Effects of Temperature on Intra-Band Photoluminescence in Zinc Oxide (ZnO) Semiconductor

By

Getu Endale Gebramichael

A Thesis Submitted to

The department of Applied Physics

School of Applied Natural Science

Presented in Partial fulfillment of the requirements for the degree of Master's in Physics

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Declaration

I hereby that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis has been duly acknowledged.

Name: Getu Endale Gebramichael

Signature……..

This MSc Thesis has been submitted for examination with my approval as thesis advisor.

Name: Dr. Megersa Wodajo Shura

Signature……..

Acknowledgement

At the moment when I just finished typing the very last word in this thesis, a kind of release suddenly came out from my bottom heart and run through entire body. All the scenes happened within last two years in Adama Science and Technology University are suddenly flashing back. Many people who ever contributed to the work and helped me in the life slowly came into my mind one by one. I truly appreciate and cherish what all of you have done for me, even though my gratitude is beyond words.

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List of Symbols and Abbreviations

CBM	Conduction Band Minimum
VBM	Valance Band Maximum
E_T	Localized Trap Energy
$g_c(E)$	The density of quantum states in conduction band
$g_V(E)$	The density of quantum states in valence
$E_g^{(0)}$	Band gap energy at absolute zero on the Kelvin
$E_g^{(T)}$	Band gap energy at any temperature
$\delta n. \delta p$	Excess charge concentration for electron and hole density (cm^{-3})
G_{th}	Thermal equilibrium Generation rate Electron and hole ($cm^{-3}s^{-1}$)
n_T, P_T	When occupied by electron and hole on the trap level (cm^{-3})
E_T	Electron occupation of a trap located at energy in the band gap(Ev)
$U_{n,p}$	Net recombination rate of electron and hole ($cm^{-3}s^{-1}$)
m_0	Rest mass of the electron (kg)
m_n^*, m_p^*	Electron and hole Effective mass (kg)
T	Temperature(K)
e	Charge of electron ($1.6x10^{-19}$ C)
h	Planck's constant ($1,054x10^{-34}\ Js$)
K_B	Boltzmann constant ($1.38x10^{-23} Jk^{-1}$)
PL	Photoluminescence

E_{photon}	Energy of photon (eV)
E_g	Energy band gap (eV)
N_c, N_v	Electron and hole density of accessible state (cm^{-3})
EHP	Electron-hole pair
C_R	Radiative recombination coefficient(cm^3s^{-1})
E_i	Intrinsic Fermi energy (eV)
c	Speed of light vacuum ($^m/_s$)
E_F	Fermi energy (eV)
E_a, E_d	Energy of acceptor and donor (eV)
E_c, E_V	Energy of conduction band and valance band(eV)
n_0, p_0	Thermal equilibrium concentration of electron and hole (cm^{-3})
$\delta n, \delta p$	Excess carrier charge concentration of electron and hole (cm^{-3})
n, p	Non-thermal equilibrium Concentration of Electron and hole (cm^{-3})
τ_R	Carrier life time in Radiative(ns)
n_T, p_T	When occupied by electron and hole on the trap level (cm^{-3})
n_{0T}, p_{0T}	The thermal equilibrium electron and hole occupancy (cm^{-3})
C_{nT}, C_{pT}	Capture coefficient of electron and hole of the state (cm^3s^{-1})
N_T	Density of localized state are a given as a number/ unit volume (cm^{-3})
ZnO	Zinc oxide
C_{CT}	Conduction band to Trap Radiative Recombination capture coefficient (cm^3s^{-1})
C_{TV}	Trap to Valence band Radiative Recombination capture coefficient (cm^3s^{-1})

τ_{CT}	Conduction band to Trap Radiative Recombination Lifetime(s)
τ_{TV}	Trap to Valence band Radiative Recombination Lifetime(s)
n_1	The concentration of electrons in valence band
p_1	The concentration of holes in the conduction band
I_{CV}	The intensity of light in the Conduction to valence band radiative recombination
I_{CT}	The intensity of light in the Conduction band to trap level radiative recombination
I_{TV}	The intensity of light in the trap level to valence band radiative recombination

Abstract

In this research work, the theoretical description of the photoluminescence in Zinc Oxide semiconductor due to the intra-band and band to band transition of free carriers is performed. First, the excitation of free carriers from the valence band to conduction band and from different localized state to the conduction band by the illumination of sufficient energy is considered. Then, the radiative recombination rates of photo-generated carriers from the conduction band to different energy levels within the forbidden gap, from the conduction band to the valence band and from different energy levels within the band gap to the valence band are described in detail. A theoretical model for minority carrier trapping is also investigated to explain the dependence of the photoluminescence on the trap energy. By using illumination, and net rate of recombination, the intensity of light emitted during recombination of free carriers is determined by assuming one incident photon ejects one electron at a time. Finally, variation of photoluminescence intensities along with localized state energy and transition energy is considered at different temperatures. The obtained results show that, for the variation of photoluminescence intensities with transition energy, at very low temperature, there is no recombination taking place between the conduction band and the localized state; and between the localized states and the valence band. As temperature increases the photoluminescence due to the transition of free electrons from the conduction band to the valence band, I_{CV}, from the conduction band to the localized states, I_{CT} and from the localized states to the valence band, I_{TV} are increasing.

Chapter 1

Introduction

1.1 Background

The beginning of semiconductor research is marked by Faraday's 1833 report on negative temperature coefficient of resistance of Silver sulfide . This is the first observation of any semiconductor property. In his 1833 paper, "Experimental Researches in Electricity" Faraday disclosed this observation. This observation was in distinction from the usual properties of metals and electrolytes in whose case resistance increases with temperature. The next significant contributor to semiconductor field is the French experimental physicist Edmond Becquerel. In 1839, he reported the observation of photovoltage in the silver chloride coated Platinum electrodes. In his experiment, a AgCl coated Platinum electrode was immersed in an aqueous Nitric acid electrolyte solution. Illumination of the electrode generated photo-voltage that altered the electromagnetic field produced by the cell; in fact, it produced a reductive (cathodic) photocurrent at the AgCl coated electrode. This was the first reported photovoltaic device. Photovoltage was generated at the Ag/AgCl metal semiconductor contact, Ag at the junction was formed by the absorbed silver clusters in the AgCl electronic states [1].

The next important decade in the semiconductor research is the decade of 1870. During this period Selenium was discovered as a semiconductor, rectification at semiconductor interface came into scientists' notice. In 1873, Willoughby Smith arrived at the discovery of photoconductivity of Selenium . He was initially working with submarine cables. He set into experiments with Selenium for its high resistance, which appeared suitable for his submarine telegraphy. Various experimenters measured the resistance of Selenium bars, but the resistance as measured by them under different conditions did not agree at all. Then Smith discovered that the resistance actually depends on the intensity of incident light. When the Selenium bars were put inside a box with the sliding cover closed, the resistance was the highest. When glasses of various colours were placed in the way of light, the resistance varied according to the amount of light passing through the glass. But, when the cover was removed, the conductivity increased. He also found that the effect was not due to temperature variation [2].

Zinc oxide is an inorganic compound with the chemical formula ZnO. It occurs as a white powder that is nearly insoluble in water. It crystallizes in two main forms, hexagonal wurtzite and cubic zinc blende structures. The wurtzite structure is more stable than the zinc blende structure. It is a wide-bandgap semiconductor of the II-VI semiconductor group. Zinc oxide finds applications in the following: It is used for preventing corrosion in nuclear reactors, It is used as a pigment in paint, Coatings, Cigarette filters, Medicine etc.[3].

For different semiconductor devices, one needs materials with different parameters, like energy band-gap. Physical properties are very different among different semiconductors due to distinct characteristics of energy band-gaps and impurities. These impurities play a major role in determining the electrical and optical properties of semiconductors. Almost all of today's technology involves the use of semiconductors, with the most significant aspect being the integrated circuit (IC). One of the most commonly used techniques to investigate properties in semiconductors is Photoluminescence (PL). PL has become a standard method for the characterization of semiconductors properties. It can be used to determine energy levels, concentration of impurities, defects and fundamental properties of semiconductors. One of the most common examples of photoluminescence is the fluorescent lamp [4].

The basic difference between direct gap and indirect gap transitions is that, when the CBM and the VBM occur at the same value of wave number,k the material is said to be direct band-gap material. Conversely, when the CBM and the VBM occur at different values of k , the material is said to be indirect band-gap material. Electronic transitions between the two bands, CBM and VBM in a direct material can take place with little or no change in crystal momentum. On the other hand, conservation of momentum during an inter-band transition is a major concern in indirect band-gap materials. There is a process, which involves the capture of electrons from the conduction band (or holes from the valence band) by the trap, followed by the recombination with holes in the valence band (or electrons in the conduction band). When electron-hole pairs (EHPs) recombine, energy is released through phonon emission and the localized state is called the recombination center. If the localized state captures free carriers temporarily and then re-emits them back to their original band, the center is called a free carrier trap. The localized trap states may be created by deep impurities, dislocations, radiation defects, grain boundaries, point defects and their complexes. The presence of defects in a semiconductor crystal due to impurities or crystallographic imperfections such as dislocations

produces discrete energy levels within the band-gap. These defect levels, also known as traps, greatly facilitate recombination through a two-step process where a free electron from the conduction band first relaxes to the defect level and then relaxes to the valence band where it annihilates a hole [5].

In this study, the competition between different localized states and their involvement in radiative recombination mechanisms described. The effects of doping, injection level, temperature and the energy level of the localized states on the photoluminescence of Zinc Oxide is studied.

1.2 Objectives of the study

The general objectives of this study will be to determine the effects of different localized states on the photoluminescence of Zinc Oxide compound semiconductors. The specific objectives of the study will be:

- the description of the free charge carriers capture effects of different localized states in Zinc Oxide compound semiconductor,
- the investigation of free carriers' generation-recombination effect at different localized states in Zinc Oxide compound semiconductor,
- the determination of the photoluminescence of different localized states in Zinc Oxide compound semiconductors.

1.3 Thesis Outline

In this work the effects photoluminescence of Zinc Oxide compound semiconductor is studied. Determining the luminescence intensity for band -to-band, conduction band-to-localized state and localized state-to-valence band radiative recombination of Zinc Oxide compound semiconductors is basic work in this study. The thesis is organized into five chapters. **Chapter two** is literature review. Theoretical back ground of direct band gap semiconductors and intensity of light for different radiative recombination mechanisms were discussed in this chapter. **Chapter three** describes the overall methodology by which important data is collected and analyzed. **Chapter four** covers the results and discussion of the study. **Chapter five** gives the conclusion and outlook of the thesis.

Chapter 2

Literature Reviews

This topic describes the theoretical background of the thermal equilibrium properties and the photo-responses of Zinc Oxide (ZnO) Semiconductor. First, the theories of energy band gap of ZnO is described, then the theory of thermal equilibrium carrier concentration in semiconductors is described. Finally, the theory of the photo-response to any illumination is described in terms of the free carrier generation-recombination mechanisms and the intensities of photoluminescence of different localized states in the band gap of ZnO.

2.1. Energy band gap in semiconductors

The energy band gap is a major factor in determining the electrical conductivity of a solid. Energy band gap is a gap of energy in solids where no electron states can exist. Energy band gap, also called an energy gap or band gap. The band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. The closest point between the top of the valance band curve and the bottom of the conduction band is called the materials Energy Gap. For insulating materials, this gap can be greater than ten electron volts. However, for semiconductor electronic devices operating a reasonable voltage, the gap has to be a few electron volts [6].

The band gap of a semiconductor, given by the energetic difference between its valence band maximum and conduction band minimum, has important implications for both the semiconductor's light absorption properties and the maximum photo voltage that can be expected from a corresponding device. In order to absorb a photon, an electron generally must be excited from the valence band of the semiconductor to the conduction band. Thus, a photon must possess energy greater than or equal to that of the semiconductor band gap in order to be absorbed and create an excited electron-hole pairs. The processes excitation of free carriers must obey the law of energy and momentum conservations. This, in particular, leads to the fact that the minimum quantum energy sufficient to excite electron from the valence band to the conduction band is equal to the band gap of the semiconductor. The energy bands may be occupied or unoccupied. The highest occupied band is called the valence band at energy E_V, and

contains the valence electrons. The lowest unoccupied band is called the conducting band that lies at the energy level E_C. The energy bands can be empty, partly full or completely full and determines the properties of the solid. The band gap energy, E_g is the energy deference between the valence and the conduction band [7].

$$E_g = E_C - E_V. \quad (1)$$

The thermal excitation of electrons from the valence band to the conduction band creates free carriers in both bands. A large band gap will make it more difficult for a carrier to be thermally excited, hence the concentration of thermal carriers is lower in higher band gap materials.

Band gap in semiconductors are classified into two. These are indirect and direct band gap semiconductors.

2.1.1 Direct band gap semiconductors

The materials for which maximum of valence band and minimum of conduction band lie for same value of wave vector, k, are called direct band gap semiconductors. Direct band semiconductors are like GaAs, InP, InSb, GaSb, ZnO and etc. These semiconductors have different energy gap. Some are small, wide and large direct band gap. The gallium antimonide is small direct band gap semiconductor and Zinc Oxide is large band gap semiconductor. A contraction of the crystal lattice with decreasing temperature usually leads to a strengthening of the inter atomic bonds and an associated increase in the band gap energy. The first empirical relation for the band gap shift with temperature developed by varshini *et al.* was given by:

$$E_g(T) = E_{g0} - \frac{\alpha T^2}{\beta + T}, \quad (2)$$

where α and β are constants choosen to obtain the best fit to experimental data and E_{g0} is the limiting value of the band gap at zero Kelvin. It was found that E_{g0} = 3.360 eV, α = 5.05×10^{-4} eV/K and β = 900K for Zinc Oxide [8].

From (2), it is observed that the energy band gap of zinc oxide semiconductors decreases with the increasing temperature because of the lattice expansion and the electron-phonon interaction, which soft the lattice bonds, resulting in a decrease of the bonding energy. The

band-gap shrinkage with temperature is due to the thermal lattice expansion, and the electron-phonon coupling.

2.2. Intrinsic and Extrinsic semiconductors

The semiconductors may be divided into two categories; the pure un doped semiconductor, which is usually referred to as the intrinsic semiconductor, and the doped semiconductor, which is also called the extrinsic semiconductor. The total thermal equilibrium density of electrons in a semiconductor is given by [9].

$$n_0 = N_C \exp\left(-\frac{E_C - E_F}{k_B T}\right), \tag{3}$$

where

$$N_c = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} \tag{4}$$

is the effective density of the conduction band states, m_n^* is effective mass of electrons in the conduction band and h is the known Planck's constant. The hole thermal equilibrium density in the valence band is also given by:

$$p_0 = N_V \exp\left(-\frac{E_F - E_V}{k_B T}\right), \tag{5}$$

where

$$N_V = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{3/2} \tag{6}$$

E_F is the Fermi level, m_p^* is effective mass of holes in the valence band. The values of m_p^* and m_n^* for ZnO is given by [10]:

$$m_p^* = 0.59 m_n \quad \text{and} \quad m_n^* = 0.24\, m_n, \tag{7}$$

where, m_n is the rest mass of electron which is equal to 9.11×10^{-31}kg.

2.2.1. Intrinsic semiconductors

Semiconductors are considered to be as intrinsic semiconductors if it's thermally generated carrier density represented by n_i is much larger than the background doping or residual impurity densities. At zero temperature ($T = 0K$), an intrinsic semiconductor behaves like an insulator because the conduction band states are totally empty and the valence band states are

completely filled. However, as the temperature increases, some of the electrons in the valence band states are excited into the conduction band states by thermal energy, leaving behind an equal number of holes in the valence band. Suppose that $\Re$ is the concentration of electron-hole pairs thermally generated in the respective bands and $\Re_R$ is the concentration of electron hole annihilated after the generation, the free carrier concentrations in the conduction and valence bands adjust for the intrinsic semiconductor to be:

$$n_0 = \Re - \Re_R = n_i = p_0. \tag{8}$$

Since the non-degenerate relations are obviously valid for an intrinsic semiconductor, the intrinsic carrier concentrations are given as follows:

$$n_i = N_C \exp\left(-\frac{E_C - E_i}{k_B T}\right) = N_V \exp\left(-\frac{E_i - E_v}{k_B T}\right), \tag{9}$$

where, E_i is intrinsic energy level and k_B is Boltzmann constant which is equal to $1.38 \times 10^{-23}\text{JK}^{-1}$.

The intrinsic Fermi energy derived from (9) as follows:

$$E_i = \frac{E_C - E_V}{2} + \frac{k_B T}{2} \ln\left(\frac{N_V}{N_C}\right). \tag{10}$$

or

$$E_i = \frac{E_V + E_C}{2} + \frac{3}{4} k_B T \ln\left(\frac{m_p^*}{m_n^*}\right), \tag{11}$$

which indicates that if $m_p^* = m_n^*$ or $T = 0$ the Fermi level in an intrinsic semiconductor is positioned at mid-gap. In real cases $m_p^* \neq m_n^*$, resulting in small deviation of the fermi level from mid-gap.

The equilibrium density of electrons and holes in a non-degenerate semiconductor is constant at a given temperature. The product of the electrons and holes density, in a non-degenerate semiconductor at equilibrium, is always equal to the square of the intrinsic carrier density [11].

$$n_i{}^2 = p_0 n_0 \tag{12}$$

The intrinsic carrier density (which is specific to a given semiconductor) is related to the effective density of conduction and valence band, i.e.

$$n_i = \sqrt{N_C N_V} \exp\left(\frac{E_V - E_C}{2 k_B T}\right). \tag{13}$$

This relationship, referred to as the law of mass action, which allows (at thermal equilibrium) to determine the electron density if the hole density is known or vice versa. It should be noted that this equation signifies that, the electron-hole pairs may be continuously generated and recombined; the product of the concentration (averaged in time) stays constant. This equation also indicates that, for a non-degenerate material in equilibrium, the $p_0 n_0$ product depends on the effective conduction and valence band densities of states, the energy band gap of a semiconductor, and the temperature. It is independent of the Fermi level position and of the individual electrons and holes densities. In other words, the $p_0 n_0$ product is constant at a given temperature regardless of doping [12].

2.2.2. Extrinsic Semiconductors

The availability of charge carriers in the valence and conduction bands greatly affected by the presence of impurities (*i.e.*, foreign atoms incorporated into the crystal structure of a semiconductor). In semiconductors, some impurities are deliberately introduced to produce materials and devices with desired properties. The process of putting impurities into the lattice is doping. The contribution of free carriers by dopants requires them being ionized (i.e., the dopants have donated or accepted an electron). The ionization of the dopants depends on the thermal energy and the position of the impurity level in the energy gap of a semiconductor. In an extrinsic semiconductor, electrons are majority carriers and holes are minority carriers in n-type semiconductor. In p-type material, electrons are minority carriers and holes are majority carriers [13].

As shown in the Figure 1 below, at low temperature, the donor impurity levels are filled. But with increasing T, the electron in the donor levels are excited into the conduction band and similarly the holes in the acceptor levels are excited into the valence band. With a small temperature, these donors or acceptors can be thermally excited into the band. Therefore, the donor impurities donate free electrons to the conduction band, whereas the acceptor impurities give free holes to the valence band. However, at very low temperature, these carriers are bound back to their respective nuclei so that they can no longer carry electricity, a phenomenon known as carrier freeze out [14].

Figure 1 also shows that, when donor impurities are added, at zero temperature, these states are near the top of the band gap, and are filled. Thus, the Fermi energy is moved up to the

top of the band gap. On the other hand, when acceptors are added, the acceptor states near the bottom of the band gap are empty. (Remember it is a bound state of a hole to a nucleus!). Thus, the Fermi energy is moved down to the bottom of the band gap. The presence of impurities in a material can have dramatic effects on its optical properties. There are two main optical effects of impurities. The first effect is that the impurities add charge carriers to the materials. This obviously can have some important effects on the interaction with light. The second important effect is the introduction of new energy levels within the gap. Whereas before the introduction of impurities, the lowest energy transition that can be made is the full energy of the gap, now one can have optical transitions between impurity states, or from the bands to the impurity states [15].

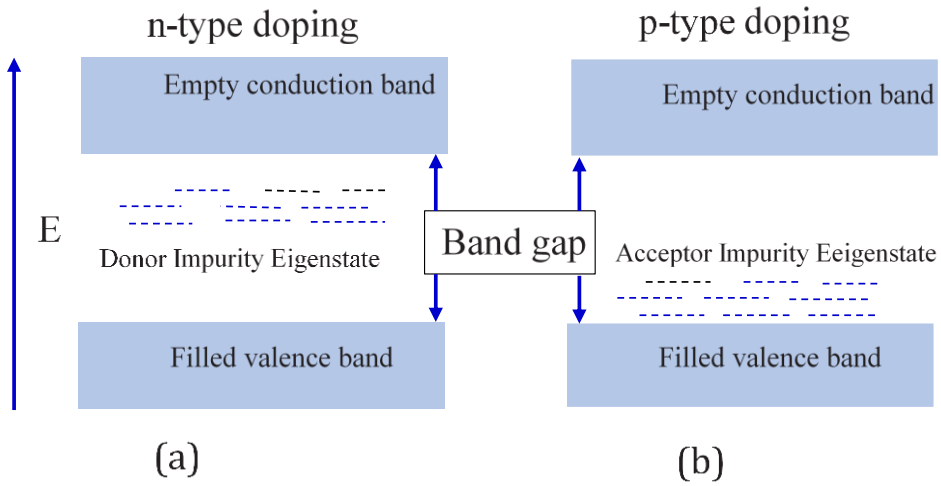

Figure 1: Doped semiconductors with (a) donor (b) acceptor impurities.

The most important and unique feature of a semiconductor material lies in the fact that its electrical conductivity can be readily changed by many orders of magnitude by simply doping the semiconductor with shallow-donor or shallow-acceptor impurities. By incorporating the doping impurities into a semiconductor, the electrons or holes density will increase with increasing shallow-donor or shallow-acceptor impurity concentrations. Adding donor or acceptor impurity atoms into semiconductor will change the distribution of electrons and holes in the material, and as a result, the Fermi energy will change.

$$n_0 = n_i \exp\left(-\frac{E_i - E_F}{k_B T}\right) \quad \text{and} \quad p_0 = n_i \exp\left(-\frac{E_F - E_i}{k_B T}\right). \tag{14}$$

The law of mass action, Eqn. (13) allows one to calculate the minority carrier density in an extrinsic semiconductor when the majority carrier density is known:

$$\text{Minority carrier density} = \begin{cases} \frac{n_i^2}{p_0} \text{ for p} - \text{type materials,} \\ \frac{n_i^2}{n_0} \text{for n} - \text{type materials} \end{cases} \quad (15)$$

The thermal equilibrium extrinsic Fermi-level position can be described from Eqn. (14) in terms of E_i and the thermal equilibrium carrier concentrations as:

$$E_F = E_i - k_B T \ln\left(\frac{p_0}{n_i}\right) = E_i + k_B T \ln\left(\frac{n_0}{n_i}\right). \quad (16)$$

As the charge carrier concentrations change, the position of the extrinsic Fermi energy level varies within the band gap until the system reaches thermal equilibrium. Eqn. (16) shows that E_F lies above E_i for n-type material ($n_i > p_0$) and below E_i for p-type material ($n_i < p_0$).

2.2.3. Statistics of Donors and Acceptors

The shallow donor-acceptor levels emit their electrons (holes) to the conduction band (valence band) where they travel freely and contribute to the conductivity. The free charge carriers may be trapped by deeper levels, where they are frozen out unless enough thermal energy is provided to excite them back to the bands again. Deeper located levels can interact with both bands easily and the free charge carriers may use these defect states as recombination path. The donor electron can also interact directly with a hole, thus the charge carriers recombine without contributing to conduction or charge carrier compensation takes place [16].

The density of electrons in a shallow-donor state is given by:

$$n_d = \frac{N_d}{1 + \frac{1}{g_d} \exp\left(\frac{E_d - E_F}{k_B T}\right)}, \quad (17)$$

where n_d is the density of electrons occupying the donor level, N_d is the concentration of donor atoms, E_d is the energy of the donor level and g_d is the donor-site degeneracy factor. The concentration of ionized donors N_d^+ is then:

$$N_d^+ = N_d - n_d = \frac{N_d}{1 + g_d \exp\left(\frac{E_F - E_d}{K_B T}\right)}, \quad (18)$$

When a singly ionisable donor captures an electron it becomes neutral, and when it releases an electron, it becomes positively charged. Using the same analysis, the concentration of ionized acceptors becomes:

$$N_a^- = N_a - p_a = \frac{N_d}{1 + g_a \exp\left(\frac{E_F - E_a}{K_B T}\right)}, \tag{19}$$

where p_a is the density of holes bound to acceptors, N_a the concentration of acceptor atoms, E_a the energy of the acceptor level relative to the valence band, N_a^- the concentration of ionized acceptor atoms and g_a is the acceptor-site degeneracy factor. When a singly ionisable acceptor captures an electron it becomes negatively charged, and neutral when it releases the electron. Most authors set $g_d = 2$ to account for the spin degeneracy at the donor sites (only one parabolic band at the conduction band edge). It is likewise standard practice to argue that the acceptor sites must additionally reflect the two fold (heavy- and light-hole) degeneracy of the valence band. Thus, the acceptor degeneracy factor is $g_a = 2 \times 2 = 4$.

At sufficiently high temperatures in p-type material, all the acceptors are ionized, so that $N_a^- \approx N_a$ or $p_a \approx 0$. This leads to the conditions $E_a - E_F$ resulting in the Fermi level lying above the acceptor level for p-type materials. In the same way it can be shown that complete ionization of donors for n-type materials satisfies the conditions, $N_d^+ \approx N_d \; or \; n_d \approx 0$ and thus, $E_d \gg E_F$.

For complete freeze-out at very low temperatures in p-type material assuming zero or negligible compensation, all the acceptors are neutralized; i.e., $p_a \approx N_a \; or \; N_a^- \approx 0$. This again leads to the conditions $E_a - E_F > 0 \; or \; E_a > E_F$, with the Fermi level below the acceptor level. Similarly, for n-type materials at very low temperature, it can be shown that $N_d \approx N_d$ or $N_d^+ \approx 0$ and the Fermi level lies above the donor level ($E_d < E_F$).

2.3. Photoluminescence Theory

When electron-hole pairs are generated in a semiconductor, or when carriers are excited into higher impurity levels from which they fall to their equilibrium states, light can be given off by the material. Many of the semiconductors are well suited for light emission, particularly the compound semiconductors with direct band gaps. The general property of light emission is called luminescence. This overall category can be subdivided according to the excitation

mechanism: If carriers are excited by photon absorption, the radiation resulting from the recombination of the excited carriers is called photoluminescence [17].

2.3.1 Optical Absorption

An important technique for measuring the band gap energy of a semiconductor is the absorption of incident photons by the material. Since photons with energies greater than the band gap energy are absorbed while photons with energies less than the band gap are transmitted. It is apparent that a photon with energy $h\upsilon \geq E_g$ can be absorbed in a semiconductor, where υ is the light frequency. Since the valence band contains many electrons and the conduction band has many empty states into which the electrons may be excited, the probability of photon absorption is high. An electron excited to the conduction band by optical absorption may initially have more energy than is common for conduction band electrons. Thus, the excited electron loses energy to the lattice in scattering events until its velocity reaches the thermal equilibrium velocity of other conduction band electrons. The electron and hole created by this absorption process are excess carriers; since they are out of balance with their environment, they must eventually recombine. While the excess carriers exist in their respective bands, however, they are free to contribute to the conductivity of the material [18].

A photon with energy less than E_g is unable to excite an electron from the valence band to the conduction band. Thus in a pure semiconductor, there is negligible absorption of photons with $h\upsilon < E_g$. This explains why some materials are transparent in certain wavelength ranges. We are able to "see through" certain insulators, such as a good $NaCl$ crystal, because a large energy gap containing no electron states exists in the material. If a beam of photons with $h\upsilon > E_g$ falls on a semiconductor, there will be some predictable amount of absorption, determined by the properties of the material. Figure 2 below shows these processes clearly [19].

2.3.2 Photoluminescence process

Photoluminescence involves the irradiation of the crystal to be characterized with photons of energy greater than the band-gap energy of that material. In the case of a crystal scintillator, the incident photons will create electron hole pairs. When these electrons and holes recombine, this recombination energy will transform partly into non-radiative emission and partly into radiative emission. Photoluminescence consists of impinging relatively high frequency light

onto a material, exciting atomic electrons. Subsequent relaxation may result in the production of photons that are characteristic of the crystal or defect site that emits the light. The luminescent signals detected could result from the band-to-band recombination, intrinsic crystalline defects (growth defects), dopant impurities (introduced during growth or ion implantation), or other extrinsic defect levels (because of radiation or thermal effects). When bombarded with photons of energy greater than the band-gap of the material, an impurity energy level may emit characteristic photons via several different types of radiative recombination events, allowing the resultant PL spectra to be used to determine the specific type of semiconductor defect. This interaction provides a highly sensitive, qualitative measurement of native and extrinsic impurity levels found within the material band gap. We can briefly say photoluminescence process includes four main phases [20].

1. Excitation: Electrons can absorb energy from external sources, such as lasers, arc-discharge lamps and tungsten-halogen bulbs and be promoted to higher energy levels. In this process electron-hole pairs are created.

2. Relaxation: Carriers excited to very high energy level the corresponding band relaxes towards quasi-thermal equilibrium distributions (band edge).

3. Recombination: The energy can subsequently be released, in the form of a lower energy photon, when the electron falls back to the original ground state. This process can occur radiatively or non-radiatively.

4. **Trapping:** is the mechanism by which some of the excess EHPs, originally created in equal densities might be trapped temporarily at impurity levels before being recombined. When trapping is an issue, lifetime measurements are frequently made in the presence of background illumination to reduce the effect. Trapping is a major concern in wide band-gap semiconductors. For a given steady state photo-generation rate, an excess minority carrier concentration is created so that generation is perfectly balanced by recombination. At the same time, an additional number of electrons is trapped.

The simplest example of light emission from a semiconductor occurs for direct excitation and recombination of an EHP. If the recombination occurs directly rather than via a defect level, band gap light is given off in the process. For steady state excitation, the recombination of EHPs occurs at the same rate as the generation, and one photon is emitted for each photon absorbed.

An example of a photoluminescence process is shown in the Figure 2 below. This material contains a defect level (due to an impurity) in the band gap, which has a strong tendency to capture (trap) electrons from the conduction band or holes from the valence band. The events depicted in the figure are as follows. (a) An incoming photon with energy $h\upsilon_1$ greater than the bandgap energy E_g is absorbed, creating an EHP; (b) the excited electron gives up energy to the lattice by scattering until it nears the bottom of the conduction band; (c) electron and hole in the conduction and valence bands are moving in the applied field to conduct electric current. An electron in the conduction band can be (d) directly recombined with a hole in the valence band by emitting photon of energy $h\upsilon_2$, approximately equal to the energy band gap, E_g or (e) can be captured by the localized centre by emitting a photon of energy $h\upsilon_3$ which is less than E_g. An electron captured by the localized state (f) can be recombined with a hole in the valence band by emitting a photon of energy $h\upsilon_4$ which is less than E_g or (g) can be re-emitted thermally or optically to the conduction band to conduct electric current [21].

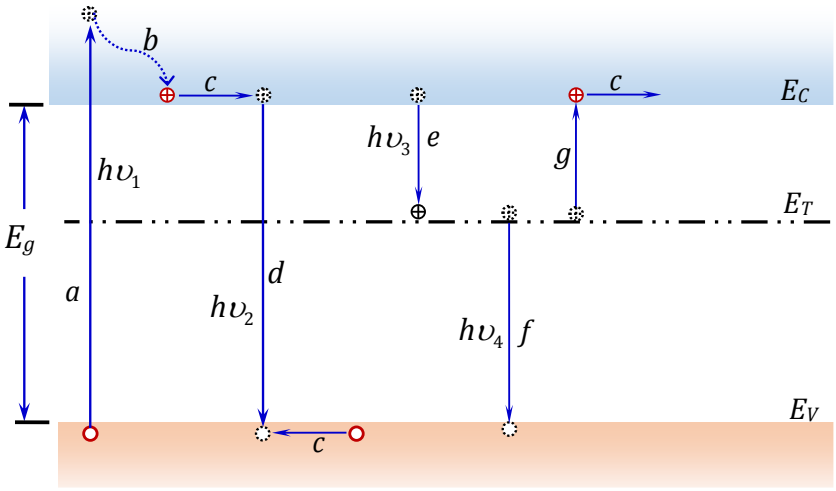

Figure 2: Excitation and recombination mechanisms in PL with a trapping.

One of the most common examples of photoluminescence is the fluorescent lamp. Typically, such a lamp is composed of a glass tube filled with gas (e.g., a mixture of argon and mercury), with a fluorescent coating on the inside of the tube. When an electric discharge is induced between electrodes in the tube, the excited atoms of the gas emit photons, largely in the visible and ultraviolet regions of the spectrum. This light absorbed by luminescent coating and the visible photons are emitted [22].

2.3.3 Generation and Recombination through localized states

Recombination of electrons and holes is a process by which both carriers annihilate each other. Both carriers eventually disappear in the process. The energy difference between the initial and final state of the electron is released in the process. Recombination of charge carriers is the opposite of generation of charge carriers, representing mechanisms that reduce the excess charge density. When there is generation of charge carriers, it is always balanced by the recombination of charge carriers at the steady state[23].

When photons with energies equal to or greater than the band gap energy are absorbed in a semiconductor, electron-hole pairs are generated. The excess charge carriers generated by absorption of photons are known as photogenerated carriers. The photo-generated carriers can dominate the conduction processes in the semiconductor material. A large concentration of excess carriers can be maintained in a semiconductor under non-thermal equilibrium conditions, and this alters the conduction properties of the specimen. While the photo-generated carriers exist in their respective bands, they are free to contribute to the conductivity of the material [24].

The localized states are spatially distributed throughout the volume of the semiconductors. Therefore, n_T, p_T and the total density of the localized states N_T are given as a number per unit volume. The total density of the trap levels occupied by electrons, n_T and holes, p_T must equal to the total density of traps N_T:

$$N_T = n_T + p_T = n_{0T} + p_{0T}, \tag{20}$$

where, N_T is the total density of traps, n_T and p_T are the non-thermal equilibrium total density of the trap levels occupied by electrons and holes respectively. n_{0T} and p_{0T} are thermal equilibrium density of the trap levels occupied by electrons and holes respectively.

Rearranging Eqn.(20) Yields:

$$\delta n_T = -\delta p_T \tag{21}$$

Equation (21) shows that the trapping of electrons by the localized state removes the same amount of p_T states.

If there is illumination, the photo-generated electrons and holes are involved in the recombination processes. For the concentrations of photo-generated electrons (δn) and holes

in the conduction band (δp), the respective changes of the concentrations of p_T and n_T states of a centre due to illumination, δn_T and δp_T are given by:

$$\delta n_T = n_T + p_{0T} \qquad \text{and} \qquad \delta p_T = p_T + n_{0T}, \tag{22}$$

where, δn_T and δp_T are excess carriers concentrations of electrons and holes on the trap level respectively. In other words, a center is either in a neutral or negatively charged state, or in a neutral or positively charged state.

Suppose that δN density of electrons and δP densities of holes pairs generated in the conduction and valence bands, respectively in a semiconductor due to illumination; the total concentrations of excess electrons (δn) and holes (δp) under conduction in the respective conduction and valence bands are then given by:

$$\delta n = \delta N - \delta n_T, \qquad \delta p = \delta P - \delta p_T. \tag{23}$$

For a system with only electron trap, $\delta p = \delta N = \delta P$, so that from Eqn. (23) gives the photo-generated charge carrier neutrality equation for the system with an electron trap center to be:

$$\delta n + \delta n_T = \delta p \tag{24}$$

Similarly, the equation for a system with a hole's trap Centre is:

$$\delta n = \delta p + \delta p_T \tag{25}$$

The distribution probability f_n for the electron occupation of a trap located at energy E_T in the band gap is given by:

$$f_n(T) = \frac{1}{1 + \exp\left(\frac{E_T - E_F}{K_B T}\right)} \tag{26}$$

The thermal equilibrium electron occupancy n_{0T} and holes occupancy p_{0T} of the localized states are given by:

$$n_{0T} = f_n N_T = \frac{N_T}{1 + \exp\left(\frac{E_T - E_F}{K_B T}\right)}, \qquad p_{0T} = N_T - n_{0T} \tag{27}$$

The probability of electron capture by a localized state (U_{cn}) at thermal equilibrium is a function of the density of electrons in the conduction band (n_0), the electron capture coefficient of the state (C_{nT}), and the density of empty traps (p_{0T}). However, the probability of emission of an electron (U_{en}) depends only on the electron emission rate (e_n) and the density of traps occupied by electrons (n_{0T}). Thus, one can write U_{cn} and U_{en} as:

$$U_{cn} = C_{nT} n_0 p_{0T}, \qquad U_{en} = e_n n_{0T} \tag{28}$$

The electron capture coefficient (C_{nT}) depends on the proximity of the Centre to the conduction band. Similarly, the probability of holes capture (U_{cp}), and the probability of holes emission (U_{ep}) are given by:

$$U_{cp} = C_{pT} p_0 n_{0T}, \qquad U_{ep} = e_p p_{0T}, \tag{29}$$

where e_p is the hole emission rate. The hole capture coefficient (C_{pT}) depends on the proximity of the center to the valance band.

According to the principle of detailed balance ($R_{th} = G_{th}$), the probability of capture and emission for each carrier is equal, so that we have:

$$U_{cn} = U_{en}, \quad U_{cp} = U_{ep} \tag{30}$$

Taking into account Eqn. (28) through Eqn. (29) Yields:

$$e_n = C_{nT} n_1, \qquad \text{and} \quad e_p = C_{pT} p_1, \tag{31}$$

where,

$$n_1 = n_i \exp\left(\frac{E_T - E_i}{K_B T}\right), \quad \text{and} \quad p_1 = n_i \exp\left(\frac{E_i - E_T}{K_B T}\right), \tag{32}$$

are the concentrations of electrons and holes in the conduction and valence bands for the case in which the Fermi-level E_F falls at E_T. The fraction of photo-generated electrons, I_n trapped at the localized Centre to the excess electrons in the conduction band is given by:

$$I_n = \frac{\delta n_T}{\delta n} = \frac{\left(\tau_{p0} p_{0T} - \tau_{n0} n_{0T}\right)}{\tau_{n0}(p_0 + p_1 + n_{0T} + \delta N) + \tau_{p0}(n_0 + n_1 + \delta N)} \tag{33}$$

where δN is the total excess electron concentration generated in the conduction band discussed in Eqn. (23), τ_{n0} and τ_{p0} are time constants for a given center and is in general a function of the electron and hole capture coefficients of the center given by:

$$\tau_{n0} = \frac{1}{C_{nT} N_T} \tag{34}$$

and

$$\tau_{p0} = \frac{1}{C_{pT} N_T}. \tag{35}$$

The time constant τ_{n0} is often called the minimum lifetime for electrons, when all the localized states are empty, and τ_{p0} is the minimum lifetime for holes, when electrons occupy all localized

states. Taking into account Eqns. (24) give the fraction of trapped photo generated holes, I_p at the localized trap state to the excess holes in the valence band to be:

$$I_p = \frac{\delta p_T}{\delta p} = \frac{\left(\tau_{n0} n_{0T} - \tau_{p0} p_{0T}\right)}{\tau_{n0}(p_0 + p_1 + \delta P) + \tau_{p0}(n_0 + n_1 + p_{0T} + \delta P)}, \tag{36}$$

where δP is the total excess hole concentration generated in the valence band described in Eqn. (23). The subscripts n and p in Eqns. (35) and (36) represent the electrons and holes concentration. For low injection level system, $N_T, p_0, p_1, n_1 \gg \delta N, \delta P$, Eqns. (35) and (36) gives:

$$I_n = \frac{\left(\tau_{p0} p_{0T} - \tau_{n0} n_{0T}\right)}{\tau_{n0}(p_0 + p_1 + n_{0T}) + \tau_{p0}(n_0 + n_1)} \tag{37}$$

and

$$I_p = \frac{\left(\tau_{n0} n_{0T} - \tau_{p0} p_{0T}\right)}{\tau_{n0}(p_0 + p_1) + \tau_{p0}(n_0 + n_1 + p_{0T})}, \tag{38}$$

where τ_{n0} and τ_{p0} are constants for a given center and is in general a function of the electron and hole capture coefficients of the center. The relation between the densities of the excess carriers in conduction process and the total free carriers generated in the respective bands can be written from Eqn. (23) ,(33) and (36) above as:

$$\delta n = \frac{\delta N}{1 + I_n}, \qquad \delta p = \frac{\delta P}{1 + I_p}. \tag{39}$$

2.3.4 Radiative Recombination Mechanisms

Optically generated charge carriers can recombine in two different ways: radiatively or non-radiatively. Radiative recombination is the opposite of optical generation of charge carriers. It occurs when the energy of the excited electron is emitted by the formation of a photon during the annihilation of an EHP. Non-radiative recombination occurs when excess energy is released as phonons. Or transferred as excess kinetic energy to another charge carrier, i.e. the excess energy is dissipated as heat during the recombination process. When the electron and hole recombine through radiative recombination, a photon is emitted and the energy of the emitted photon is dependent on the change in energy state of electron-crystal system. Photoluminescence is heavily dependent on the recombination mechanisms of a material's minority carriers. The dominating recombination mechanism is very sensitive to impurities or defects. The minority carrier lifetime is defined as the average time it takes an excess minority carrier to recombine. In indirect band gap semiconductors, the radiative lifetime is very large.

This is because the valence and conduction bands do not line up causing the direct band-to-band recombination to be far less frequent. Because the radiative lifetime is very large, it can usually be neglected [25] to [28].

I. Band-to-Band Radiative Recombination

Radiative (band-to-band) recombination occurs in direct band gap semiconductors when an electron recombines directly with a hole. Radiative recombination is dependent on the density of electrons and holes. Radiative recombination involves the annihilation of electron-hole pairs by giving out a photon of energy equal to the energy gap between the levels where the two carriers were in before recombination. Both carrier types need to be available in the recombination process. Therefore, the rate is expected to be proportional to the product of negative and positive charge carrier densities, n and p, respectively. Also, in thermal equilibrium, the recombination rate must equal the generation rate since there is no net recombination [29].

The band-to-band radiative recombination is a direct recombination mechanism, in which the electrons in the conduction band decay to the valence band (i.e. recombine with holes in the valence band). This is a very efficient process in direct band gap semiconductors. The energy lost by an electron in making the transition is released as a photon [30] to [32].

The total band-to-band radiative recombination rate R is directly proportional to the products of the concentration of electrons n available in the conduction band and the concentration of holes p available in the valence band to capture these electrons.

$$R = C_R np, \tag{40}$$

where C_R is a constant known as the coefficient of holes in the valence band for the capture of electrons from the conduction band. The capture probability C_R, is described for direct band gap materials by van Roosbroeck and Shockley, using experimentally determined values of the optical absorption coefficient and the intrinsic carrier concentration as [33].

$$C_R = e\pi\sqrt{k_\infty}\left(\frac{m_n}{m_n^* + m_p^*}\,\frac{300}{T}\right)^{\frac{3}{2}}\left(1 + \frac{m_n}{m_n^*} + \frac{m_n}{m_p^*}\right)\left[E_g^2 + 3E_g k_B T + 3.75 k_B^2 T^2\right], \tag{41}$$

where e is the elemental charge and k_∞, the high frequency dielectric constant of the material.

The respective net excess photo-generate negative and positive charge carrier densities, δn and δp during illumination can be calculated by the difference between non-thermal equilibrium and thermal equilibrium charge carrier densities as:

$$\delta n = n - n_0 \qquad \text{and} \qquad \delta p = p - p_0. \tag{42}$$

The above recombination mechanism is written under non-thermal equilibrium circumstances. At thermal equilibrium, these recombination rates are given by:

$$R^{th} = C_R n_0 p_0, \tag{43}$$

The net band-to-band radiative recombination rate, U_R of free carriers is given by the difference between the band-to-band non-thermal equilibrium recombination mechanism, and the band-to-band thermal equilibrium recombination mechanisms:

$$U_R = R - R^{th} = C_R(p_0\delta n + n_0\delta p + \delta p\delta n). \tag{44}$$

Assuming a system with no free carrier trapping center (only band to band transition), the steady-state band to band free carrier's generation lifetime is given by:

$$\tau_g = \frac{\delta N}{U_R} = \frac{\tau_{R0}\tau_k}{\tau_{R0} + \tau_k}, \tag{45}$$

where τ_{R0} and τ_k are time constants related to low and high injection band to band free carriers generation rate given by:

$$\tau_{R0} = \frac{1}{C_R(n_0 + p_0)} \tag{46}$$

and

$$\tau_k = \frac{\tau_{R0}}{\sqrt{1 + 4C_R G_0 \tau_{R0}^2}}, \tag{47}$$

where G_0 is optical generation rate of charge carriers. The ratio of the band to band recombination rate, U_R to the free carrier generation rate, G_0 which is a direct measure of the band to band photoluminescence effect is given by:

$$I_{CV} = \frac{U_R}{G_0} = \frac{C_R(p_0\delta n + n_0\delta p + \delta p\delta n)}{G_0}. \tag{48}$$

II. Conduction band-to-trap level radiative recombination

The conduction band to localized center radiative recombination rate R_{CT} is directly proportional to the product of the concentration of electrons n available in the conduction band

and the concentration of holes p_T states available in the localized state to capture electrons from the conduction band:

$$R_{CT} = C_{nT} n p_T, \tag{49}$$

where C_{nT} is a constant known as the coefficient of holes in the localized state for the capture of electrons in conduction band is given by R. N. Hall *et al*. as [34].

$$C_{CT} = 0.69 \times 10^{-12} \frac{\mu}{Z^2} \left(\frac{m_n}{m_n^*}\right)^{5/2} \left(\frac{300}{T}\right)^{1/2} (E_C - E_T). \tag{50}$$

The recombination mechanisms in Eqn. (49) can be rewritten at thermal equilibrium as:

$$R_{CT}^{th} = C_{CT} n_0 p_{0T}, \tag{51}$$

where, R_{CT}^{th} is thermal equilibrium conduction band to trap level radiative recombination rate. Again, under non-thermal equilibrium circumstances, we have:

$$p_T = p_{0T} + \delta p_T, \qquad n_T = n_{0T} + \delta n_T. \tag{52}$$

The net conduction band to localized trap center radiative recombination rate of free carriers are given by the difference between the non-thermal and thermal equilibrium recombination mechanisms:

$$U_{CT} = R_{CT} - R_{CT}^{th} = C_{CT}(p_{0T}\delta n + n_0 \delta p_T + \delta p_T \delta n) \tag{53}$$

or

$$U_{CT} = C_{CT}\left(p_{0T}\delta n + n_0 I_p \delta p + I_p \delta p \delta n\right). \tag{54}$$

Assuming only conduction band to localized state transition ($\delta n = \delta p_T$), the trap level to conduction band carrier generation lifetime, τ_{CTg} can also be described by:

$$\tau_{CTg} = \frac{\tau_{CT0}\tau_{CTk}}{\tau_{CT0} + \tau_{CTk}}, \tag{55}$$

where τ_{CT0} and τ_{CTk} are the time constants given by:

$$\tau_{CT0} = \frac{1}{C_{CT}(n_0 + p_{0T})} \tag{56}$$

and

$$\tau_{CTk} = \frac{\tau_{CT0}}{\sqrt{1 + 4C_{CT}G_0\tau_{CT0}^2}}. \tag{57}$$

The ration of the conduction band recombination rate of free carriers to the total optical generation rate of the free carriers, G_0 is given by:

$$I_{CT} = \frac{U_{CT}}{G_0} = \frac{C_{CT}\left(p_{0T}\delta n + n_0 I_p \delta p + I_p \delta p \delta n\right)}{G_0} \tag{58}$$

III. Trap Level-to-Valence Band Radiative Recombination

The localized state to valence band radiative recombination rate R_{TV} is directly proportional to the product of the concentration of n_T states available in the localized state and the concentration of holes p available in the valence band to capture electrons from the localized state [35].

$$R_{TV} = C_{TV} p n_T, \tag{59}$$

where, C_{TV} is a constant known as the coefficient of holes in the valence band for the capture of electrons in the localized states and it is given by:

$$C_{TV} = 0.69 \times 10^{-12} \frac{\mu}{Z^2} \left(\frac{m_n}{m_p^*}\right)^{5/2} \left(\frac{300}{T}\right)^{1/2} (E_T - E_V). \tag{60}$$

The recombination mechanisms in eqn.(59) is written under non-thermal equilibrium circumstances. At thermal equilibrium, this recombination rate is given by:

$$R_{TV}^{th} = C_{TV} p_0 n_{0T} \tag{61}$$

The net localized trap center to valence band radiative recombination rate of free carriers are given by the difference between the non-thermal and thermal equilibrium recombination mechanisms:

$$U_{TV} = R_V - R_V^{th} = C_{TV}(p_0 \delta n_T + n_{0T} \delta p + \delta p \delta n_T) \tag{62}$$

or

$$U_{TV} = C_{TV}(p_0 I_n \delta n + n_{0T} \delta p + I_n \delta p \delta n). \tag{63}$$

Assuming only valence band to localized state transition ($\delta p = \delta n_T$), the free carrier generation lifetime from the valence band to the localized state, τ_{TVg} is given by:

$$\tau_{TVg} = \frac{\tau_{TV0}\tau_{TVk}}{\tau_{TV0} + \tau_{TVk}}, \tag{64}$$

where τ_{TV0} and τ_{TVk} are time constants given by:

$$\tau_{TV0} = \frac{1}{C_{TV}(p_0 + n_{0T})}. \tag{65}$$

and

$$\tau_{TVk} = \frac{\tau_{TV0}}{\sqrt{1 + 4C_{TV}G_0\tau_{TV0}^2}}. \tag{66}$$

The intensity of light from the trap level to the valence band, I_{TV} is given by:

$$I_{TV} = \frac{U_{TV}}{G_0} = \frac{C_{TV}(p_0 I_n \delta n + n_{0T}\delta p + I_n \delta p \delta n)}{G_0}. \tag{67}$$

The total concentration of excess electrons generated in the conduction band is given by:

$$\delta N = \frac{G_0 \tau_g \tau_{CTg}}{\tau_g + \tau_{CTg}}. \tag{68}$$

The total concentration of excess holes generated in the valence band is also given by:

$$\delta P = \frac{G_0 \tau_g \tau_{TVg}}{\tau_g + \tau_{TVg}}. \tag{69}$$

Chapter 3

Methodology

This section gives the details explanation through which the calculations are done and the method that used. Firstly, the parameters of Zinc Oxide like Varshni parameters, capture coefficient, effective masses of holes and electrons were determined from previously studied materials. The next task is, to formulate the governing equation by considering radiative recombination mechanisms in the band-to-band, conduction band to valence band and localized trap to valence band radiative recombination mechanisms.

Next, the statistics of the accumulation of free carriers in the conduction band, valence band and different localized states are formulated by considering the band-to-band optical generation, the recombination and trapping of free carriers through different localized states. By using thermal and non-thermal equilibrium concentration of electrons and holes, the total band-to-band, conduction to trap level and trap level to valence band radiative recombination rate is determined. Then using the difference between thermal and non-thermal equilibrium recombination rate, net radiative recombination rate of free carriers in the corresponding band is determined.

Upon the determination of the steady-state expressions for the occupation of free carriers at different energy levels, one can describe the relations between $\delta n, \delta p$, δn_T and δp_T under different conditions. Then, by using illumination and net radiative recombination rate the luminescence intensity of light is determined for the corresponding radiative recombination mechanisms by assuming one photon ejects one electron at a time.

Then, by substituting the typical values for energy band gap, capture coefficients, acceptor energy levels, and carrier's concentrations of the zinc oxide semiconductor, the competition between the photoluminescence of different localized states are described. This can be done by varying the doping level, energy of the illumination, injection level (incident photo flux density) and temperature of the samples. This was done by inserting the necessary formula on the excel data and copying this data to the origin to plot and formatting the graph. Then by making semi-log the result obtained, the graph of photoluminescence intensity of different localized states as a function of localized trap energy was plotted.

Chapter 4

Results and Discussions

In this topic the factors that affect the free carrier's density and the factors that affects the intensities of the lights emitted due to the radiative recombination of free carriers in between different energy levels in ZnO semiconductor is described in detail.

4.1. Trapping Effects

Figure 3 depicts the variation of free carriers trapping intensity with localized state energies, showing (a) the effects of different localized energies on the trapping intensity at constant temperature and (b) the effects of temperature on the trapping intensities for ZnO semiconductor at low injection level. The temperature values considered are 60 K, 300 K, 600 K and 900 K. The doping concentration, N_a and the density, N_T of the localized centers considered are equal and 10^{17}cm^{-3}. All the figure of trapping intensities in this work were drawn using relations (33) and (36) under different conditions.

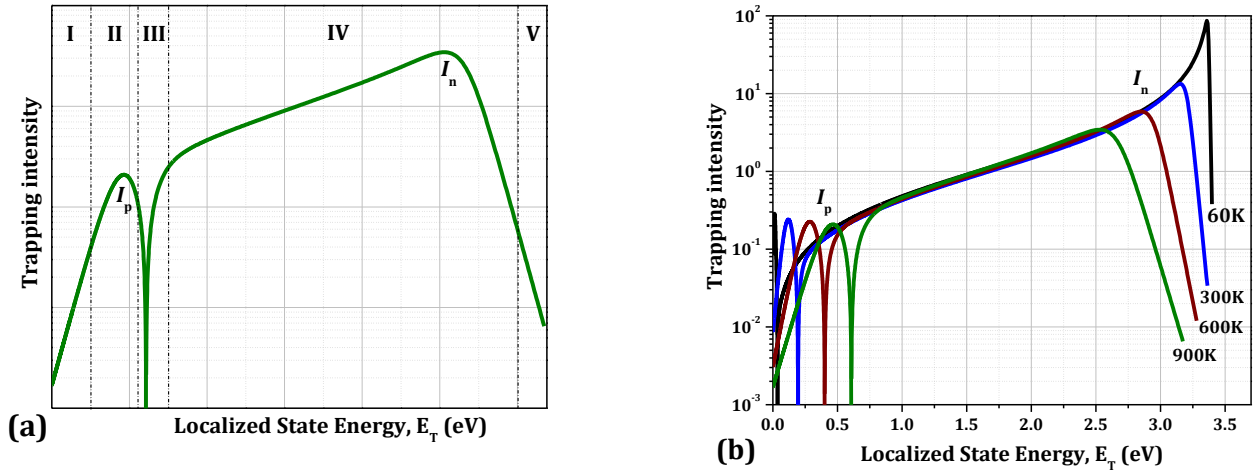

Figure 3: Variation of free carriers trapping intensity with localized state energy, showing (a) the effects of different localized energies on the trapping intensity at constant temperature and (b) the effects of temperature on the trapping intensities for ZnO semiconductor at low injection level. The temperature values considered are 60 K, 300 K, 600 K and 900 K. The doping concentration and the density of the localized centers considered are equal and 10^{17}cm^{-3}.

The localized energy dependence of trap intensity described above can be divided into five regions based on the interactions of the localized states with the conduction or valence bands as shown in Figure 3(a). These are:

I. Acceptor region: This region comprises all the energy levels very closer to the valence band edge. Most of the impurities are in the n_T states and the holes emission rate to the valence band

by the localized states in this region is very high. The effects of the traps of a localized center becomes small and the localized center hence act as acceptor levels.

II. Holes trap region: This region encompasses the localized centers far above the valence band edge and far below the Fermi level. Most localized states are still in the n_T states and the hole emission rate has decreased and the free holes trapping effect becomes dominant.

III. Recombination region: This region also encompasses all the regions very closer to the Fermi level, where the localized levels are partially ionized, the electron and holes capture rates are almost equal. The centers has equal probabilities to capture free holes and electrons. So that, the effects of free charge carriers traps are negligibly small and recombination becomes dominant in this region.

IV. Electron trap region: This region comprises all the regions that are very close to the intrinsic Fermi level and most of the regions far above the intrinsic Fermi level. Most localized states are in the p_T states and the holes capture rate is very low. The electron trap effect becomes the most dominant.

V. Donor region: This region consists of all the localized Centre closer to the conduction band. All the localized states in this region are in the p_T states. The hole capture rate is negligibly small and the electron emission rate is extremely very high. Hence, the free carriers trap effect in this region is very negligibly small and all the localized centers act as donor levels.

The interaction of the localized states with the respective energy bands is varied with temperature. In general, free carrier traps are relatively more active at low temperatures. Only deep levels can trap free carriers at higher temperatures as shown in Figure 3 (a). The minority carrier traps farther away above the intrinsic level become more effective with decreasing temperature as shown in Figure 3 (b). At very low temperatures, the carriers have insufficient thermal energy to become excited into the conduction (or valence) band. Free carrier traps are more effective at low temperatures, when compared to high temperatures. The minority carrier traps farther away above the intrinsic level and below the donor level becomes more effective with decreasing temperature. The probability of emission of carriers by the center increases with increasing temperature. The electron trap localized centers become the most dominant electron trap centers at lower temperatures [36].

4.2. Variation of photoluminescence with localized state energy

In this section, the localized energy dependences of the photoluminescence intensities of Zinc Oxide are described at different temperatures. The photoluminescence intensities for the conduction band to valence band, I_{CV}, conduction band to localized states I_{CT}, and for the localized states to valence band, I_{TV} transitions are described using relations (48), (58) and (67) above respectively.

As already discussed in Figure 3 (b) above, densities of the trapped excess electrons in the localized states below the mid-gap is negligibly very small. For localized states above the mid-gap, the trapping increases with increasing energy and decreasing the temperature of the body. Hence, in the presence of the localized states below the mid-gap, the conduction band has sufficient excess electron density and the valence band has also sufficient excess holes density to capture excess electrons in the conduction band. In the presence of the localized states above the mid-gap the conduction band has very small excess electron density due to the capture of excess electrons by the localized states. Hence, more band to band recombination is enhanced in the presence of lower energy localized states [37]. Figure 4 illustrates the variation of low injection level photoluminescence intensities due to various electronic transition levels with localized energies at (a) 60 K, (b) 500 K and (c) 900 K for the sample used in Figure 4. As depicted in Figure 4 (a), the conduction band to valence band photoluminescence, I_{CV} is very high at the low energy regimes because of the absence of free electrons trap by the low energy localized states. However, the conduction band to valence band photoluminescence, I_{CV} is decreasing with increasing the energy of the localized states above the mid-gap due to the small free electrons density in the conduction band due to the increase in the free electrons trap by the localized states. The conduction band to valence band photoluminescence, I_{CV} increases in the donor region towards the valence band because of the reduction (absence) of free electrons trap by the localized states.

At very low temperature, most of the localized states are occupied by the trapped free carriers and hence there is no (very small) recombination taking place between the conduction band and the localized state; and between the localized states and the valence band as shown in Figure 4 (a). As the temperature increases, the free carriers trapping effect by the localized states decreases. This facilitates the radiative recombination rates between all the energy

levels. As a result, the photoluminescence due to the transition of free electrons from the conduction band to the valence band, I_{CV}, from the conduction band to the localized states, I_{CT} and from the localized states to the valence band, I_{TV} are increasing as shown in Figure 4 (a) to (c).

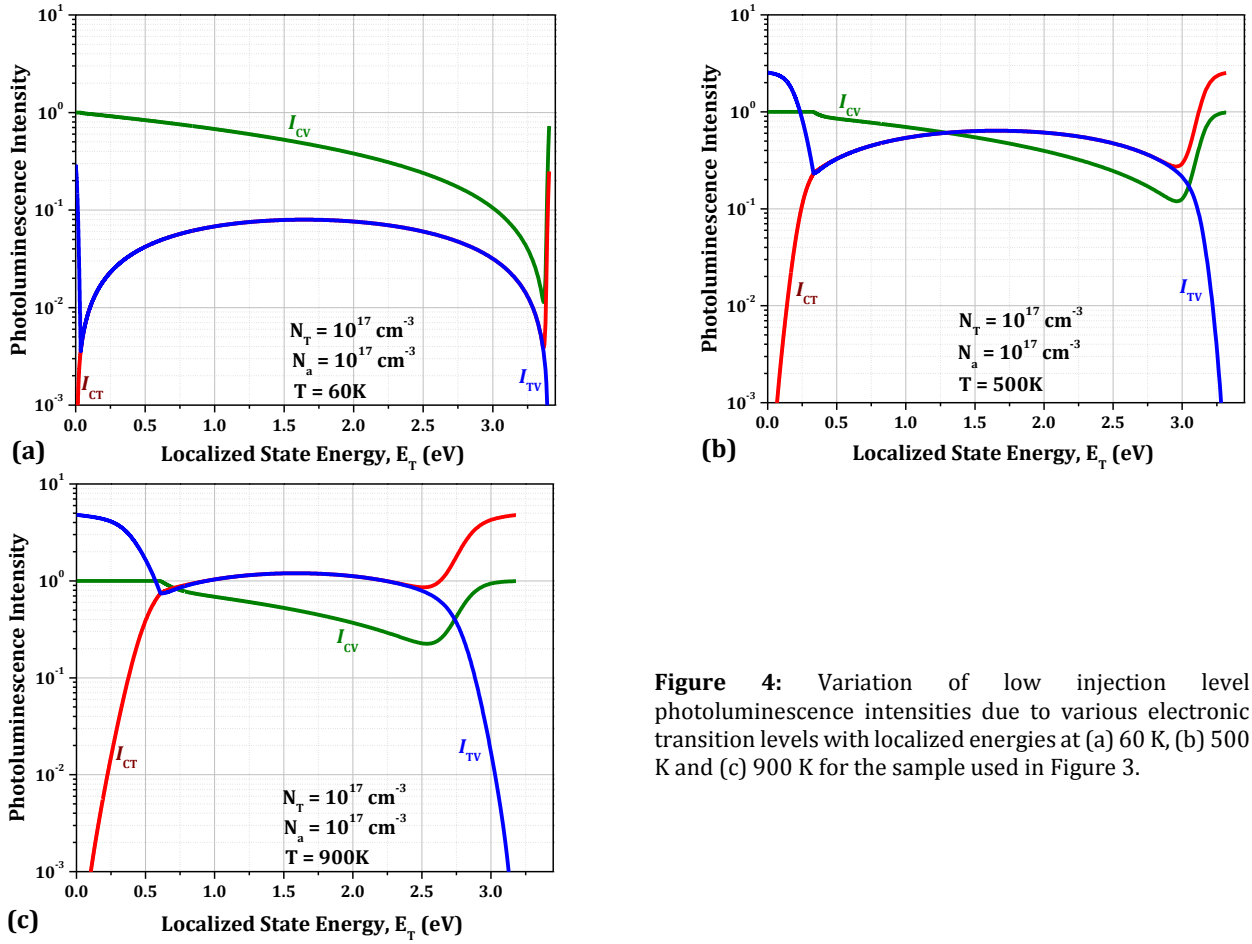

Figure 4: Variation of low injection level photoluminescence intensities due to various electronic transition levels with localized energies at (a) 60 K, (b) 500 K and (c) 900 K for the sample used in Figure 3.

All the localized states above the acceptor level and below the donor level have equal probability for the recombination of free electrons in the conduction band with the available holes in the localized states; and free electrons in the localized states with holes in the valence band. Since they are in the same electronic states, there is no transition of free electrons from the conduction band to the acceptor levels; and from the donor level to the valence band. However, there is very high degree of electron transition (photoluminescence) from conduction band to donor levels; and from acceptor levels to the valence band [38] to [40].

Note that, the band to band photoluminescence intensity dominates at very low temperature and the localized state to valence band photoluminescence intensity dominates at

very high temperature (Figure 4 (a) and (c)). At the intermediate temperature, the band to band photoluminescence dominates the lower energy regimes and the localized states to the valence bands photoluminescence dominates the higher energy regimes as depicted in Figure 4 (b). The acceptor level to valence band and the valence band to donor level free electron transition rates are the most dominant at very high temperature as depicted in Figure 4(c).

4.3. Variation of photoluminescence with transition energy

Photoluminescence measures the intensities of photons generated during radiative recombination of electrons in the higher energy level with holes in the lower energy levels in terms of the energy through which the transition of free electrons take place. If we assume the generation of a photon during the recombination of an electron-hole pairs, the rate at which photons are generated can be described in terms the radiative recombination rate of the free carriers as we did in section 4.2 above. The conduction band to valence band photoluminescence intensity is described only by a single transition energy $E_C - E_V$ at constant temperature. The conduction band to localized state photoluminescence intensity is described using the variation in $E_C - E_T$. The localized state to valence band photoluminescence intensity is described using the variation in $E_T - E_V$ [41].

Figure 5 illustrates the variation of low injection level photoluminescence intensities due to various electronic transition levels with transition energies at (a) 60 K, (b) 500 K and (c) 900 K for the sample used in Figure 4. Please, refer to the description of Figure 4 for more detail of the effects of localized energy states the photoluminescence intensities of different transition levels. As it can be seen in Figure 5 (a) to (c), the conduction band to valence band photoluminescence under goes only a single transition energy of $E_C - E_V$ at constant temperature. This energy transition level is relatively shifted to low energy level with increasing temperature, since the band gap is decreasing with increasing temperature. In conduction band to the localized state transition of free carriers, $E_C - E_T$ is considered as low transition energy for E_T above the mid-gap and vice versa. Hence, in the description of the photoluminescence intensities as a function of $E_C - E_T$, the red graphs of I_{CT} in Figure 4 above have to be inverted horizontally as shown in Figure 5. In the localized state to valence band transition of free carriers, $E_T - E_V$ is considered as low transition energy for E_T below the mid-

gap and vice versa. Hence, in the description of the photoluminescence intensities as function of $E_T - E_V$, the blue graphs of I_{TV} in Figure 4 above have to be remained as they are as shown in Figure 5.

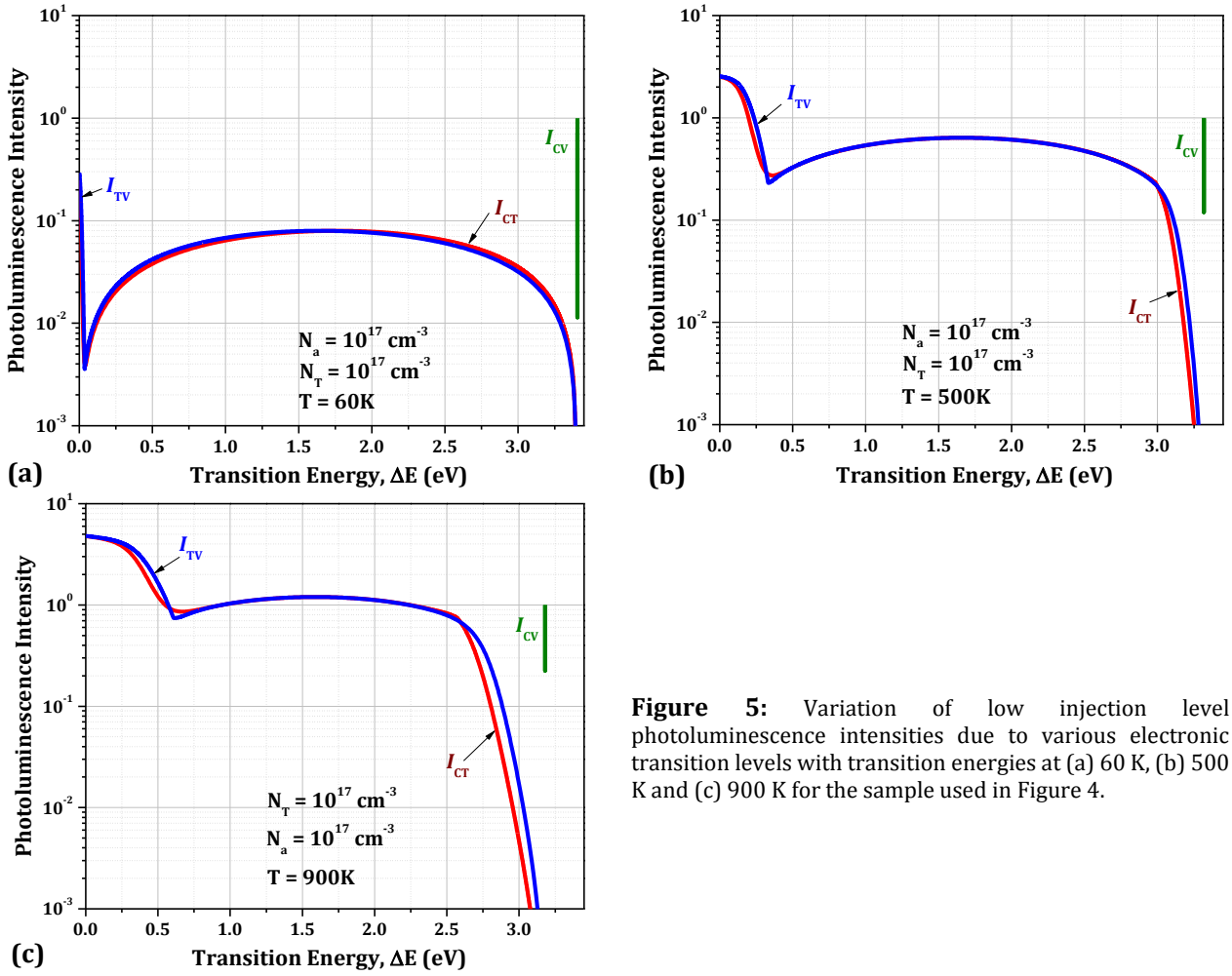

Figure 5: Variation of low injection level photoluminescence intensities due to various electronic transition levels with transition energies at (a) 60 K, (b) 500 K and (c) 900 K for the sample used in Figure 4.

Hence, except the reduction of the lower and higher transition energies conduction band to localized photoluminescence, I_{CT} depicted in Figure 5 (b) and (c), the variation of I_{CT} and I_{TV} with transition energy is similar at the intermediate transition energies at all temperatures. The variations of high temperature I_{CT} and I_{TV} at the lower and higher transition energies are attributed to the high intensity of the capture of free electrons in the deep donor levels in low energy transition regimes and due to the highly ionized acceptor levels in the high transition energy regimes. The increase in the minimum value of I_{CV} with increasing temperature depicted in Figure 5 (a) to (c) is due to the reduction of carrier trapping discussed in section 4.2 above.

One can conclude from Figure 5 that, if an intensive photoluminescence is observed closer to band edge, its source could be most probably band to band free carrier transition, but not localized state band free carrier transition. The other photoluminescence intensities observed at transition energies far below the band edge energy could be attributed to the conduction band to localized state or localized state to valence band free carrier transitions.

Chapter 5

Conclusion and Outlook

5.1. Conclusion

This thesis has discussed the photoluminescence of zinc oxide compound semiconductor. The intensity of light depends on the amount of illumination and net rate of recombination of excess electrons in the corresponding radiative recombination mechanisms. It shows the amount of light in the bands and the more luminescent bands. Since there is no effects of traps in the conduction to valence band radiative recombination, rate of recombination is high and photoluminescence intensity of light becomes high. The intensity of light decreases with increasing localized trap energy in this band. It was shown that due to trap effects in the conduction band to trap level radiative recombination, the recombination rate reduces and hence decreases the intensity of light in the band. The intensity of light increases with increasing localized trap energy in this band. Due to the effects of trap, only small amount of electrons on localized Centre and excess of holes in the valence band. These decreases the recombination rates and hence decreases the intensity of light in the Trap level to valence band radiative recombination.

It has been shown that, the trapping intensities varies with temperature. At low temperatures, free carrier traps are relatively more active. The minority carrier traps farther away above the intrinsic level become more effective with decreasing temperature. Free carrier traps are more effective at low temperatures, when compared to high temperatures. The probability of emission of carriers by the center increases with increasing temperature. The electron trap localized centers become the most dominant electron trap centers at lower temperatures.

Photoluminescence is varied with localized state energy and transition energy at different temperatures. Under variation with localized state energy, at very low temperature, there is no (very small) recombination taking place between the conduction band and the localized state; and between the localized states and the valence band. As the temperature increases, the photoluminescence due to the transition of free electrons from the conduction band to the valence band, I_{CV}, from the conduction band to the localized states, I_{CT} and from the localized states to the valence band, I_{TV} are increasing. The band to band photoluminescence intensity

dominates at very low temperature and the localized state to valence band photoluminescence intensity dominates at very high temperature. At the intermediate temperature, the band to band photoluminescence dominates at the lower energy regimes and the localized states to the bands photoluminescence dominates the higher energy regimes. The acceptor level to valence band and the valence band to donor level free electron transition rates are the most dominant at very high temperature.

It was concluded that, under variation of Photoluminescence with transition energy, the conduction band to valence band photoluminescence energy transition level is relatively shifted to low energy level with increasing temperature. the variation of I_{CT} and I_{TV} with transition energy is similar at the intermediate transition energies at all temperatures.

5.2. Outlook

In these work the effects of photoluminescence of zinc oxide is studied. The developed methods can be applied for other types of wide and direct band gap semiconductors. In the future, this research will be extended into three directions. One is further studying of the remaining parameters of zinc oxide under different temperature and excess carrier concentrations. The second is the effects of doping, the injection level, the temperature and the energy level of the localized states on the photoluminescence for zinc oxide samples needs to be subjected to different laboratory. Therefore, further studies are required to be done in order to see the effects of photoluminescence of wide and direct band gap semiconductors. The third is focusing on the application of zinc oxide.

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Declaration

I here under signed declare that the thesis is my original work, has not been presented for a degree in any other university and that all sources of material used for the thesis have been fully acknowledged.

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Signature:_____

This thesis has been submitted for the examination with my Approves as Adama Science and Technology university advisor.

Name: Dr. Megarsa Wodajo

Signature: _____