Photo Emission Characteristics of CNT based Light Emitting Diode

A thesis Submitted to

The department of Electrical and Electronic Engineering

of

BRAC university

in partial fulfillment of the requirement

for the degree of

BACHELOR OF SCIENCE IN ELECTRONICS AND COMMUNICATION ENGINEERING

Submitted by

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BRAC UNIVERSITY

AUGUST, 2013

The thesis entitled "Photo Emission Characteristics of CNT based Light Emitting Diode" submitted by Jinnah Barkatul Alim, Std ID: 09310007 and Tasauf Islam, Std ID: 09110045 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of BACHELOR OF SCIENCE IN ELECTRONICS AND COMMUNICATION ENGINEERING.

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Dedication

To Our Parents

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Acknowledgements

We wish to offer our heartiest gratitude and profound respect to our thesis supervisor Dr. Sharif Mohammad Mominuzzaman, Proffessor, Department of Electrical and Electronic Enigineering (EEE), Bangladesh University of Engineering and Technology (BUET) for giving us the opportunity to work with him and for his continuous guidance, suggestions and wholehearted supervision throughout the progress of this work. We are indebted to him for acquainting us with the world of advanced research.

We are grateful to the Head of Department, Electrical and Electronic Engineering (EEE), BRAC university for giving us the permission to work in this thesis. We are grateful to our families and friends for their encouragement in our study. Finally, we are grateful to Almighty Allah for giving us strength and courage to complete the work.

Abstract

At present time, different types of LEDs are available in the market. Currently, most widely used semiconducting material to make LEDs is silicon (Si). But there are some problems associated with Si. The major & main problem is, Si is an indirect bandgap material. That's why; electrons cannot easily move to valence band from conduction band. That is why, in this thesis we have worked to find out a possible alternative and that is carbon nanotube (CNT). The major advantage of CNT is, here we can control the peak emission. That's why; at first we have worked with unipolar & ambipolar emission and observed a huge difference in intensity. First of all, we have fitted the unipolar EL spectrum curve & obtained six major peaks. On the other hand, after fitting the ambipolar EL spectrum curve we have obtained three major peaks. The peak intensity of unipolar emission was 4.61 (arb units). On the other hand, the peak intensity of ambipolar emission was 28.2 (arb units). After that, for bipolar emission we have analyzed the EL spectrum of CNT based LED for different drain-source current I_{DS}. Applying the fitting technique on each curve, we have obtained few peaks. After obtaining the fitted curves, we have plotted curves for different position, intensity & FWHM of peak1 & peak2, corresponding the drain-source current I_{DS}. Then we have observed that the position of peak1 does not remains constant. With increasing I_{DS}, it moves towards the lower energy. Up to I_{DS}=155 nA, it keeps the trend unchanged. After that it starts to move towards the higher energy. But peak2 shows a different trend. Just like peak1 it moves towards the lower energy up to I_{DS}=155 nA. But after that, it becomes stable. When we observed the intensity of peak1, corresponding the drain-source current I_{DS}, we have seen that the intensity of peak1 increases with increasing I_{DS}. But when I_{DS} reaches to 155 nA, it starts to decrease. For peak2, intensity also increases with I_{DS} but it does not decrease. After that we have observed the FWHM of peak1. The FWHM of peak1 decreases with increasing I_{DS}. But when I_{DS} reaches to 120 nA, it starts to decrease drastically. And when I_{DS} reaches to 180 nA it starts to increase. But for peak2, we have observed a different scenario. The FWHM of peak2 almost remains constant up to 120 nA. After that it starts to increase. And when I_{DS} reaches to 155 nA, it decreases drastically. And when I_{DS} approaches to 180 nA it drastically increases. We have also plotted the ratio of intensity of peak2 & peak1, corresponding the drain-source current I_{DS}. We have observed that the ratio of intensity increases with I_{DS}. And when I_{DS} reaches to

155 nA, it increases rapidly. After that, we have plotted the ratio of area of peak2 & peak1, corresponding the drain-source current I_{DS} . Here we have seen that the ratio of area increases rapidly with I_{DS} . And when I_{DS} reaches to 120 nA, it rapidly decreases. Again when I_{DS} approaches to 155 nA it starts to increase. In this thesis we have worked with two peaks only. But, in the fitted curves there are some other peaks too which could be a mean for further research.

Chapter 1

Introduction

A light emitting diode (LED) is a semiconductor light source.^[10] LEDs are used as indicator lamps in many devices and are increasingly used for other lighting. Appearing as practical electronic components in 1962,^[17] early LEDs emitted low-intensity red light, but modern versions are available across the visible, ultraviolet and infrared wavelengths with very high brightness.

When a light-emitting diode is switched on, electrons are able to recombine with holes within the device, releasing energy in the form of photons. This effect is called electroluminescence and the color of the light (corresponding to the energy of the photon) is determined by the energy gap of the semiconductor. An LED is often small in area (less than 1 mm²), and integrated optical components may be used to shape its radiation pattern. LEDs present many advantages over incandestant light sources including lower energy consumption, longer lifetime, improved physical robustness, smaller size and faster switching. However, LED is powerful enough for room lightening are relatively expensive and require more precise current and heat management than compact fluorescent lamp sources of comparable output.

Light emitting diodes are used in applications as diverse as aviation lighting, digital microscopes, automotive lightening, advertising, general lighting and traffic signals. LED has allowed new texts, video displays and sensors to be developed while their high switching rates are also useful in advanced communications technology. Infrared LEDs are also used in the remote control units of many commercial products including televisions, DVD players and other domestic appliances. LEDs are also used in seven-segment display.

Electroluminescence as a phenomenon was discovered in 1907 by the British experimenter H.J. Round of Marconi Labs using a crystal of silicon carbide and a cat's-whisker detector. [19][20] Russian Oleg Vladimirovich Losev reported creation

of the first LED in 1927.^[21] His research was distributed in Russian, German and British scientific journals, but no practical use was made of the discovery for several decades.^{[22][23]} Rubin Braunstein of the Radio Corporation of America reported on infrared emission from gallium arsenide (GaAs) and other semiconductor alloys in 1955.^[24] Braunstein observed infrared emission generated by simple diode structures using gallium antimonide (GaSb), GaAs, indium phosphide (InP) and silicon germanium (SiGe) alloys at room temperature and at 77 Kelvin.

In 1961 American experimenters Robert Biard and Gary Pittman, working at Texas Instruments, [25] found that GaAs emitted infrared radiation when electric current was applied and received the patent for the infrared LED.

The first practical visible-spectrum (red) LED was developed in 1962 by Nick Holonyak, Jr, while working at General Electric Company. Holonyak first reported this breakthrough in the journal Applied Physics Letters on the December 1, 1962. Holonyak is seen as the "father of the light-emitting diode". M.George Craford a former graduate student of Holonyak, invented the first yellow LED and improved the brightness of red and red-orange LEDs by a factor of ten in 1972. In 1976 T.P. Pearsell created the first high brightness; high efficiency LEDs for optical fiber telecommunications by inventing new semiconductor materials specifically adapted to optical fiber transmission wavelengths.

In the present time the most widely used semiconducting material is silicon (Si) and also gallium arsenide (GaAs). In the chip manufacturing industry they use Si to make transistor. As chip materials continue to grow smaller, more and more current is able to escape from the transistors to fail. There are other problems with Si too. Silicon is an indirect band material. That's why electrons from valence band cannot easily reach the conduction band. It creates further problems to make LED with silicon.

Some people think GaAs as a possible solution but it has some other problems too. GaAs is very rare and difficult to obtain. On the other hand arsenic is toxic. It is toxic so much that its minimum use creates problems with handlings and disposal

of GaAs circuits. Moreover, arsenide has poor thermal conductivity. That's why for all these drawbacks a new semi conducting material is now a demand of time.

Carbon nanotube shows a new hope to solve the above problems with currently used semiconductors. First of all, it conducts electricity better than any other material at room temperature. That's why it could be the best possible replacement for conventional chip making materials. Secondly, the mobility of carbon nanotube is about 70 times higher than that of silicon and 25 percent higher than any other known semiconducting materials. It measures how fast electrons can move through a material. Because the carbon atoms are more tightly bound together than the metals currently used in transistor production, electrons flowing through the tubes have less room to veer of track. This allows a greater amount of current to move even faster through carbon nanotubes than through the copper interconnects of today's chips. The carbon nanotubes not only carry current at higher speeds than silicon transistors but also detect electrical changes with a greater degree of precision than silicon. This allows the nanotube to function as a highly responsive sensor.

Chapter 2

2.1 Review on current LEDs

The first commercial LEDs were commonly used as replacements for incandescent and neon indicator lamps, and in seven-segment displays, [32] first in expensive equipment such as laboratory and electronics test equipment, then later in such appliances as TVs, radios, telephones, calculators and even watches.

Conventional LEDs are made from a variety of inorganic semiconductor materials. The following table shows the available colors with wavelength range, voltage drop and material:

Table 2.1 Available LED's material, colors with wavelength range and voltage drop.

	Color	Wavelengh[nm]	Voltage drop [ΔV]	
SSe	Infrared	<u>∆</u> > 760	<u>∆</u> V < 1.63	Gallium arsenide (GaAs) Aluminium gallium arsenide (AlGaAs)
	<u>Red</u>	610 < λ < 760	1.63 < Δ <i>V</i> < 2.03	Aluminium gallium arsenide (AlGaAs) Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium(III)phosphide (GaP)

<u>Orange</u>	590 < λ < 610	2.03 < ΔV < 2.10	Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium(III) phosphide (GaP)
<u>Yellow</u>	570 < λ < 590	2.10 < ΔV < 2.18	Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium(III) phosphide (GaP)
<u>Green</u>	500 < λ < 570	$1.9^{[33]} < \Delta V < 4.0$	Traditional green: Gallium(III) phosphide (GaP) Aluminium gallium indium phosphide (AlGaInP) Aluminium gallium phosphide (AlGaP) Pure green: Indium gallium nitride (InGaN) / Gallium(III) nitride (GaN)
<u>Blue</u>	450 < λ < 500	2.48 < Δ <i>V</i> < 3.7	Zinc selenide (ZnSe) Indium gallium nitride (InGaN) Silicon carbide (SiC) as substrate Silicon (Si) as substrate—under development
<u>Violet</u>	400 < λ < 450	2.76 < Δ <i>V</i> < 4.0	Indium gallium nitride (InGaN)

<u>Purple</u>	multiple types	2.48 < Δ <i>V</i> < 3.7	Dual blue/red LEDs, blue with red phosphor, or white with purple plastic
<u>Ultraviolet</u>	λ < 400	3.1 < Δ <i>V</i> < 4.4	Diamond ^[34] (235 nm) Boron nitride ^{[35][36]} (215 nm) Aluminium nitride (AIN) (210 nm) Aluminium gallium nitride (AIGaN) Aluminium gallium indium nitride ^[37] (AIGaInN)—down to 210 nm
<u>Pink</u>	multiple types	ΔV ~ 3.3 ^[38]	Blue with one or two phosphor layers: yellow with red, orange or pink phosphor added afterwards, or white with pink pigment or dye. ^[39]

2.2 Review on ultraviolet and blue LEDs

Current bright blue LEDs are based on the wide band gap semiconductors GaN (gallium nitride) and InGaN (indium gallium nitride). They can be added to existing red and green LEDs to produce the impression of white light. Modules combining the three colors are used in big video screens and in adjustable color fixtures.

By the late 1990s, blue LEDs had become widely available. They have an active region consisting of one or more InGaN, called cladding layers. By varying the relative In/Ga fraction in the InGaN quantum wells, the light emission can in theory be varied from violet to amber. Aluminum gallium nitride (AlGaN) of varying Al/Ga fraction can be used to manufacture the cladding and quantum well layers for ultraviolet LEDs, but these devices have not yet reached the level of efficiency and technological maturity of InGaN/GaN blue/green devices. If unalloyed GaN is used in this case to form the active quantum well layers, the device will emit near-ultraviolet light with a peak wavelength centered around 365 nm.

With nitrides containing aluminum, most often AlGaN and AlGaInN, even shorter wavelengths are achievable. Ultraviolet LEDs in a range of wavelengths are becoming available on the market. Near–UV emitters at wavelengths around 375-395 nm are already cheap and often encountered, for example as black light lamp replacements for inspection of anti-counterfeiting UV watermarks in some documents and paper currencies. Shorter wavelength diodes, while substantially more expensive, are commercially available for wavelengths down to 240 nm. As the photosensitivity of microorganisms approximately matches the absorption spectrum of DNA, with a peak at about 260 nm, UV LED emitting at 250-270 nm are to be expected in prospective disinfection and sterilization devices. Recent research has shown that commercially available UVA LEDs (365 nm) are already effective disinfection and sterilization devices.

Deep-UV wavelengths were obtained in laboratories using aluminum nitride (210 nm), boron nitride (215 nm) and diamond (235 nm).

2.3 Review on RGB systems

White light can be formed by mixing differently colored lights: the most common method is to use red, green, and blue (RGB). Hence the method is called multicolor white LEDs (sometimes referred to as RGB LEDs). Because these need electronic circuits to control the blending and diffusion of different colors, and because the individual color LEDs typically have slightly

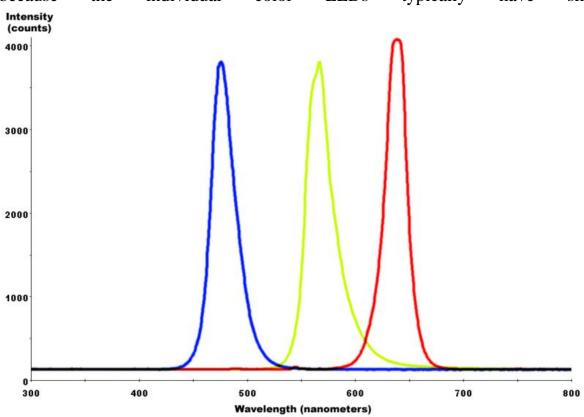


Fig 2.3 Combined spectral curves for blue, yellow-green, and high brightness red solid state semiconductor LEDs.

different emission patterns (leading to variation of the color depending on direction) even if they are made as a single unit, these are seldom used to produce white lighting. Nevertheless, this method is particular interesting in many uses because of the flexibility of mixing different colors, [42] and in principle this mechanism also has higher quantum efficiency in producing white light.

There are several types of multi color white LEDs: di-, tri-, and tetra chromic white LEDs. Several key factors that play among these different methods include color stability, color rendering capability, and luminous efficacy. Often, higher efficiency will mean lower color rendering, presenting a trade-off between the luminous efficiency and color rendering. For example, the dichromatic white LEDs have the best luminous efficacy (120 lm/W), but the lowest color rendering capability. However, although tetra chromatic white LEDs have excellent color rendering capability, they often have poor luminous efficiency. Trichromatic white LEDs are in between, having both good luminous efficacy (>70 lm/W) and fair color rendering capability.

One of the challenges is the development of more efficient green LEDs. The theoretical maximum for green LEDs is 683 lumens per watt but today few green LEDs exceed even 100 lumens per watt. The blue and red LEDs get closer to their theoretical limits.

Multi-color LEDs offer not merely another means to form white light but a new means to form light of different colors. Most perceivable colors can be formed by mixing different amounts of three primary colors. This allows precise dynamic color control. As more effort is devoted to investigating this method, multi-color LEDs should have profound influence on the fundamental method that we use to produce and control light color. However, before this type of LED can play a role on the market, several technical problems must be solved. These include that this type of LEDs emission power decays exponentially with rising temperature, resulting in a substantial change in color stability. Such problems inhibit and may preclude industrial use. Thus, many new package designs aimed at solving this problem have been proposed and their results are now being reproduced by researchers and scientists.

2.4 Review on Phosphor based LEDs

This method involves coating LEDs of one color (mostly blue LEDs made of (InGaN) with phosphors of different colors to form white light, the resultant LEDs

are called phosphor-based white LEDs^[44]. A fraction of the blue light undergoes the stoke shift being transformed from shorter wavelengths to longer. Depending on the color of the original LED, phosphors of different colors can be employed. If several phosphor layers of distinct colors are applied, the emitted spectrum is broadened, effectively raising the color rendering index (CRI) value of a given LED.^[45]

Phosphor based LED efficiency losses are due to the heat loss from the Stokes shift and also other phosphor-related degradation issues. Their efficiencies compared to normal LEDs depend on the spectral distribution of the resultant light output and the original wavelength of the LED itself. For example, the efficiency of a typical YAG yellow phosphor based white LED ranges from 3 to 5times the efficiency of the original blue LED because of the greater luminous efficacy of yellow compared to blue light> Due to the simplicity of manufacturing the phosphor method is still the most popular method for making high-intensity white LEDs. The design and production of a light source or light fixture using a monochrome emitter with phosphor conversion is simpler and cheaper than a complex RGB system, and the majority of high-intensity white LEDs presently on the market are manufactured using phosphor light conversion.

Among the challenges being faced to improve the efficiency of LED-based white light sources is the development of more efficient phosphors. Today the most efficient yellow phosphor is still the YAG phosphor, with less than 10% Stoke shift loss. Losses attributable to internal optical losses due to re-absorption in the LED chip and in the LED packaging itself account typically for another 10% to 30% of efficiency loss. Currently, in the area of phosphor LED development, much effort is being spent on optimizing these devices to higher light output and higher operation temperatures. For instance, the efficiency can be raised by adapting better package design or by using a more suitable type of phosphor. Conformal coating process is frequently used to address the issue of varying phosphor thickness.

The phosphor-based white LEDs encapsulate InGaN blue LEDs inside phosphor coated epoxy. A common yellow phosphor material is cerium-doped yttrium aluminum garnet (Ce³⁺:YAG).

2.5 Types of LEDs

The main types of LEDs are miniature, high power devices and custom designs such as alphanumeric or multi-color. [46]

2.5.1 Miniature

These are mostly single-die LEDs used as indicators, and they come in various sizes from 2 mm sink to 8 mm, through-hole and surface mount packages. They usually do not use a separate heat sink.^[47] Typical current ratings range from around 1mA to above 20 mA. The small size a natural upper boundary on power consumption due to heat caused by the high current density and need for a heat.

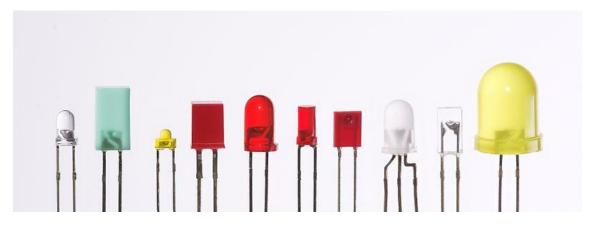


Fig 2.6.1 LEDs of different shapes and sizes.

Common package shapes include round, with a domed or flat top, rectangular with a flat top (as used in bar-graph displays), and triangular or square with a flat top. The encapsulation may also be clear or tinted to improve contrast and viewing angle.

There are three main categories of miniature single die LEDs:

• Low-current typically rated for 2 mA at around 2 V (approximately 4 mW consumption).

• Standard 20 mA LEDs (ranging from approximately 40 mW to 90 mW) at around:

1.9 to 2.1 V for red, orange and yellow,

3.0 to 3.4 for green and blue,

2.9 to 4.2 for violet, pink, purple and white.

• Ultra-high-output 20mA at approximately 2 V or 4-5 V, designed for viewing in direct sunlight

5 V and 12 V LEDs are ordinary miniature LEDs that incorporate a suitable series resistor for direct connection to a 5V or 12 V supply.

2.5.2 Mid-range

Medium-power LEDs are often through-hole—mounted and mostly utilized when an output of just a few lumens is needed. They sometimes have the diode mounted to four leads (two cathode leads, two anode leads) for better heat conduction and carry an integrated lens. An example of this is the Superflux package, from Philips Lumileds. These LEDs are most commonly used in light panels, emergency lighting and automotive tall-lights. Due to the larger amount of metal in the LED, they are able to handle higher currents (around 100 mA). The higher current allows for the higher light output required for tail-lights and emergency lighting.

2.5.3 High-power

High-power LEDs (HPLED) can be driven at currents from hundreds of mA to more than an ampere, compared with the tens of mA for other LEDs. Some can emit over a thousand lumens. [48][49] LED power densities up to 300W/cm² have been achieved. [50] Since overheating is destructive, the HPLEDs must be mounted on a heat sink to allow for heat dissipation. If the heat from a HPLED is not removed, the device will fail in seconds. One HPLED can often replace an incandescent bulb in a flashlight, or be set in an array to form a powerful LED lamp.

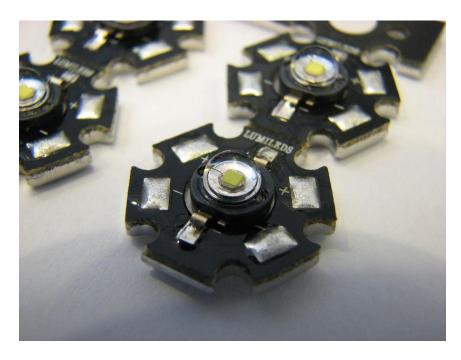


Fig 2.6.3 High power light-emitting diodes

Some well-known HPLEDs in this category are the Nichia 19 series, Lumileds Rebe Led, Osram Opto Semiconductors Golden Dragon, and Cree X-lamp. As of September 2009, some HPLEDs manufactured by Cree Inc. now exceed 105 lm/W.^[51] (e.g. the Xlamp XP-G LED chip emitting Cool white light) and are being sold in lamps intended to replace incandescent, halogen, and even fluorescent lights, as LEDs grow more cost competitive.

The impact of Hait'z law which describe the exponential rise in light output of LEDs over time can be readily seen in year over year increases in lumen output and efficiency. For example, the CREE XP-G series LED achieved 105 lm/W in 2009, while Nichia released the 19 series with a typical efficacy of 140 lm/W in 2010. [52]

LEDs have been developed by Seoul Semiconductor that can operate on AC power without the need for a DC converter. For each half-cycle, part of the LED emits light and part is dark, and this is reversed during the next half-cycle. The efficacy of this type of HPLED is typically 40 lm/W.^[53] A large number of LED elements in series may be able to operate directly from line voltage. In 2009, Seoul Semiconductor released a high DC voltage LED capable of being driven

from AC power with a simple controlling circuit. The low-power dissipation of these LEDs affords them more flexibility than the original AC LED design.^[54]

2.6.1 Advantages

- **Efficiency**: LEDs emit more light per watt than incandescent light bulbs. ^[55] The efficiency of LED lighting fixtures is not affected by shape and size, unlike fluorescent light bulbs or tubes.
- Color: LEDs can emit light of an intended color without using any color filters as traditional lighting methods need. This is more efficient and can lower initial costs.
- **Size**: LEDs can be very small (smaller than 2 mm² [56]) and are easily attached to printed circuit boards.
- **On/Off time**: LED light up very quickly. A typical red indicator LED will achieve full brightness in under a microsecond. ^[57] LEDs used in communications devices can have even faster response times.
- **Cycling**: LEDs are ideal for uses subject to frequent on-off cycling, unlike fluorescent lamps that fail faster when cycled often, or HID lamps that require a long time before restarting.
- **Dimming**: LEDs can very easily be dimmed euther by pulse-width modulation or lowering the forward current. This pulse-width modulation is why LED lights viewed on camera, particularly headlights on cars, appear to be flashing or flickering. This is a type of Stroboscopic effect.
- Cool light: In contrast to most light sources, LED s radiate very little heat in the form of IR that can cause damage to sensitive objects or fabrics. Wasted energy is dispersed as heat through the base of the LED.
- **Slow failure**: LEDs mostly fail by dimming over time, rather than the abrupt failure of incandescent bulbs.^[59]
- **Lifetime**: LEDs can have a relatively long useful life. One report estimates 35,000 to 50,000 hours of useful life, though time to

complete failure may be longer.^[60] Fluorescent tubes typically are rated at about 10,000 to 15,000 hours, depending partly on the conditions of use, and incandescent light bulbs at 1000 to 2000 hours. Several DOE demonstration have shown that reduced maintenance costs from this extended lifetime, rather than energy savings, is the primary factor in determining the payback period for an LED product.^[61]

- **Shock resistance**: LEDs being solid-state components are difficult to damage with external shock, unlike fluorescent and incandescent bulbs, which are fragile.
- Focus: The solid package of the LED can be designed to focus its light. Incandescent and fluorescent sources often require an external reflector to collect light and directly it in a usable manner. For larger LED packages total internal reflection (TIR) lenses are often used to the same effect. However, when large quantities of light is needed many light sources are usually deployed, which are difficult to focus or collimate towards the same target

2.6.2 Disadvantages

- **High initial price**: LEDs are currently more expensive, price per lumen, on an initial capital cost basis, than most conventional lighting technologies. As of 2010, the cost per thousand lumens (kilolumen) was about \$18. The price is expected to reach \$2/kilolumen by 2015. [62] The additional expenses partially stems from the relatively low lumen output and the drive circuitry and power supplies needed.
- **Temperature dependence**: LED performance largely depends on the ambient temperature of the operating environment or "thermal management" properties. Over-driving an LED in high ambient temperatures may result in overheating the LED package, eventually leading to device failure. An adequate heat sink is needed to maintain long life. This is especially important in automotive,

- medical and military uses where devices must operate over a wide range of temperatures, which require low failure rates.
- **Voltage sensitivity**: LEDs must be supplied with the voltage above the threshold and a current below the rating. This can involve series resistors or current-regulated power supplies.^[63]
- **Light quality**: Most cool-white LEDs have spectra that differ significantly from a black body radiator like the sun or an incandescent light. The spike at 460 nm and dip at 500 nm can cause the color of objects to be perceived differently under cool-white LED illumination than sunlight or incandescent sources, due to metamerism, ^[64] redsurfaces being rendered particularly badly typical phosphor-based cool-white LEDs. However, the color rendering properties of common fluorescent lamps are often inferior to what is now available in state-of-art white LEDs.
- **Area light source**: Single LEDs do not approximate a point source of light giving a spherical light distribution, but rather a lambertian distribution. So LEDs are difficult to apply to uses needing a spherical light field, however different fields of light can be manipulated by the application of different optics or "lenses". LEDs cannot provide divergence below a few degrees. In contrast, lasers can emit beams with divergences of 0.2 degrees or less. [65]
- Electrical polarity: Unlike incandescent light bulbs, which illuminate regardless of the electrical polarity, LEDs are only light with correct electrical polarity. To automatically match source polarity to LED devices, rectifiers can be used.
- Blue hazard: There is a concern that blue LEDs and cool-white LEDs are now capable of exceeding safe limits of the so-called blue-light hazard as defined in eye safety specifications such as ANSI/IESNA RP-27. 1-05: Recommended Practice for Photo biological Safety for Lamp Systems. [66][67]
- Blue Pollution: Because cool-white LEDs with high color temperature emit proportionally more blue light than conventional outdoor light sources such as high- pressure sodium vapor lamps, the strong wavelength dependence of Rayleigh scattering means that

cool-white LEDs can cause more light pollution than other light sources. The International Dark-Sky Association discourages using white light sources with correlated color temperature above 3.000 K.^[68]

• **Droop**: The efficiency of conventional InGaN based LEDs decreases as one increases current above a given level. [69][70][71][72]

2.7 Review on CNT LED

2.7.1 Introduction

Advances in fabrication, purification, and processing techniques have allowed carbon nanotubes to show great potential in many areas of physics, chemistry, and engineering. ^[9] Existing in two forms, multiwalled and single-walled, this form of carbon has been shown, both experimentally and theoretically to have excellent mechanical and electrical properties. Individual nanotubes have elastic moduli in the region of 1 TPa, and in powder samples, bulk conductivity as high a 10⁵ S/m has been measured.

However, while many potential applications have been suggested for carbon nanotubes, few practical uses have emerged. The main difficulties relate to the poor purity and processability of nanotube containing powders. Using nanotubes to improve the performance of existing functional organic devices would be one of the most accessible applications. One of the most studied of these devices types over the last 10 yr has been the organic light emitting diode (OLED).

Efficient organic electroluminescence requires the optimization of four factors: balance of injection of electrons and holes, transportation of these carriers as polarons within the polymer, recombination of carriers to form singlet excitons, and the radiative decay of these excitons. In order to achieve the optimization of these factors, heterojunction using hole- and electron-transport layers are generally used.

While many organic materials can be as hole-transport layers, materials that work effectively as electron-transport layers are not so common. There are various reasons for this, n-type undoped polymers are rare while electron mobilities tend to be low as a result of the efficient trapping of negative carriers by impurities, etc. One possible alternative to polymers or molecular materials as electron-transport layers would be to use a high mobility material such as carbon nanotubes. In fact, these carbon nanocrystals can individually be extremely conductive with high mobilities for both electrons and holes.

2.7.2 Electroluminescence

2.7.2.1 Review on unipolar and ambipolar FETs

A CNT field-effect transistor is a three terminal switching device in which the current from the source to the drain through the CNT is controlled by an applied voltage at a capacitive coupled gate. ^[14] In addition to modulating the carrier density in the CNT, the gate voltage also modulates the injection of carriers at the source and drain Schottky barriers. The polarity of the device depends on the Schottky barriers heights for electrons and holes, and can be engineered to some degree by adjusting the metal work functions. For example, for palladium contacts, the Schottky barriers for holes are small and devices are p-type, whereas annealed titanium contacts produce ambipolar devices with intermediate Schottky barrier heights for electron and holes.

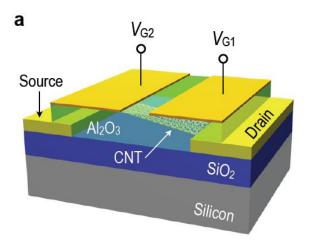


Fig 2.7.2.1 Schematics of a CNT p-n junction.

Ambipolar CNT field-effect transistors (FETs) are not particularly desirable for logic operations, because they lack a well-behaved off state. As a result, ways have been developed to regain a unipolar device characteristic by using a double gate or by chemically doping the contact region. On the other hand, ambipolar

transistors enable the injection of electrons and holes from opposite contacts into the CNT, and thus are very useful for electro-optic applications.

2.7.2.2 Electron-hole recombination in ambipolar nanotubes

Electron-hole pairs in semiconductors may recombine by a variety of mechanisms. ^[14] In most cases, the energy will be released as heat (phonos), but a fraction of the recombination events may involve the emission of a photon. This electroluminescence (EL) process is widely used to produce solid-state light sources such as LEDs. To produce an electroluminescent device that emits a significant amount of light, a large number of electrons and holes must recombine. In an LED, this is achieved at an interface between a hole-doped (p-doped) and an electron-doped (n-doped) material. In ambipolar CNT-FETs, electrons and holes can be simultaneously injected at opposite ends of the CNT channel. This enables radiative recombination to take place in the CNT and EL is generated. Although the emission mechanism is the same as that in LEDs, ambipolar CNT-FETs do not require any chemical doping, a significant simplification of the fabrication process.

Carbon-nanotube EL exhibits a number of interesting properties. The emitted light, as with photoluminescence, is polarized along the tube axis, and the radiation has a characteristic energy that depends on the diameter and chirality of the excited single-walled CNT. The length of the electroluminescent region is of the order of the recombination length which is less than or equal to 1 µm. At a gate voltage halfway between the value of the source and drain voltages, about an equal numbers of electrons and holes are injected. The total current is minimized, but the amount of light generated is maximized. In short devices, the light emission encompasses the entire CNT. In long devices, where electron-hole recombination is fast compared with carrier transit times through the channel, light emission originates from a small part of the CNT, where electrons and holes coexist and can annihilate. As a result, the emission is localized to where the concentrations of electron and holes overlap most strongly. In the regions above

and below this recombination spot, transport is unipolar and charge carriers are of opposite sign. Most importantly, because no chemical doping is involved, the electron-hole overlap region and thus the region of light emission can be physically moved along the CNT using the gate electrode. A CNT-EL device is thus a translatable light source.

In long CNT-FETs, a simple drift transport model accounts well for the main features of the movement of the light emission. For intermediate-length devices numerical calculations for the light emission have been performed. The EL spectra can be similar to photoluminescence spectra. However, electrical pumping is usually much stronger than optical pumping, excitation densities are much higher, and a broad emission with a low-energy onset at the E_{11} exciton energy is usually observed.

2.7.2.3 Hot-carrier induced excitation and unipolar emission

In addition to photon irradiation and electron-hole recombination, excitation of CNTs can be achieved through energic – 'hot' – carriers flowing through the CNT. $^{[14]}$ This is an impact-scattering mechanism that involves coulombic interactions between electrons. Electron-electron interactions are very strong in 1D materials such as CNTs. Indeed, calculations suggest that impact-excitation processes in CNTs are much more efficient (about four orders of magnitude stronger) than in conventional bulk semiconductors. The carriers are accelerated by the applied electric field, gain energy and then lose some of it to phonons, primarily optical phonons. When an energy threshold, E_{th} , is reached, electronic excitation of the CNT across the bandgap can take place. The value of E_{th} is determined not only by the E_{11} energy, but also by the requirement to conserve the circumferential angular momentum of the CNT in the impact-excitation process.

Solving the Boltzman equation shows that the exciton production probability, P, varies exponentially with F, that is P ~ exp(- $E_{th}/eF\lambda_{op}$), where e is the charge of an electron, E_{th} ~ 1.5 E_{11} and λ_{op} (about 20-40 nm) is the electron mean free path with respect to optical-phonon

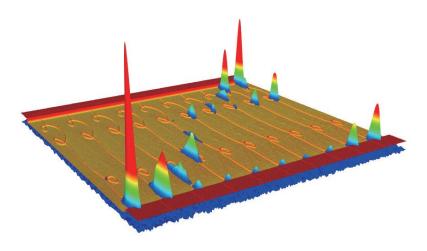


Fig 2.8.3 Localized and mobile EL from a looped CNT.

scattering. The hot-carrier-induced impact excitation of CNTs can be used to create an efficient EL source . The current is carried by only one type of carrier (either electrons or holes), and inhomogeneities actively generate electron-hole pairs by impact excitation. The emission occurs near defects, trapped charges in the gate insulator, CNT-CNT contacts, the Schottky contacts, or any other inhomogeneities that produce large, local electric fields that can accelerate the carriers to energies above E_{th} . For example, for the straight CNT, there are at least three stationary spots that do not move with the gate voltage. Each of them appears to the negative voltage side of the ambipolar spot, where the corresponding CNT segment has become n-type. They disappear past the ambipolar spot. Experiments like these suggest that locally p-doped segments act as n-p-n junctions during electron conduction, owing to pockets of trapped electrons in the SiO_2 used as the gate dielectric. Thus, monitoring localized EL provides a tool for detecting defects in CNT devices.

Figure 2.8.3 shows looped nanotubes, where hot carriers tunnel from one end of the CNTs to the other end across the base of the loop and produce light by impact excitation. Different loops on the same CNT may or may not show unipolar EL, depending on the microscopic properties of the junction. An analogous variation in contact properties has been observed in photovoltage measurements of looped CNTs that, unlike EL measurements, probe the low-bias behavior of devices. The light emission also depends on the charge in the surrounding CNT segments,

which can be changed by moving the ambipolar spot across the base of the loop using the gate bias. For example, in Fig 2.8.3 two of the loops become active for hole conduction. Note that the ambipolar infrared spot never moves through the interior of the loop and instead jumps across the CNT-CNT contacts, which suggests strong intertube electron-hole coupling.

Artificial structures can also be fabricated to create the abrupt change in the potential that is required to generate localized light emission by impact excitation. It consists of a back gated CNT-FET in which a trench has been cut in the gate oxide by etching so that a portion of the CNT channel is suspended. The difference in the coupling to the gate of the oxide-supported and the suspended part of the CNT leads to band-bending at the interface of the twp segments. Carriers reaching this interface are accelerated and, through impact excitation, can produce excitons or electron-hole pairs that recombine radiatively.

Light intensity, I, from unipolar devices depends exponentially on the applied electric field, I (photon) α exp(- F_{th}/F), where F_{th} is the threshold field required for electronic acceleration within the band. Furthermore, impact excitation is not subject to the same selection rules as photoexcitation spectra. Although interband transitions are suppressed in favor of exciton transitions in photoexcitation, impact excitation does produce free electron-hole pairs. Thus using internal impact excitation, both exciton and bandgap CNT emission can be observed. In suspended metallic tubes under high-bias conditions, light emission was also observed as a result of the hot carrier distribution.

2.7.3 Advantages of CNT LED

Single-walled CNT films are conductive, optically transparent and flexible. ^[14] These properties have been used to make anodes for organic LEDs. The advantage over the traditionally used indium tin oxide films is their cheaper price, flexibility and resilience to corrosion. For example, polymer OLEDs with CNT anodes that have maximum light output of 3,500 cd m⁻² and a current efficiency of 1.6 cd A⁻¹ have been reported.

Another way to use CNT in light-emitting devices is in the form of composites with conjugated polymers. Indeed, enhanced EL in such composites has been reported by many authors, and enhanced photovoltaic behavior was also observed in such composites.

Chapter 3

3.1 Work Analysis

The objective of this work is to investigate the advantage of carbon nanotube over other materials especially in the field of optoelectronics. In the field of optoelectronics, Si based devices is expected to reach its limiting size. Carbon nanotube is one among the most promising alternatives due to its superior optoelectronic properties. In this thesis, the performance of nanotube based devices will be investigated.

3.1.1 Experimental detail

Comparing with CNT LEDs, Si based LEDs are not that much efficient in terms of luminous intensity. One of the main reasons behind it, is Si is an indirect bandgap material. That's why, electrons cannot easily reach to conduction band from valence band. This is a major obstacle to make LEDs with Si. On the other hand, carbon nanotube is a highly conductive material. And semiconductor CNTs are direct bandgap material. Here optical transition occurs according to the Van Hove singularities. If E_{11} optical transition occurs, it is said to be the first Van Hove optical transition and second Van Hove optical transition for E_2

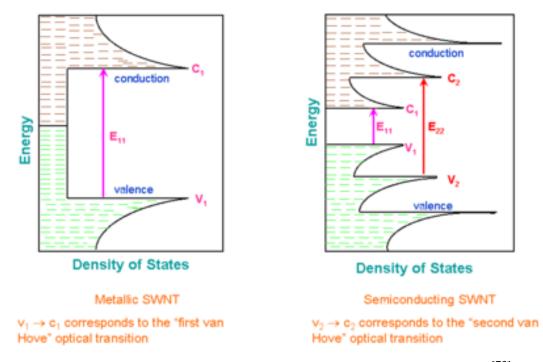


Fig 3.1.1Density of states of metallic & semiconducting CNT^[73]

The main focus of this experiment is on CNT FET, where the channel is made of CNT with two gate biasing voltages. One gate bias injects holes and other injects electrons from two opposite directions. And the recombination occurs at the channel. Another big advantage of CNT FET which will be examined and discussed thoroughly later in this chapter is, here we can control the peak emission. This is a unique characteristic of CNT over other semiconductive materials. In this experiment we will examine the change of peak position, peak intensity, FWHM and the ratio of area and intensity of two different peaks.

3.1.2 Comparison between unipolar and ambipolar emission

We have experimental data available for unipolar and ambipolar emission. The following figures are for the comparison between two types of emissions in terms of their peak position, intensity and FWHM.

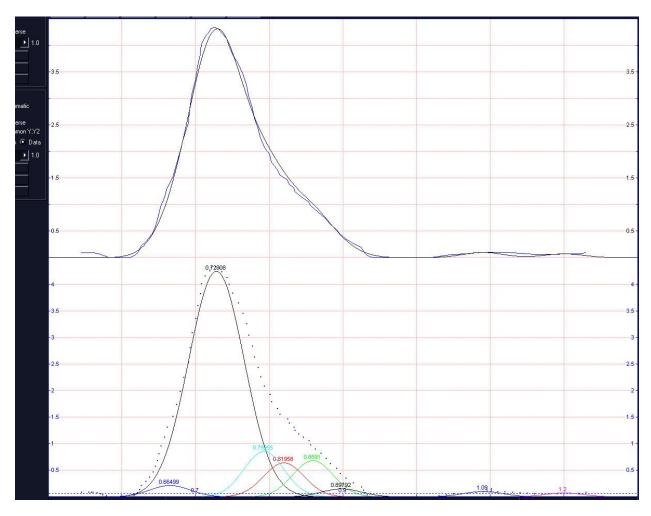


Fig 3.1.2.1 Fitted curve of unipolar light emission. [6]

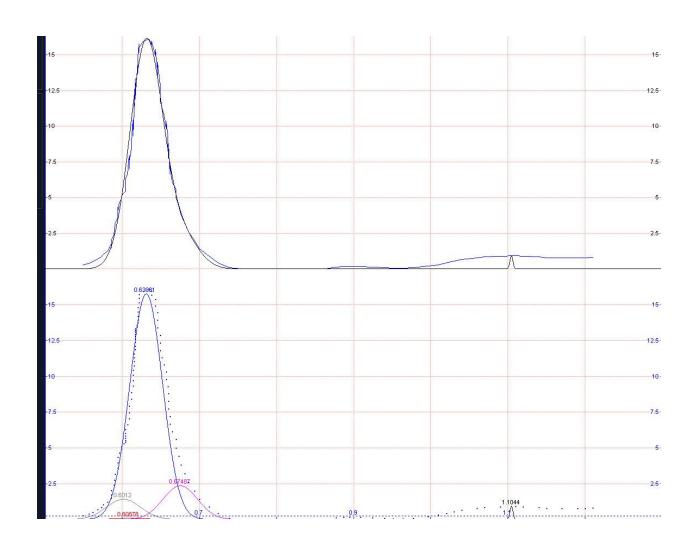


Fig 3.1.2.2 Fitted curve of ambipolar light emission. [6]

Table 3.1.2 comparison between unipolar and ambipolar emission

	Peak position	Peak intensity	FWHM
Unipolar	0.72808	4.61	0.0887348
Ambipolar	0.63061	28.2	0.0495697

It is being clearly seen from the above table and the graphs the big difference of unipolar and ambipolar emission in terms of peak intensity. It is mainly because of the biasing difference between two types of emission. In unipolar mechanism, biasing is either positive or negative. That's why only holes or electrons can be injected here. As a result, at unipolar biasing non-radiative recombination dominates over radiative recombination.

On the other hand, in ambipolar mechanism biasing is bipolar. That's why; both electrons and holes are injected over here. As a result, here radiative recombination dominates over non-radiative recombination.

For the above reasons, at unipolar biasing peak intensity decreases to a large extent and that reduces the electroluminescence intensity.

3.1.3 Electroluminescence spectrum at different drain-source current $I_{DS}\,$

The following curves are to examine the different EL intensity at different I_{DS} at bipolar biasing condition.

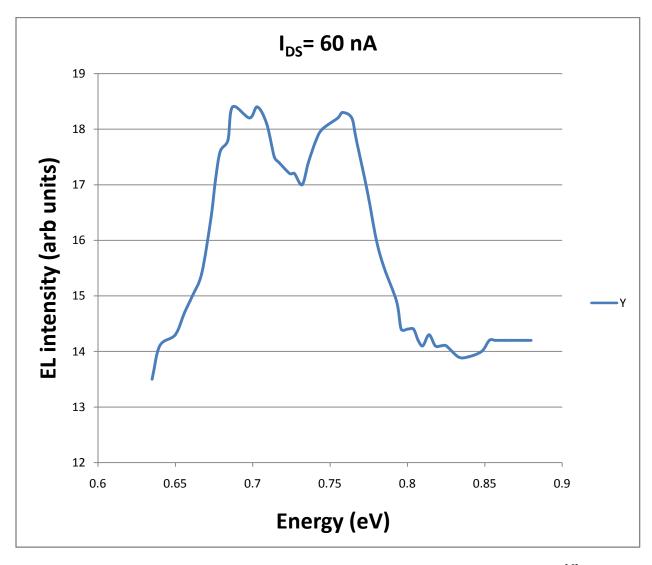


Fig 3.1.3a EL spectrum of nanotube diode recorded at I_{DS} =60 nA. [6]

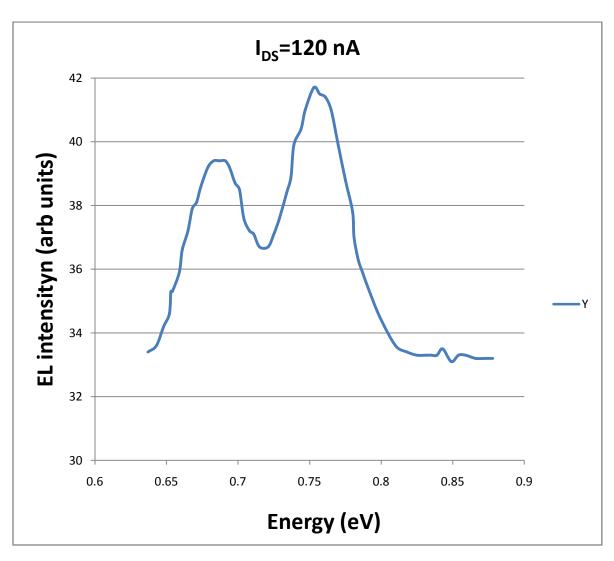


Fig 3.1.3b EL spectrum of nanotube diode recorded at I_{DS} =120 nA. ^[6]

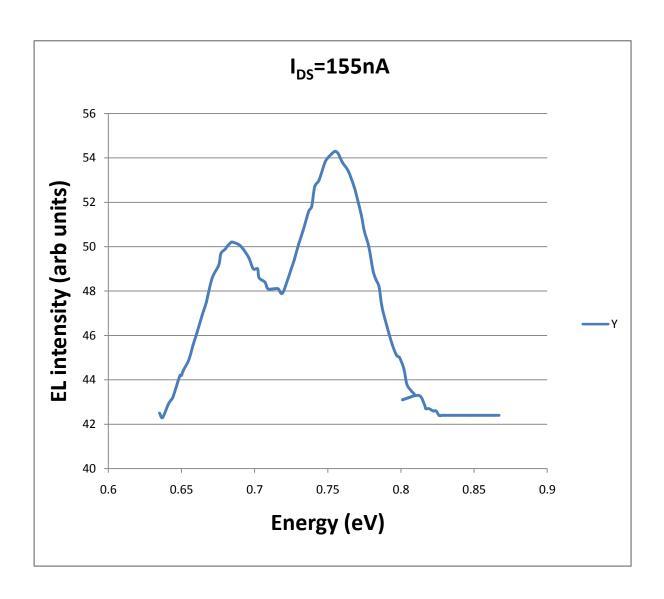


Fig 3.1.3c EL spectrum of nanotube diode recorded at I_{DS} =155 nA. ^[6]

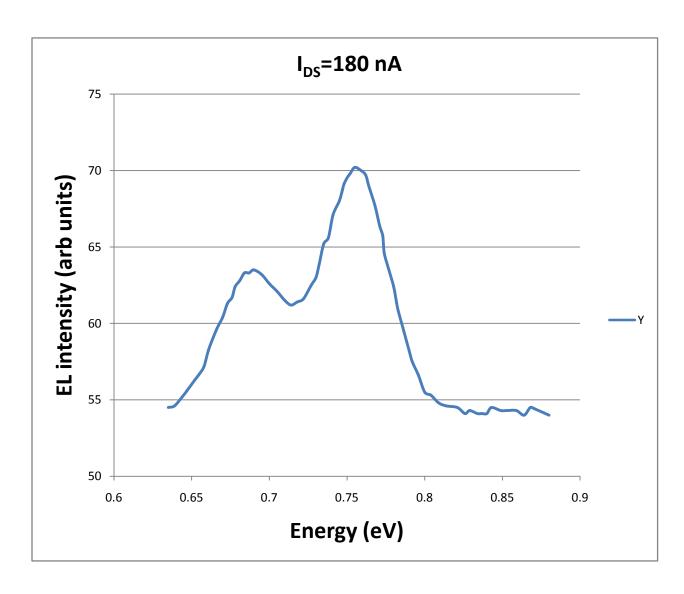


Fig 3.1.3d EL spectrum of nanotube diode recorded at I_{DS} =180 nA. [6]

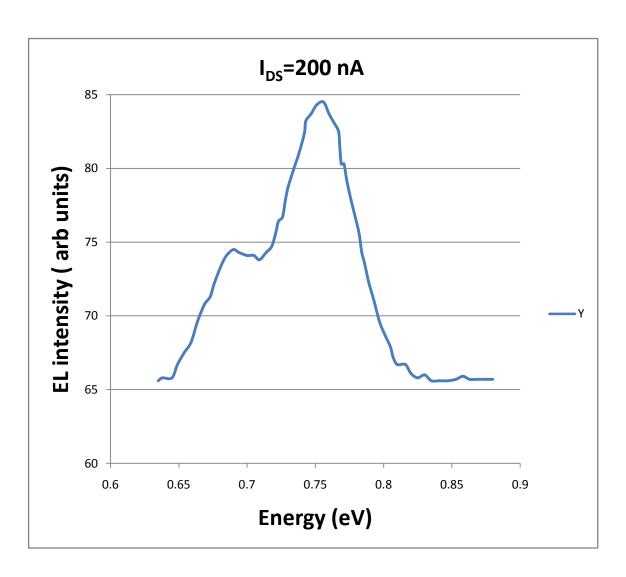


Fig 3.1.3e EL spectrum of nanotube diode recorded at I_{DS} =200 nA. [6]

At first, we have applied the fitting technique on the curve I_{DS} =60 nA. And for best fitting, we have obtained three peaks in that. Following figure shows the main curve with the fitted curve with three peaks.

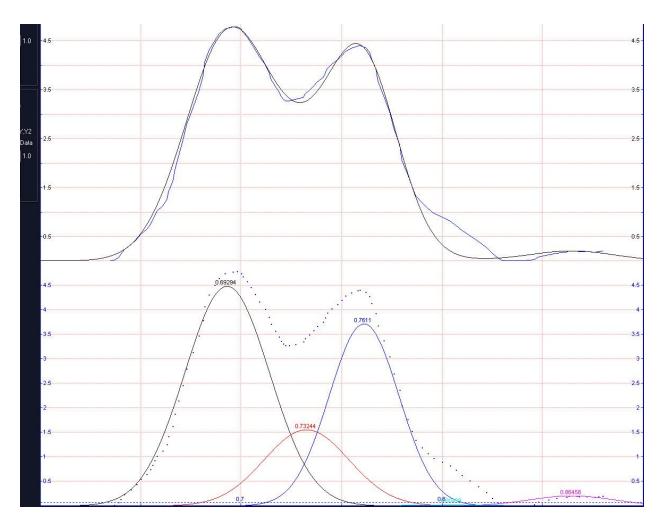


Fig 3.1.3f Fitted curve of EL spectrum of nanotube diode recorded at I_{DS} =60 nA.

Then we have applied the fitting technique on the curve I_{DS} =120 nA. And here for best fitting we have obtained two peaks. Following figure shows the fitted curve with the main curve.

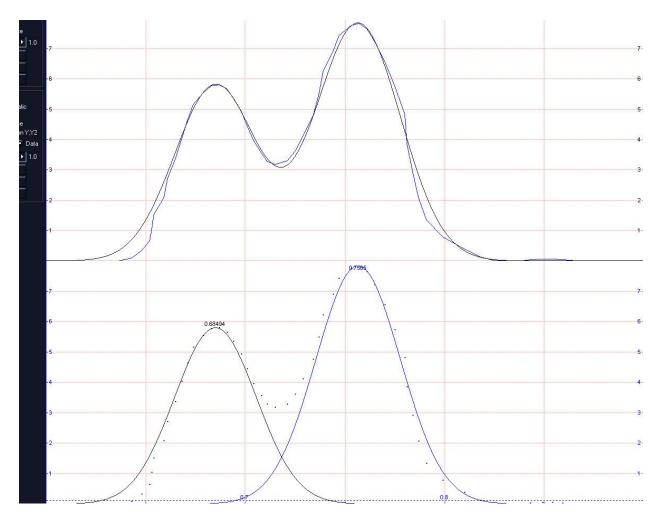


Fig 3.1.3g Fitted curve of EL spectrum of nanotube diode recorded at I_{DS} =120 nA

After that we have applied the fitting technique on the curve I_{DS} =155 nA. Here we have obtained three peaks for best fitting. Following figure shows both the fitted curve and the main curve.

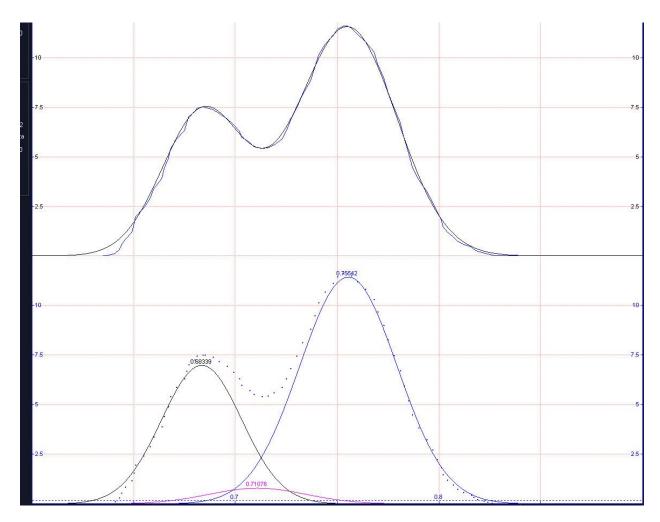


Fig 3.1.3h Fitted curve of EL spectrum of nanotube diode recorded at I_{DS} =155 nA

Next we have applied the fitting technique on the curve I_{DS} =180 nA. Here we have obtained three peaks for best fitting. Following figure shows the main curve with the fitted curve.

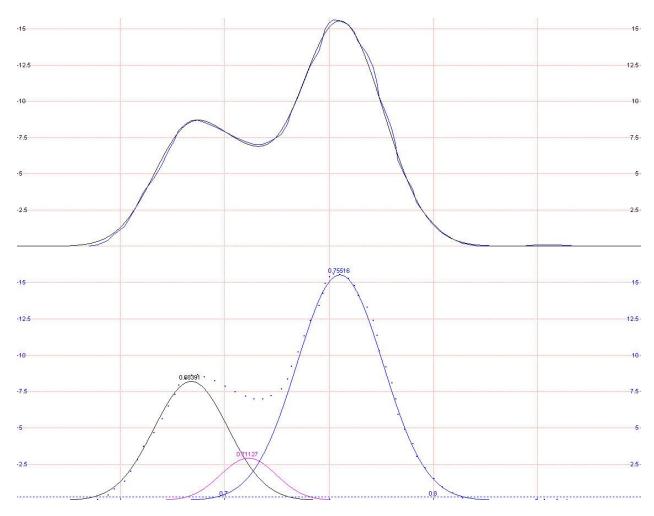


Fig 3.1.3i Fitted curve of EL spectrum of nanotube diode recorded at $I_{DS}\!\!=\!\!180~\text{nA}$

Lastly, we have applied the fitting technique on the curve I_{DS} =200 nA. For best fitting we have obtained three peaks over here. Following figure shows the fitted curve with the main curve,

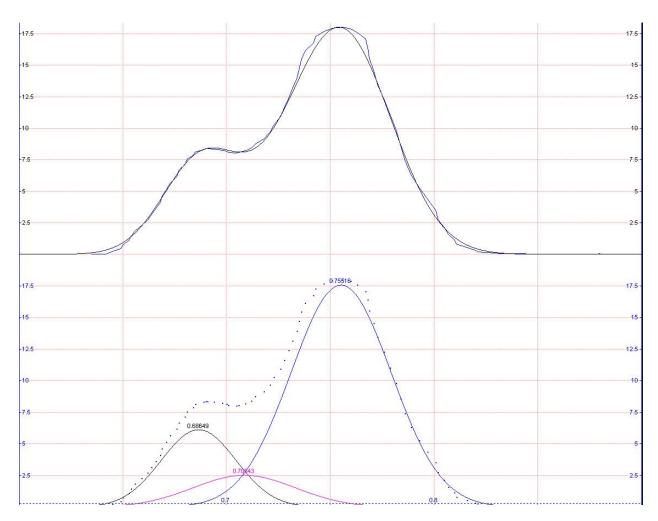


Fig 3.1.3j Fitted curve of EL spectrum of nanotube diode recorded at I_{DS} =200 nA

Now, observing the position of peak1 corresponding the drain-source current I_{DS} , we have seen that the position of peak1 moves towards the lower energy with increasing I_{DS} . But when I_{DS} approaches approximately 155 nA, it starts to move towards the higher energy. Following curve shows the trend.

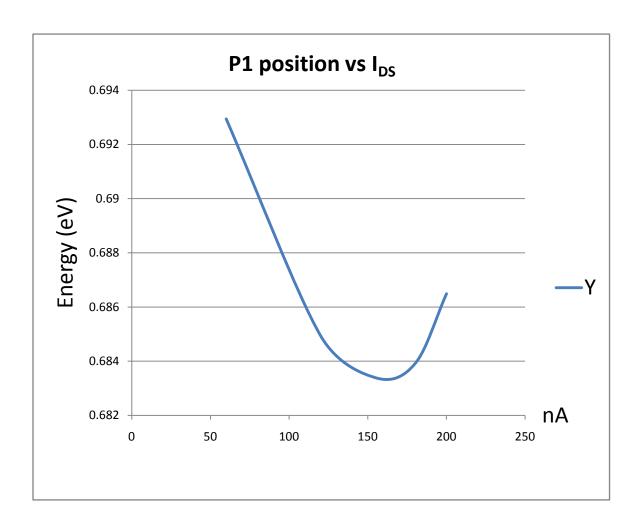


Fig 3.1.3k Different position of first peak vs I_{DS}

After that observing the intensity of peak1 corresponding the drain-source current I_{DS} , we have seen that the intensity of peak1 increases with increasing I_{DS} . But when I_{DS} approximately approaches to 180 nA it starts to decrease. Following curve shows the trend.

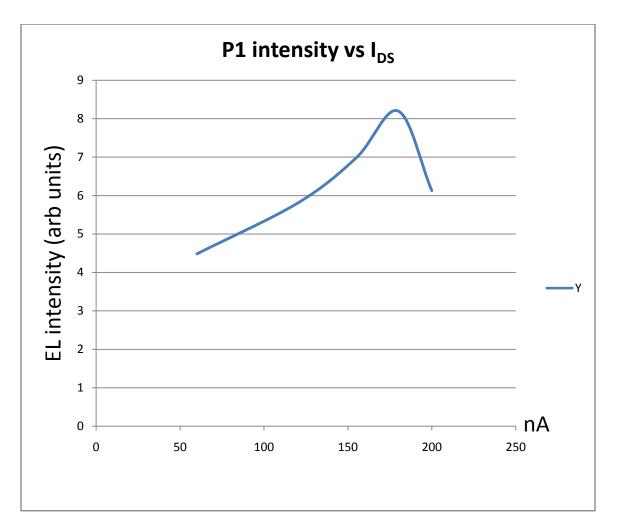


Fig 3.1.31 Different intensity of second peak vs I_{DS}

Then we have observed the FWHM of peak1 corresponding the drain-source current I_{DS} . The FWHM of peak 1 decreases with increasing I_{DS} . Initially it decreases slowly but when I_{DS} approaches approximately 120 nA it decreases drastically. Again when I_{DS} reaches to 180 nA approximately the FWHM of peak1 slightly increases. Following curve shows the trend.

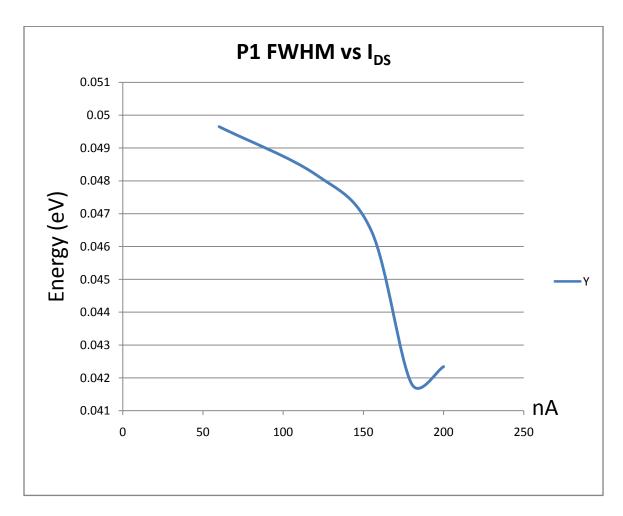


Fig 3.1.3m Different FWHM of first peak vs I_{DS}

Now, observing the position of peak2 corresponding the drain-source current I_{DS} we have seen that the position of peak2 moves towards the lower energy with increasing I_{DS} . And when I_{DS} reaches to 155 nA approximately it becomes stable. Following curve shows the trend.

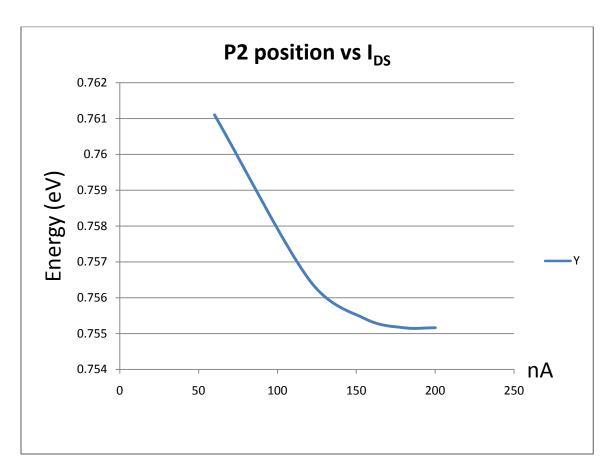


Fig 3.1.3n Different position of second peak vs I_{DS}

After that we have observed the intensity of peak2 corresponding the drain-source current I_{DS} . The intensity of peak2 increases with increasing I_{DS} . Following curve shows the trend.

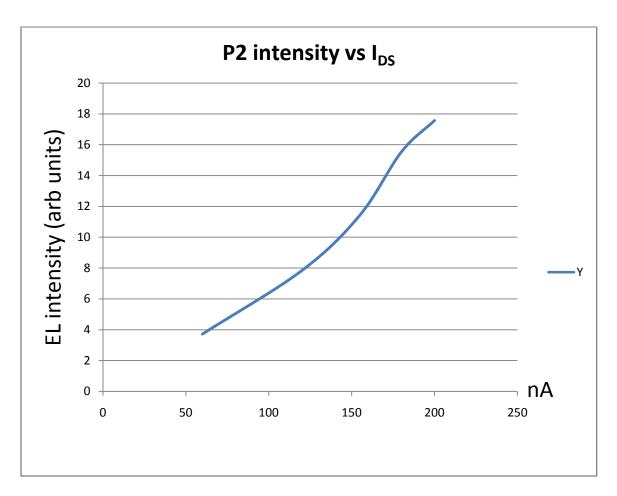


Fig 3.1.30 Different intensity of second peak vs I_{DS}

Then we have observed the FWHM of peak2 corresponding the drain-source current I_{DS} . The FWHM of peak2 shows a different characteristic. It is being almost stable up to I_{DS} =120 nA approximately. After that it slightly increases. When I_{DS} reaches to 155 nA approximately, it drastically decreases and when I_{DS} approaches to 180 nA approximately it increases drastically.

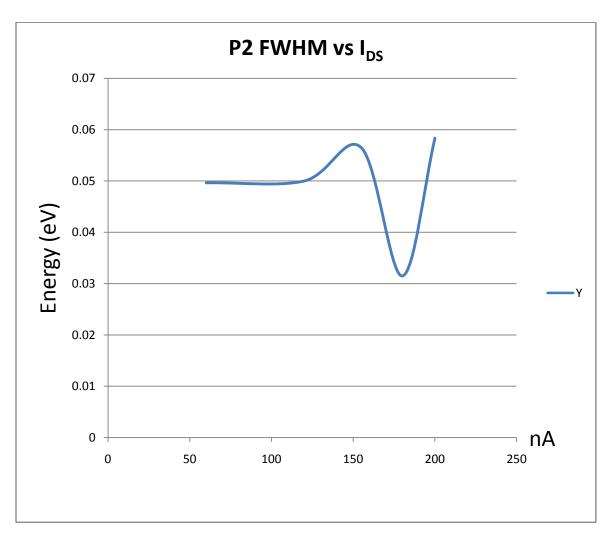


Fig 3.1.3p Different FWHM of second peak vs I_{DS}

Plotting the ratio of intensity of peak2 & peak1 corresponding the drain-source current I_{DS} we have seen that ratio of intensity increases with I_{DS} . And when I_{DS} reaches to 155 nA approximately it increases rapidly. That means the intensity of peak2 dominates over peak1. Following curve shows the trend.

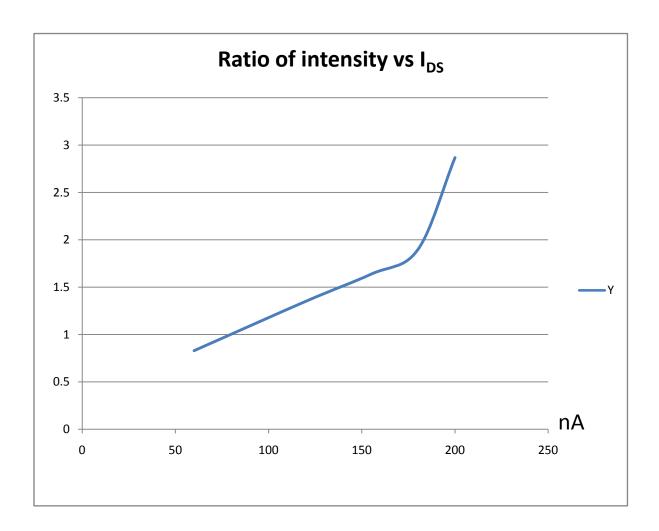


Fig 3.1.3q Ratio of intensity vs I_{DS}

After that, plotting the ratio of area of peak2 & peak1 corresponding the drain-source current I_{DS} we have seen that the ratio of area increases with increasing I_{DS} up to 120 nA approximately. After that it drastically decreases and when I_{DS} reaches to 155 nA it starts to increase again. Following curve shows the trend.

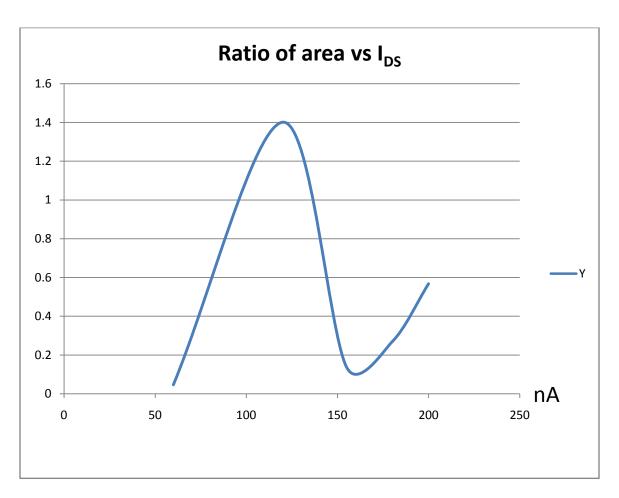


Fig 3.1.3r Ratio of area vs I_{DS}

Table 3.1.3 Data for peak 1 & peak 2

	P1	P1	P1	P2	P2	P2	Ratio	Ratio
	positio	intensit	FWHM	positio	intensit	FWH	of	of area
	n	y		n	y	M	intens	(P2/P1
							ity)
							(P2/P	
							1)	
60	0.6929	4.482	0.049648	0.7611	3.7162	0.0496	0.829	0.0457
nA	4					484		2
120	0.6849	5.8018	0.048199	0.7565	7.8373	0.0500	1.350	1.4013
nA	4					023	8	
155	0.6833	6.982	0.046472	0.7554	11.43	0.0564	1.637	0.1372
nA	9			2		747		
180	0.6839	8.1982	0.041824	0.7551	15.529	0.0314	1.894	0.2679
nA	1			6		974	1	
200	0.6864	6.1261	0.042341	0.7551	17.568	0.0583	2.867	0.5674
nA	9			6		477	7	

In this thesis, we have used the data of only two peaks for our analysis and observation. But in the fitted curve there are some other peaks too. This could be the mean for further research & study in this field.

3.1.4 Light emitting mechanism and others

The main and major advantage of CNT LED is, here we can control the peak emission and also the FWHM. But in Si which is the most common and used material for LED we cannot do that.

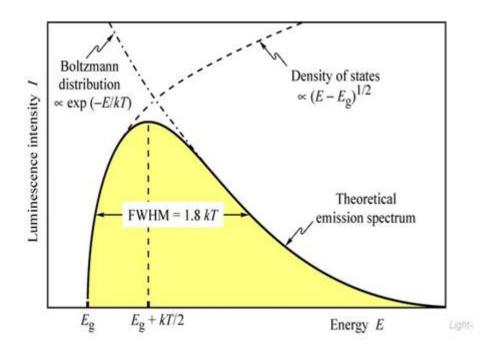


Fig 3.1.4a emission spectrum of silicon

In CNT FET structure the gate voltage is mainly used to modulate the injection efficiency of electrons (or holes). At a large negative bias i.e. V_g =-5V the hole is the majority carrier type injected into the CNT channel. These injected holes may recombine with electrons injected from the Sc contact via tunneling and emit photon. However, the electron is the majority carrier type in the CNT channel with i.e. V_g =5V. The electrons injected from the Sc electrode may recombine with holes injected from the Pd contact via tunneling and emit photon.

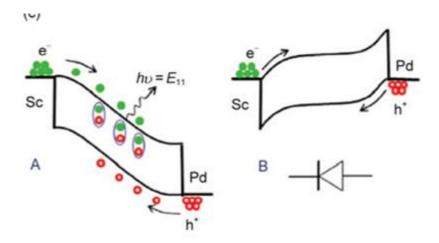


Fig 3.1.4b Band diagrams which correspond to two representative points A (forward bias) and B (zero or small reverse bias)^[2]

To obtain efficient light emission from CNT devices, we propose that large numbers of carriers can be injected from two electrodes at the same time without the Schottky barrier, and they can then radiatively recombine with high efficiency.

Chapter 4

Conclusion

In summary we can say, semiconducting CNTs are direct-bandgap materials, with strongly bound 1D excitons, whose transition energies are inversely proportional to the CNT diameter. [14] These energies can be further tuned by placing them in different dielectric environments. Such excitons can be excited by light absorption, electron-hole recombination or internal impact excitation by hot carriers flowing through the CNTs. Their radiative decay leads to fast luminescence characteristics. Ambipolar CNTs can be used to form LED-like three-terminal devices without the need for external doping. Furthermore, the origin of the resulting emission can be translated along the tube at will by the gate field. Even stronger, localized EL can be excited by hot carriers under unipolar conditions. Higher-energy exciton states produce photocurrents and photovoltages that can be used for the spectroscopic identification of CNTs and to determine important device parameters, such as band-bending and Schottky barriers, or to fabricate nanoscale photodetectors. However, this is only the beginning of the study and of the application of nanotube photonics. As the production of pure CNTs advances, we expect to see applications in biology, where sensors, are nonlinear devices. Applications in biology, where CNTs are already used as fluorescent probes, photosensitizers and sensors, are expected to grow. An understanding of 1D optics, exciton localization and excitonexciton interactions would also greatly benefit from the study of these model systems.

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Appendix 1

P1 position vs I_{DS},

$$y = 1E-10x^4 - 5E-08x^3 + 1E-05x^2 - 0.001x + 0.728$$

P1 intensity vs I_{DS},

$$y = -3E-07x^4 + 0.000x^3 - 0.031x^2 + 2.502x - 63.76$$

P1 FWHM vs I_{DS},

$$y = 7E-10x^4 - 4E-07x^3 + 8E-05x^2 - 0.006x + 0.217$$

P2 position vs I_{DS},

$$y = -1E-12x^4 - 5E-10x^3 + 7E-07x^2 - 0.000x + 0.770$$

P2 intensity vs I_{DS},

$$y = -3E - 07x^4 + 0.000x^3 - 0.025x^2 + 2.085x - 54.99$$

P2 FWHM vs I_{DS},

$$y = 8E-09x^4 - 4E-06x^3 + 0.000x^2 - 0.063x + 1.809$$

Ratio of intensity vs I_{DS},

$$y = 7E-08x^4 - 4E-05x^3 + 0.006x^2 - 0.503x + 14.07$$

Ratio of area vs I_{DS},

$$y = -1E-07x^4 + 7E-05x^3 - 0.015x^2 + 1.408x - 42.01$$