronic transition energy [or also known as Zero Phonon Line (ZPL), $\hbar \omega_{eg}$].³⁷ Here we take the LO phonon as the only primary phonon in the

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model, so $\omega_j = \omega_{LO}$. The LO phonon frequency ω_{LO} is assigned to be the spacing between adjacent phonon side bands. One of the advantages of using MBO is that one could locate the 0-0 electronic transition energy which is difficult to determine by visual inspection.

The spectral density of the MBO model can be written as

$$\tilde{C}''(\omega) = \frac{2\lambda\omega_{LO}^2\omega\gamma(\omega)}{\omega^2\gamma^2(\omega) + [\omega_{LO}^2 + \omega\Gamma(\omega) - \omega^2]^2} \quad (3-10)$$

where $\Gamma(\omega)$ is the real part of the self-energy and the Stokes shift is given by

$$2\lambda = \frac{m\omega^2 d^2}{\hbar} \quad (3-11)$$

Alternatively, we can write $\lambda = S\hbar\omega_{LO}$. Here we adopt a simple form of the MBO model in this work. In this model, the spectral distribution function $\gamma(\omega)$ is assumed to be in its Ohmic limit (i.e., $\gamma(\omega) = \text{constants}$). Under these simplifications, the spectral density function has following form

$$C''(\omega) = \frac{2\lambda\omega_{LO}^2\omega\gamma}{\omega^2\gamma^2 + (\omega_{LO}^2 - \omega^2)^2} \quad (3-12)$$

where the self-energy term $\Gamma(\omega)$ is set to zero.

The spectral response function $g(t)$ can be expressed in terms of the correlation function described in Eq. (3-12) as

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$$g(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{C''(\omega)}{\omega^2} [1 + \coth(\beta \hbar \omega / 2)] (e^{-i\omega t} + i\omega t - 1) \quad (3-13)$$

Finally, the PL line shape can be calculated from

$$I_{PL}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} \exp[i(\omega - \omega_{eg} + \lambda)t - g^*(t)] dt \quad (3-14)$$

Previously, the MBO model was successfully implemented to study the green bands of ZnO across a wide range of temperatures.⁶⁵ Some of the parameters used can be implemented as constraints in our work in order to fit our spectra with the MBO model. Firstly, we fix the difference in the two ZPL lines separated by 30 meV as observed in the literature.^{3,65} The two Huang-Rhys factors S_1 and S_2 are constrained to have a common value while γ_1 and γ_2 are fixed at 65 cm⁻¹ and 60 cm⁻¹, respectively. These γ_1 and γ_2 values are obtained from the PL spectra at room temperature. The weight coefficients used to calculate the overall emission spectra are fixed at 1 and 1.5 for $\hbar\omega_{e1g^0}$ and $\hbar\omega_{e2g^0}$. We determined our LO phonon frequency (to be discussed in details in Chapter 4) to be 583.7 cm⁻¹ and 582.1 cm⁻¹ for the ZnO with Type I and Type II defects, correspondingly.⁶⁶ These frequencies are used as the primary oscillator in the MBO model.

CHAPTER 4:

NATURE OF QUASI-LO PHONON IN ZINC OXIDE

4.1 Introduction

Raman spectroscopy explores the vibrational modes of the crystal, hence it is possible to detect changes when defects are found. Although the vibrational modes of ZnO is proposed as far back as in the 1960s, it is only during an investigation on ZnO thin film using Raman spectroscopy that led to a brief discussion on the appearance of anomalously high intensity “E_{1LO} Raman peak” at about 579 cm⁻¹ which maybe correlated with the excess zinc.^{6,67} However, it was later suggested that this peak may be assigned as a silent mode.⁶⁸

In this work, we carry out a systematic investigation on this vibrational mode on ZnO with defect formation. The importance of the position and the shape profile of this peak which has been neglected in the past will be discussed. Subsequently, this result will be correlated with the photonic behavior of these defects in ZnO in an attempt to reveal the nature of Quasi-LO phonon in ZnO.

4.2 Results and Discussions

4.2.1 Electron Micrograph of ZnO in Different Environment

There are various characterization techniques to determine the properties of ZnO, one of the most direct methods to understand the property differences is through observing the morphological changes pertaining to these samples.

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Additionally it is possible to determine their particle size distribution. Electron micrograph for the as-received ZnO is done on Transmission Electron Microscopy (TEM) using a Jeol 2010 operating at 200 KeV whereas for the annealed samples, the results are determined using Jeol SM 6340 Scanning Electron Microscope (SEM).

Fig 4.1: Electron micrographs of ZnO with (a) Type I defects, (b) Type II defects and (c) as-received ZnO.

Fig 4.1 shows one of many electron micrographs of ZnO with Type I (annealed in reduction environment for 24 hrs at 900°C) and II (annealed in ambient

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environment for 24 hrs at 900°C) defects respectively as well as the as-prepared samples. During grain growth stages at the annealing temperature and long times, the particle size of the annealed samples are much larger than the as-received ZnO. We have calculated the size and size distribution of these samples [Table 4.1]. The size distribution is relatively uniform with the standard deviation smaller than the mean size.

Table 4.1: Particle Size Distribution

	As-Received ZnO	ZnO with Type I Defects	ZnO with Type II Defects
Size/ μm	0.174	1.92	1.61
Standard Deviation/ $\pm$ μm	0.035	0.54	0.38

4.2.2 Diffuse Reflectance

One of the methods to determine the quality of the materials can be achieved by determining the absorption edge of the semiconductor crystal. Here, we make use of the Diffuse Reflectance Spectroscopy that is able to characterize the optical properties of powdered samples. 0.4 g of powder from each annealing conditions are compacted into a pellet at 5000 psi using a hydraulic press to achieve uniform packing density. These are in preparation for diffuse reflectance measurement. The absorption spectra were derived from the diffuse reflectance using Perkin Elmer

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Lamda 900 UV/VIS/NIR using a dual beam in 200 – 800 nm range. This is made possible by using an integrating sphere that helps to collect the diffuse spectra. One of the inherent properties of a diffuse reflectance spectrum is that the spectra are made up of the scattering and absorption characteristics of the component of the powdered sample. On the other hand the diffuse reflectance spectra are influenced by many physical parameters such as (1) particle size and size distribution, (2) packing density or (3) homogeneity of the investigated powder mixtures that may alter the scattering coefficient that causes different reflectance values for chemically similar samples. This issue has been minimized as we determined from the previous section (Section 4.2.1) that the particle size distribution is relatively uniform as well as the packing density. Since the ZnO as-prepared are single phase, the risk of inhomogeneity can be neglected.

The diffuse reflectance data are converted to absorptivities by the Kubelka-Munk function⁶⁹ using the following equation

$$F(R) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{\alpha}{s} \quad (4-1)$$

Where $R = (I/I_0)$ diffuse, the diffuse reflectivity from the powder measured from diffuse reflectance spectroscopy. α is the absorptivity in units of cm^{-1} , and S is the scattering factor. The optical band-edge obtained from diffuse reflectance would be an average value since the former is dependent on the crystallographic direction. However, it remains useful because the presence of defect or impurity states would

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cause a band tailing (smearing) of the absorption edge. This is in fact relevant to our current study. The absorption edge study is derived from following equation:

$$F(R)XE = (E - E_g + E_p)^{(1/n)} \quad (4-2)$$

Where E_g is the bandgap while E is the range of energy measured. Since ZnO has a direct bandgap, the quality of the crystal can be determined by plotting plotting $[F(R) \times E]^2$ versus energy E in electron volts. Here, the value of n is 2 which implies a direct allowed transition.

The absorption spectra derived from the diffuse reflectance shown in Fig 4.2 indicates that the as-received sample is a higher quality sample than the annealed samples

Fig 4.2: Absorption spectra of the ZnO prepared at different conditions.

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with a much steeper slope as well as a well-defined absorption edge. The ZnO with Type I and II defects has a smearing of the absorption edge due to the presence of defects causing the band tailing to appear.⁶⁹

4.2.3 Raman Scattering of ZnO

(A) Comparison of Raman Spectra of ZnO with Type I and Type II defects

The phonon modes of wurtzite ZnO have been identified previously, having a total of 12 phonon modes. Our interests are focused on the LO component of the A₁ and E₁ phonons modes, which is associated with macroscopic electric fields.⁶ This peak is found at $585.6 \pm 0.9 \text{ cm}^{-1}$ for the as received ZnO [Fig 4.3]. It is in between the A_{1LO} mode of 574 cm^{-1} and the E_{1LO} mode of 590 cm^{-1} and therefore maybe assigned as a quasi-LO phonon.⁷⁰

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Fig 4.3: Quasi-LO phonon mode of ZnO prepared under different conditions. The profiles are accompanied with their curve fittings using split-Pearson VII function.

The A_{1LO} and E_{1LO} phonon modes can be distinctly observed in single crystal when they are excited by the laser in a specified scattering orientation. As the Raman peak of interest falls in between these modes, it is often misinterpreted as either A_{1LO} or E_{1LO} mode.^{67,71} The appearance of A_{1LO} or E_{1LO} mode is known by others as B1(high) silent mode and is accompanied by a lower density B1(low) silent mode at 275 cm^{-1} .¹³ The absence of B1(low) in our polycrystalline samples (Fig 4.4) suggests the observed phonon peak at

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Fig 4.4: Raman spectra of ZnO that show the absence of B1 silent mode at $\sim 275 \text{ cm}^{-1}$.

$585.6 \pm 0.9 \text{ cm}^{-1}$ may not be a silent mode. Instead, it is believed that the influence of random orientation of the polycrystalline powder would give rise to a quasi-LO mode, which is an angular averaging frequency appearing between the A_{1LO} and E_{1LO} mode.⁷⁰ Although it is noted that the quasi-LO mode is observed under resonant mode, the possibility of the observed quasi-LO phenomenon in our measurements with a non-resonant mode can be influenced by the presence of defects.^{70,72}

The presence of defects can manifest itself under the LO phonon mode in a few ways. One of the most direct observable effects is the change in the vibrational mode's position. The LO phonon mode for a perfect ZnO crystal is at its maximum

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near the center of Brillouin zone ($q \approx 0$).⁷³ When the presence of impurities such as defects induces crystal disorder it led to an observable breakdown of momentum conservation rules, thus relaxation of $q \approx 0$ occur and allows the position of LO modes to shift.⁷⁴ The material annealed in ambient atmosphere has the largest red shift from 585.6 cm^{-1} (as-received ZnO) to 582.1 cm^{-1} while the sample that is annealed in reduction environment has a smaller shift from 585.6 cm^{-1} to $583.7 \pm 0.3 \text{ cm}^{-1}$. The larger magnitude of the red shift suggests that the material annealed in ambient atmosphere has a larger degree of relaxation as the appearance of defects disrupts the periodicity of the crystals.

(B) Non-Linear Least Square Fitting of Raman Spectra of ZnO

By apply the non-linear least square fitting to our Raman Spectra, we determined that the as-received ZnO has the largest asymmetry factor $\Gamma_a/\Gamma_b \approx 1.38$, where Γ_a is the half width at half maximum (HWHM) on the left of the peak position, Γ_b is the HWHM on the right of the peak position. ZnO with Type I and Type II defects have an asymmetrical factor of $\Gamma_a/\Gamma_b \approx 1.27$ and $\Gamma_a/\Gamma_b \approx 1.16$ respectively. The presence of asymmetry maybe due to (1) the presence of size effect or the (2) presence of the defects.⁷⁴ The discussions are as below pertaining to these two factors.

(1) Size Effect

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The aforementioned results and analysis indicate the as-received sample has the largest Raman-shift position which has the lowest defect concentration as supported by its sharp absorption edge. The size effect in the as-received sample is therefore suspected. The calculated grain size of the as-received ZnO is 138.5 ± 3.8 nm, is consistent with the observation made using TEM [Fig 4.1(c)]. The size effect on materials performance would appear when the grain size approaches 100 nm.⁷⁵ The grain size is about 401.6 ± 7.2 nm and $410.4 \text{ nm} \pm 2.4 \text{ nm}$ for the materials annealed in ambient and reduction atmospheres respectively. Therefore, the crystal growth in the annealed materials diminishes the size effect and reduces the asymmetry. The wavefunction of the phonon which is originally coupled to an infinitely large crystal has to be modified in response to an act of localization when a finite size of the crystal is considered. This localization generates non vanishing values of the phonon transition matrix at $q \neq 0$ hence relaxation of the crystal momentum conservation and decay of phonons in such crystals is observed through the Raman spectrum when the nature of the shift and its broadening depends on the phonon dispersion.⁷⁶

The nanostructured material behaves differently from its bulk counterpart when a specific wavelength of the laser is used. As the size is reduced, so is the material's density which deteriorates its own thermal conductivity. Consequently, laser heating causes drastic thermal expansion (volume change) thus alters the vibration frequencies. The increased localized heating will cause a red shifting of the Raman spectra as a function of the decreasing size.⁷⁷ We deduced that localized heating on our samples is absent as the power of the laser is of an average of 15 mW.

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It is known that the effect of heating induced red shifting can be avoided if the laser power is below 100 mW.⁷⁸ Additionally, the increased size of our samples after annealing are accompanied by the red shifting, therefore this mechanism cannot be applied in our case.

(2) Presence of Defects

The asymmetry of the as-received ZnO maybe due to the localization mechanism. Notice that while the asymmetry factor of the treated ZnO is lowered, their residual asymmetry may not be solely due to the diminishing size effect as their Quasi-LO Raman spectra continues to shift to lower wavenumber which is an indication of the presence of defects. Since ZnO's optical phonon branch has the maximum frequency ω_o at the zone center, the cross section of the phonon-impurity (or defects) scattering will vanish at $\omega = \omega_o$ while increases for $\omega^2 < \omega_o^2$. This cause the Raman line to exhibit an asymmetrical nature.^{73,79}

A unique phenomenon that can be observed in Raman spectra is the appearance of the LO-plasmon coupling effect. The LO-plasmon coupling occurs in a non-inverted symmetry polar semiconductor e.g. ZnO. Its net electric dipole moment will couple with the LO phonons with the longitudinal plasma oscillations of the free carriers.⁸⁰ The coupling depends on the effective mass and the carrier mobility and ZnO has a heavier effective mass and much lower carrier's mobility as compared to GaAs. [GaAs-mobility, $\mu = 3100 \text{ cm}^2/\text{Vs}$, effective mass, $m^* = 0.074 m_o$, ZnO $\mu = 210\text{-}410 \text{ cm}^2/\text{Vs}$, $m^* = 0.27 m_o$, where m_o is the mass of free electron].^{78,81} As a result, a

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coupling mode will appear and can be observed at the higher Raman shift of the LO phonon mode.

In the case of ZnO, it is known that the presence of this coupling mode remains close to the main LO phonon such that a broadened peak is observed instead.⁷⁸ Despite similar grain size, ZnO with Type I and II defects have an asymmetrical factor of $\Gamma_a/\Gamma_b \approx 1.27$ and $\Gamma_a/\Gamma_b \approx 1.16$ respectively. The decrease of Γ_a/Γ_b seems to be associated with the enhancement of Γ_b . This might indicate that the higher frequency mode as a result of LO-plasmon coupling effect begins to appear. Thus the increased Γ_b suggests that the carrier concentration is increased when ZnO is annealed yielding Type II defects. It is necessary to evaluate the carrier concentration because the origin of carrier generation is perhaps correlated to defect concentration.⁸² Likewise, the absence of LO-plasmon coupling with a stronger asymmetrical factor in the as-received and ZnO with Type I defects qualitatively suggest that the carrier concentrations in these materials are lowered, therefore specific defect concentrations are also lower.

(C) Correlation between Raman Spectra and Photoluminescence of ZnO

The enhancement of the quasi-LO or A_{1LO}/E_{1LO} phonon (due to defect concentration increment) are often associated with the presence of oxygen vacancies that have a strong influence on the appearance of the green emission.⁷¹ It is therefore anticipated that the green emission from ZnO should follow a similar trend, for example, ZnO with Type II defects should have the highest green emission intensity

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normalized by the intensity of the UV emission light: A weaker Raman shift Quasi-LO phonon is associated. Comparing between Fig 4.3 and Fig 4.5 reveal such a relationship in a different light: A weaker Raman shift Quasi-

Fig 4.5: Relative intensity of the green emission of ZnO annealed in different environments. Intensity is normalized with reference to UV emission at ~381 nm.

LO phonon is associated with a strong higher energy green emission (~2.465 eV, 503.4 nm,) for ZnO with Type I defects while a stronger Raman shift Quasi-LO phonon gives a weaker lower energy green emission (~2.294 eV, 540.9 nm) for ZnO with Type II defects.

In this Raman scattering experiment, the transparency of ZnO to the red exciting laser made the signal rather insensitive to the surface as calculated from the

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optical detection depth which is estimated to be a few tens of micrometers [Appendix A].⁸³⁻⁸⁴ The collected signals are contributed mostly from the thick layer of materials underneath the surface. It may be possible to correlate ZnO with Type II defects with the presence of oxygen vacancies underneath the surface that cause the low energy green emission. It follows the energy transition mechanism for deep energy level defects as aforementioned in the introduction.³⁶ It is improbable for ZnO with Type I defects, to assign a lower concentration of specific defect such as oxygen vacancies through the interpretation of the Quasi-LO phonon profile with a high intensity green emission, hence such a relationship cannot be established. Although it is not clear how the high energy green emission (504.5 nm, ~2.45 eV) for ZnO with Type I defects is formed, Li. *et. al.* recently showed that by coating the surface of ZnO with surfactant, its green emission is suppressed, suggesting that a possible origin of this green emission maybe attributed to the surface modification such as oxygen vacancies near the surface.⁴⁹

The quantum size effect in the case of ZnO (typically <6 nm) would widen the bandgap and shift the band edge emission as well as the defect induced visible emission (green band) to higher energy. But this is not applicable to our case¹⁰ This is because the visible emission for the as-received sample is at a much lower energy than the annealed sample although its grain size is much smaller than the annealed samples.

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4.3 Summary

The largest red-shifting of the Quasi-LO Raman mode for the ZnO with Type II defects is attributed to a more dominant specific defect such as the oxygen vacancies. The lower asymmetrical factor is associated with the LO-plasmon coupling effects, supporting the notion of dominant specific defects in this material. It is believed that the formation of oxygen vacancies changes the translational symmetry and relaxes the selective rules for a randomly oriented powder samples. This causes a strong green emission from ZnO with Type II defects while the green emission observed from ZnO with Type I defects maybe originated from the surface modification.

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CHAPTER 5:

CORRELATION BETWEEN THE CHARACTERISTIC GREEN EMISSIONS AND SPECIFIC DEFECTS OF ZINC OXIDE

5.1 Introduction

In the present work, we discriminate the surface defects from the bulk defects and investigate their interaction that result in the observed subtle variation of the green emissions. Such a variation can be divided into two particular individual emissions referred to as the high energy and low energy green emissions. This finding may provide some new insights into the fundamental principle of manipulating the emission spectra with defect chemistry for practical applications.

5.2 Results and Discussions

5.2.1 PL Results and Multimode Brownian Oscillator Model (MBO)

Fig. 5.1 plots the spectra of the normalized emission intensity versus energies for the materials with Type I and Type II defects induced at 900°C. The spectra with Type I defects exhibits a high energy green emission peaked at 2.465 eV (503.4 nm labelled with "A") while spectra with Type II defects has a low energy green emission with peak intensity at 2.294 eV (540.9 nm, labeled with "B"). These differs from the spectra of the as-received ZnO which possess a yellow emission at 2.103 eV (590.0

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nm labelled with “C”). The green band which includes the phonon sideband is associated with the interactions between the electronic

Fig 5.1: PL spectra of the as-received ZnO and ZnO with high and low energy green emissions with Type I and II defects respectively annealed at 900°C for 24 hours.

degrees of freedom and optical phonons. Therefore, it is interesting to simulate the green emission band with the multimode Brownian oscillator (MBO) model and then extract the useful information on electron-phonon coupling of the materials. The MBO model has been described in Chapter 3.

Fig 5.2 shows the typical measured and calculated emission spectra associated with Type I and II defects while Table 5.1 shows the fitting results. The PL emissions associated with Type I defects [Fig 5.2 (a)] can be fitted well with the MBO

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model on the higher energy side. Fig 5.2 (b) shows the MBO fitting for the PL emissions of ZnO with Type II defects. It exhibits a shoulder beside the lower energy green emission. This could be due to the residual peak from the as-received sample (Fig 5.1). This shoulder is believed to be related to the yellow and orange emissions but their origins remain unknown as several types of defects might be responsible for these emissions.⁶ Although we cannot identify the exact nature of this impurity or defect, nevertheless, the remains and disappearance of the shoulder peak under ambient and reduction environment respectively suggest that the impurity/defects' out diffusion could be influenced by the nature of the annealing environment. The impurity that results in the residual (shoulder) emission is not effectively removed under ambient annealing environment. On the other hand, the impurity could be effectively removed under reduction environment such that the emission shoulder is removed.

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Fig 5.2: MBO model fitting of ZnO of (a) Type I and (b) Type II defects annealed at 900°C respectively.

Table 5.1:MBO Parameters

	$\hbar\omega_{e1g^0}$	$\hbar\omega_{e2g^0}$	ω_{LO}	$S_1 = S_2$
Type I Defects annealed at 500°C, 24hrs	2.951	2.981	583.7	7.3
Type I Defects annealed at 700°C, 24hrs	2.981	3.011	583.7	8.1
Type I Defects annealed at 900°C, 24hrs	3.021	3.051	583.7	8.65
Type II Defects annealed at 500°C, 24hrs	2.841	2.871	582.1	8.2

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Type II Defects annealed at 700°C, 24hrs	2.841	2.871	582.1	8.4
Type II Defects annealed at 900°C, 24hrs	2.911	2.941	582.1	8.85

Although the shoulder emission causes the overall fitting to be less satisfactory, the objective of this work is to extract information on the green band, hence MBO fitting is needed on the higher energy side of the low energy green emission associated with Type II defects. This region allows the MBO fitting to provide valuable information on the 0-0 transition energies (ZPL) as well as the Huang-Rhys factor that are responsible for the green emission [Fig 5.2 (b)]. We have also done the MBO fitting at different temperatures which is presented in Appendix B.

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Fig 5.3: (a) 0-0 transition energy for ZPL-2, $\hbar\omega_{e2g}^0$ and (b) Huang Rhys factor, S for ZnO of Type I and II defects annealing at different temperature respectively. Note that only ZPL-2 is shown for simplicity since $\hbar\omega_{e1g}^0$ and $\hbar\omega_{e2g}^0$ are constrained by a difference of 30 meV. The blue dash lines in both figures shows a clear difference between the nature Type I and Type II defects.

From Fig 5.3, it can be seen that the 0-0 transition energies for both high and low energy green emissions have a slight increase with increasing inducing temperature. On the other hand the electron-phonon coupling strength represented by the Huang-Rhys factor also increases with increasing temperature in the emissions associated with both types of defects. Both the increasing 0-0 transition energy and the Huang-Rhys factor could be attributed to the amount of surrounding mean lattice distortion which increases with defect concentration as a function of temperature.⁸⁵⁻⁸⁶

Although the 0-0 transition energy of the emission associated with Type I defects is always higher than that with Type II defects [Fig 5.3(a)], it does not follow that ZnO would have a higher concentration of Type I defects than that of Type II. This is because the Huang-Rhys factor as observed in high energy green emission is always lower than that of the low energy one [Fig 5.3(b)]. It implies that the Huang-Rhys factor is dependent on the nature of defects.³⁷ This observation suggests that the mechanism of high energy and low energy green emissions may be different.

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5.2.2 Influence Beneath the Surface

Fig 5.4 (a) shows the increase in the relative emission intensities with the defect inducing temperature. They could be attributed to the increment of the emission transition site concentration which is directly related to the defect of interest thus indicating that the defect concentration increases with inducing temperature.⁸⁷

Fig 5.4: XRD Rietveld Refinement shows (a) relative PL intensity (normalized with reference to UV emission) trend with increasing temperature and (b) unit cell volume of ZnO with Type I and II defects respectively as a function of inducing temperature.

On the other hand, Fig 5.4 (b) shows the unit cell volume determined from Rietveld Refinement of the XRD results for the ZnO with Types I and II defects. It is necessary to take note that the unit cell volume contraction is smaller at the inducing temperature of 700°C for ZnO with Type I defects which would imply a lower defect concentration. This is unexpected as the observed increasing high energy green emission intensity implies an increasing defect concentration [Fig 5.4 (b)].

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Therefore, the donors/defects that cause the unit cell volume contraction may not be responsible for the high energy green emission. The gradual volume contraction for ZnO with Type II defects indicating a continuous increase in defect concentration is however consistent with its increasing relative intensity of the lower energy green emission. This indicates that the defects may have originated from the bulk. It also suggests that the defects are found within the absorption depth of the He-Cd laser (~ 70 nm).⁸³⁻⁸⁴

For a deeper understanding of the specific defects that influence the PL emissions, we also treated the ZnO in pure oxygen atmosphere. Fig 5.5 shows the emission spectra of the ZnO processed in such atmosphere and the low energy green emission associated with Type II defects with peak emissions at 2.186 eV (567.5 nm) and 2.294 eV (540.9 nm) respectively. The difference is clear. Despite the fact that the ZnO particles are annealed with a similar zinc partial pressure, it is less likely that they have a similar defect origin that relates to their emissions such as zinc vacancies. In fact, by reducing the oxygen partial pressure from 1 atm to 0.21 atm, the emission intensity peaked at 2.186 eV becomes weaker while the low energy green emission associated with Type II defects becomes dominant (also see Appendix C). The oxygen vacancies have been the dominant defects that are responsible for the green emission. Earlier, we determine that Zn vacancy is less likely to be responsible for the green emission. Other various kind of defects such as O/Zn interstitials, Frenkel and Shottky defects are discussed here. The formation energies of the

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Cation Frenkel, Anion Frenkel and Schottky defects which can be found in the works of Tomlins *et al.*⁸⁸

Fig 5.5: PL spectra of ZnO with Type II defects annealed at 900°C for 24 and under O₂ atmosphere at 900°C for 24 hrs.

Table 5.2: Formation Energies of Defects

Disorder Type	Formation Energy (per defect)
	(kJ/mol)
Cation Frenkel	424
Anion Frenkel	418

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Schottky

339

The formation energies for cation and anion frenkel defects are higher than the Schottky defects. The oxygen interstitials concentration are negligible as the wurtzite structure has no space for them, therefore anion frenkel defects are most likely to be absent.⁸⁹ The cation Frenkel defects (zinc vacancies and zinc interstitials) are expected to be dominant when we annealed ZnO in 100% oxygen atmosphere, however, we did not observe any green emission. Therefore it is also unlikely that the cation Frenkel defects to be responsible for the green emission.

The ZnO is a semiconductor material, the charge neutrality can be determined in this form;

$$n + [V'_{Zn}] + 2[V''_{Zn}] = p + [V^+_o] + 2[V^{++}_o] \quad (5-1)$$

where V'_{Zn} and V''_{Zn} are the singly and doubly charged ionized acceptors respectively and V^+_o and V^{++}_o are the singly and doubly charged ionized donors. The negative charges are provided by electrons and ionized acceptors, while the positive charges are holes and ionized donors. The concentrations of electrons and holes are related through the interband equilibrium coefficient, $K_i = np$. ZnO is an intrinsically an n-type materials, therefore the electron carrier concentrations are dominant in the system. The overall downwards surface band bending in the ZnO that has annealing in ambient and reducing atmosphere suggested that the material is an n-type semiconductor with relatively large carrier concentration. The charge neutrality is therefore maintained by the presence of ionized donors such as the presence of charged oxygen vacancies. While the presence of the Schottky defects are possible, they might not be the dominant defects as it will implied

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a drastic reduction of the carrier concentration in the materials which does not reflect our results. Therefore, the Schottky defects might not be responsible to the green emission.

The as-received ZnO powder has the following impurities as highlighted on the container. The as-received ZnO has been calcinated, although the exact calcination temperature

Table 5.3: Impurities in As-received ZnO

	Impurities	Percentage (%)
1.	Carbonate	0.2
2.	Chlorides Cl^-	0.002
3.	Phosphates PO_4^{3-}	0.015
4.	Nitrate NO_3^{2-}	0.062
5.	Sulphate SO_4^{2-}	0.014
6.	Ammonium Sulphate $(\text{NH}_4)_2(\text{SO}_4)$	0.18
7.	Fe	0.003
8.	As	0.0005
9.	Mn	0.005
10.	Ca	0.005
11.	Cu	0.0005
12.	Pb	0.01
13.	Cd	0.001

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14.	Zn metal	0.002
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is not highlighted. The peak emission for the as-received ZnO is found at 2.103 eV (~590 nm), which is in the yellow region. It is therefore unlikely that impurities are related to the presence of the green emission. Although copper impurity is found to be related to the green emission, the presence of this impurity in our as-received sample does not show any valid relationship.³ Literature reviews have also shown that the rest of the impurities are not related to the green emission.⁹⁰⁻¹⁰⁴

5.2.3 Influence from Surface Modification

To identify the nature of defects and understand how the specific defects give rise to the particular green emissions, the surfaces of the as-prepared materials were characterized with XPS. The as-received ZnO, which serves as the reference, has a core level Zn 2p 3/2 binding energy (BE) at 1021.2 eV. The BE of Zn 2p 3/2 for the ZnO with Type I defects is 1.8 eV higher (1023.0 eV) while the ZnO with Type II defects shifts towards lower energy by 0.5 eV [Fig 5.6 (a)]. This shows that the core level BE of ZnO with both green emissions shifts in the opposite directions to that of the as-received materials. It is interesting to note that the other measured core level orbital BE, Zn 3s has a small distinctive shift of 0.2 eV for ZnO with Type I defects [Fig 5.6 (b)].

The BE shift that occurs at Zn 2p 3/2 core level may be associated with the sensitivity of the maximum sampling depth of XPS characterization. The electron's

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inelastic mean free path (IMFP) $\propto (\text{\AA})$ could be estimated at a particular binding energy using Tanuma, Powell, and Penn TPP2M formula.¹⁰⁵ The maximum sampling depth was subsequently derived from the decaying function $\exp[-d/\alpha]$,¹⁰⁶ where d is the approximated sampling depth. Since d is approximated by 3α , in this depth $\sim 95\%$ of all the photoelectrons would be scattered by the time they reach the surface. The calculation shows that the estimated maximum sampling depth for Zn $2p_{3/2}$ is about 3.5 nm while it

(c)

(d)

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Fig 5.6: (a) XPS spectra of Zn 2p $3/2$, (b) Zn 3s for the ZnO with Type I and II defects respectively annealed at 900°C for 24 hrs. High resolution TEM image of ZnO with (c) Type I defects (annealed at 900°C, 24 hrs) with an ultra thin modified layer (arrowed) and (d) with Type II defects (annealed at 900°C, 24 hrs).

is approximately 7.6 nm for Zn 3s respectively. This indicates that a dominant modification may have occurred on the surface of the material processed in the reducing atmosphere and the depth of the modified layer underneath the surface was less than 3.5 nm.

Pertaining to the first observation, as the shift for ZnO with Type I defects is much larger, an extensive modification may have taken place on the surface. Since the core level BE of Zn 3s has shifted slightly, little modification occurred at the corresponding sampling depths. The XPS results are supported by the high resolution TEM image in Fig 5.6 (c) and Fig 5.6 (d). The high resolution image in Fig 5.6 (c) shows that the ZnO with Type I defects has a core shell-like structure with the

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shell thickness of ~ 4.0 nm, having a good agreement with the XPS results. Since the shift of the 2p $3/2$ core level BE of ZnO with Type II defects is much smaller than that of ZnO with Type I defects, the modification on the surface as shown in the TEM image is not apparent [Fig 5.6 (d)].

The surface modification in ZnO with Type I defects should be the predominant factor of the high energy green emission. Such a phenomenon can be explained with the presence of surface band bending. The as-received ZnO has a hydroxylated surface that contributes electrons to form a downwards band bending with an accumulation layer.¹⁰⁷ Since the BE of ZnO with Type I defects shifts to higher energy, there is an increase downwards band bending with the core levels as well as the valence band maximum¹⁰⁸ shifting away from the Fermi level. This could be due to an increased electron accumulation layer possibly from the surface oxygen vacancies which is an electron donor.¹² The ZnO with Type II defects should have a lower degree of downwards band bending as a result of reduced oxygen vacancies concentration.¹⁰⁹ However, such a observation should be accompanied by an increase in oxygen vacancy concentration as a function of depth and would dominate in the bulk as characterized by the XRD and Raman spectroscopy.^{66,109} The nature of band bending found in ZnO probably leads to different electronic transition such as the high energy and low energy green emissions. In addition, it should be noted that the calculated defect transition level of surface oxygen vacancies also appears to be different from that of the bulk oxygen vacancies, leading to these two types of emissions.¹¹⁰

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5.2.4 Possibility of Hydrogen Effects on the Green Emission

It is unclear whether the hydrogen in a reducing atmosphere would be doped into the materials, thus making its own contribution to the high energy green emission. In general, hydrogen could be a shallow donor; it dissolves interstitially so that it can be completely ionised to protons, thus residing on oxide ions as hydroxide ion defects and electrons. Such hydrogen easily dominates the defect structure as well as the electrical and photonic properties directly or indirectly. In the reducing atmospheres, hydrogen could be trapped in ZnO above 500 °C, leading to the dissolution of protons and electrons. In the as-reduced materials, the induced defects such as protons and electrons etc. would be frozen and trapped in the quenching processing.

The question is: Does hydrogen play a direct role in the development of the high energy green emission? To isolate the contribution of hydrogen and oxygen on the specific green emissions, we annealed the ZnO in dry N₂ at 700°C for 24 hrs. The PL spectra of the materials processed in dry N₂ and % H₂ + 97 % Ar at 700°C for 24 hrs were plotted in Fig.

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Fig 5.7: (a) PL spectra of ZnO with Type I defects and one that annealed under nitrogen atmosphere at 700°C for 24 hrs and (b) MBO model fitting of ZnO annealed under nitrogen atmosphere at 700°C for 24hrs.

5.7(a) for comparison. Fig. 5.7 (b) shows the PL emission spectra of ZnO processed in N₂ at 700°C with its fitting results using the same MBO parameters obtained from the Type I defects induced at similar temperature. It demonstrates that the MBO fitting is satisfactory at the high energy band side. A similar emission mechanism appeared in the materials processed in H₂ free atmosphere; it shows that the high energy green emission is not originated from hydrogen. In addition, it has been reported that the presence of hydrogen in ZnO enhances the efficiency of UV emission while it suppresses the defect emission, for example, green emission.^{46,111} However, the relative intensity of the high energy green emission [Fig 5.4 (b)] was enhanced instead in our experiments by the processing temperature. Hence hydrogen may not have played a direct role in the origination of this green emission.

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5.4 Summary

The intrinsic variants of green emissions in ZnO were investigated to separate the subtle interplay among the specific defects. Through systematic experimental separations, advanced materials characterizations and physical modeling, the subtle variation of the green emission was deemed significant and was closely related to the defects residing at different locations. It was found, for example, that the defects residing on the surface and in the bulk give rise to the high energy (peak value of 2.465 eV) and low energy green (peak value of 2.294 eV) emissions respectively. Importantly, the ZnO with Type I defects that are associated with the surface defects was found to be responsible for the high energy green emission as evidenced by the downwards band bending through a binding energy shift of Zn 2p $3/2$ orbital and the observation of a modified surface layer. The downward band bending caused by the electron accumulation layer could be due to the formation of the surface oxygen vacancies acting as the electron donors. On the other hand, the correlation between the unit cell volume contraction through XRD and PL intensity of the low energy green emission suggests that the Type II defects are the oxygen vacancies distributed beneath the surface. The experimental results also demonstrate that the green emissions are independent of hydrogen doping. This finding provides a new insight that could possibly assist the precise manipulation of the photonic emissions of ZnO for optoelectronic applications in the future.

CHAPTER 6:

SPECIFIC DEFECTS, SURFACE BAND BENDING AND CHARACTERISTIC GREEN EMISSIONS OF ZINC OXIDE

6.1 Introduction

Following the previous chapter, it was found that ZnO with Type I and Type II defects have different types of green emissions, namely the higher energy and lower energy green emissions. By means of XPS, the Zn 2p $3/2$ core level binding energy of the prepared ZnO samples is shown to be very different from each other. In combination with the TEM, the Type I defect could be related to surface defects. Such a core level shift is suggested to be due to the presence of surface band bending.

In this chapter, we analyse the XPS result in depth and attempt to correlate this relationship with the green emission. The mechanism of the surface band bending caused by the specific defects and the underlying chemical physics are studied in detail.

6.2 Results and Discussions

As observed in Fig 5.1 the high energy green emission caused by Type I defects has a peak energy of 2.46 eV (~ 504.4 nm) while the low energy green emission induced by the Type II defect has a peak energy of ~ 2.26 eV (~ 549.0 nm).

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ZnO

The relative intensities of these green emissions normalized to their respective UV emissions, increase as a function of the processing temperature. The relative intensity of the green emission is related to the concentration of the specific defects acting as the emission center. Unlike the transition metals that would have multiple ion valence states, Zn only has limited ion valence states e.g. +1 and +2.¹¹² This suggests that it is very difficult to quantitatively determine the variation of chemical compositions caused by the processing in different atmospheres with the state-of-the-art characterization techniques. This is true as the phase diagram of ZnO shows an extremely narrow range of possible chemical composition (e.g atomic percent of Zn change is less than 0.0001%).¹¹³ The correlation among the intensity of green emission, concentration of defects, processing temperatures and environments were qualitatively investigated by the PL spectroscopy and crystallographic structural characterization using X-ray Diffraction in Chapter 5.¹¹⁴ The results showed that, in ambient environment, the unit cell volume decreased as the processing temperature increases. This was associated with the increase of the concentration of Type II defects, exhibiting the behaviour of the defect in bulk.

Fig. 6.1 shows the core level and valence band binding energy shift as a function of the relative intensity of the characteristic green emissions for the materials with Type I and Type II defects respectively. For the ZnO with Type I defects, the Zn 2p 3/2 core level binding energy shifts gradually to higher binding energy from 1021.1 eV to 1023.0 eV as the relative intensity of high energy green emission increases from 1.66 to 7.08 [Fig. 6.1 (a)]. Similar correlation between

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shifting of the VBM and the relative intensity of high energy green emission are also observed experimentally in Fig. 6.1 (b).

Different from the phenomena observed in the ZnO with Type I defects, the Zn 2p 3/2 core level binding energies generally decreases with increasing relative intensity of the low energy green emission in the ZnO with Type II defects. It is interesting to note that

Fig 6.1: (a) Zn 2p 3/2 Core Level Binding Energy of ZnO with Type I and Type II defects. The relative green emission intensity with respect to the UV emission is denoted as 'R', (b) Valence Band Maximum(VBM) of ZnO with Type I and Type II defects.

while Zn 2p 3/2 core level binding energies shifted to lower energy, the VBM shifted to higher binding energy. This is distinct from [Fig 6.1 (b)] that of ZnO with Type I defects.

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Such phenomena may be explained with the characterization of XPS results within the framework of surface band bending mechanism.¹¹⁵ Fig 6.2 shows the schematic diagrams of the surface band bending mechanism interpreted by core level binding energy or VBM in XPS. For a hypothetical semiconductor with an absent of band bending, the VBM hypothetically determined from XPS has an energy of χ eV from the Fermi level, $E_F = 0$ eV as shown in Fig 6.2 (a). On the other hand, this VBM can be represented as a horizontal red

Fig 6.2: Schematic Diagram of the relationship between (a) XPS using valence band maximum and (b) Downwards surface band bending.

dotted line in the band diagram shown in Fig 6.2 (b). This red dotted line represents the flat band condition from the bulk to the surface for this hypothetical semiconductor. We assume an n-type semiconductor has a Fermi level pinned to the surface and its VBM in XPS [Fig 6.2 (a)](now shifted γ eV away from E_F , where $\gamma > \chi$ in value. Therefore, its VBM (as represented by the black continuous line) as shown in the band diagram of Fig 6.2 (b) would shift downwards from the E_F by γ eV [Fig

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6.2(b)]. It is noted that γ eV, which is the amount of band bending, is found at a probing depth of σ determined by the XPS [Fig 6.2 (b)]. Such downward band bending indicates an accumulation of electrons contributed by donor defects near the surface for an n-type material. Likewise, if the binding energy shifts towards the E_F , it would indicate the formation of a surface depleted of electrons, thus an upward banding would be observed. The effects of an accumulation or depletion layer not only influence the VBM but also the core level binding energy in a similar manner.¹⁰⁸ The nature of the surface band bending is also influenced by the absorption of atoms or molecules of interest.¹¹⁶⁻¹¹⁷ It is therefore noted that the as-received ZnO absorbed moisture from the environment, thus having a hydroxylated surface. Through a reaction of $H + O^{2-} \rightarrow OH^- + e^-$, a shallow donor state may be formed to allow an increase in the carrier concentration on the space charge layer by many folds. This implies that the as-received sample most likely would have an accumulation layer.¹⁰⁷

The surface banding phenomenon can be applied to our XPS results provided that the probing depth of XPS is also considered. In Chapter 5, the calculation shows that the estimated maximum sampling depth for Zn 2p 3/2 is approximately 3.5 nm while it is approximately ~8.2 nm for the VBM region. The ZnO with Type I defects induced at 900°C has its core level Zn 2p 3/2 shifted to a higher binding energy by 1.9 eV while its VBM shifted to higher energy by only 0.35 eV with reference to the as-received ZnO. Therefore, the downwards surface band bending is more severe at a shallower depth. The overview of the core level as well as the VBM shift in the form

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of surface band bending is illustrated in Fig 6.3(a). Such a surface band bending effect indicates that the active donor concentration is dominant in the surface layer (~ 3.5 nm) but reduces along the depth and finally reaches the concentration of the bulk. It has been reported that an accumulation of electron near the surface layers may be associated with oxygen vacancies, V_o which are electron donors [Fig 6.3(b)].¹²

The observation of VBM and the core level shift for the ZnO with Type II defects is more complex. The Zn 2p $3/2$ core level has a shallower probing depth (~ 3.5 nm) and yields a lower binding energy as referenced by the as-received ZnO [Fig 6.3(a)]. Therefore, the degree of downwards band bending in this particular material is lower. Compared with

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Fig 6.3: (a) Schematic Diagram of downwards band bending of ZnO with Type I and Type II defects annealed at 900°C. (b) Schematic diagram of ZnO with the location of Type I and II defects. (c) Electronic transition of Type I and II defects that give rise to the high and low energy green emission respectively.

the materials processed in both hydrogen and nitrogen, the relatively high oxygen partial pressure at ambient atmosphere resulted in a lower concentration of oxygen vacancies near the surface. Therefore, the electron concentration from the oxygen vacancies (defect donor) is lower due to the compensation of the holes associated with the acceptors. A homogenous distribution of the point defect in the bulk particle is not expected as determined by the XPS results. This has been observed by Mahan

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et. al. ¹⁰⁹ He explained that the reason that caused the inhomogeneity could be due to the rapid reduction of the diffusivity as the temperature is lowered. As a result, the oxygen vacancies become frozen in with this non-uniform distribution. This non-uniform distribution of the defects spans a distance of around 10 nm from the surface [Fig 6.3 (b)] and this is the range we are investigating through XPS.¹⁰⁹ This led the oxygen vacancies to be more dominant at a deeper depth (~8.2 nm) onwards [Fig 6.3 (b)]. The donor/electron concentration subsequently increases beneath the surface and consequently, the VBM shifted to a higher energy as compared to that of the as-received ZnO. It is important that an elaborated work must be carried out to study the thermodynamics of the vacancies diffusion under various conditions in the future.

In Fig 6.3 (c), we separate the surface band bending for the ZnO with Type I and II defects. The aforementioned Type I defects should be the oxygen vacancies that are concentrated near the surface, thus resulting in the downwards surface band bending. Since the oxygen vacancies is a deep level defect of localized state, the band bending effect should have little influence in altering its energetic position as compared to those shallow donor/acceptors.¹¹⁸ Hence, the electronic transition from the deep level state to the VBM occurs at a higher energy (0-0 transition, ZPL = 3.051 eV), giving rise to high energy green emission. On the other hand, oxygen vacancies which are mostly present in the bulk should be the Type II defects such that low energy (0-0 transition, ZPL = 2.941 eV) green emission occurs in the flat band region.

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The nature of the core level binding energy as well as the VBM shift could also be affected by several factors. The first is a chemical shift associated with the nature of the chemical bonding state.¹⁰⁶ Since ZnO doesn't have multiple oxidation state, the charge transfer is associated with the change of coordination number. It was reported that the 3d 5/2 core level binding energy of Rh ions shifts to higher binding energy when the coordination number to oxygen increases. This electron charge transfer that causes the higher binding energy shift is consistent with the valence band region.¹¹⁹ Such chemical shift is not observed in the ZnO with Type I defects where the surface has a number of oxygen vacancies. It is also unlikely to apply this chemical shift to the ZnO with Type II defects as the Zn 2p 3/2 core level shifts to lower energy while Zn 3d core level and VBM shifted to higher binding energy. This is supported by our work in Chapter 7 in which we studied the role of electron charge transfer in the presence of broken bonds for ZnO nanocrystals.

The Madelung energy is another factor that plays a role in the core level shift. For metal ions with higher coordination number, the Madelung energy component lowers its binding energy shifts while the binding energy of oxygen ions shifts to higher energy.¹²⁰ Table 6.1 shows the O 1s binding energy of ZnO with the high and low energy green emissions that are associated with Type I and Type II defects respectively. For the ZnO with Type I defects, the O 1s generally increases in its binding energy which shares the same trend as the Zn 2p 3/2 core level. For the ZnO with Type II defects, the O 1s core level binding energy generally shifts to lower binding energy, similar to the Zn 2p 3/2 core level binding energy. However, neither

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ZnO

of these materials shows the Madelung energy to be dominant. The above considerations favour our assignment of the binding energy to the observation of band bending.

Table 6.1: O 1s Core Level Binding Energies of ZnO with Type I and II defects with their respective green emissions of increasing relative intensities.

Type I Defect, Relative Green Emission	Type II Defect, Relative Green Emission	O 1s (TYPE I, eV)	O 1s (TYPE II, eV)
-	-	530.1	530.1
1.66	0.41	530.1	529.9
5.07	0.62	530.3	529.7
7.08	4	530.4	529.8

For the ZnO that was processed in pure nitrogen atmosphere without hydrogen and oxygen, the material has Zn 2p 3/2 core level binding energy at 1021.3 eV shifted by 0.2 eV with reference to the as-received sample. Its VBM shifts to 2.44 eV from 2.37 eV with the same reference. Such a substantial downwards band bending further supports notion of the accumulation layer formation. Nitrogen is an active acceptor and is therefore unlikely to contribute electrons to the surface if they

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are successfully doped into the as-prepared material.¹²¹ The downward band bending for this material suggests that under low oxygen vapour pressure, oxygen vacancies may form and act as active donors to contribute electrons near the surface. The electronic transition between the defect state and the downwards band bending region give rise to the high energy green emission.¹²² While the presence of nitrogen creates a low oxygen vapour pressure environment, such that oxygen vacancies are preferably formed, on the other hand, the XPS suggested that the nitrogen does not act as a defect level in contributing to the green emission.

It is believed that the donor defects would likely contribute to a downward band bending at the low index surfaces, such as (0001), (000-1), (10-10) as they are thermodynamically stable as compared to other crystal surfaces.^{12,107,123} They are also the favorable surfaces of the as-grown crystals. Therefore, a downward surface band bending is mainly contributed by the introduction of donor defects.

6.3 Summary

We have determined the core level binding energy as well as the VBM of the materials with different specific defects. For the ZnO with Type I defects, both the core level and the valence band shift to higher binding energy, indicating a further downwards band bending due to the formation of an accumulated layer of electrons. The presence of electrons is attributed to the donor concentration and the localized oxygen vacancies near the surface which act as the Type I defects. The defect state in

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the downwards bending region is responsible for the observed high energy green emission. On the other hand, the Zn 2p $3/2$ core level binding energy for the ZnO with Type II defects shifts to lower binding energy while the VBM shifts to higher binding energy. It demonstrates that the shallower region probed by the Zn 2p $3/2$ core level has an increasing concentration of acceptors, which partially compensate the existing accumulated layers. The formation of higher concentration of oxygen vacancies occurs at a deeper depth (~ 81.8 nm) due to the relatively fast cooling rate. These oxygen vacancies are the Type II defects, rendering the low energy green emission. The location of oxygen vacancies as shown in the results determines the characteristic green emissions with different energies, as observed.

CHAPTER 7:

CHEMICAL SHIFT OF ZN 2P 3/2 BINDING ENERGY IN NANOCRYSTALLINE ZINC OXIDE

7.1 Introduction

ZnO nanocrystals have initiated enormous scientific interests both in understanding the phenomena and in exploiting their remarkable intrinsic performance for optoelectronics.^{30,124} Nanocrystalline ZnO possesses unique properties by enhancing or suppressing existing bulk properties.¹²⁵⁻¹²⁹ In this work, we report the size dependence of the electron structure in ZnO by investigating the binding energy variation of nanocrystalline ZnO as a function of average crystal size. These results support of the surface band banding mechanism proposed in Chapter 6.

7.2 Results and Discussions

Transmission electron microscopy (TEM) was employed to verify the crystal sizes determined by X-ray Diffraction (XRD). Fig. 7.1(a) shows that the prepared ZnO nanomaterials have an

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Fig 7.1: TEM morphology shows that the prepared ZnO materials have an average crystal size of ~3.0 nm.

average crystal size of ~3.0 nm (also see Appendix D), demonstrating a well controlled size dispersion in our experiment. High resolution TEM image in Fig. 7.1(b) also exhibits that the high quality nanocrystalline materials were produced by the employed technique. Quantitative analysis indicated that except for size variation and modulation of structural parameters, no other chemical reactions occurred during the milling process.

The phases were verified by the Rietveld refinement. By visual inspection, using phases such as ZnO, WC and the Al₂O₃ NIST standard, no major mistift e.g unfitted peaks can be identified during the refinement. Hence, the Rietveld refinement did not show any additional phase that has not been accounted for. Fig 7.2 shows that the quality of the fitting is relatively good. Furthermore, the R_{bragg} is about 2.274 which is an indication that

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the selection of the ZnO phase for refinement has a close matching with our experimental data.¹³⁰

Fig 7.2: Rietveld Refinement of the High Energy Ball Milled ZnO with a crystal size of ~3.0 nm.

In addition, mechanical contamination from unreacted WC with less than 0.5 wt % was detected in samples with the longest milling durations as determined from Rietveld Refinement (Table 7.1). The phase composition is calculated in the table below

Table 7.1: Phase Composition wt %.

Phase Composition wt % (Spiked with 20 wt% of Al ₂ O ₃ NIST Standard)			
Size (nm)	ZnO	Amorphous ZnO	WC
8.5	77.13	22.5	0.37
3.0	60.17	39.4	0.43

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The composition is determined by the XPS and is shown in the table as determined by the the XPS. It must be noted that this is a relative chemical composition, therefore the qualitative result shows the present loss of oxygen atoms with reducing sizes.

Table 7.2: Relative Chemical Composition at%

Relative Chemical Composition at%		
ZnO	Zn	O
As-received	50	50
Size = ~8.5 nm	50	41.27
Size = ~3.0 nm	50	36.13

Since the major impurity is the tungsten carbide (WC) which is less than 5 wt%, the presence of this little amount impurity phase is unlikely to affect the grain size. One of the most likely surface contaminant would be the interaction between the WC and the surface of ZnO nanocrystals. Fig 7.3 below shows the W 4f 7/2 binding energy of W. From the figure, we observed that the peak position of the W 4f 7/2 remains the same suggesting that there is no interaction with the ZnO nanocrystals. The binding energy shift of the Zn 2p 3/2 (shown later) should not be related to presence of WC.

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Fig 7.3: Binding energy of W 4f 7/2 of HEBM ZnO Nanocrystals.

All XPS spectra were fitted with the reported fitting guideline.⁵⁷ The XPS spectra of the high purity starting material was symmetrically fitted with a single peak, as an asymmetrical peak should be assigned to the interaction of the positive core hole with the conduction electrons in a metal like conducting system.⁵⁸ In each case, the spectra broadening caused by chemical, structural and electronic fluctuations in the surroundings of the emitting atoms of the peaks was refined using a procedure as implemented on Fresenius.⁵⁹

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The individual ZnO particle in the starting material having an average size of 2.9 μm consists of many submicron crystals (202 nm). The XPS spectra of the starting material exhibits a main core level binding energy (BE) of Zn-2p_{3/2} located at 1022.0 eV [Fig. 7.4(a)],

Fig 7.4: XPS spectra show core level binding energies of Zn-2p_{3/2} of ZnO with crystal sizes of (a) 202 nm and (b) 8.5 nm, respectively.

well within the errors after calibration and the value agrees well with NIST XPS database.¹³¹ It is of interest to note that there is a small BE peak at 1023.0 eV which is independent of crystal size and appears in all XPS spectra. The origin for the appearance of this peak remains unclear. It may be related to the zinc vacancies which have been observed in the materials annealed at very high temperature in ambient.¹³²

When the crystal size of ZnO is reduced to 8.5 nm, the BE peak for Zn-2p_{3/2} is broadened and shifted towards a lower binding energy [Fig. 7.4(b)]. Two new BE peaks are subsequently identified at 1021.2 eV and 1020.8 eV through peak deconvolution. The overall shift (the original broad peak) suggests a change in the

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binding state of Zn ions which can physically be described by a loss in the number of oxygen ions (oxygen vacancies) in nanocrystalline ZnO. The charge transfer from zinc to oxygen is therefore reduced, thus increasing the shielding effect of the valence electrons in Zn ions which decreases the binding energy of the core electrons in the Zn ion. From Fig. 7.4(b), it is discernable that the integrated intensity for the BE peak at 1022.0 eV, which represents the concentration of stoichiometric ZnO, decreases. This may be attributed to the formation of a large fraction of non-stoichiometric ZnO in the sample. This supports the notion of oxygen vacancy formation induced by the size reduction. As a matter of clarification, such oxygen variation is solely intrinsic as the consequence of size reduction, different from the extrinsic oxygen variation caused by thermal treatment.

Fig. 7.4(b) also shows that the BE peak of 1021.2 eV is dominant in the spectra followed by the BE peaks at 1022.0 eV and 1020.8 eV. This phenomenon may be related to the variation of broken bonds caused by size reduction. Ideally, zinc cations are tetrahedrally co-ordinated with four oxygen ions in the bulk. Consider a tetra-coordination with four oxygen ions is equivalent to zero broken bond, there is a direct relationship between the number of broken bonds and the number of oxygen ions removed from the lattice points surrounding a zinc ion. An increase in the number of broken bonds is proportional to the number of oxygen ions removed from the lattice points associated with the particular zinc cation (e.g., a broken bond is a result of an oxygen ion removed from the coordination lattice point of the zinc ion and so on). With increasing broken bonds, the amount of charge

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transfer from zinc ion to oxygen ions will be further reduced, thus lowering the binding energy of the core electrons of Zn ions. Based on this consideration, the BE peak at 1021.2 eV can be assigned to zinc ions with a broken bond while BE peak at 1020.8 eV is assigned to zinc ions with two broken bonds.

From a thermodynamic view point, when a ZnO crystal is cleaved normal to the c axis in a manner which breaks the fewest interatomic bonds, two different polar surfaces, such as (0001)-Zn and (000 $\bar{1}$)-O surfaces, are formed on opposite sides of the crystal with cleavage energy of ~ 4.0 J/m².¹²³ Therefore, the (0001) plane is frequently observed in high resolution TEM characterization as shown in Fig. 7.3(b). On an ideal surface of ZnO, such as the surface with infinite radius, Zn ion in stoichiometric ZnO would bond to three oxygen atoms with a broken bond on (0001) plane. The (0001)-Zn with positive charge and (000 $\bar{1}$)-O with negative charge always co-exist because of charge neutralization. It is believed that these polar surfaces do not need to be stabilized by reconstruction or presence of adsorbates.^{123,133} Even though the oxygen absorption might occur at the dangling bonds on (0001)-Zn, it would be minimized at the lowest level to maintain the charge neutralization.

Different from the atomic structure of the surface, the zinc ions beneath the surface would be fully coordinated. When the crystal size of ZnO is reduced to 8.5 nm, oxygen vacancies tend to form on the surface layer, initially to compensate the surface shrinkage caused by the size reduction, therefore some of the surface zinc ions would acquire an extra terminated bond (e.g. two broken bonds), creating a

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new binding energy of 1020.8 eV. In thermodynamics, the higher concentration of oxygen vacancies on the surface would cause a further occurrence of vacancies in a few layers beneath the surface. The formation of such vacancies results in a part of the interior zinc ions having a broken bond with binding energy of 1021.2 eV. This gives rise to zinc ions beneath the surface which are no longer fully-coordinated with oxygen ions, different from the bulk materials. It is important to note that there are two factors that account the dominant BE peak at 1021.2 eV at this crystal size. The surface atom percentage is taken into account and it is relatively small (33%) by assuming one unit cell as the monolayer on the surface. Another consideration is the sampling depth which is estimated to be 3.5 nm for XPS as calculated in Chapter 6.¹³⁴ This implies that considerable XPS detection is in fact derived from the interior zinc ions away from the surface. As a result, these interior zinc ions with one broken bond are responsible for the dominant BE peak positioned at 1021.2 eV.

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Fig 7.5: (a) XPS spectra show core level binding energy of Zn-2p_{3/2} of nanocrystal ZnO with crystal size of 3.0 nm. (b) A schematic atomic structure of nanocrystalline ZnO shows the corresponding positions of oxygen vacancies (dashed-dotted circle) and zinc ion associated to one (continuous circle marked B) and two broken bonds (dashed circle marked A) on both surface and underneath layers.

For nanocrystal ZnO of 3.0 nm, the relative percentage of integrated intensity of peak binding energies of 1021.2 eV and 1020.8 eV changes, indicating that the BE peak at 1020.8 eV in the XPS spectra becomes prominent [Fig. 7.5(a)]. The percentage of surface atoms calculated has increased from 33% to 74%, suggesting that in this case, there is a negligible influence of sampling depth and the surface detection becomes extremely important. It implies that the percentage of the surface zinc ions associated with two broken bonds as a result of oxygen vacancies in the materials increases with further decrease in crystalline size. It can be seen that the increased surface area becomes extremely unstable, allowing a high concentration of high oxygen vacancies to be favourably formed on the surface instead. Fig. 7.5(b) is a schematic atomic model showing the possible positions of oxygen vacancies (dashed-dotted circle) associated to the broken bonds in ZnO with crystal size of 3.0 nm. This model exhibits how oxygen vacancies on the surface layer result in two broken bonds around a zinc ion (dashed circle marked as A) whilst oxygen vacancies at the layer underneath surround another zinc atom (continuous circle marked as B) and causes at least one broken bond. Fig. 7.5(b) also shows a possibility that zinc ions at the sub-surface can have two broken bonds if two oxygen vacancies are able to form around it. This may suggest an extra contribution to the increased intensity of the BE peak at 1020.8 eV which is the predominant binding state of the material.

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The additional BE peaks at the end of the lower tail should be due to the impurities as they appear to be present even in the as-received materials.

7.3 Summary

In summary, the size dependence of electron structure of ZnO has been studied in detail. The results show a complicated alteration in the zinc binding state (equivalent to the splitting of oxygen state) which is associated with the variation in the number of broken bonds per zinc ion due the severe size reduction. Two binding states at 1021.2 eV and 1020.8 eV are observed in nanocrystalline ZnO of 8.5 nm and 3.0 nm, respectively. These energies are lower than the binding energy of stoichiometric ZnO with a crystal size of 202 nm. It suggests that oxygen vacancies may be generated by surface shrinkage due to the size reduction and the two binding energies are therefore assigned to the zinc ions with one and two broken bonds respectively. It is believed that the increase of broken bonds associated with zinc ions in the ZnO of 3.0 nm causes localized structural distortion or variation.

CHAPTER 8:

SURFACE BAND BENDING: THE MECHANISM OF GREEN EMISSION VARIATION IN ZNO

8.1 Introduction

In the Chapter 4-6, we determined how the nature of Type I and Type II defects are related to their locations in ZnO and hence behave differently. Particularly, Type I defects residing near the surface results in downwards band bending that leads to a higher energy green emission. In this chapter the origin of the characteristic green emission is investigated in detail and a universal mechanism is established to describe how the characteristic green emissions are stimulated by the defects beneath and near the surface.

8.2 Flat Band Condition Defect Beneath the Surface

The green emission is a radiative transition which can be described using the configurational coordinate model. The photoluminescence bandshape with temperature above $T = 0$ K can be described as a function of temperature by

$$I_{ab}(E) = I_0 \sum_{p=-\infty}^{\infty} \exp(-S(1+2n)) \left(\frac{1+n}{n}\right)^{p/2} I_p(2S\sqrt{n(n+1)}) \delta(E_0 - p\hbar\omega_{LO} - E) \quad (1)$$

Where $n = [\exp(\hbar\omega_{LO}/k_B T) - 1]^{-1}$ is the mean thermal occupancy in the vibrational mode, and $I_p(x)$ is the modified Bessel function. S is the Huang-Rhys factor which describes the strength of electron-phonon coupling.¹³⁵ For the green

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emission emitted from ZnO, $E_o = \hbar\omega_{eg}$ is also known as the 0-0 electronic transition energy [or Zero Phonon Line (ZPL)] that ranges from 2.859 eV to 2.927 eV^{3,5} while the S factor is around 6.4 - 6.9.^{5,39,65} In Chapter 5, we determine the 0-0 electronic transition energy as well as the S factor. Since ZnO is intrinsically n-type, the dominant defects should be electron donors. The green emission mostly involves an electronic transition between a donor and the valence band^{9,50} Due to the finite temperature conditions, such a transition would involve a strong electron-phonon coupling.¹³⁵

We first applied Eq. (1) to either beneath the surface or near an ideal surface with a flat band condition. In this process, despite taking place at different depth, the donor defects have a similar transition as shown in Fig 8.1(a). This provides a distinct emission bandshape consisting of multiple electronic-vibrational lines as shown in Fig 8.1(b). These multiple electronic vibrational lines can be described by the Dirac function in Eqn 1 but it is unable to account for the finite broadening of linewidth. Such broadening is important to the electronic vibrational lines because it determines visibility of the fine structures in the emission band. In Chapter 3 and 5, we describe the emission bandshape with inclusion of the finite linewidth with the multi-Mode Brownian oscillator (MBO) model. In MBO model, The key parameters of the model are: (1) the frequencies of the primary oscillators ω_j , (2) the damping coefficient γ that controls the system-bath coupling strength, and (3) the Huang-Rhys factor S that reflects the electron-phonon coupling strength. Other controlling parameters include the bath temperature T and the 0-0 electronic transition energy

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(ZPL, $\hbar\omega_{eg}$) as aforementioned earlier.¹³⁶ The only primary phonon used in our analysis, the LO phonon $\omega_j=\omega_{LO}$. ($\omega_{LO} = 574.1 \text{ cm}^{-1}$), is assigned to be the space between adjacent phonon side bands. Compared with the information obtained from Fig 8.1(b) we simulate the green emission band at 10K and $\gamma = 60 \text{ cm}^{-1}$ using the parameters given in Fig 8.1(c). One can observe a fine structure emission of the electron-vibrational lines with a finite linewidth.

Fig 8.1: a) Schematic Diagram of a single 0-0 electronic transition at flat band condition, b) Emission band of a single 0-0 electronic transition at flat band condition, c) Emission band of single 0-0 electronic transition using MBO model.

8.3 Surface Band Bending Condition Defects Near the Surface

In an actual surface, a donor defect near the surface cannot be neglected. This is because donor defects near the surface produce an electron accumulation layer. The concentration of the donors can be many times higher than that beneath the surface.¹²² As a result, downwards band bending occurs.^{12,108} It is unlikely to have an upwards band bending as ZnO would have a hydroxylated surface in the ambient containing shallow donors that would donate electrons to the surface.¹⁰⁷ This has been explained in Chapter 6. From the schematic diagram in Fig 8.2(a), we therefore expect the ZPL to increase to a maximum value on the surface [Fig 8.2(a)]. Comparing the emission bandshape of single donor defects in bulk and on the surface [Fig 8.1(a) and 8.2(a)], it can be seen that the deep level defect is a strongly localized state, hence the energy level of this defect state in the bandgap remains unchanged.¹¹⁸ However, we observed that the emission bandshape remains similar but has shifted by 0.2 eV as a result of band bending at a particular depth near the surface [Fig 8.2(b)]. This demonstrates that downwards surface band bending play an important role in shifting the green emission from 2.855 eV to 3.055 eV.

The He-Cd laser with wavelength of 325 nm would probe all emission entities in ZnO to about 70.8 nm giving rise to the resultant emission band.⁸⁴ This implied that the emission is affected by the influence of surface band bending on 0-0 electronic transitions. To simplify the case, the deep level defects are divided into 5 categories that are located at different positions from the surface to the downwards

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band bending region [Fig 8.2(c)]. The different degree of band bending implied different 0-0 electronic transition (ZPL).

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Fig 8.2: Schematic Diagram of (a) a single 0-0 electronic transition at downwards band bending condition, b) Emission band of a single 0-0 electronic transition at downwards band bending condition, c) Schematic Diagram of five 0-0 electronic transition at downwards band bending condition, d) Emission band of a five 0-0 electronic transition at downwards band bending condition and e) Emission band of five 0-0 electronic transition using MBO model.

Fig 8.2(d) shows that the resultant electronic-vibrational lines for different categories are offset from each other while the Huang-Rhys factor remains unchanged for each 0-0 electronic transition. In fact, the correlation between the surface band bending and the electronic transition suggests that in the downwards band bending, the 0-0 electronic transition shifts to higher energy and we obtain a summed emission bandshape of higher energy as shown Fig 8.2(d). For example, the peak of this summed emission in Fig 8.2(d) is ~ 2.556 eV while the peak emission of the electronic-vibrational line under the flat band condition is at ~ 2.427 eV [Fig 8.1(b)]. In actual experimental observations the band bending effects invoked a continuous variation of the 0-0 electronic transitions at different depths from the surface; therefore a shift in the peak emission spectra to higher energy is expected.

In Fig 8.2(e), we use the MBO model [Eq.(2)] to simulate the effect of downwards surface band bending for a material consisting of the same 5 categories of 0-0 electronic transitions similar to that shown in Fig 8.2(c). Here we fix the S factor and γ coupling strength with equal weighting. Fig 8.2(e) shows the emission bandshape with fine structures of the electronic vibrational lines. As one notices, the fine discrete structure of the green emission appears to smooth out [Fig 8.2(e)] compared to the emission of single 0-0 electronic transition [Fig 8.1(c)]. The degree of the structured green emission is reduced as the number of 0-0 electronic

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transitions increases because the fine structures of the electronic vibrational lines are offset from each other during the superimposition. In addition, it is important to note that the peak emission of Fig 8.1(c) is at 2.427 eV while the peak emission of Fig 8.2(e) is at 2.522 eV. This supports the notion of a shift between the structured and the diminishing fine structured emission band.

It has been reported that the green emission is either a structured or structureless

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Fig 8.3: a) Experimental result from Garces *et. al.*² structured and structureless green emission of single crystal ZnO and b) Simulated MBO model for structured and structureless green emission.

emission. This is illustrated in Fig 8.3 (a) based on experimental results presented in the open literature.^{2-3,5,41} The structured emission band can be seen to have been displaced from the structureless emission and the former is positioned at a lower energy, similar to our simulated result in Fig 8.3(b). In our simulation, only the single 0-0 electronic transition was considered in the structured green emission due to the presence of donor defects in the bulk, which has a flat band condition. For the donor defects found near the surface, we started the summation from the surface with the downward band bending (which has an electronic transition of 3.055 eV) to the flat band condition in the bulk (which has an electronic transition of 2.855 eV) at 20 intervals. Here, we simulate a sum of 21 electronic transitions to simplify the calculation in the downward band bending conditions. It is worth noting that our simulated results as shown in Fig 8.3 (b) are in good agreement with the observed structureless emission band at the higher energy [Fig 8.3 (a)]. This simplification is considered valid because the downwards band bending should be continuous. The agreement between our simulated results and the observed data suggests that the effect of downwards band bending dominates the emission band shifting.

From the observed experimental results as shown in Fig 8.3(a), it is less likely that the damping coefficient γ , which controls the system-bath coupling strength of each electronic-vibrational line dominates the structureless green emission. In Fig 8.4, we showed the simulated emission band using MBO as a function of γ . Despite

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the fact that the structured emission band diminishes and is gradually replaced by the structureless emission band with increasing γ , the peak emission shifts towards lower energy from point A (at 2.496 eV when $\gamma = 30 \text{ cm}^{-1}$) to point B (at 2.424 eV when $\gamma = 200 \text{ cm}^{-1}$). This is different from the

Fig 8.4: Effect of γ of different values on the simulated green emission.

results shown in Fig 8.3(a), where the structureless green emission band was observed experimentally to be positioned at a higher energy (2.485 eV) as compared to the observed structured green emission (2.432 eV). Our proposed mechanism using the surface band bending may thus better describe the origin of the shifted emission band as well as its structureless nature.

It is also unlikely that the presence of surface defects which often provide a non-radiative pathway would suppress the emission band. Recent investigation

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suggests that the green emission originates from the surface and that its band can be suppressed when the surface is “passivated”.⁴⁹

In our work we have assumed that the donor defect is similar in the flat band as well as in the downwards band bending region. This assumption is considered valid as donor defect such as oxygen vacancies, can either dominate in the bulk or the surface making it possible to discriminate the band bending conditions.^{12,137}

8.4 Summary

The presence of structured (lower energy) and structureless (higher energy) green emission is influenced by the presence of defects in the bulk and near the surface respectively. In addition, the knowledge of the localized deep level defect, the surface electronic band bending near the surface as well as physical models are requisites to explain the observation of these green emissions. In both locations, the oxygen vacancies are the dominant defects. However in the bulk, flat band condition allows a single electronic transition between the defect energy state and the valence band while defects near the surface resulted in an electron accumulation layer leading to a downward surface band bending. This led to an increasing electronic transition as the band bending increases toward the surface. Subsequently the summed emission band increases in energy and diminishes the sharp electron-vibrational lines in the phonon sideband. The proposed mechanism and simulated emission are in agreement with the experimental observation.

CHAPTER 9:

CONCLUSIONS AND SUGGESTING FUTURE WORKS

The origin of the green emission of ZnO has been discussed in the literature review section (Chapter 2). Various kinds of point defects are hypothesized to be potential candidates for the green emission. However, the origin of the green emission needs further concrete analysis. In this work, the investigation of the green emission involved takes on a different approach and makes several key findings. This chapter summarizes these and discusses the major contributions.

9.1 Conclusions

The LO vibrational mode of the prepared ZnO was investigated using Raman Spectroscopy. It has been determined to be a Quasi-LO vibrational mode as it is considered as an angular averaging frequency appearing between the A_{1LO} and E_{1LO} modes under resonant mode. The Raman Spectroscopy result shows that the largest red-shifting of the mode for the ZnO with Type II defects is attributed to a more dominant specific defect such as the oxygen vacancies. The presence of defects induces a crystal disordering which leads to an observable breakdown of momentum conservation rules. This is in turn responsible for the position of LO modes to red-shift where the most important consideration is the transparency of ZnO to the red exciting laser. This makes the signal rather insensitive to the surface, therefore, the shift of the Quasi-LO vibrational mode and the alternation of its asymmetrical shape is due to changes in the bulk of the ZnO. It is necessary to understand that the lower asymmetrical factor might be associated with the LO-plasmon coupling effects,

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supporting the notion of a dominant specific defect in the bulk of this material. Importantly, the formation of oxygen vacancies changes the translational symmetry and relaxes the Raman selective rules for a randomly oriented powder sample. This causes a strong green emission from ZnO with Type II defects while the green emission observed from ZnO with Type I defects may have originated from the surface modification.

The green emissions were analysed in depth and were found to vary within the green energy range of the visible spectrum. Such variation is divided into high energy and low energy green emissions respectively. Through systematic experimental separations, advanced material characterizations and physical modeling, the subtle variation of the green emission is deemed significant and was closely related to the defects residing at different locations. Physical modeling using the multi-mode Brownian oscillator (MBO) model showed that the electron phonon coupling factors of these two types of green emission are different from each other indicating that their origins are different. High Resolution TEM showed that the surface of ZnO with Type I defect has been modified thus the higher energy (peak value of 2.465 eV) green emission is most probably related to defects residing near the surface. This is also evidenced by the downwards band bending through a binding energy shift of Zn 2p $3/2$ orbital. On the other hand, the correlation between the unit cell volume contraction through XRD and PL intensity of the low energy green (peak value of 2.294 eV) emission suggests that the Type II defects are the oxygen vacancies distributed beneath the surface.

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We discussed the XPS result in depth as we determined the core level binding energy as well as the VBM of the materials with different specific defects. ZnO with Type I defects has both the core level and the valence band shift to higher binding energy. This indicates a further downwards band bending due to the formation of an accumulated layer of electrons. The presence of electrons is attributed to the localized oxygen vacancies which act as donors near the surface. It is likely that these near-surface oxygen vacancies are the Type I defects. The defect state in the downwards bending region is responsible for the observed high energy green emission. On the other hand, the Zn 2p $3/2$ core level binding energy for the ZnO with Type II defects shifts to lower binding energy while the VBM shifts to higher binding energy. It shows that the shallower region probed by the Zn 2p $3/2$ core level has an increasing concentration of acceptors which partially compensate for the existing accumulated layers. The formation of higher concentration of oxygen vacancies occurs at a greater depth which has a flat band condition (~ 81.8 nm) due to the relatively fast cooling rate. These reinforce the evidence that oxygen vacancies are the Type II defects resulting in the low energy green emission. The result is therefore consistent with other characterization techniques used in our work. The location of oxygen vacancies as shown in the results determines the characteristic green emissions with different energies as observed. Using controlled samples, we also determined that other suggested defects are unlikely origins of the green emissions.

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The origin of the shift of the XPS can be different for size dependent ZnO. When the size of the ZnO is physically reduced, the Zn 2p $3/2$ core level binding energy would shift to lower energy. The results show a complicated alteration in the zinc binding state which is associated with the variation in the number of broken bonds per zinc ion due to the severe size reduction. It suggests that oxygen vacancies may be generated by surface shrinkage due to the size reduction and the two binding energies of 1021.2 eV and 1020.8 eV are therefore assigned to the zinc ions with one and two broken bonds, respectively. The increase in broken bonds associated with zinc ions in the ZnO of 3.0 nm is associated with localized structural distortion or variation.

Finally, we hypothesize the behavior of the green emission using MBO at low temperatures. It was observed that while the low energy green emission maybe found to be highly structured as a result of the appearance of the electronic-vibrational modes, the presence of the surface downwards band bending diminishes the structured green emission which then leads to a structureless green emission.

9.2 Suggesting Future Work

While we have determined that the nature of defects and locations are the factors that determine the high and low energy green emissions, there are possible future works that are worth mentioning to enhance the understanding of the mechanism of the green emission. The suggesting future works are listed below:

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- 1) While it has been deduced that the oxygen vacancies play a role in the green emission, the nature of the charge on oxygen vacancies remains unclear. It may possess a neutral, +1 or +2 charge and therefore the corresponding electronic transitions remain unknown. It is thus important to determine the charge state of the defects. In particular, changes between them during excitation and relaxation process might be of interest to the scientific community as the changes would be correlated with each other. This would shed some light on their relationship with the variation of the green emission.
- 2) The Density Function Theory (DFT) using different approaches has been applied to identify the dominant defects in ZnO for many years. As reported in the literature review, there are some flaws in the current DFT methodology pertaining to defect identification. Particularly, the problem of band gap underestimation as well as the limited supercell size led to problems in estimating accurate formation energy. An accurate formation energy is needed to determine the defect energy level in the bandgap. This problem could possibly be addressed if the band gap is estimated correctly. This could be achieved with a better DFT approach such as using the GW approximation. While many studies have made use of GW approximation to calculate the band gap energy it is uncommon to use this method to determine the formation energy of the defects in the material.

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Other DFT approach such as the Time Dependent DFT (TDDFT) can be used to investigate the properties and dynamics of many-body systems in the presence of time-dependent potentials, such as electric or magnetic fields. The effect of such fields on ZnO can possibly be investigated with TDDFT to extract features such as excitation energies, frequency-dependent response properties, and photo absorption spectra. These could contribute important clues that will enhance our understanding of the green emission.

- 3) While DFT could determine the formation energies of the defects theoretically, there is little experimental data to verify these calculated parameters. It is important to understand the thermodynamic properties of the defects in the materials, such as the diffusion behavior as well as the formation energies of the defects in the system experimentally. Synthesis processes that involve temperature, time and environment will determine the thermodynamic properties of the defects. Such understanding will be very important to our investigated results and are critical in proposing strategies to suppress the defects.
- 4) Finally, low temperature photoluminescence spectroscopy is recommended to determine the structure and unstructured green emission of ZnO. This will verify the hypothesis proposed in Chapter 7 pertaining to the presence of Type I and Type II defects. On the other hand, various factors that will affect the green emission such as the Huang Rhys Factor, gamma and 0-0 Transition can be determined and cross comparison made with the work of others. This

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allows a verification of the various types green emission observed and reported in the open literature.

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Appendix A: Optical Depth of Detection

APPENDIX A : OPTICAL DEPTH OF DETECTION

The penetration depth of the excitation beam depends on the excitation source as well as the absorption coefficient of ZnO.

The total scattered light intensity integrated from the surface to depth d , I_s , is expressed as

$$I_s = (I_o R) \int_0^d \exp(-2 \alpha x) dx = \left(\frac{I_o R}{\gamma} \alpha\right) [1 - \exp(-2 \alpha d)] \text{-----}(3)$$

And that from depth d to infinity I_d is expressed as

$$I_d = (I_o R) \int_d^\infty \exp(-2 \propto x) dx = \left(\frac{I_o R}{2} \propto \right) \exp(-2 \propto d) \text{-----(4)}$$

Where I_0 , R , and α are the incident light intensity, the Raman scattering cross section and the photoabsorption coefficient of the probed materials. Suppose that the penetration depth d is given by the depth that satisfies the relationship

$$\frac{I_d}{I_s + I_d} = 0.1 \text{-----} (4)$$

Then this depth is given by

$$d = \frac{-\ln 0.1}{2\alpha} = \frac{2.3}{2\alpha} \text{-----} (5)$$

Calculation indicates the penetration depth of a laser (using a 325 nm HeCd Laser) to be around 70 nm while a red laser (633 nm laser) can penetrate to a depth up to a few tens micrometers.

Appendix B: Multimode Brownian Oscillator Model

APPENDIX B: MULTIMODE BROWNIAN OSCILLATOR MODEL

Fig. B-1 shows the measured and calculated emission spectra of the ZnO annealed in different atmospheres at different temperatures. For the ZnO that is annealed in the reducing environment shown in Fig B-1 (a)-(c), it is shown that the MBO model can be fitted well on the higher energy side. The fitting on the lower energy side is however, slightly less satisfactory for the sample annealed at 500°C [Fig B-1 (a)]. There is progressive improvement in the spectra fitting at the lower energy side as the annealing temperature increases from 500 to 700°C because the peak shoulder diminishes [Fig B-2]. The spectrum of the sample annealed at 900°C in the reducing environment has the best fit as the lower energy emission completely diminishes.

Fig B-1 (d) – (f) on the other hand shows the MBO fitting for ZnO annealed under the ambient environment. As observed in Fig B-1 (d), the shoulder peak and an additional emission band at the higher energy side (labelled 'H') of the green band are fitted empirically, together with the MBO modelled green emission band

Appendix B: Multimode Brownian Oscillator Model

Appendix B: Multimode Brownian Oscillator Model

Fig B-1 MBO model fitting of ZnO annealed under reducing atmosphere at (a) 500°C, (b) 700°C, (c) 900°C and in ambient atmosphere at (d) 500°C, (e) 700°C , (f) 900°C. The green and blue curved in (d) refers to additional empirical fitting and summed curved respectively.

Appendix B: Multimode Brownian Oscillator Model

Fig B-2 Overlaid spectra of ZnO annealed in reducing atmospheres of different temperature.

to give a more accurate result for the ZnO annealed in the ambient atmosphere at 500°C [Fig B-1(d)]. We attempted to implement the result of the empirical fit of the higher energy emission onto the ZnO annealed in ambient atmosphere at 700°C and 900°C respectively, however the fit was not good suggesting that this emission band diminished at higher annealing temperature. Although the shoulder emission (at the lower energy) causes the overall fitting to be less satisfactory, the objective of this work is to extract information on the green band. We have achieved this by fitting reliably in the higher energy side of the spectra which contain the information on the 0-0 transition energies (ZPL) that are responsible for the green emission as well as the Huang-Rhys factor [Fig B-1 (e)-(f)].

Appendix C: Shift of Emission of ZnO annealed in Different Oxygen Partial Pressure

APPENDIX C: SHIFT OF EMISSION OF ZNO ANNEALED IN
DIFFERENT OXYGEN PARTIAL PRESSURE

In this appendix, we showed the variation of the visible emission as a function of oxygen partial pressure. The ZnO was annealed in different partial pressure of oxygen with nitrogen at 900°C for 24 hrs. Figure D-1 shows the variable of the emission with different

Fig.C-1 Emission variation as a function of oxygen partial pressure.

oxygen partial pressure. Notice that the visible emission is very broad and extend to low energy when the ZnO is annealed with 100 % oxygen. As the oxygen partial pressure is reduced to the that of ambient atmosphere, one could observed that the peak energy shifts to low energy green emission region ~2.355 eV. This supports the

Appendix C: Shift of Emission of ZnO annealed in Different Oxygen Partial Pressure

suggestion that the reduce oxygen partial pressure induces oxygen vacancies in ZnO that give rise to the green emission e.g the lower energy green emission due to the presence of Type I defects.

Appendix D: TEM Images of other Zinc Oxide Nanocrystals of Size ~3.0 nm

**APPENDIX D: TEM IMAGES OF OTHER ZINC OXIDE
NANOCRYSTALS OF SIZE ~3.0 NM**

Fig.D-1 TEM micrographs of the prepared ZnO materials with average crystal size of ~3.0 nm.

Appendix E: List of Author's Publications

APPENDIX E: LIST OF AUTHOR'S PUBLICATIONS

Journal Publications:

- 1) S. Xing, Y. Feng, **Y.Y. Tay**, T. Chen, J. Xu, M. Pan, J. He, H.H. Hng, Q. Yan, H. Chen, "Reducing the Symmetry of Bimetallic Au@Ag Nanoparticles by Exploiting Eccentric Polymer Shells", *Journal of the American Chemical Society*, Ref:Ja-2010-02591z, Accepted (2010)
- 2) **Y.Y. Tay**, T.T. Tan, M. H. Liang, F. Boey, S. Li, "Specific Defects, Surface Band Bending and Characteristic Green Emissions of ZnO", *Physical Chemistry Chemical Physics, Physical Chemistry Chemical Physics*, v12, 6008-6013 (2010)
- 3) **Y.Y. Tay**, T.T. Tan, F. Boey, M. H. Liang, J. Ye, Y. Zhao, T. Norby, S. Li, "Correlation between the Characteristic Green Emissions and Specific Defects of ZnO", *Physical Chemistry Chemical Physics*, v12, 2373-2379 (2010).
- 4) **Y.Y. Tay**, T.T. Tan, M.H. Liang, F. Boey, S. Li, "Nature of Quasi-LO Phonon in ZnO", *Applied Physics Letters*, v93, 111903 - 111905 (2008).
- 5) **Y.Y. Tay**, S. Li, M. L. Liang, "Defect Mediated Photonic Behavior of ZnO Nanocrystals", *Advanced Materials Research*, v31, 83-85 (2008).
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- 7) **Y.Y. Tay**, S. Li, F. Boey, Y.H. Cheng and M.H. Liang, "Growth Mechanism of Spherical ZnO Nanostructures Synthesized Via Colloid Chemistry", *Physica B*, v394, 372-376 (2007).
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- 9) Y.H. Cheng, L.K. Teh, **Y.Y. Tay**, H. S. Park, C.C. Wong and S. Li, "Coating Process of ZnO Thin Film on Macroporous Silica Periodic Array", *Thin Solid Films*, v504, 41-44 (2006).

Appendix E: List of Author's Publications

- 10) S. Li, **Y.Y. Tay** and C.Q. Sun, "Separation of Lattice Structural and Electronic Effects on Physical Properties with Nanotechnology", *Ceramics Transactions*, v172, 247-255 (2005).
- 11) T.T. Tan, S. Li, S.P. Lau, **Y.Y. Tay**, S.H. Zhou and S.X. Dou, "Texture optimization studies of powder-in-tube processed (Bi, Pb)₂Sr₂Ca₂Cu₃O₁₀/Ag superconductor tape by using electron backscattered diffraction", *Superconductor Science and Technology*, v16, 885-892 (2003).

Conference Publications:

- 1) H. Yan, **Y. Y. Tay**, M. H. Liang, Z. Chen, C. M. Ng, J. S. Pan, H. Xu, C. Liu, V. V. Silberschmidt "Amorphous Metallic Thin Films as Copper Diffusion Barrier for Advanced Interconnect Applications", *Proceedings of 11th Electronic Packaging Technology Conference*, published by IEEE, pp. 567-572, Singapore, December 9-11, 2009
- 2) **Y.Y. Tay**, S. Li, M. L. Liang,, ""Defect Mediated Photonic Behavior of ZnO Nanocrystals", *International Conference on Materials for Advanced Technologies (ICMAT 2007)*, Materials Research Society, Singapore, July 1 – 6, 2007.
- 3) **Y.Y. Tay**, S. Li, Y.H. Cheng and M.H. Liang, "Growth Mechanism of Spherical ZnO Nanostructures Synthesized Via Colloid Chemistry", *7th International Conference on the Electrical, Transport and Optical Properties of Inhomogeneous Media (ETOPIM 7)*, Australia, July, 9-13, 2006.
- 4) Y.H. Cheng, L.K. Teh, **Y.Y. Tay**, H. S. Park, C.C. Wong and S. Li, "Coating Process of ZnO Thin Film on Macroporous Silica Periodic Array", *International Conference on Materials for Advanced Technologies (ICMAT 2005)*, Materials Research Society, Singapore, July 3 – 18, 2005.
- 5) **Y.Y. Tay**, P. Chen, J. Plevert, S.J. Chua, C.C. Wong and S. Li, "Photonic Behavior of Nanoparticles ZnO," *3rd International Conference on Materials Processing for Properties and Performance (MP³)*, Singapore, November 24-26, 2004.