Characterization of Cylindrical and Conical Like Zinc Oxide Light Emitting Diode Structures

by

Nik Nur Atiqah Binti Saidi
(1632212108)

A thesis submitted in fulfillment of the requirements for the degree of Master of Science in Photonic Engineering

School of Microelectronic Engineering
UNIVERSITI MALAYSIA PERLIS

2018

ACKNOWLEDGMENT

First and above all, I praise Allah SWT, the almighty for providing me this opportunity and granting me the capability to proceed successfully. This Master's final report appears in its current form due to the assistance and guidance of several people. I would, therefore, like to offer my sincere thanks to all of them.

Associate Professor Dr. Mohamad Halim bin Abd. Wahid, the supervisor for master's research, my cordial thanks for accepting me as a student under your supervision. The trust, the insightful discussion, and the valuable advice are given by you during the whole period of the research are very helpful in order for me to adapt to the new environment. This project excellently a success is because of your guidance.

Besides that, I would like to thank Associate Professor Dr. Prabakaran A/L Poopalan, the co-supervisor, for your help regarding my lab session, experimental setup and the progress of this project. The task was challenging at first, however, I manage to finish and understand them because of your help and advice.

Associate Professor Ir. Dr. Rizalafande bin Che Ismail, which is the dean for School of Microelectronic Engineering and my academic advisor during my study in Universiti Malaysia Perlis (UniMAP), thank you for your warm encouragement, thoughtful guidance, critical comments, and correction for this research especially during the process of proposal defense.

I also would like to thank Mr. Zulkarnail bin Abd. Hamid, laboratory assistance for your excellent technical assistance in the lab and your kindly answers to my general questions regarding the procedure of the lab. All the postgrad students, as well as the undergrad, are able to finish their research given is because of your help to provide an excellent and comfortable environment in the laboratory.

Miss Nur Atirah, Miss Ummi Khairiah, Miss Najwa Sarihah, Miss Nursyamimi, Miss Nur Hafika, and Miss Nur Zahidah, I greatly appreciate for the useful suggestions and for assisting me in many different ways during the preparation of the task and handling the report.

I cannot finish without thanking my family, Tuan Hj. Saidi bin Hassan and Puan Hjh. Nik Yah binti Mahamood. I warmly thank and appreciate my parents not only for the undivided love but also for their constant material support and spiritual encouragement in all aspects of my life. Honestly, without your supports and encouragements, I could not have finished this research.

Lastly, I can just say thanks for everything and may all of you the best in return.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

2D	Two-dimensional
3D	Three-dimensional
Ag	Silver
Al	Aluminum
AlGaAs	Aluminum gallium arsenide
AlGaInP	Aluminum gallium indium phosphide
AlGaP	Aluminum gallium phosphide
As	Arsenic
BeO	Beryllium oxide
CdO	Cadmium oxide
CdS	Cadmium sulfide
CdTe	Cadmium telluride
CFL	Compact fluorescence lamp
Cl	Chlorine
CRI	Color rendering index
CRT	Cathode ray tubes
Cu	Copper
Cu:Zn	Cooper-zinc
EQE	External quantum efficiency
Ga	Gallium
GaAs	Gallium arsenide
GaN	Gallium nitride
GaP	Gallium phosphide
Ge	Germanium
GGA	General gradient approximation
HID	High-intensity discharge
I	Iodine
In	Indium
IQE	Internal quantum efficiency
I-V	Current versus voltage
InGaN	Indium gallium nitride
IR LED	Infrared LED

K	Potassium
LCD	Liquid crystal display
LDA	Local density approximation
LED	Light emitting diode
Li	Lithium
LPE	Liquid-phase epitaxy
MBE	Molecular beam epitaxy
Mg	Magnesium
MgO	Magnesium oxide
MIS	Metal-insulator-semiconductor
MQW	Multiple quantum well
N	Nitrogen
Na	Sodium
O	Oxygen
O^{2-}	Oxygen ion
P	Phosphorus
PCB	Printed circuit board
PhC	Photonic crystal
PL	Photoluminescence
PLCC	Plastic leadless chip carrier
Sb	Antimony
Si	Silicon
SiC	Silicon carbide
Si:H	Hydrogenated Amorphous Silicon
SiO_2	Silicon dioxide
SPE	Scattered photon extraction
SRH	Shockley-Read-Hall
TFT	Thin film transistor
UV	Ultraviolet
Zn	Zinc
ZnO	Zinc oxide
ZnS	Zinc sulfide
ZnSe	Zinc selenide

$ZnSO_4$	Zinc sulphate
ZnSO4.7H2O	Zinc vitriol
ZnTe	Zinc telluride

LIST OF SYMBOLS

cm	Centimeter
C	Coulomb (unit)
E_{gap}	Energy bandgap of semiconductor
E	Applied electric field intensity in $\frac{V}{cm}$
e, q	electron charge constant (1.6021x 10^{-19}C)
eV	Electron volt
f(E)	Distribution function
h_con_n	Height of ring structure
h_dom	Thickness of LED
h_p	thickness of p-type layer
hv	Photon energy
I	Diode current
I_0	Saturation current of diode
$i/_e$	Injected photon flux
J	Joule (unit)
J_n	Drift of current density due to free electrons
J_p	Drift of current density due to free holes
k	Boltzmann's constant (1.380 x 10^{-23}J/K)
K	Kelvin (unit)
m_0	Free electron mass
n	Number of free electrons in cm^{-3}
N	Doping concentration in cm^{-3}
N_c	Effective density of state of conduction band
N_V	Effective density of state of valence band
nm	Nanometer (unit)
P_o	Output optical power
p	Number of free holes in cm^{-3}
$\boldsymbol{r}$	Axis of symmetry (radial position)
r	Recombination
r_r	Radiative recombination coefficient
r_{nr}	Non-radiative recombination coefficient

r_fill	Fillet radius
s	Second (time)
T	Absolute temperature (means in degree kelvin)
V	Applied voltage in Volts
V	Volt (unit)
v	Emission frequency
V_n	Voltage supply at n contact
V_p	Voltage supply at p contact
w_con_n	Width of ring structure
w_con_p	Width of p contact
w_dom	Width of LED
~	Approximation
μ	Micro (unit)
μ_n	Electron mobility
μ_p	Hole mobility
º	Degree (angle)
ºC	Degree Celsius (temperature)
Å	Ionic radius
η_{int}	Internal quantum efficiency (IQE)
η_{ent}	External quantum efficiency (EQE)
η_e	Proportion of photons generated in the active region that escape from the device
ρ	Resistivity
Ω	Ohm (unit)
τ	Lifetime
τ_r	Radiative recombination lifetime
τ_{nr}	Non-radiative recombination lifetimes
ϕ_o	Output photon flux
%	Percentage
$\boldsymbol{z}$	Axis of symmetry (axial position)

Pencirian Struktur Silinder dan Kon Diod Pancaran Cahaya Zink Oksida

ABSTRAK

Berbeza dengan sistem pencahayaan tradisional, penggunaan teknologi pencahayaan cahaya diod (LED) dapat mengekalkan pertumbuhan ekonomi disebabkan oleh penurunan penggunaan tenaga secara drastik, dapat mencegah malapetaka kepada pengguna akibat penghasilan haba, dan juga dapat mengurangkan kesan rumah hijau. Berbeza dengan sistem lampu konvensional, teknologi LED memiliki ciri sistem pencahayaan mesra alam. Kajian ini telah menggunakan Zink oksida (ZnO) sebagai bahan utama cip LED. Ini adalah kerana ZnO bukan sahaja murah tetapi juga mudah untuk diperolehi dalam pasaran semasa. Oleh itu, kos awal pemprosesan LED boleh dikurangkan dan menjadikannya lebih rendah berbanding harga pasaran LED yang sedia ada. Tujuan utama kajian ini adalah untuk mengkaji kesan ketebalan dopan dan voltan dalam struktur cip yang berbentuk silinder dan kon. Kesemua keputusan yang diperoleh telah direkodkan dan dibandingkan mengikut ciri-ciri voltan semasa (I-V), kadar pelepasan dan kecekapan kuantum dalaman. Kedua-dua struktur geometri ini mempunyai diameter dan ketebalan yang sama iaitu 50μm dan 10μm. Di samping itu, bahagian bawah struktur silinder dan kon dilampirkan dengan penghubung n yang berbentuk seperti cincin. Cincin logam ini terdiri daripads 5μm lebar dan 2μm ketebalan yang menjadikan diameter bawah untuk struktur silinder dan kon seperti 60μm. Sementara itu, penghubung p direka di bahagian atas struktur secara langsung mewujudkan cakera logam. Ketebalan dopan divariasi dari 1μm lapisan p-jenis dengan 9μm ketebalan lapisan n-jenis. Lapisan ini selanjutnya diubah-ubah sehingga menjadi 9μm jenis p dengan ketebalan 1μm jenis n. Nilai voltan kemudiannya ditetapkan pada 6V. Hasilnya, dimensi silinder menunjukkan voltan putaran yang lebih tinggi dan peratusan kecekapan kuantum dalaman yang lebih tinggi berbanding struktur kon. Di samping itu, peratusan kecekapan kuantum dalaman untuk kedua-dua struktur juga meningkat kerana ketebalan lapisan jenis p dipertingkatkan. Struktur seperti kon menunjukkan kadar pelepasan yang lebih baik berbanding struktur silinder. Oleh itu, cip kon menghasilkan pelepasan cahaya yang lebih cerah. Penyelidikan ini kemudiannya diteruskan dengan memvariasikan jumlah bekalan voltan. Ketebalan dopan ditetapkan kepada 5μm untuk lapisan jenis p dan jenis n. Berdasarkan hasil yang diperolehi dari lengkungan I-V, keseluruhan kategori menggambarkan nilai voltan penghidupan yang sama iaitu 1V. Selain itu, kedua-dua struktur menunjukkan hasil yang lebih baik apabila voltan yang lebih tinggi dibekalkan melalui penghubung p-n. Struktur seperti kon mempunyai peratusan yang lebih rendah dalam kecekapan kuantum dalaman berbanding dengan dimensi silinder. Peratusan itu juga berkurangan apabila bekalan voltan meningkat untuk kedua-dua struktur geometri. Oleh kerana kualiti LED berkaitan rapat dengan kecerahan, cip berbentuk kon adalah struktur yang lebih baik untuk LED.

Characterization of Cylindrical and Conical Like Zinc Oxide Light Emitting Diode Structures

ABSTRACT

Unlike the traditional lighting system, the usage of light emitting diode (LED) lighting technology be able to sustain the economy growth due to drastically drop in power usage, be able to prevent harmful occurrences to the user due to the production of heat by electricity waste, and also be able to reduce the greenhouse effect. In contrast with the conventional lighting system, LED's technology possesses a characteristic of an environmental friendly lighting system. In this work, zinc oxide (ZnO) is used as the main material of LED's chip. This is because of ZnO not only low-in-cost but also readily available in the current market. Therefore, the initial cost of LED can be reduced and lowered compare to the existing LEDs. The main purpose of this study is to investigate the effect of doping layer thickness as well as the bias voltage in cylindrical and conical-like LED chips structure. All results are recorded and compared in terms of current-voltage (I-V) characteristic, emission rate and internal quantum efficiency (IQE). Both geometrical structures, cylindrical and conical like, hold an equivalent diameter and thickness which is 50μm and 10μm respectively. Besides, the bottom edge of cylindrical and conical-like structures is attached with a ring of n-contact. The metal ring is composed of 5μm of width and 2μm of thickness, making the bottom diameter for the cylindrical and conical-like structure 60μm. Meanwhile, the p-contact is designated at the top of the structures, creating a metal disk. The doping layer thickness is varied from 1μm of p-type layer with 9μm of n-type layer thickness. This layer is further diverted until it reaches 9μm of p-type with 1μm of n-type thickness. A fixed value of driven voltage is maintained at 6V. As a result, the cylindrical dimension shows a higher turn-on voltage and a higher percentage of IQE compares to the conical-like structure. In addition, the percentage of IQE for both structures is also increased as the p-type layer thickness is enhanced. The conical-like structure demonstrates more favorable results of emission rate than the cylindrical shape of LED chip. Therefore, the conical-like chip is able to produce a brighter emission of light. The research is then preceded by varying the amount of voltage supply. A constant value of doping layer thickness is adopted which is 5μm for p-type and n-type layers. Based on the obtained results from I-V curve, the entire category illustrates a similar value of turn-on voltage which is 1V. Other than that, both of cylindrical and conical like structures indicate a better result of emission rate when a higher voltage is supplied through the p-n junction. The conical-like structure possesses lower percentages of IQE in comparison to the cylindrical dimension. The percentage also decreases as the voltage supply is increased for both geometrical structures. Since the performance of LED is greatly related to the brightness, the conical-like dimension is a better structure for LED chip.

CHAPTER 1

INTRODUCTION

1.1 Introduction

In this chapter, a general overview about light emitting diode (LED) and zinc oxide (ZnO) is introduced for a better understanding on its behaviours. An investigation on previous works on ZnO crystal structure and lattice parameter, electrical properties, optical properties as well as the doping of ZnO is summarized and concluded in this chapter. The objectives of this study are also highlighted as well as the problem statements, the aims and motivation, and the scope and strategy.

1.2 General Overview

Nowadays, technology advancement has made the world a great and convenient place to live in. It is undeniable that technology is represented as one of the most valuable tools available and it endlessly has made life better and easier. However, the unstoppable inventions of technology also lead to unavoidable environmental impacts which caused a great damage to the world. For instance, the inventions of the vehicle provide people the ability to travel to unlimited distance with a minimum of time. Unfortunately, the burning fossil fuel used to produce electricity for transportation release numerous amount of carbon dioxide (Goudie, 2013; U.S. Patent Application, 2009). It is one of the main gasses that responsible for increasing the greenhouse effect and global warming (Goudie, 2013; U.S. Patent Application, 2009; Haszeldine, 2009).

This is a great example of a current technology which consists of undeniable preference and burden. Therefore, the innovations of modern technology also have to consider the world freedom from any damage and pollution because ‘we are responsible to our home’.

Lighting system has become one of the important prerequisites in order to increase the smoothness, satisfaction and harmonious of daily activities. However, the safeness of the lighting technology is still questionable. This is proved recently when incandescent light bulb not only harmful because of the electricity wasted in producing heat but also because of a substantial amount of carbon dioxide emitted. In order to overcome the inconvenience, compact fluorescence light bulb (CFL) is invented. Although less power needed to light it, each CFL used 5mg of mercury that might be dangerous to some individual and have potential to cause serious injuries if inhaled (Sparavigna, 2014). Due to the increasing demand in environmental-friendly lighting facilities, a further study regarding LED is conducted. The development of LED’s technology be able to reduce the greenhouse effect and to sustain the economy growth due to drastically drop in power usage.

1.2.1 Research Overview of LED

The foundation of LED’s technology is discovered by early pioneers like H.J Round, Oleg Losev and Rubin Braunstein since the first half of 20th century. Electroluminescence was first discovered in 1907 by H.J Round who was a British experimenter of Marconi Company. He had noticed that silicon (Si) carbide crystal emits yellowish light when a voltage is applied across it. In the year 1927, a study

regarding LED's technologies by Oleg Losev was reported by Soviet, German and British scientific journals. However, during that time, there is still no practical used is made on the application of LED. Research development regarding the use of LED is preceded till 1955 when Rubin Braunstein which is from Radio Cooperation of America reported that simple diode structure using gallium arsenide (GaAs) and other semiconductor alloys which connected to current source be able to produce infrared (IR) emission (U.S. Patent Application, 2009; Sparavigna, 2014). Based on the studies, first non-radio communication for short distance is invented in 1957. A half decade later in October 1962, the first practical LED was commercialized which operating a pure GaAs crystal.

LED is extraordinary diode which be able to create light by a process called electroluminescence that occurs within the semiconductor material (U.S. Patent Application, 2009; Sparavigna, 2014; Destriau & Ivey, 1955; Mottier, 2010). Generally, electroluminescence is an optical and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field (Sparavigna, 2014; Destriau & Ivey, 1955). In order to actualize electroluminescence process, LED technology is invented by connecting two layers with different density of electron which is an n-type layer and p-type layer. Both of them are joined inside a single crystal of semiconductor. The p-type layer which represents the positive side contains an excessive amount of hole while n-type layer which represents the negative side consist an excess of electrons (Mottier, 2010; Shockley, 1949). Electroluminescence is the result of radiative recombination of electron and hole in the material. As a matter of fact, radiative recombination occurs when an electron from

conduction band loses energy and recombines with a hole in valance band and release photon which has energy similar to bandgap (Shockley, 1949).

Besides that, LED is a specialized form of the p-n junction diode. When the junction is formed, the gradient of electron and hole density between two connecting layers is tremendous (Shockley, 1949). Therefore, the majority carriers in each layer begin to diffuse into the opposite regions. The charge transfer of electron and hole across the p-n junction is known as diffusion. The diffusion process starts when free carriers move from high concentration to low concentration region (Shockley, 1949; Lutz, 2007; Werner, 1994). Free electrons that diffuse into the p-type region leave behind positively charge ions in n-type region. The electrons are combined with holes and produced negatively charge ions in p-type region. Likewise, holes from the p-type region near the interface diffused into n-type region (Lutz, 2007; Werner, 1994). Holes are then combined with the electron in opposite side and formed negatively charge ions inside the p-type region while leaving behind negatively charged ions (Werner, 1994). As a result, both of the regions lost their neutrality and most of the mobile carriers. A space charge built up in between the layer, creating a depletion region which inhibits any further electrons and holes transfer (Sparavigna, 2014; Lutz, 2007; Werner, 1994). Figure 1.1 shows the result of diffusion process that occurred in p-n junction structure of LED.

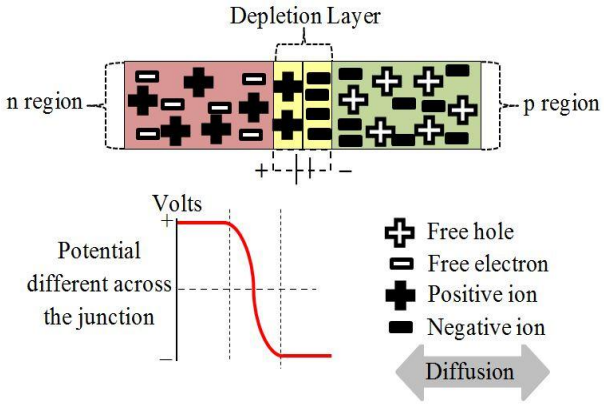

Figure 1.1 P-n junction structure.

Moreover, when the majority carriers no longer diffuse to the opposite side of the regions, it means that the junction equilibrium is achieved. Equilibrium of junction is the result of Coulomb force from positive ions inside the n-type region and negative ions in p-type region (Lutz, 2007; Israelachvili, 2011). Coulomb's Law states that, if the bodies are similarly charged, the force between them becomes repulsive (Israelachvili, 2011). Conversely, if the bodies are oppositely charged, the force becomes attracted toward one another. As a result, the remaining free electrons in n-type layer and the remaining free holes in p-type layer are unable to diffuse into the opposite region. This is because the electrons are repelled by negative ions while holes are repelled by the positive ions. Therefore, in order to overcome this problem, free charges require extra energy to overcome the Coulomb force that exist and be able to diffuse across the depletion region. In order to solve this complication, an application of a voltage using forward direction, referred as forward bias is applied.

In forward bias, the p-type region is connected to positive voltage terminal while negative terminal is joined with n-type region (Lutz, 2007; Werner, 1994). Holes in p-type region and electrons in the n-type region are pushed toward the junction and

neutralized the positive and negative ions. Besides that, due to high attraction from positive voltage terminal, valance bond which creates the ions in p-type region is broken. Therefore, an electron is escaped and shifted toward the positive terminal. Likewise, the hole which is escaped from the valance band in n-type region is shifted toward the negative voltage terminal. As a result, the thickness of depletion region decreases and at the same time reduces the electrical resistance of the junction (Mottier, 2010; Lutz, 2007; Werner, 1994). Free electrons are also able to diffuse from holes to holes toward the positive voltage terminal. Likewise, the holes are also able to diffuse into the opposite direction toward the negative voltage terminal. Forward bias junction only allows current to flow in one direction (Jagadish & Pearton, 2011; U.S. Patent, 1993; U.S. Patent, 2004). The higher value of forward voltage be able to produce high quality of LED depends on the type of semiconductor material used and its temperature.

LED is an example of advance innovation in lighting system because of the ability to convert electricity to light with a minimum wasteful creation of heat (U.S. Patent, 2014). The quality of LED lighting system depends on two types of recombination which are radiative recombination and non-radiative recombination that occur in the semiconductor materials. Recombination is a process in the form of spontaneous emission where electrons in the conduction band lose energy and recombine with the holes in the valance band (Lutz, 2007; Werner, 1994; Van Zeghbroeck, 2011a). Radiative recombination (band-to-band recombination) is dominated and significant only in direct bandgap semiconductor (Van Zeghbroeck, 2011a). When radiative recombination occur, electrons from conduction band directly recombine with holes in the valence band and emit photons (light) with the wavelength corresponding to the energy of bandgap. Meanwhile, non-radiative recombination is a

process where recombination between electrons and holes produce wasteful heat (phonon) instead of photons (Werner, 1994; Van Zeghbroeck, 2011a). Two types of non-radiative recombination in semiconductor LED are Shockley-Read-Hall (SRH) recombination and Auger recombination. Figure 1.2 shows the differences between radiative recombination, SRH recombination and Auger recombination.

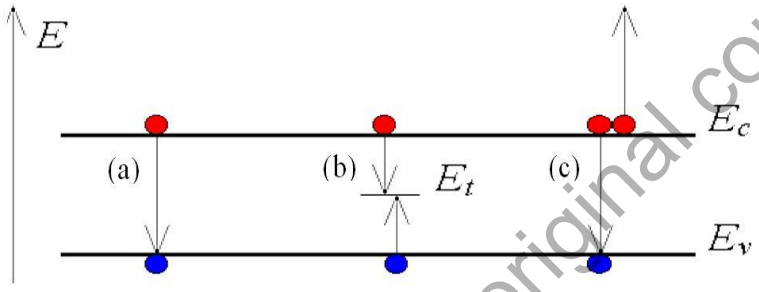

Figure 1.2 (a) Radiative recombination, (b) SRH recombination and (c) Auger recombination (Van Zeghbroeck, 2011a).

SRH recombination (trap-assisted recombination) is significant in indirect bandgap semiconductor and direct bandgap with low carrier density. SRH recombination does not take place in perfectly pure and undefeated material. SRH recombination occurs when an electron or hole falls into bandgap energy level due to the present of a structural defect in the material. This process can be envisioned as the termination of electrons and holes which meet in the trap, thereby completing the recombination process. Meanwhile, Auger recombination is a process where electrons and holes recombine in band-to-band transition (Van Zeghbroeck, 2011a). However, the resulting energy is given to the third carrier. As a result, the third carriers move to another higher energy level and will normally lose the excess energy to thermal vibration. In 2013, the causing of LED droop is identified as Auger recombination (Iveland, Martinelli, Peretti, Speck, & Weisbuch, 2013).LED droop is a phenomenon

where LED efficiency decreases at a higher connection of electrical current (Laubsch, Sabathil, Baur, Peter, & Hahn, 2010; Piprek, 2010; Xie, et al., 2008). However, Auger recombination is important at high carrier concentration caused by heavily doping.

LED is a high-level lighting technology that is invented in order to replace traditional lighting systems such as the incandescent light bulb, compact fluorescence (CFL) and high-intensity discharge (HID) lamp. LED technology can be used in unlimited places and spaces due to availability in smaller sizes compare to the conventional lighting system. Besides that, LED also has a longer lamp life compare to CFL and incandescent light bulb. It can achieve until 80 000+ hours of lamp life which approximately equal to 10 years compare to the incandescent bulb which only lasts for 750 to 2 000+ hours of life which maximally equal to three month. This means that the need to replace failed lamp is decreased. As a matter of fact, LED's mechanism decreases the production of heat and be able to save energy (Whitaker, 2005a). In a conventional light, the high loss of energy due to the increasing of wasteful heat is very common. Moreover, due to heat lost in the traditional lighting system, only 20% of energy efficiency is produced while the remaining is lost as heat. In LED, 80% to 90% of energy efficiency is produced (Whitaker, 2005a). LED is also cool and safer to handle during the installation and maintenance process.

Besides that, LED is bright enough to be seen even in daylight. The color temperature range of LED is available from warm white (2500K) until daylight (6500K) making them suitable for any application. Color rendering index (CRI) is a metric to measure the quality of light out of 100. A quality LED can have CRI up to 90+. Moreover, the output from LED can range from red (~700nm wavelength) to blue-

violet (~400nm wavelength). Some LED devices can emit infrared energy (~850nm wavelength) which is known as Infrared LED (IR LED). Traditional incandescent light bulbs use a filter to produce color, the method is extremely inefficient (Foster & Gómez, 2005). However, colors of LED can be blended together and produce millions of color options. LED is also environmental friendly because it does not contain any toxic chemical and 100% recyclable. LED is encapsulated in an epoxy resin enclosure, which means LED is sturdier, compared to the incandescent light bulb or fluorescent tube which made of fragile material. Therefore, LED is able to withstand shock, vibration and extreme temperature (Whitaker, 2005a). Other than that, LED is fast switching which means that it can turn on and off many times without affecting LED's lifetime or light emission (Sparavigna, 2014). Figure 1.3 shows the variation of LED's color and its wavelength.

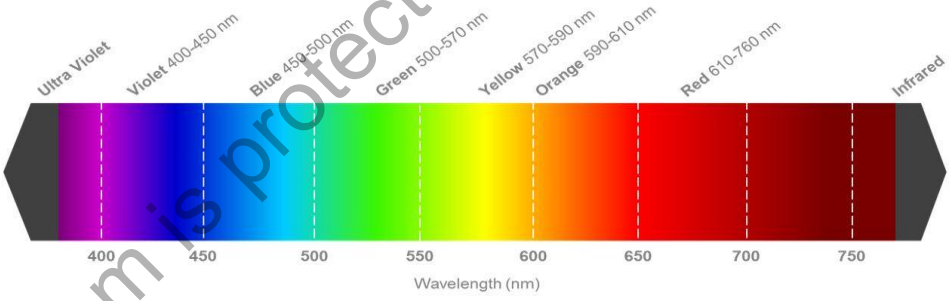

Figure 1.3 Colors of LED and its wavelength (RKC Industrial, 2013).

Although LED is one of the most advanced technology in the 20th century, there are still several disadvantages which unavoidable. The main circumstance is due to expensive prices compared to traditional lighting technology (Sparavigna, 2014; Whitaker, 2005a). However, when considering the total cost including maintenance and power supply, LED far surpasses incandescent light bulb and begins to threat compact fluorescent lamp. Besides that, the performance of LED largely depends on the ambient

temperature. Over-operating of LED especially at a high temperature of ambient will lead to device failure (Whitaker, 2005a; RKC Industrial, 2013). This means that the longevity of LED lamp life also depends on the environmental condition. LED also tends to shift color due to temperature and age. Other than that, there is concerned regarding blue and cool white (blue-white color) LED which might be unsafed to be regularly used. The blue color of LED is dangerous and may cause disorder to human eyes (RKC Industrial, 2013).

Nowadays, LEDs have become the preferred lighting solution for both professional and residential users. Therefore, LEDs is used in a variety of different application including residential lighting, automotive, broadcasting, electronic instrumentation, entertainment, military gadgets, traffic, and transportation. In the entertainment industry, LED technology is used for stage performance because it is easy to control and available in a variety of color. LED is a number one choice for residential lighting due to low maintenance cost and energy saving. LED is also used inside electronic instrumentation such as flat screen television and monitors. This is because LED is able to generate active backlighting and produce a visible image for the application (Sparavigna, 2014). Besides that, the quality of application such as television also depends on the expected lifespan of LED. Traffic operation also one of application that uses LED lighting system. This is due to low energy consuming and easy to maintain. LED also be able to operate and withstand any weather condition including hot, rain or snow because of plastic encapsulation. Table 1.1 shows the available color of LED with wavelength range, voltage drop and material.

Table 1.1 Classification of LED (RKC Industrial, 2013).

Color	Wavelength (nm)	Voltage (V)	Semiconductor Material
Infrared	λ > 760	ΔV < 1.9	Gallium arsenide (GaAs) Aluminium gallium arsenide (AlGaAs)
Red	610 < λ < 760	1.63 < ΔV < 2.03	Aluminium gallium arsenide (AlGaAs) Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium(III) phosphide (GaP)
Orange	590 < λ < 610	2.03 < ΔV < 2.10	Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium(III) phosphide (GaP)
Yellow	570 < λ < 590	2.10 < ΔV < 2.18	Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium(III) phosphide (GaP)
Green	500 < λ < 570	1.9[31] < ΔV < 4.0	Indium gallium nitride (InGaN) / Gallium(III) nitride (GaN) Gallium(III) phosphide (GaP) Aluminium gallium indium phosphide (AlGaInP) Aluminium gallium phosphide (AlGaP)
Blue	450 < λ < 500	2.48 < ΔV < 3.7	Zinc selenide (ZnSe) Indium gallium nitride (InGaN) Silicon carbide (SiC) as substrate Silicon (Si) as substrate — (under development)
Violet	400 < λ < 450	2.76 < ΔV < 4.0	Indium gallium nitride (InGaN)
Purple	multiple types	2.48 < ΔV < 3.7	Dual blue/red LEDs, blue with red phosphor, or white with purple plastic
Ultraviolet	λ < 400	3.1 < ΔV < 4.4	diamond (235 nm) Boron nitride (215 nm) Aluminium nitride (AlN) (210 nm) Aluminium gallium nitride (AlGaN) Aluminium gallium indium nitride (AlGaInN) — (down to 210 nm)
White	Broad spectrum	ΔV = 3.5	Blue/UV diode with yellow phosphor

The main semiconductor materials that are used to produce LEDs includes indium gallium nitride (InGaN), aluminum gallium indium phosphide (AlGaInP), aluminum gallium arsenide (AlGaAs), aluminum gallium phosphide (AlGaP), gallium phosphide (GaP), gallium nitride (GaN), zinc selenide (ZnSe), silicon carbide (SiC) and diamond. One of the differences between these LEDs is the color of emitted light. InGaN produces blue, green, violet and ultraviolet (UV) high-brightness LED whilst AlGaInP be able to emit yellow, orange, green and red in color. AlGaAs LED produces red and infrared spectrum meanwhile GaP LED be able to produce a red, orange, yellow and green color of high brightness LED. GaN be able to produce LED that can emit green light while ZnSe and SiC LED be able to emit a blue color of light emission. Meanwhile, diamond produces UV LED. Besides that, each color of LED possesses different value of wavelength and voltage drop. The Infrared color is the highest

wavelength among all followed by red, orange, yellow, green, blue, violet, purple, UV and white (RKC Industrial, 2013).

1.2.2 Research Overview of ZnO

Long before the discovery of zinc (Zn) as a metal, early humans already used Zn ore to produce cooper-zinc (Cu:Zn) alloy brass as well as Zn salt for medical purpose (Özgür et al., 2005; Rheinzink, 2006.; Kharakwal & Gurjar, 2006). The inventions of objects build from brass was acknowledged from Babylonia and Assyria since 3000 B.C and Palestine from 1400 B.C until 1000 B.C. In 500 B.C, the addition of Zn together with Cu inside brass material is proven for the first time from a piece of jewellery which found in Rhodes (Rheinzink, 2006). Meanwhile, Marco Polo from Venice reported that the usage of Zn in the medical field was rapidly spread all over Persia since 1254 (Rheinzink, 2006; Kharakwal & Gurjar, 2006). During that time, Persia used a solution of zinc vitriol ($ZnSO_4.7H2O$) to treat eyes inflammation and zinc sulphate ($ZnSO_4$) as antiseptic until today (Rheinzink, 2006). Marco Polo also had mentioned regarding the manufacture of ZnO in Persia during the 13th century (Rheinzink, 2006; Kharakwal & Gurjar, 2006). Technically, Zn will only be found in nature in the form of a compound which is carbonate of Zn, also known as Zn salt (Rheinzink, 2006). The source regarding the first person who isolated the element always differs. However, historians are believed that Guyton de Morveau who reported the white pigment which they are believed as the first discoverer of ZnO (Douma, 2008).

ZnO is used in medical field for centuries. A 500 B.C Indian medical text, Charaka Simhita, had mentioned that ZnO is used as a treatment for eyes and open wound. A Greek physician, Dioscorides, also acknowledged the impressiveness of ZnO ointment during the 1st century. Meanwhile, the Canon of Medicine written by Avicenna in the year 1025 also mention that ZnO was a preferred treatment for a variety of skin condition including skin cancer (Özgür et al., 2005). Other than that, ZnO is also used in the production of watercolor. For example, in the year 1794 and 1796, paterns were issued for the manufacture of ZnO to the English colormaker, John Atkinson at Harington near Liverpool (Douma, 2008). However, ZnO is only accepted as a watercolor in 1843. The first usage of ZnO material for electronic application was constructed into radio sets in the year 1920's. By connecting the ZnO crystal with copper (Cu) wire, a Schottky barrier is created, providing the desired rectification for converting AC radio waves to DC signal. However, the usage of ZnO still not widely spread until the invention of nonlinear resistor devices known as varistors. Without the reliable protection from varistors, the use of electronic application at home would be impossible without constantly replacing the fried component (Jagadish & Pearton, 2011).

Although the research of ZnO falls behind too many decades, the interest of research community is renewed due to the high quality and numerous promising ZnO properties. ZnO is a major inorganic compound in this research. With the possession of semiconductor characteristic, ZnO be able to partially conduct electrical current within the compound. For centuries, ZnO is only recognized as a substrate for GaN and other related alloys. However, this material has now gained substantial interest in the research community to turn their research for electronic and photonic devices using ZnO

material in its own right. The example of an application that is designated using ZnO compound material including blue/UV optoelectronics such as LED, transparent electronics, spintronic devices and sensor application (Jagadish & Pearton, 2011). The quality of ZnO-based devices is highly related to the general properties itself encompassing crystal structure, electrical properties and optical properties.

1.3 General Properties of ZnO

ZnO is a major element in this research. ZnO exhibits the characteristic of semiconductor and piezoelectric properties. Lack of the symmetry of wurtzite combined with strong electromechanical coupling, help to produce strong piezoelectric in ZnO (Olsen, 2015; Wang, 2004). ZnO is an intrinsic semiconductor but naturally almost exist as n-type (Jagadish & Pearton, 2011). However, it still can be doped both n-type and p-type. ZnO which is from II-VI group, consist of direct wide bandgap ($3.437eV$), large free exciton binding energy (60mV), and low thermal energy at room temperature (25mV) (Jagadish & Pearton, 2011; Wang, 2004; Tsay, Fan, Chen, & Tsai, 2010a; Tsay, et al., 2010b). A wide bandgap material consist the ability to work in high voltage and high temperature. Since, this binding energy is much greater than thermal energy at room temperature, efficient excitonic recombination leads to room temperature lasing in ZnO. High electron mobility, high thermal conductivity, and high exciton binding energy make ZnO suitable for wide range devices. Besides that, ZnO has high transparency to visible light at room temperature, non-toxicity, and ease of doping. ZnO can be made highly conductive by doping. This material is also cheap and ready availability in the current market (Tsay, et al., 2010a).

1.3.1 Crystal Structure and Lattice Parameter

ZnO is originated from group II-VI inorganic compound semiconductor which ionicity resides at the borderline between covalent and ionic semiconductor. The possible crystal structure of ZnO material comprised wurtzite (B4), Zn blende (B3) and rocksalt which has also known as Rochelle salt (B1). Several differences between three phases of crystal structure is diagnosed and published in Strukturbericht journal, which is the original crystallographic report. Wurtzite symmetry is the representation of thermodynamically stable phase under ambient conditions (Morkoç & Özgür, 2007). Meanwhile, a stabilized structure of Zn blende ZnO phase can only be achieved by heteroepitaxial growing on a cubic substrate such as zinc sulfide (ZnS), GaAs and Si. Unfortunately for rocksalt phase, this structure can only be obtained at relatively high pressure (approximately form at ~10GPa) and impossible to epitaxially stabilize (Jagadish & Pearton, 2011; Morkoç & Özgür, 2007). Besides that, the cohesive energy between the phases was also thoroughly investigated. The results show that the energy different between wurtzite, Zn blende and rocksalt is small for local density approximation (LDA) and general gradient approximation (GGA). However, the differentiation values are relatively large for Hartree-Fock approximation. Based on the result obtained, wurtzite is energetically favorable compared to Zn blende and rocksalt form (Morkoç & Özgür, 2007). Figure 1.4 shows the type of crystal structure including rocksalt, Zn blende, and wurtzite.

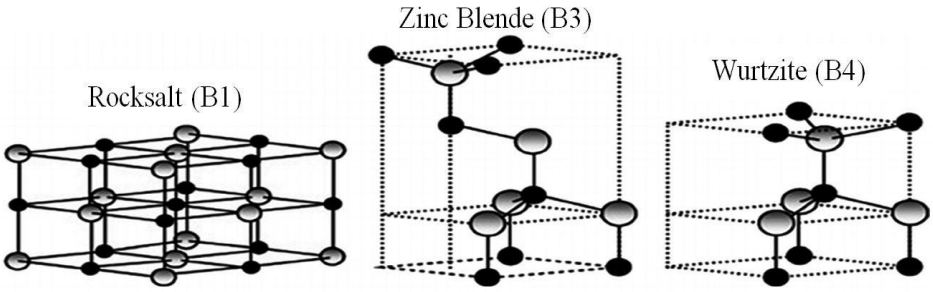

Figure 1.4 Type of crystal structure (Morkoç & Özgür, 2007).

Mostly, common II-VI compound semiconductors are stable thermodynamically with the Zn blende crystal structure (Jagadish & Pearton, 2011; Morkoç & Özgür, 2007; Ashrafi & Jagadish, 2007). However, for II-O (O-atom, oxidizing agent) materials such as ZnO and beryllium oxide (BeO) are stable with wurtzite phase whilst for cadmium oxide (CdO) and magnesium oxide (MgO) are stable in rocksalt structure (Morkoç & Özgür, 2007; Ashrafi & Jagadish, 2007). The stability of ZnO is highly related to numbers of a hexagonal unit cell, as it is the main component to form wurtzite structure (Morkoç & Özgür, 2007; Özgür, et al., 2005). The physical dimension of the hexagonal unit cell is known as hexagonal lattice, which is characterized by two interconnecting sub-lattices of Zn^{2+} and O^{2-}, such that each Zn ion is surrounded by O ions in tetrahedral manner and vice versa. Tetrahedral means that a central atom is located at the center with four substituents are located at the corner of a tetrahedron. The tetrahedral coordination gives rise to polar symmetry along the hexagonal axis. The polarity is responsible for the number of ZnO properties including piezoelectricity, spontaneous polarization and also a key factor in crystal growth, etching and defect generation. There are four most common face termination of wurtzite ZnO which is already identified by Miller Indices. The face termination is divided into two, the polar Zn-terminated (0001) and O-terminated $(000\bar{1})$ faces (c-axis oriented), and the non-polar $(11\bar{2}0)$ (a-axis) and $(10\bar{2}0)$ faces which both contain an equal number of Zn and O

atoms (Jagadish & Pearton, 2011). Miller Indices is a method to describe the orientation of planes and to specify the direction in a crystal structure. Aside from causing the inherent polarity in ZnO crystal, the tetrahedral coordination of this inorganic compound also provides an indicator of covalent bonding (Morkoç & Özgür, 2007). Figure 1.5 shows the axis orientation of wurtzite ZnO.

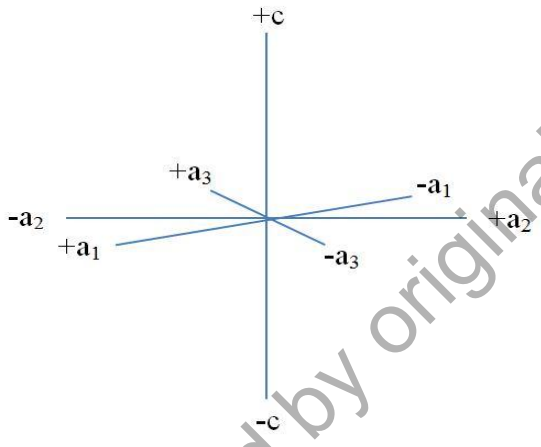

Figure 1.5 Axis orientation of wurtzite ZnO.

As mention earlier, Zn blende ZnO crystal structure can be stabilized only by growing on selected cubic structure for the purpose to overcome the intrinsic tendency of forming wurtzite phase. Unfortunately for the case of highly mismatch substrates, there is usually a certain amount of Zn blende phase of ZnO separated by crystallographic defects form the wurtzite phase. A crystallographic defect is a form of irregular pattern that interrupts the regular position of atom or molecule that is already determined by the unit cell parameter (Hirth & Lothe, 1992). There are three types of defect including a planar defect, line defect, and bulk defect. Besides that, wurtzite ZnO also can be transformed into rocksalt structure at relatively modest external hydrostatic pressure.

1.3.2 Electrical Properties

As a direct and wide bandgap material (Jagadish & Pearton, 2011; Wang, 2004; Tsay, et al., 2010a; Tsay, et al., 2010b; Morkoç & Özgür, 2007), ZnO attract much attention for a variety of electronic and optoelectronic applications. Advantages associated with a large bandgap include high-temperature and high-power operation, lower noise generation, higher breakdown voltage and ability to sustain large electric fields (Morkoç & Özgür, 2007). The electron transport in ZnO semiconductor can be considered for low and high electric field. However, the electrical properties of ZnO are difficult to quantify due to large variance of the quality of available samples. The largest reported n-type doping is ~10^{20} electrons cm^{-3} and largest reported p-type doping is ~10^{19} holes cm^{-3}. The effective density of state of valence band, N_V and conduction band, N_C is 10^{17} cm^{-3} and 10^{18} cm^{-3} respectively. Although such high levels of p-conductivity are questionable, it still not experimentally verified. Besides, the ZnO semiconductor gains substantial interest in the research community in part because of its large exciton binding energy that could lead to the innovation of high-quality optoelectronic device application. The electron mass of ZnO is $0.24m_0$ and the hole effective mass is $0.59m_0$. The corresponding electron Hall mobility at 300K for low n-type conductivity is μ_n = 200 $\frac{cm^2}{Vs}$ and for low p-type conductivity is μ_p = 5 to 50 $\frac{cm^2}{Vs}$ and the largest 180 $\frac{cm^2}{Vs}$ (Jagadish & Pearton, 2011).

1.3.3 Optical Properties

One of the unique properties of direct bandgap ZnO semiconductors that revolutionized the optoelectronic field is their ability to produce light emission (Morkoç & Özgür, 2007). Light emission through any process other than blackbody radiation is called luminescence and required excitation as it is a non-equilibrium procedure. In the case of LEDs and lasers, the recombination of electron and hole that occur due to the voltage that applied across a forward biased p-n junction, resulting in light emission called electroluminescence (Destriau & Ivey, 1955). The emitted photon has energy equal to the energy of electron and hole recombination process. In the indirect semiconductor, the emission of light is inefficient compared to ZnO material or other direct semiconductors unless highly spatially localized centers, such as N in GaP, are used. Another term of light emission is Photoluminescence (PL) which a result of incident photon absorption that generates electron-hole pairs and produces emission of a photon of a different wavelength. Light emission can also be induced by raising the temperature of ZnO semiconductor which known as thermoluminescence. Meanwhile, ZnO semiconductor material can also undergo cathodoluminescence process by subjecting the semiconductor to electron irradiation or other high-energy particle radiation in order to generate light emission.

Those characteristic and properties of ZnO are the reason that attracts researcher to explore more on ZnO in order to produce high quality of product and invention. ZnO offers some potential especially in photonic, spin-based devices optical, electronic field and encouraging progress is made in the research phase. This is because of the demands in making advanced technologies which can fulfill human needs are increased.

Numerous materials are exploited for this reason including ZnO. The production of devices and application of ZnO is increased in order to replace and improve the quality of traditional appliances, for example, ZnO-based thin film transistor (TFT) is used to replace Hydrogenated Amorphous Silicon (a Si:H) thin-film in liquid crystal display (LCD) due to low photosensitivity (Tsay, et al., 2010a; Tsay, et al., 2010b). Transparent thin-film transistors, ZnO-based transparent oxides and laser structure exploiting the large exciton binding energy of ZnO are also among the application invented from ZnO semiconductor material. The task is made more difficult by highly successful GaN that competes for a similar application (Jagadish & Pearton, 2011). However, some application of ZnO which are not addressed by GaN might pave the way for ZnO.

1.3.4 Research properties of ZnO

Table 1.2 below shows the main properties of ZnO semiconductor. Each of the following properties is taken into account during the simulation process and it is used to construct the LED.

Table 1.2 List of ZnO properties.

Property	Name	Value	Unit
Relative permittivity	epsilonr	8.5	1
Band gap	Eg0	3.437	V
Electron affinity	chi0	2.0870	V
Effective density of states, valence band	Nv	1.0*10^17[cm^...	$1/m^3$
Effective density of states, conduction band	Nc	5.75*10^20	$1/m^3$
Electron mobility	mun	200[cm^2/(V*s)]	$m^2/(V{\cdot}s)$
Hole mobility	mup	180[cm^2/(V*s)]	$m^2/(V{\cdot}s)$
Auger recombination factor, electrons	Cn	1e-31[cm^6/s]	m^6/s
Auger recombination factor, holes	Cp	1e-31[cm^6/s]	m^6/s

1.4 Doping of ZnO

Doping is a process of adding impurities into intrinsic semiconductor under the intention to modify the material properties. In all cases, unintentionally doped ZnO is observed to be n-type. This means, ZnO which is slightly n-type condition is attributed to the presence of intrinsic defects and impurities. Intentional n-type doping is relatively well established through the substitution of group III elements which are aluminum (Al), gallium (Ga) and indium (In) on the Zn sites, producing highly conductive n-type ZnO. However, all the efforts to obtain reliable p-type doping in ZnO have so far being mainly unsuccessful. The same intrinsic defect responsible for n-type conductivity tends to aggravate the efforts for p-type doping by compensating the potential acceptors. The predilection for unipolar doping is not that surprising in wide bandgap semiconductors. GaN, cadmium sulfide (CdS), ZnS and ZnSe are also easily doped to n-type whereas p-type doping is difficult to achieve. The situation is opposite for zinc telluride (ZnTe) and cadmium telluride (CdTe), where p-type doping is easily obtained whereas n-type doping is extremely difficult (Morkoç & Özgür, 2007).

In general, these issues arise from the fact that wide-gap semiconductor has either a low valence band maximum or a high conduction band minimum with respect to the vacuum level. As a result, some materials which valance band is relatively closed to the vacuum level have preferably p-type conductivity. In contrast, materials with valance band relatively far from the energetic position of the vacuum level have preferable n-type conductivity. Elements such as Al, Ga, and In on the Zn sites and chlorine (Cl) and iodine (I) on the O sites can potentially form shallow donors in ZnO. Element such as lithium (Li), sodium (Na), potassium (K), Cu and silver (Ag) on the Zn

sites and nitrogen (N), phosphorus (P), antimony (Sb) and arsenic (As) on the O sites have the potentials of forming acceptor in ZnO.

1.4.1 N-type doping

ZnO with a wurtzite structure is naturally an n-type semiconductor due to the presence of intrinsic defects such as O vacancies (V_O) and Zn interstitials (Zn_i). Undoped ZnO shows n-type conductivity with electron densities as high as $10^{21}\ cm^{-3}$, a value that fortunately is reduced by molecular beam epitaxy (MBE) to about $10^{1}\ cm^{-3}$ and by hydrothermal growth to below $10^{14}\ cm^{-3}$. Besides that, there are also suggested that the n-type conductivity of unintentionally doped films is only due to hydrogen that acts as a shallow donor with an ionization energy of about 30meV (Morkoç & Özgür, 2007). This opinion is supported by the fact that hydrogen is always presented in all growth methods and can easily diffuse in ZnO in large amount even at temperature as low as 600˚C due to its large mobility.

Group III element Al, Ga and In as substitutional elements for Zn are probably more suitable for n-type doping of ZnO due to their lower vapor pressure compared to group VII element such as Cl and I. Group VII have memory effect in low pressure deposition system such that the residual electron concentration would not be lowed after usage. Oxidation of Al also become a problem because of its high reactivity with O. Ga and In are less reactive than Al. Furthermore, Ko et al. estimated covalent bond length of Ga-O to be slightly smaller than the covalent bond length of Zn-O whereas the bond length for In-O is estimated higher. This condition is unsurprisingly considered the large ionic radius of In. The Ga-O is expected to cause only small deformation of the

ZnO lattice even in the case of high concentration of Ga (Morkoç & Özgür, 2007). However, the larger bond of In-O would deform the ZnO more disastrously. That is why Ga is likely an optimum choice for doping ZnO.

1.4.2 P-type doping

As mentioned, it is very difficult, to vary the degrees, to obtain p-type doping in wide bandgap semiconductors. This condition is attributed to low-energy native defects with a propensity to n-type doping. The low solubility of the dopant in the host material and precipitate formation are also possible causes. Besides, deep impurity level can also be a source of the doping problem causing significant resistance to the formation of shallow acceptor level. This compensation problem is the most challenging phenomenon in wide bandgap semiconductors and ZnO in particular. The p-n junction is also reported, but the efficiency of light emission is low, the emission width is arguably wide and the source of emission is controversial and not well understood.

Known acceptors in ZnO include group I elements such as Li, Na, K, Cu and Ag as well as group V elements such as N, P, Sb and As. However, many of these form deep acceptors and do not contribute sufficiently to p-type conduction. It is believed that the most promising dopants for p-type ZnO are the group V elements even though theory mentions some difficulty in achieving shallow acceptor level (Morkoç & Özgür, 2007). Among these candidates, N element is known to provide the shallowest acceptor impurity and the most likely a genuine p-type dopant. N has the smallest ionic radius which is 1.68Å, which is very close to O ionic radius of 1.38Å. However, N has low

solubility making it imperative to decrease the back-ground donor concentration and increase solubility by codoping.

1.5 Research Objective

The main purpose of this work is to design different structural dimensions of LED chip by using ZnO. Instead of using a typical rectangular or square structure, cylindrical and conical like structures are used to fulfill the main objective. Besides that, there are also several specific objectives in order to improve the quality of studies and to ensure this research is parallel with the theories of LED. The objectives are,

I. To investigate the effect of doping layer thickness in cylindrical and conical like structures of LED chip.
II. To examine the effect of bias voltage supply in cylindrical and conical like structures of LED chip.
III. To explore the characteristic of ZnO LED by analyzing the I-V characteristic curves, two-dimensional (2D) emission rate, relation of total emission rate and current, and internal quantum efficiency (IQE) with current variation.
IV. To evaluate the drift and diffusion process of carrier flows in cylindrical and conical like structures.

1.6 Statement of Research Problem

The main issue that limits the production of LED is the achievement of p-type material. This is the case for most wide bandgap semiconductors including ZnO as well