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Implementation of ‘Hole confinement’ for efficient Inverted and un-doped bilayer Organic Light Emitting Diodes using a buffer layer

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Implementation of ‘Hole confinement’ for efficient Inverted and undoped bi-layer Organic Light Emitting Diodes using a buffer layer

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ABSTRACT

Organic Light Emitting Diode (OLED) technology has attracted a great deal of attention over the past ten years in the field of display and lighting. OLED have the advantage of being environment friendly, which is one of the major reasons for the large focus it is being given. The other advantages of displays made from OLEDs include low power consumption, light weight, flexibility, high brightness, high contrast, wide viewing angle and broad color gamut. The rapid growth in the field has led to efforts being devoted to improve OLED efficiency and lifetime and their compatibility. In this thesis we demonstrate improved efficiency of green and blue inverted OLEDs using the hole confining concept. Also the effect of adding a buffer layer of TPBI (1, 3, 5 - tri (phenyl - 2- benzimidazole) – benzene) to conventional green OLEDs is discussed. In the first part, the various steps involved in the fabrication of inverted green and blue OLEDs are discussed. Then the concept of hole confinement is discussed and the luminance of inverted OLEDs is improved by using BCP (Bathocuproine) as the hole confining layer. In the second part the hole confinement concept is implemented on conventional green light emitting OLED using a buffer layer of TPBI. Further, the effect of having a constant emitting layer thickness and variation of TPBI layer thickness is also discussed. Finally, suggestions for future work are offered.
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Chapter 1 Introduction

1.1 Outline

Organic Light Emitting Diodes (OLEDs) are devices made up of layers of organic materials which emit light when a voltage is applied across them. Similar to a diode, an OLED has a cathode and an anode between which the organic materials are sandwiched. Since their invention, OLEDs have received widespread attention due to their potential for applications in full color displays and solid state lighting. OLEDs offer a greener (eco-friendly) solution when compared to the current lighting and display industry. In this chapter, we give a brief history and background of OLEDs followed by a description of their potential applications and advantages over present displays and lighting sources. Then we discuss the basic operation, working mechanism and performance parameters of an OLED. The goal of the thesis is to improve the efficiency of inverted OLEDs (in which the anode is at the bottom of the stacked layer) using a hole confining layer of Bathocuproine (BCP). The effect of adding a buffer layer of 1, 3, 5 - tri(phenyl - 2- benzimidazole) - benzene (TPBI) to OLED is also investigated in this thesis.

1.2 Background

Certain materials emit light in response to the passage of electric current through them or to the application of a strong electric field across them. This electro optical phenomenon is called electroluminescence (EL). When organic materials emit light the phenomenon is called organic electroluminescence. Bernanose et al. [1] made the first report of organic electroluminescence in AC mode in 1953 following which Pope and co-workers reported single crystal anthracene based organic light emitting devices in DC mode in 1963 [2]. These single crystals were very thick and required high voltages (nearly 50 V) to be operated [3], [4]. Consequently, in 1967 AC EL was
achieved using an emissive polymer [5]. These organic crystals required high drive voltages due to their thicknesses being in the order of micrometers and millimeters. The high working voltages resulted in low device efficiencies and lifetimes when compared to the existing non-organic light emitting devices. Therefore, not much of research was focused on organic materials.

A major impetus towards research in OLEDs occurred in 1987 after Tang and VanSlyke at Eastman Kodak Company reported a device consisting of a junction between a thin layer of vacuum deposited small molecular weight hole transporting triarylamine, followed by another thin layer of electron transporting green fluorescent emitting molecule, tris(8-hydroxyquinoline) aluminum (Alq$_3$) [6]. The two thin layers were deposited on an Indium Tin Oxide (ITO) anode and a Magnesium-Silver (Mg-Ag) cathode. This device demonstrated high EL efficiency, fast response, low driving voltage and simple fabrication methods. Further impetus was given to the small molecular weight OLEDs in 1990 with the demonstration of the first PLED (polymer OLED) by the Cambridge group led by Friend and co-workers [7]. The PLED consisted of the luminescent poly (para-phenylene vinylene) (PPV) layer fabricated by using a spin coating precursor polymer onto a transparent conducting ITO anode substrate, thermally converting the precursor to PPV, and finally evaporating Al thin film as cathode. The electroluminescence was observed from PPV.

1.3 Advantages and applications of OLEDs

The major advantage of OLEDs compared to their inorganic counterparts is that the former can be fine tuned to obtain the desired emitting wavelength (color) by chemical means. The fact that organic thin films can be easily deposited on any substrates, namely glass, plastic or thin metal
foils etc by using vapor deposition techniques has been a motivation for researchers and engineers all over the world [8], [9]. The flexibility of the substrates allows the displays to be rolled up in very small volumes and is also lightweight, which is not the case with existing display mediums. The other advantages of OLED displays include high brightness, wide color gamut, printability, flexibility, faster response, low power consumption, wide viewing angle etc. The OLED displays do not require backlighting which results in thinner and lighter displays. As they emit light from only necessary pixels rather than the entire panel their power consumption is also reduced.

Applications of OLED displays include colorful cellular phone displays, full color personal communicators, low cost organic lasers, heads-up instrumentation for aircraft and automobiles, wearable electronic displays (watches), compact MP3 players, and lightweight thin laptop screens.

Two types of OLED displays are available today, namely – active matrix (AMOLED) and passive matrix (PMOLED) displays. The electrode material is deposited in a matrix of rows and columns such that a pixel at the intersection forms an OLED for both types of displays. In the passive matrix OLED display the image is created by a sequential scan of the rows and columns. Where as in an active matrix display there is an electronic backplane integrated to each pixel to obtain high resolution and each pixel (OLED) contains a thin film transistor (TFT) in series with it. These TFTs have high switching speeds and high current carrying capacity, which is used to control the brightness and current flowing through the OLED [10].

Pioneer Electronics introduced the first major commercial application of passive matrix OLED display for the front panel display of a car in 1997. After which there have been many AMOLED
and PMOLED displays reported by various companies around the world as recently reviewed by Becker et al. [11] and Young [12]. Companies such as LG, Samsung, and Motorola have commercialized various cellular phone displays using PMOLED and AMOLED displays. Eastman Kodak-Sanyo commercialized the first digital camera Kodak Easy Share LS633 having a full color AMOLED display. Sony then introduced the XEL-1 an 11-inch, 3mm thick AMOLED high-resolution digital television for commercial purposes. Samsung has also showcased a larger OLED TV measuring 31-inches and 4.3 mm with AMOLED display. It has also announced the development of a prototype 40-inch, OLED based TV and a 12.1-inch AMOLED display laptop screen.

In addition to displays, OLEDs also have enormous potential for solid state lighting applications, where the market is driven by brightness, low power consumption, thinness and wide gamut of colors. Rapid advances have been made in the field of Solid state lighting with OLEDs also. Green molecular PHOLEDs with peak efficiencies up to 70 lm/W have been reported in early 1990s. Currently many companies are working on producing commercially viable solid state lighting using OLEDs. Universal Display Corporation has already reported an OLED with an efficiency more than 100 lm/W. Moreover, OLED being self emitting light sources the need for fixtures and diffusers to reduce glare and dissipate heat is avoided. The highest polymer OLED efficiency are approximately 20% because the OLED efficiencies are measured for devices on flat glass substrates, where the maximum out-coupling obtained is only 20%. The matching up of the external efficiencies with the internal efficiencies is a significant challenge remaining for OLEDs. When a solution to this is achieved with a low cost method, OLEDs would become the most efficient light source available. The OLED market has grown by 63% from US $84 million
in 2001 to US $1.7 billion in 2007 [13]. Nanomarkets have forecasted the revenue in OLEDs to reach the US $6 billion by the year 2015.

1.4 Basic operation of an OLED

The first bi-layer organic light emitting diode was reported by Tang and Van Slyke. This revolutionized the field of organic electroluminescence [6]. It had a simple structure which consisted of the transparent anode - ITO, a hole transport layer (HTL) deposited on top of the anode, an electron transport/emitting layer (ETL/EL) deposited on top of the HTL and a metal cathode as shown in Figure 1-1. The HTL and the ETL/EL were deposited by thermal evaporation. In the basic operation mode of the bi-layer OLED, when forward biased, the holes are injected from the transparent anode into the HTL and the electrons are injected from the cathode into the ETL/EL, similar to that of the operation of a p-n junction diode. There exists a triangular barrier for the injection of holes as well as electrons form the anode and cathode to the HTL and ETL, respectively. These injected carriers then move through the organic layers and recombine at the heterojunction of the two organic layers to form excitons. These excitons radiatively decay to release energy in the form of photons thus producing light.

The energy band diagram of a bilayer OLED consisting of a HTL and an ETL is shown in Figure 1-2; where \( E_f \) denotes the Fermi Energy level for the electrodes. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is analogous to the valence band and the conduction band in semiconductors, respectively.
Figure 1-1: Cross section of the first bi-layer OLED reported by Tang and Van Slyke [6]. The hole transport and electron transport layer are sandwiched between the anode and cathode.

Figure 1-2: Energy band diagram of a simple bilayer OLED under biased condition. The HUMO and LUMO levels are bent because of biasing, and the carrier recombination and light emission occurs at the ETL/HTL interface.
1. 5 Working Mechanism of an OLED

The electronic structure of thin films is based on the HOMO and LUMO levels of individual molecules. The weak Van der Waal forces between the molecules causes the conduction and the valance band to narrow out. The electronic structure can be described using the ionization potential \( I_p \), electron affinity \( E_a \), charge carrier densities and the mobilities. The energy from the HOMO level of the molecule to the vacuum level is the ionization potential. Similarly the energy from the LUMO level of the molecule to the vacuum level is the electron affinity of the molecule. The ionization potential and the electron affinity influence the charge injection property of the molecule while the charge carrier density and the mobility influence the charge transport property. The intrinsic carrier densities and mobility of organic semiconductors are around \( 10^5 - 10^{10} / \text{cm}^3 \) and \( 10^{-3} \text{ cm}^2/\text{Vs} - 10^{-7} \text{ cm}^2/\text{Vs} \) [4]. The disorders and traps in the small molecule due to the defects and impurities in amorphous thin films are attributed to such low values of carrier densities and mobilities. Though these properties seem unfavorable at first, the ability to fabricated ultra thin films of these organic semiconductors has led to their widespread use. Due to the very small thickness of thin films (order of nanometers and angstroms), when a small voltage of \( 5 - 10 \text{ V} \) is applied a very high electric field is produced. This high electric field induces carrier injection and space charge limited current. The working mechanism of an OLED consists of carrier injection, carrier transport, recombination and emission.

1. 5. 1 Carrier Injection

There are basically two possible mechanisms to inject charge carriers into the organics:

1) Schottky thermal injection,

2) Fowler-Nordheim Tunneling injection.
**Schottky thermal injection**: The Schottky thermal injection is described by Eq. (1.1) and Figure 1-3 [14],

\[ J = \frac{4\pi q m k^2 T^2}{\hbar^3} \exp \left( -\frac{q \Phi_{Bn}}{kT} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right] \quad (1.1) \]

Where \( m \) is the effective mass of the electron (hole), \( k \) is the Boltzmann’s constant, \( h \) is the Planck’s constant, \( T \) is the temperature in Kelvin, \( q \) is the elementary charge, \( \Phi_{Bn} \) is the barrier height and \( V \) is the applied voltage.

![Diagram of Schottky injection](image)

Figure 1-3: Schottky type carrier injection via impurity of structural disordered levels with thermal assistance [4].

The injection mechanism is through the structural defects and the impurities present in the molecule, as shown in Figure 1-3. When thermal assistance is present, the injection of carriers takes place through structural disorders and impurities. Once a contact is established between the electrode and the organic, an initial injection of electrons from the electrode into the organic trap sites take place resulting in the formation of an image force potential. This potential is formed due to the Coulomb attraction between the electrons and the holes left behind in the metal. This
potential lowers the energy of the interface barrier height thus rendering them energetically available for the hopping of charges form the Fermi level. This image force potential varies as a function of the distance from the electrode and reduces as we move towards the bulk of the organics. In order to make the bulk of the organics also energetically available for charge hopping an external electric field is applied so as to lower the energy of the available states in the bulk.

**Fowler-Nordheim Tunneling Injection:** Carrier injection is described using Fowler-Nordheim Tunneling injection as shown in Figure 1-4. Electrons from the metal Fermi level can tunnel through the thin triangular energy barrier and hop into the energetically available state in the bulk of the organics in the presence of an electric field due to band bending. The total current injected in this case is given by the Eq. (1.2) [14].

\[
J = \left( \frac{q^2 V^2 m_0}{8 \pi h m^* \Phi_{Bn}} \right) \exp \left( \frac{-8 \pi (2m^*)^{0.5} \Phi_{Bn}^{1.5}}{3h q V} \right),
\]

(1.2)

where \(m_0\) is the mass of free electron and \(m^*\) is the effective mass, \(q\) is the elementary charge, \(\Phi_{Bn}\) is the barrier height and \(V\) is the applied voltage.

### 1. 5. 2 Carrier transport

In an OLED, carriers are transported across the organic layers through charge hopping under the influence of an electric field [4]. The charge transport in organics can be divided into four different regimes: namely,
Ohmic carrier transport: When the applied electric field is typically very low (less than $10^4$ V/cm) and the injected carrier density is less than the intrinsic carrier density, then the current flow is limited by the contact interface between the electrodes and organic layers. The current flow is governed by Ohm’s law.

Space-charge carrier transport: As the applied electric field increases, the injected carrier density exceeds the intrinsic carrier density. Thus more holes are injected from the anode into the HTL and electrons form cathode into the ETL, respectively. These holes and electrons drift or hop across the HTL and ETL and reach the internal interface. Here, as the mobility of the holes
in ETL and electrons in HTL is low in the order of $10^{-5}$ to $10^{-3}$ cm$^2$/Vs, accumulation of the carriers at the interface takes place. This accumulation causes a charge buildup. Thus the injected carriers form space charges which enhance the internal electric field. The current density is now described by Eq. (1.3) [14]

$$J = \frac{9\varepsilon\mu V^2}{8L^3},$$  \hspace{1cm} (1.3)$$

where $\varepsilon$ is dielectric constant and $L$ is the sample thickness. $I$ - $V$ curves are super linear, quadratic in the absence of traps, a characteristic of space charge limited current (SCLC). The SCLC type mechanism is generally found to rule the conduction in devices where strong injection is achieved from both electrodes.

**Trap charge limited carrier transport:** When traps are present, typically due to impurities and defects in the organic films, the current is lower and the quadratic dependence is present only when the traps are filled. When the electric field increases the traps start getting filled up and the current tends to increase faster. The current now follows a high exponent power law $I \alpha V^\alpha$, where ‘$\alpha$’ (the disorder parameter) varies from 7 and 9 [15],[16]. This current is referred to as trap charge limited current.

**Trap filled space charge limited carrier transport:** After all the traps in the organics have been filled by carriers, the additional carriers are free to move in the presence of space charge effects only, without any influence form the trapped charges. This is called trap filled space charge limited carrier transport regime [15].
1. 5. 3 Carrier recombination and emission process

The transported electrons and hole recombine in the emitting layer via Coulomb interaction to form excitons [2]. They are also called ‘neutral excited species’. This recombination of electrons and holes generate two types of excitons, namely: Singlet and Triplet excitons. Anti-parallel spin pairs recombine to form singlet excitons (SE) and parallel spin pairs recombine to form triplet excitons (TE). Singlet excitons decay to emit photons in fluorescent OLEDs while both singlets and triplets decay to emit photons in phosphorescent OLEDs. Spin statistics reveal that the singlet to triplet formation ratio is 1:3 [17].

\[
4 \text{e} + 4 \text{h} \rightarrow 1 \text{SE} + 3 \text{TE} \quad (1.4)
\]

Our research is only on undoped fluorescent OLEDs; hence we focus on the formation of singlet excitons which are the source of light emission in our OLEDs.

1. 6 Efficiency of OLEDs

There are various performance parameters for OLEDs such as Luminance, Radiance, Lifetime, External quantum efficiency, luminous efficiency, radiance efficiency, etc. Of these parameters efficiency is a key parameter which indicates both energy consumption and durability of the device. A low I-V product for a given luminance would indicate that the power consumed is less, in turn implying a lower ohmic heating and better life.

The three principal efficiency measurements for an OLED are [18]

1. External quantum efficiency,
2. Luminous efficiency,
3. and Power efficiency.
1.6.1 External quantum efficiency

External quantum efficiency (EQE) is defined as the number of photons emitted through the front face of the device per injected electron [4]. In other words, it is the ratio of the photons to electrons. The number of electrons is taken into consideration while calculating the efficiency since they are the limiting factor. This is due to the fact that the mobility of holes is higher than that of electrons in organics. The equation for external quantum efficiency is written as follows

\[ \eta_{EL} = \varepsilon \gamma r_{ST} \eta_{PL} \]  

(1.5)

where \( \eta_{EL} \) is the external quantum efficiency, \( \varepsilon \) is the out coupling efficiency, \( \gamma \) is the charge balance factor, \( r_{ST} \) is the ratio of singlet excitons to triplet excitons and \( \eta_{PL} \) is the photoluminescence quantum yield [4]. Our goal is to maximize the efficiency, which requires each term in Eq. (1.5) to have maximum value.

**Out coupling efficiency (\( \varepsilon \)):** It is the ratio of the number of photons that are emitted from the surface of the device to the number of photons generated inside the device. Photons are lost due to self absorption in the organic layers, wave guiding within the device, and absorption by the cathode. This factor plays a major role in the loss of the external quantum efficiency of the device. The out-coupling efficiency is given by Eq. (1.6). (For a first degree approximation) as follows

\[ \varepsilon = 0.5/n^2 \]  

(1.6)
where ‘n’ refers to the refractive index of the emitting layer [19]. For typical materials the value of n is 1.7 which limits the value of ε to 0.17 or 17%. Thus, implying that more than 80% of the light emitted is lost due to internal reflection. This places a maximum limit of 20% on the EQE of the device. Methods such as a micro array of lenses, reflective surface, distributed Bragg reflectors are being investigated to improve the out-coupling efficiency.

**Charge balance factor (γ):** It is the measure of the number of electrons to the number of holes present in the device and their probability of recombining. The maximum and ideal value of γ is unity (every electron recombining with a hole). This factor can be optimized by varying the composition and/or thickness of the ETL and HTL and by monitoring the I–V curves [17]. The devices in this thesis were designed to improve the charge balance factor by the introduction of hole confining layers so as to balance out the number of holes and electrons in the emitting layer.

**Singlet excitons to triplet excitation ratio (r_{ST}):** As described earlier, the electron hole pairs that recombine tend to generate both singlet and triplet excitons. Spin statistics demand that the ratio of singlets to triplets be 0.25. In this thesis, we focus only on undoped fluorescent OLEDs and thus the r_{ST} is limited to 0.25. It should also be noted that the photon formation is only due to the radiative decay of singlets. Thus the EQE is also limited by one fourth due to spin statistics.

**Photoluminescence quantum yield (η_{PL}):** It is the measure of the radiative yield of the singlet excitons. Many dyes exhibit η_{PL} of 100%, but their yield drops as the concentration of the dye is increased in solid state devices. This is attributed to the “concentration quenching” effect due to the creation of non-radiative decay paths. PL as high as 60% have been reported till date.
1. 6. 2 Luminous efficiency

It is defined as the ratio of the luminance (cd/m$^2$) to the current density (A/m$^2$). The unit of luminous efficiency is cd/A. The cd/A value is widely used in the OLED display industry for characterizing and determining the OLED performance. The luminous efficiency acts as a gauge for the influence of current on the device performance. The luminance efficiency is a photometric unit and not a radiometric one. Photometry is the measure of the light in the visible spectrum. It depends upon the spectral response of the eye.

\[
\text{Luminance Efficiency} = \frac{\text{Luminance}}{\text{Current Density}}
\]  
(1.7)

1. 6. 3 Power efficiency

It is defined as the ratio of the light output in lumens to the electrical power in Watts. The derived unit is lm/W. It is more widely used for OLED solid state lighting applications. A typical incandescent bulb has a power efficiency of 15 lm/W while a fluorescent bulb has nearly 60 lm/W. White OLEDs with power efficiency of 100 lm/W have been demonstrated.

An important factor that needs to be accounted in the measurement of efficiency is that the OLED is a Lambertian emitter, i.e., the intensity observed form the surface of an OLED is directly proportional to the cosine of the angle between the observer’s line of sight and the surface normal. Thus, a more rigorous model has to be constructed to account for the device geometry, reflection of light from cathode, finite thickness of glass, total internal reflection at the glass-air interface, etc, for the proper measurement of the efficiency [20].
1. 7 Types of OLEDs

There are various ways of classifying OLEDs: based on the number of layers they are classified as single layer, bilayer or multilayer OLEDs. Based on the excitons causing emission of light, they are classified as fluorescent (only singlets emitting) and phosphorescent (both singlet and triplet emitting) OLEDs. Based on the order in which the materials are deposited on the substrate they are classified as conventional OLED (anode in contact with substrate) and inverted OLEDs (cathode in contact with the substrate).

1. 7. 1 Conventional OLEDs

These are the most common type of OLEDs fabricated. In this type of OLED the anode is in contact with the substrate. They are also known as bottom emitting OLEDs. The light is emitted from the bottom layer of the structure; generally a transparent layer of ITO is used as the transparent substrate. Plastic and glass are other materials used as transparent substrates. The organic layers are then deposited on the transparent layer, and then a highly reflective cathode layer is deposited. The most widely used cathode material is aluminum. Silver and Magnesium are the other materials used for cathode. Figure 1-5 shows the cross section of a conventional (bottom) emitting OLED.
In this type of OLED the cathode is in contact with the substrate instead of the anode like a conventional OLED. The organics are then deposited in the reverse order to that of the conventional OLED and finally the anode is deposited on top of the organics. Figure 1-6 shows the cross section of an inverted OLED. In this thesis, we fabricate and characterize some inverted OLEDs. Inverted OLEDs are beginning to play a very important role in the ever developing display industry. They are used in AMOLED displays due to the fact that they allow easy integration with n-type thin film transistors (TFTs).
Figure 1-6: Cross section of an inverted OLED. Cathode is in contact with the substrate, with the organic stack (ETL, HTL) deposited on top of it and then the anode.

1.8 OLED structure design

After the development of the bi-layer OLED by Tang and VanSlyke in 1987 [6], significant research work has been carried out to enable a better understanding of the device physics which has subsequently led to improvements in structure of OLED producing an improvements in their performance. The most significant aspect is the multilayer structure consisting of the ETL, HTL, hole blocking layer, and electron blocking layer. With the appropriate placement of these additional layers the charge carriers have been confined in the emitting layer and carrier injection and transport have been balanced [21]. In addition to carrier confinement, the multilayer structures further help in keeping the energy of the molecular excitons from dissipating into the metal electrodes [4]. Advanced multilayer structured OLEDs have multiple hole/electron transport layers, where each layer has a specialized carrier injection or transport property and the
charge carriers encounter smoother energy barriers. Taking these into consideration we have designed OLEDs in this thesis using multilayered structure consisting of hole injecting layer, hole/electron transport layer and hole blocking layers to implement the ‘hole confining’ concept. The device structure is described in detail in the following chapters.

1.9 Thesis outline

In the above sections, we discussed the operating mechanism, the device physics governing the carrier injection, transport, recombination and emission process and the various efficiencies that are used in evaluating the OLED performance. Researchers all over the world are striving to improve the device performance as the demand for high efficiency OLED is continually on the rise to meet the requirements of display and lighting industry. In this thesis, we report an improvement in the efficiencies of undoped inverted green and blue emitting OLEDs. The mobility of holes in hole transport layer is higher than that of electrons in the electron transport layer [22]. If we could reduce the hole mobility and confine them in the emitting region, the efficiency can be improved. This idea of ‘hole confinement’ was suggested by K. Garre, a former Ph.D student of Dr. Cahay [23]. This concept of hole confinement was studied by S. H. Mohan [24] and N. K. Bhandari [25] using BCP on green light emitting OLEDs and by A. Rakurthi on white light emitting OLEDs [26]. In this thesis, Inverted OLEDs implementing the hole confining concept were fabricated and tested in Dr. Cahay’s Spintronics and Vacuum Nanoelectronics Laboratory. Also the concept of hole confinement using TPBI as the hole blocking buffer layer was studied by fabricating and testing green light emitting diodes at Universal Display Corporation. The rest of this thesis is mainly divided into three chapters.
Chapter 2 consists of two parts. The first part describes the various steps involved in the fabrication of inverted OLEDs in Dr. Cahay’s lab. These include preparation of the ITO substrate and the various steps involved in it and then the vacuum thermal evaporation of the various layers of the inverted OLED. The second part of this chapter describes the concept of hole confinement in detail. The experimental results for green and blue light emitting inverted OLEDs based on the concept of hole confinement using BCP as the hole blocking layer.

In Chapter 3, the electric field profile in a bilayer OLED is discussed. Following which the experimental results for undoped green light emitting OLEDs fabricated at Universal Display Corporation, implementing the concept of hole confinement using a buffer layer of TPBI as the hole blocking layer is discussed. It is divided into two parts. First the experimental results for devices with varying thickness of the TPBI buffer layer are presented. Then the experimental results for devices having a constant emitting layer thickness are discussed.

In Chapter 4, we present our conclusions and suggest a few possibilities for future work.
Chapter 2 Fabrication of inverted OLEDs using Hole confinement concept

2.1 Outline

This chapter outlines the various steps involved in fabricating inverted OLEDs and explains the concept of ‘hole confinement’ and its implementation in inverted OLEDs. In the first part of the chapter, the device structure, material selection and the fabrication procedure of inverted OLEDs are described. In the second part, the ‘hole confinement’ and its implementation are discussed in detail along with the experimental results for green and blue emitting inverted OLEDs.

2.2 Device Structure and Material Selection

K. Garre [23] and P. Draviam [27] were the first students in our lab to replicate the small molecule OLED similar to the one reported by Tang and VanSlyke [6]. The OLED structure they used was ITO/TPD/Alq3/Al. This was a basic bi-layer device. They also used structures with LaS or Al – LaS bi-layer cathodes. The material used as the anode was a thin layer of Indium Tin oxide (ITO) on a glass substrate. ITO is the most widely used anode material owing to its superior electrical and optical properties. It is transparent in the visible region of the electromagnetic spectrum, thus enabling the light to come out of the OLED. Furthermore, ITO assists in easy injection of holes into the OLED as it has a high work function of 4.7eV. The work function of ITO is dependent on its oxygen content and can be varied by varying the amount of oxygen. A maximum work function of 5.1eV can be achieved this way [28], [29]. The most widely used material for the cathode is Aluminum, because of its low work function of 4.3eV. This promotes electron injection from the cathode into the OLED. The anode and the
cathode sandwich the organic layers which consist of the hole transporting material, electron transporting material and the emitting layer. TPD (N, N’-diphenyl-N, N’-(3-methyl phenyl)-[1, 1’-biphenyl]-4, 4’-diamine) is the most popularly used hole transport layer. It has a hole mobility of \((1-2 \times 10^{-3} \text{ cm}^2/\text{Vs})\) [30]. Alq\(_3\) (8-hydroxyquinoline aluminum salt) is used as the electron transporting material as well as the emitting layer. It has an electron mobility of \(1.4 \times 10^{-6} \text{ cm}^2/\text{Vs}\) [31]. The (HOMO, LUMO) levels of TPD and Alq\(_3\) are \((5.4\text{eV}, 5.7\text{eV})\) and \((2.2\text{eV}, 3.1\text{eV})\), respectively. There exists a barrier for both electrons and holes at the interface of TPD and Alq\(_3\), as seen in Figure 2-1. The electrons and holes tend to recombine at this interface forming excitons. These excitons undergo radiative decay and emit a photon. The wavelength of the emitted photon in this device is near 520nm, which falls in the green region of the visible electromagnetic spectrum. The emission in the green region is due to the presence of the Alq\(_3\) layer.

This structure was modified by implementing a bi-layer cathode consisting of Lithium Fluoride /Al in place of Al. A thin layer of LiF of the order of few angstroms before the Al is found to enhance electron injection [32]. The LiF layer pulls the vacuum level down, thereby lowering the work function of the cathode to 3.5eV. In this work, the materials were deposited in reverse order on the ITO substrate to fabricate an inverted OLED. Thus the Al/Liq bilayer cathode was deposited first on the ITO substrate followed by the emitting layer (Alq\(_3\)), and the hole transport layer (TPD).

Y. Lee et al. [33] have demonstrated an inverted OLED with the structure ITO/Al/Liq/Alq\(_3\)/NPB/WO\(_3\)/Al. They have shown that Al/Liq can be used as an electron injection layer for inverted OLEDs. The inverted OLEDs with Al/Liq showed improved performance compared to ITO/Al or ITO/Mg cathode. Al/Liq along with Alq\(_3\) was found to
reduce the electron injection barrier by 0.91eV, thus, helping in better electron injection and producing better luminance.

![Flat band energy diagram of a basic ITO/TPD/Alq3/Al device](image)

Figure 2-1: Flat band energy diagram of a basic ITO/TPD/Alq3/Al device

For the light to come out of the top of device a very thin layer of Aluminum is deposited on the hole transport layer. This layer of Aluminum is made as thin as possible so that the transparency of the device is not lost. Since this thin layer of Aluminum is damaged while making contacts, an additional thicker layer of Aluminum is deposited on top of it so that contacts can be made using this layer without damaging the transparent layer. Instead of Aluminum, Silver can also be used as the transparent layer. However, Silver tends to oxidize rapidly when exposed to atmosphere than aluminum. The flat band energy diagram of the modified structure,
ITO/Al/LiF/Alq₃/TPD/Al for the inverted OLED is shown in Figure 2-2. In this device Alq₃ is the emitting layer. This device emits green light and is used as the control device in this thesis.

When the Alq₃ layer is replaced by BCP, the device emits in the blue region of the electromagnetic spectrum due to the excitons being confined in the TPD layer. Thus the control device for an inverted blue emitting OLED has the following structure, ITO/Al/LiF/BCP/TPD/Al/Al. The flat band energy diagram of the inverted blue emitting OLED is shown in Figure 2-3.

For the hole confining experiment on the inverted green OLED, a thin layer of BCP was incorporated before TPD layer. The reason is that a thin layer of BCP would partially block holes and further improve hole confinement. In addition to this, since the mobility of holes is greater than the mobility of electrons in organics, we inserted another layer of BCP before the emitting layer of Alq₃ so as to confine the fast moving holes within the emitting layer. Thus the final structure of the inverted OLED is as follows: ITO/Al/LiF/BCP/Alq₃/BCP/TPD/Al. The hole confining structure is explained in detail in the later part of the chapter.

For the hole confining experiment on inverted blue emitting OLED, the TPD layer was confined between two BCP layers. Thus the final structure of the inverted OLED is as follows: ITO/Al/LiF/BCP/TPD/BCP/Al.
Figure 2-2: Flat band energy diagram of an inverted green OLED, ITO/Al/LiF/Alq3/TPD/Al which is used as the control device in our experiment.

Figure 2-3: Flat band energy diagram of an ITO/Al/LiF/BCP/TPD/Al inverted Blue emitting OLED used as the control device in our experiment.
2. 3 Fabrication Procedure

The inverted OLEDs fabricated in our lab have the generic form, ITO/Al/LiF/organic stack/Al (for transparency)/Al (for contact). The different fabrication steps required to fabricate these inverted OLEDs are

1) Substrate preparation,

2) Thermal evaporation of cathode,

3) Thermal evaporation of organics,

4) Defining the emitting area using shadow masks and formation of the contact layer

We will now consider each of the processes individually in greater detail.

2. 3. 1 Substrate Preparation

As already mentioned in section 2.2, ITO has widely been used as the anode in OLEDs. ITO thin films deposited on float glass were purchased from Delta Technologies, Inc. in Minnesota. A 1200Å thick film of ITO was e-beam evaporated on to a thick glass substrate. This deposition was preceded by application of a passivation layer of SiO₂. The nominal sheet resistance of the delivered substrates was between 30 - 60 Ω/sq.

Substrate preparation and surface treatment includes three main processes namely:

a. Substrate cutting,

b. Etching,

c. and Cleaning
2. 3. 1. 1 Substrate Cutting

A 3 inch by 2 inch ITO coated glass was cut into four 1.5 inches by 1 inch substrates using a diamond scriber. The “scribe and break” method was used to cut the substrates. The scribing was done on the glass side so as to prevent the creation of roughness on the ITO surface which could lead to shorts or degradation in the performance of the OLED. After cutting the substrates were washed in running de-ionized (DI) water for a couple of minutes to wash out any minute glass residue and then dried using 99.9% pure nitrogen gas (N\textsubscript{2}) using a blower.

2. 3. 1. 2 Etching of ITO substrates

![Figure 2-4: Kapton tapes stuck on ITO substrate for selective etching of ITO](image-url)
The substrates were selectively patterned in order to clearly define the area for the anode and cathode of the device. Kapton tape was used for the patterning of the ITO substrates. The tapes are stuck as shown in Figure 2-4. The etching of the substrates is performed by immersing them in a solution consisting of 20% HCl and 5% HNO₃. The solution is heated to a temperature of 55°C and the substrates are left in the etching solution for a period of 6 minutes. The etching process is carried out in an acid resistant container under a fume hood. After the etching process the substrates are removed and rinsed thoroughly with DI water. The etched substrate is shown in Figure 2-5. The resistance of the etched regions is measured using a digital handheld multimeter. The complete etching of the ITO is indicated by a very high resistance. In case of any marks left by the Kapton tape on the substrate, it is removed by scrubbing it with detergent solution. The substrates are then cleaned using DI water to remove any detergent left on it.

Figure 2-5: Picture of the etched ITO substrate with a ‘T’ shaped pattern
2. 3. 1. 3 Substrate Cleaning

The etched substrates have to be cleaned before thermal evaporation can be done. The cleaning is done by immersing the etched substrates in a 20% solution of ethanolamine in de-ionized water. The solution is heated to a temperature of 80°C in an ultrasonic bath. The solution is placed on a stir/hot plate and magnetic stir bars are used to achieve homogeneity in the solution by heating and spinning. The substrates are immersed in the solution for 10 – 15 minutes while maintaining the temperature. The substrates are then washed using DI water and then dried using 99.9% pure nitrogen gas. These substrates are then used for the fabrication of OLEDs or stored in a glove box for future use.

2. 3. 2 Thermal evaporation of Cathode

The deposition of the cathode is done in a vacuum chamber using a Revap-3000 resistive heating unit from MDC Vacuum Products, Inc. A schematic of the vacuum chamber is shown in Figure 2-6 and a photograph of the chamber is shown in Figure 2-7. The etched ITO substrate is mounted on the substrate holder facing downwards towards the heating electrodes. The substrate holder with the substrate is placed vertically above the cathode source. The distance of separation between them is around 15 cm. The substrate is mounted on the holder with the help of a molybdenum strip, which can be loosened by unscrewing. The substrate is then inserted beneath the strip and the screws are tightened to hold it in position. The strip acts as a mask for the substrate from the deposition of the cathode. Figure 2-8 shows the substrate placed in the substrate holder and held by the molybdenum strip which also acts as the mask. After loading the substrate the chamber is closed and pumped down to a pressure of 2x10^{-6} Torr. The regeneration and operation procedure of the vacuum chamber is detailed in the appendix. An Al/LiF bilayer
cathode is used. The Aluminum evaporation is done using a thin wire of aluminum one inch long placed on a tungsten coil. The LiF crystals are powdered and placed in an alumina oxide crucible with tungsten filaments purchased from R. D. Mathis Company. The bi-layer cathode is then deposited by firing up the resistive Revap-3000 unit. After the deposition of Aluminum layer, one of the lead connections to the electrode is manually removed and connected to the other electrode to allow the heating and deposition of the LiF layer. The copper leads are accessed through feedthroughs on the bottom plate of the bell jar. The shifting of the lead from one electrode to another takes a couple of minutes. The thicknesses of the thin films deposited are monitored using a crystal rate monitor, which is installed in the bell jar and is connected externally to the Revap – 3000 unit. The amount of power applied, the rate of deposition in Å/sec, the thickness in Å, and the plot of percentage power vs. time are all controlled using the Revap thickness control monitor.

2.3.3 Thermal evaporation of Organics

The next step in the fabrication of the inverted OLED is the deposition of the organic layers. After the cathode has been deposited the chamber is brought down to atmospheric pressure to load the organics. In order to lower the amount of contaminants, the loading should be done as quickly as possible. The organic materials to be deposited are held either in a molybdenum boat or a crucible. The molybdenum boats were purchased from R. D. Mathis Company. Crucibles have the advantage of better deposition control over molybdenum boats. Molybdenum boats are used for the evaporation of TPD and crucibles are used for the evaporation of BCP and Alq₃. The thermal evaporation of BCP and Alq₃ need better deposition control, hence crucibles were chosen for holding them. The organics are then deposited in the following order: BCP/Alq₃/BCP/TPD.
Figure 2-6: Schematic of vacuum chamber and Revap-3000 configuration used to deposit various materials. The latter is sandwiched between two copper leads conducting a current provided by a power supply located outside the vacuum chamber [23], [24], [27].
After the cathode has been deposited the chamber is brought down to atmospheric pressure to load the organics. In order to lower the amount of contaminants, the loading should be done as quickly as possible. The leads are shifted from BCP to Alq$_3$ and again back to BCP and then to TPD, so as to obtain the hole confining structure.

Figure 2-7: Picture of Revap-3000 resistive heating unit showing lead connections to the molybdenum boat and the tungsten filament with the crucible boats that house the organic materials. When a high enough current is passed between the leads, the boat eventually starts glowing due to resistive heating. The Revap-3000 unit can be used to evaporate substances with melting point approaching 1700°C [24].
Figure 2-8: (a) Schematic and actual picture of the molybdenum strip that acts a mask for cathode and organic deposition. (b) The shaded area represents the cathode and organics deposited regions

2.3.4 Defining emitting area using shadow mask & formation of contact layer

The next step is to define the emitting area of the inverted OLED. For this a shadow mask is placed on top the deposited organic layers as shown in Figure 2-9 and Figure 2-10. The shadow mask is made from a molybdenum sheet and is patterned to cover the entire substrate, except for two strips about 0.75 inch long and 0.5 cm wide evenly spaced in order to define two emitting area for two separate inverted OLEDs. The molybdenum strip present on the substrate holder is also used as a shadow mask on the other side of the substrate such that the effective exposed region is square shaped having an area of 0.25 cm$^2$ as shown in Figure 2-10. This being a manual
step also involves the pumping down of the chamber. This has to be done as quickly as possible to avoid contaminants. The emitting area is deposited with a thin transparent layer of Aluminum as before using a tungsten coil and an inch long Aluminum wire. This transparent layer is needed so as to allow the light emerging from the inverted OLED to come out. The anode contact is made by depositing another thick layer of Aluminum in contact with a small part of the thin layer such that it is away from the defined emitting area and does not cause a short in device. This additional thick layer of Aluminum is used in order to avoid the damaging and puncturing of the transparent layer of Aluminum due to the sharp contacts from the electrode. This is done by bringing the chamber back to atmospheric pressure again and replacing the shadow mask with another one having a rectangular cross section cut at the edges as shown in Figure 2-11 and Figure 2-12, so that the defined emitting region is now masked. Once the evaporation is done, the device is tested or transferred to a nitrogen glove box so as to minimize the exposure to humidity and atmospheric oxygen. The operation of the glove box and its regeneration are described in the appendix. The schematic of the final device is shown in Figure 2-13.

Figure 2-9: Picture of the shadow mask used to define the device area
Figure 2-10: Schematic representation of the shadow mask placement for defining emitting area.

Figure 2-11: Picture of the mask used to define the contact region
2.4 Concept of Hole Confinement

One of the main parameters in the performance of an OLED is its efficiency. With the increasing number of applications in the OLED industry the improvement in efficiency plays an important role for the devices. As stated before, for small molecule OLEDs, the mobility of holes in a hole transport layer is generally higher than the mobility of electrons in the electron transport layer. For example, in our green emitting device with structure ITO/Al/LiF/BCP/Alq$_3$/BCP/TPD/Al/Al reports indicate that the hole mobility in TPD is $1-2 \times 10^{-3}$ cm$^2$/Vs, while the electron mobility in BCP (used here as the emission layer/electron transport layer) is $6 \times 10^{-7}$ cm$^2$/Vs [34]. Also the electron mobility in Alq$_3$, one of the widely used electron transport layers, is about $1.4 \times 10^{-6}$
cm²/Vs [31]. This mismatch in the mobility of holes and electrons results in one charge carrier moving faster through the device than the other, thus inducing hole leakage towards the cathode before the electron reaches the hole transport layer. This hole leakage causes a reduction in the efficiency of the device. For the devices to have better efficiency, the charge balance factor $\gamma$, (i.e., the probability of every injected hole recombining with an injected electron in the emitting layer) should ideally be unity. One possible solution would be to improve the structure of the device such that the hole mobility is reduced before they reach the emitting layer, so that effective hole – electron recombination would take place thus improving the efficiency. Furthermore, if the hole could be held captive in the emitting layer after reaching there, an enhancement in the recombination can be obtained. This enhancement would lead to improved charge balance factor ($\gamma$) in turn improving the efficiency of the device. This concept of hole confinement was suggested by K. Garre of our lab [23].

The concept of hole confinement has been studied by S. H. Mohan, N. K. Bhandari and A. Rakurthi in our lab, for undoped green and white OLEDs, respectively [24], [25], [26]. Their combined studies have shown an improvement of 15 % for an undoped green OLED and a 13.5% improvement in the efficiency of white OLED with optimized device structure [24], [25], [26].

In this thesis, we have studied whether the concept of hole confinement can be implemented for inverted green and blue emitting OLEDs to improve the luminance and efficiency of the device.
Figure 2-13: Final device after deposition of contact layer of Aluminum on the transparent layer.

The orange shaded region is the contact layer used as the anode. The emitting area is represented by the blue and green region. Since the grey region is formed by a thin transparent layer of Aluminum, the light comes out from the top. The OLED in this case is called a top – emitter.

### 2.5 Hole Blocking nature of BCP

BCP has widely been used as a hole blocking layer in OLEDs. The molecular structure of 2, 9 – Dimethyl-4, 7 – diphenyl -1, 10-phenanthroline-Bathocuproine (BCP) is shown in Figure 2-14.

Figure 2-14: Molecular structure of Bathocuproine BCP, source: www.sigmaaldrich.com
Previous studies report the HOMO level of BCP from 6.4 to 6.7 eV [35], [36] and LUMO levels at 3.2 eV [37]. The important feature of BCP is its deep HOMO level due to its large ionization potential. Kijima demonstrated a blue OLED with BCP as the hole blocking layer [38]. Following this work, O’Brien et al. demonstrated highly efficient electro phosphorescent diodes by incorporating the hole blocking BCP between the emitting layer and the electron transport layer [39]. Since BCP has a large ionization potential compared to Alq3, it blocks the passage of holes out of HTL. When placed between a doped HTL and an Alq3 ETL, it was found that light originated from the HTL suggesting that the LUMO of BCP freely allowed the transport of electrons resulting in the formation of excitons in the HTL. The inference from the experiment is that BCP blocked holes and also confines excitons in the emitting layer. Since then, several reports of BCP being used as a hole-blocking layer to effectively confine excitons in the emitting region have been made [35]. Wang et al. studied the multiple roles of BCP incorporated as a buffer layer before the aluminum cathode [40] and reported that for very thin layers of BCP, the improvement in the electron injection will lead to improvement in the performance of the OLEDs. For thicker layers of BCP, the improvement in the electron injection, hole-blocking and electron-transporting will be a function of BCP.

2.6 Inverted OLEDs with proposed hole confining structure

As seen in Sec 2.2, the structure of the control device is ITO/Al/LiF/Alq3/TPD/Al/Al for a green emitting inverted OLED. Since BCP can be used as a hole blocking layer, the addition of a thin layer of BCP between the HTL (TPD) and the EL (Alq3), as shown in Figure 2-15, would create a barrier for the transportation of holes at the Alq3/BCP interface leading to the blocking of holes at the interface. This would reduce the number of holes leaking to the cathode. Consequently, the
recombination of electrons and holes would be enhanced in the emitting layer leading to increased exciton formation and hence improvement in luminance and efficiency. The flat band energy diagram of this structure is shown in Figure 2-16. The barrier for hole at the TPD/BCP interface is around 1.3eV considering TPD and BCP have a HOMO level of 5.4eV and 6.7eV, respectively. Similarly the barrier for holes at the Alq3/BCP interface is 1eV considering the HOMO level for Alq3 is 5.7eV. The thickness of BCP layer after TPD is kept very thin so as to allow the holes to tunnel through or hop across and reach the Alq3 layer.

Figure 2-15: Cross section of the inverted green emitting OLED with hole confining structure implemented in this thesis. BCP is used as the hole confining layer.
Figure 2-16: Flat band energy diagram of inverted green emitting OLED with hole confining structure. BCP is used as the hole blocking layer before and after the emitting layer.

The structure of the control device employed for an inverted blue emitting OLED as discussed Sec 2.2 is as follows, ITO/Al/LiF/BCP/TPD/Al. The hole blocking BCP layer is used on either side of the TPD layer to form the hole confining structure. The BCP layer after TPD acts as the hole blocker while the BCP layer before TPD layer acts as the electron injection layer. Thus TPD layer is locked between two BCP layers and consequently the emission takes place from the TPD layer due to confining of excitons in it, leading to a blue emission from TPD. The final structure
of the hole confined blue emitting OLED is shown in Figure 2-17 and its flat band energy diagram is shown in Figure 2-18.

Figure 2-17: Cross section of the inverted blue emitting OLED with hole confining structure implemented in this thesis. BCP is used as the hole confining layer.
Figure 2-18: Flat band energy diagram of inverted blue emitting OLED with hole confining structure. BCP is used as the hole blocking layer before and after the emitting layer.

### 2.7 Experimental results

The devices were fabricated as described in Sec. 2.3. The cathode, organic and the transparent Aluminum layer deposition were carried out by pumping the chamber to a pressure of $1 \times 10^{-6}$ Torr. We fabricated two green emitting OLEDs and two blue emitting OLEDs referred to as G1, G2 and B1, B2 respectively. Device G1 was the reference (inverted green emitting) device, ITO/Al/LiF/Alq3/TPD/Al. In device G2, we implemented a hole confining structure by adding
BCP on both sides of Alq$_3$ layer. The thickness and the rates of deposition of the various layers are listed in Table 2-1. Device B1 was the reference (inverted blue emitting) device, ITO/Al/LiF/BCP/TPD/Al. In device B2, we implemented a hole confining structure by the addition of another layer of BCP before TPD layer. The thickness and the rates of deposition of various layers are listed in Table 2-2.

### Device G1

<table>
<thead>
<tr>
<th>Layers</th>
<th>Thickness ($\text{Å}$)</th>
<th>Rate of Deposition ($\text{Å/s}$)</th>
<th>Thickness ($\text{Å}$)</th>
<th>Rate of deposition ($\text{Å/s}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>326</td>
<td>7</td>
<td>318</td>
<td>6.5</td>
</tr>
<tr>
<td>LiF</td>
<td>9</td>
<td>0.1</td>
<td>11</td>
<td>0.2</td>
</tr>
<tr>
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<td>None</td>
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<td>1.2</td>
</tr>
<tr>
<td>Alq$_3$</td>
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<td>236</td>
<td>2.5</td>
</tr>
<tr>
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<td>21</td>
<td>0.5</td>
</tr>
<tr>
<td>TPD</td>
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</tr>
<tr>
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<td>45</td>
<td>3.1</td>
</tr>
<tr>
<td>Al</td>
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<td>8</td>
<td>521</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 2-1: Thickness of different layers of green light emitting inverted devices G1 and G2

OLED performance characterization primarily includes J-V characterisrics and luminescence measurements. A Tektonix TM5006 was used as a source voltage and the current drawn by the device was measured. Luminous intensity measurements were recorded using a USB2000 controller purchased from Ocean Optics. The USB2000 controller provides an interface between the computer and fiber optic cable. The fiber optic cable was placed on the emitting area and the
information was transmitted to the controller. The Ocean Optics OOI rad version 2.05 PR6 software was used for data acquisition. This software interprets data from the fiber optic cable and represents it as reflectance, relative irradiance or arbitrary counts thus, giving a direct measurement of lux, lumens and peak wavelength.

<table>
<thead>
<tr>
<th>Layers</th>
<th>Thickness (Å)</th>
<th>Rate of Deposition (Å/s)</th>
<th>Thickness (Å)</th>
<th>Rate of deposition (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>323</td>
<td>7.5</td>
<td>314</td>
<td>7.5</td>
</tr>
<tr>
<td>LiF</td>
<td>7</td>
<td>0.1</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>BCP</td>
<td>153</td>
<td>0.6</td>
<td>147</td>
<td>0.6</td>
</tr>
<tr>
<td>TPD</td>
<td>295</td>
<td>2.1</td>
<td>303</td>
<td>2.3</td>
</tr>
<tr>
<td>BCP</td>
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<td>None</td>
<td>28</td>
<td>0.3</td>
</tr>
<tr>
<td>Al</td>
<td>47</td>
<td>3.2</td>
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</tr>
<tr>
<td>Al</td>
<td>526</td>
<td>9</td>
<td>514</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 2-2: Thickness of different layers of blue emitting inverted devices B1 and B2

A systematic approach was followed for the electrical and optical measurements. The voltage applied across the inverted OLED was varied in steps and the corresponding current values are noted using a LABVIEW module. The absolute current (I) was then divided by the emitting area to obtain the current density (J). The emitting area of the device, defined using a cathode mask previously, was estimated to be 0.25cm². Plot of current density (mA/cm²) versus voltage (V) for devices G1, G2 and B1, B2 are shown in Figure 2-20.
Figure 2-19: J - V curves of devices G1, G2 (green) inverted OLEDs

Figure 2-20: J - V curves of devices B1, B2 (blue) inverted OLEDs
The J-V curves show pure diode behavior as seen from Figure 2-19 and Figure 2-20. The introduction of the hole confining layers of BCP leads to an increase in the driving voltage of the device. This is consistent with the findings of S.H. Mohan and N. Bhandari [24], [25] from our lab and also with the report of Divayana et al. that the field across the BCP layer is non-linear [41].

![Cd/m² vs J for green light emitting inverted OLEDs](image)

**Figure 2-21:** Luminance vs current density plot for inverted green OLEDs (G1 & G2)

For the luminance characteristic the lux of the device is measured using OOIIRad software for increasing voltages. The lux value is then converted to cd/m² to obtain luminance value. OLED being a Lambertian emitter

\[
\text{Lux}/\pi = \text{cd/m}^2
\]
Plot of luminance (cd/m$^2$) versus current density (mA/cm$^2$) for devices G1, G2 and B1, B2 are shown in Figure 2-21 and Figure 2-22, respectively.

**Cd/m$^2$ vs J for blue light emitting inverted OLEDs**

![Graph of Cd/m$^2$ vs J for blue light emitting inverted OLEDs](image)

Figure 2-22: Luminance vs current density plot for inverted blue OLEDs (B1 & B2)

It is seen that the device with the hole confining structure has a better luminance compared to the control device. The confining BCP layers reduce the hole leakage and confines holes and excitons in the emitting layer leading to better recombination. The increase in the luminance is attributed to the better confinement of holes in the emitting layer. The maximum luminance value for the reference green emitting inverted OLED (device G1) is 1628 cd/m$^2$ and for the hole confined device (device G2) it is 1861 cd/m$^2$ which corresponds to an improvement of 14.31% in the luminance. Similarly the maximum luminance value for the reference blue emitting inverted OLED (device B1) is 1285 cd/m$^2$ and for the hole confined device (device B2) is 1456 cd/m$^2$.
which corresponds to an improvement of 13.3% in the luminance. The devices are shown in Figure 2-23 (green emitting and blue emitting respectively).

![Figure 2-23: Pictures of the green and blue light emitting inverted OLED implementing the hole confining structure discussed in Sec. 2.6]

We believe further improvements in the luminance is possible by optimizing the thickness of the two BCP layers used for hole confining. Also the lifetime and luminosity of the devices can be increased by encapsulating it as soon as it is taken out from the chamber so that the device is not exposed to atmospheric oxygen and moisture while being tested.
Chapter 3  Investigation of the effect of addition of a hole confining buffer layer of TPBI on a NPB/Alq\textsubscript{3} Bi-layer Organic Light-Emitting Diode

3. 1 Outline

In this chapter, we first discuss the electric field profile in a Bi-layer Organic light emitting diode. First, we review some prior work on the electric field distribution in an OLED based on experimental and simulation studies. Then using the concept of hole confinement in a bi-layer device, a structure is proposed with TPBI as the hole confining buffer layer. The thickness of this buffer layer is varied and the effects on the OLED performance are studied. The results show an improvement in the luminance, luminous efficiency and external quantum efficiency of the devices. In the second half of this chapter, the total thickness of the electron transport layer is maintained constant while varying the thickness of its constituents (Alq\textsubscript{3} and TPBI) and the effect on the OLED performance is studied. The addition of the TPBI buffer layer leads to an improvement in the OLED performance.

3. 2 Literature review of electric field in a bi-layer device:

Since the report of the first ever OLED by Tang and VanSlyke in 1987 [6], the physical and chemical mechanisms taking place inside an OLED has been an intensive research area. The internal electric field in a bilayer device with ITO/NPB/Alq\textsubscript{3}/Al was investigated by S. J. Martin et al [42]. They used a drift – diffusion model to study the electric field distribution in a bilayer device and compared it with experimental results. The electric field distribution was explained
on the basis of charge carrier accumulation at the interface of two organic layers due to the band offsets in the HOMO and LUMO levels and the charge injection into the device. They reported that under small forward bias the electric field was homogenous throughout the device and, as the bias was increased, the holes injected from ITO into NPB gathered at the NPB/Alq₃ interface leading to an increase in the field across the Alq₃ layer as it acted as hole blocker. Similar hole accumulation at the interface was reported by Matsumura et al [43] in a TPD/Alq₃ device. With further increase in the bias the electrons injected from the Al into the Alq₃ layer started gathering at the interface causing a negative charge build up and thus increasing the field in the NPB layer as the NPB layer acted as an electron blocker. In a ITO/NPB/Alq₃/Al:Li device the injection of electrons was reported to be greater than the Al device as the injection barrier at the Al:Li interface was lower than that at the ITO/NPB interface. When a Mg:Ag cathode was used the field across the Alq₃ layer was more than that in the NPB layer as the electron injection barrier went up. Similarly, the average field across the Alq₃ layer being higher than that across the NPB layer was also reported by Yamada et al [44] by using electro-absorption spectroscopy. They also reported that the electric fields were dependent on the work functions used in the simulations and were largely independent of the thickness of the organic layers.

Similar results were reported by E. Tutis, D. Berner and L. Zuppiroli for an ITO/CuPc/NPB/Alq₃/LiF/Al structure[22], both experimentally and by device modeling. They reported that the space charge effects caused by the large number of carriers accumulated at the Alq₃ bulk due to the high electron barrier and low mobility of holes in bulk Alq₃ was more pronounced at low voltage than at high voltage. As the voltage increased, the accumulation of electrons in the Alq₃ side of the NPB/Alq₃ interface increased thus diminishing the leakage
current by providing an increasing cross section for the recombination zone and consequently reducing the space charge effect in the Alq₃ layer. The space charge effect in the NPB layer was reported to be negligible as the holes had higher mobility in NPB layer and only few electrons entered the NPB layer due to a higher barrier at the NPB/Alq₃ interface. They showed there was a large leakage of holes through the ETL to the cathode, particularly at low voltage, which led to a loss of efficiency of the OLED at low current densities. Similar devices without CuPc layer also exhibited relatively low EQE at low current densities [45], [46] for the same reasons. The authors suggest that this low efficiency can be improved by either blocking the escape of these holes or by confining them within an emitting zone. Though several authors have reported the use of hole blocking materials, to the best of our knowledge, very little work has been reported about the inefficiencies of NPB/Alq₃ devices at low current densities. The use of hole blocking layers and quantum well structures have resulted in improvement in the performance of undoped OLEDs [47], [48], [49], [35], [50], [51]. Both these methods aim at improving the efficiency of the OLEDs by improving the utilization of all injected carriers.

3.3 Proposed Structure and experimental details

As previously mentioned, the concept of hole confinement for the improvement of the efficiency of the OLED was suggested by K. Garre in our lab [23]. S. H. Mohan [24], N. K. Bhandari [25] and A. Rakurthi [26] studied the concept of hole confinement by using BCP as the hole blocking layer. This led to an addition in the driving voltage of the device. In this thesis, we have studied the effect of a hole blocking - buffer layer of TPBI - 1, 3, 5 - tri (phenyl - 2- benzimidazole) - benzene, to see if similar improvements in the efficiency can be observed specifically at lower
current densities and whether the addition in the driving voltage of the devices can be eliminated or reduced.

TPBI is a commonly used electron transporting layer as well as a hole blocking layer. The structure of TPBI is shown in Figure 3-1. Previous studies report the HOMO levels of TPBI around 6.2 to 6.7eV [52], [53], [54]. The electron mobility of TPBI was reported to be of the order of 10^{-6}-10^{-5} cm^2/Vs, which is slightly higher than that in Alq3. Furthermore, its mobility was found to be dependent on the electric field as measured by transient EL spectroscopy [55], [56]. In either case the important feature to be noted is the deep HOMO level which is attributed to the large ionization potential of the molecule. S. Lo et al [53] have demonstrated high efficiency devices (55 cd/A) based on solution processible phosphorescent green emitter using TPBI as a hole blocking and electron transport layer. Similarly J. Lu et al [57] have demonstrated OLED with TPBI as a hole blocking layer. Following this work, X. Jiang et al [58] demonstrated white organic light emitting diodes by incorporating a doped hole blocking layer of TPBI between the hole transport layer and electron transport layer. The basic idea behind using TPBI as a hole blocking layer is that it has a large ionization potential compared to Alq3, and thus blocks the passage of holes out of the HTL. In addition to the blocking of the holes, the barrier for the passage of electrons was also reduced when compared to BCP by using TPBI. Furthermore it was reported by Hung et al [56] that the operating voltage is also reduced when BCP was replaced by TPBI.

With reference to the structure used by E. Tutis et al [22] as discussed in section 3.2, we added a buffer layer of TPBI as the hole blocking layer between the cathode and Alq3 the emitting layer. TPBI also doubled up as the electron transport layer and instead of CuPc, we used
Hexaazatriphenylenehexacarbonitrile, (HAT-CN) as the hole injection layer. The modified structure of the OLED is ITO/HAT-CN/NPB/Alq3/TPBI/LiF/Al, as shown in Figure 3-1.

Figure 3-1: Cross section of the OLED implemented in this thesis with a buffer layer of TPBI between the emitting layer and the bi-layer cathode
Figure 3-2: Flat band energy diagram of the ITO/HAT-CN/NPB/Alq₃/TPBI/LiF/Al OLED. The thicknesses of the different layers are different from the actual values. The Alq₃ and the TPBI layer thickness are varied for the various devices.
3. 4 Structure and Properties of Organic Materials Used

In this section the structure and properties of the organic materials used in this thesis are described.

3. 4. 1 TPBI: 1, 3, 5 - tri (phenyl - 2- benzimidazole) – benzene

Figure 3-3: Molecular structure of TPBI. Source: www.chemicalbook.com

Figure 3-3 shows the structure of TPBI. TPBI is commonly used as an electron transporting layer and an exciton blocking layer. It has a band gap of 3.5eV. It has a LUMO level of 2.7eV and a HOMO level of 6.2eV [52]. It also doubles up as a hole blocking layer. The mobility of electrons in TPBI is found to be of the order of the hole mobility in Alq3 [55]. It also has high electron mobility compared to other electron transport layers [46] thus increasing the probability of the formation of more excitations and thus increasing the possibility of a more efficient OLED. TPBI, being a planar molecule is known to migrate through the pores of amorphous organic materials [59] which cause, the degradation of the OLEDs.
3. 4. 2 Alq₃: tris (8 - hydroxyquinioline) Aluminum

Figure 3-4: Molecular structure of Alq₃.

Figure 3-4 shows the structure of tris (8 - hydroxyquinioline) Aluminum, commonly known as Alq₃. It is generally used as an emitting layer in OLEDs. The electron mobility in Alq₃ has been reported to be around $1.4 \times 10^{-6}$ cm$^2$/V s [31] and the hole mobility has been reported to be in the order of $10^{-10}$ to $10^{-8}$ cm$^2$/V s [60]. The LUMO and HOMO levels of Alq₃ are 3.2eV and 5.7-5.9eV [61], respectively.

The emission spectrum of Alq₃ peaks at a wavelength of 545 nm which falls in the green region of the visible electromagnetic spectrum. Though Alq₃ is the most commonly used emission layer in small molecule organic light emitting diodes, it is found to degrade due to the injection of holes. The transport of holes causes the decrease in the fluorescence quantum efficiency, indicating the instability of cationic Alq₃ species. The degradation of Alq₃ produces fluorescent quenchers [62].
3. 4. 3 NPB: N,N'-bis-(1-naphthyl)-N,N' - diphenyl- 4,4'-diamine

Figure 3-5 shows the structure of N,N'-bis-(1-naphthyl)-N,N' - diphenyl- 4,4'-diamine, commonly known as NPB. It is used as a hole transport layer in OLEDs. The glass transition temperature of NPB is 98°C, which is better when compared to the other commonly used hole transporting layer, TPD (N.N'- diphenyl-N,N' bis(3-methyl-phenyl) - 1,1' bi phenyl- 4,4' diamine. Also NPB is found to be more photostable and to have better morphologically stability in thin film state than TPD [63]. TPD and NPB have similar properties which enables them to be used interchangeably. The LUMO and HOMO levels of NPB are 2.4 eV and 5.2eV [64], respectively.

3. 5 Experimental Results and Discussion

3. 5. 1 Devices with varying ETL thickness

As shown in Figure 3-1, the basic device has the following structure: ITO/HAT-CN/NPB/Alq3/LiF/Al. This device is the basic device used for comparisons throughout this section. All the devices investigated in this section were fabricated at Universal Display Corporation R&D laboratories.
In order to investigate the effect of the buffer layer on device performance, a set of seven devices referred as Device A, B, C, D, E, F and G were fabricated. Device A with ITO/HAT-CN/NPB/Alq3/LiF/Al structure is the control device. The device does not have a buffer layer of TPBI. Device B & E, C & F and D & G are fabricated such that B, C and D do not contain the TPBI buffer layer whereas devices E, F and G contain the buffer TPBI layer. The different layer thicknesses of the devices are shown in Table 3-1.

<table>
<thead>
<tr>
<th>Device</th>
<th>HAT-CN (Å)</th>
<th>NPB (Å)</th>
<th>Alq3 (Å)</th>
<th>TPBI (Å)</th>
<th>LiF (Å)</th>
<th>Al (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>500</td>
<td>400</td>
<td>0</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>500</td>
<td>500</td>
<td>0</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>500</td>
<td>600</td>
<td>0</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>D</td>
<td>100</td>
<td>500</td>
<td>800</td>
<td>0</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>500</td>
<td>400</td>
<td>100</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>F</td>
<td>100</td>
<td>500</td>
<td>400</td>
<td>200</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
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<td>500</td>
<td>400</td>
<td>400</td>
<td>5</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 3-1: Layer thickness configurations of devices (A-G). The thickness of the TPBI buffer layer was varied in devices E-G and the performance of these devices were compared with devices B-D which are NPB/Alq3 bi-layer OLEDs.

The devices were encapsulated with desiccants in an atmosphere of dry nitrogen and the electroluminescent properties were evaluated at room temperature using PhotoResearch PR650 SpectraScan Colorimeter by using a programmable current source meter. Current was applied in steps to the devices and the corresponding voltage, luminance, luminous efficiency, external quantum efficiency and peak wavelength were recorded.
Being current driven devices, the OLEDs were tested by varying the source current from 0.005 mA to 10mA. The emitting area of the device was 0.02cm². Thus, the current density varied from 0.1mA/cm² to 100mA/cm². Figure 3-6 shows the current density versus voltage (J-V) characteristics of devices A-G. All of the devices exhibit diode like characteristics as expected.

The devices A, B and C are used as the control devices in this thesis. It is seen that the addition of the buffer layer of TPBI has caused an increase between 0.5 to 0.6 V in the driving voltage for the devices F & G when compared to that of devices C & D. On the other hand, there is not a significant addition in the driving voltage for the device E when compared to device B. This increase in the driving voltage of the devices is found to occur only when the thickness of the TPBI buffer layer is greater than 100 Å. The spectra of devices B & E are also found to be similar as shown in Figure 3-10. Thus it can be concluded that a buffer layer with thickness less than 100Å does not cause a significant change in the operation of the OLED. From Figure 3-6 it is also seen that the influence of the driving voltage on the current - voltage characteristics occurs only for current densities less than 10mA/cm². For current densities greater than 20mA/cm², the current voltage characteristics of devices with and without the TPBI buffer layer is found to be the same.

This can be explained as follows: First, the increase in driving voltage is due to the increased field across the Alq3 layer. The electric field across the Alq3 layer is independent of its thickness as shown by Yamada [44] and Martin [42], [65] and as can be inferred from the linearity nature of the plot in Figure 3-16. This shows that more holes need to be present at the NPB/Alq3 interfaces at fixed bias. This leads to an increased quenching (loss of holes through ETL to the cathode causing them to recombine non-radiatively) at the NPB/Alq3 interface [46]. TPBI, being
an electron transport layer [66], also acts as a hole blocking layer causing significant number of holes to be blocked at the Alq3/TPBI interface. This increase in the number of holes causes an increase in the electric field across the Alq3 layer. Thus the voltage applied has to overcome this internal electric field in order to drive the device, causing the increase in the driving voltage. We come to the conclusion that the accumulation of the holes contribute to the addition in the driving voltage of the devices at low current densities. Second, more holes also lead to more number of injected holes reaching the Alq3/TPBI interface causing another recombination zone. This new recombination zone is present either in the bulk region of Alq3 or at the Alq3/TPBI interface. Either way, as this recombination zone is displaced from the quenching prone NPB/Alq3 interface, causes the improvement in the EQE.

At high current densities there is no significant increase in the driving voltage of the devices and the electric field across the Alq3 layer remains unaltered. An increase in the EQE of the device is seen due to the increase in thickness of the buffer TPBI layer causing a displacement of the recombination zone away from the NPB/Alq3 interface. This reduces the quenching, causing the EQE to improve. Figure 3-7 shows indeed an increase in the EQE of devices F & G when compared to devices C & D.

Figure 3-7 shows the external quantum efficiency versus current density (EQE vs J) plot of devices A-G. It can be seen that the addition of the TPBI buffer layer improves the EQE of the devices. There is a steady increase in the EQE with the increase in the thickness of the buffer layer. There is an improvement of 20% in the EQE of device G compared to device D. There is also a marginal improvement in the EQE of device F compared to device C, whereas there is no
improvement in the EQE of device E compared to device B. This shows that a significant change in EQE occurs only for devices which have a TPBI buffer layer of thickness greater than 100Å similar to the effect seen in the addition of driving voltage from Figure 3-6.

As the thickness of the TPBI buffer layer is increased, the Alq₃/TPBI interface is moved away from the NPB/Alq₃ interface which causes a reduction in quenching. Simultaneously, more holes pass through to the Alq₃ layer improving the EQE of the device. In device F with a thickness of the buffer TPBI layer being 200Å, the Alq₃/TPBI interface of the device is close to the NPB/Alq₃ interface where quenching occurs and only a marginal increase in the EQE is seen. In device G with a 400Å thick TPBI buffer layer, the Alq₃/TPBI interface is farther away from the NPB/Alq₃ interface, thus reducing the percentage of quenching and in turn causing an improvement in the EQE of the device when compared to the control device D. Figure 3-8 shows the plot of the current efficiency versus the current density (Cd/A vs J) for devices A – G. The current efficiency of the devices shows a similar behavior as that of the EQE. When the buffer layer of TPBI is 100Å thick (device E), there is no improvement in the current efficiency compared to device B. As the thickness of the buffer layer is increased the current efficiency is found to increase, as seen in Figure 3-8 for devices F and G compared to devices C and D.

The plot of the luminance of the devices versus the current density (Cd/m² vs J) is shown in Figure 3-9. The luminance is also found to exhibit a behavior similar to that of EQE and current efficiency. As the thickness of the buffer TPBI layer increases the luminance of the devices also increases.
Figure 3-6: Current Density versus driving Voltage plot for devices A-G. The increase in driving voltage at low current density is visible for devices F & G.
Figure 3-7: External Quantum Efficiency versus Current density for Devices A-G
Figure 3-8: Current efficiency versus Current density for Devices A-G
Figure 3-9: Luminance versus Current density for Devices A-G
Figure 3-10 shows the normalized emission spectra plots of devices A-G. All spectra of the devices A-D are centered near 520 nm which is in the green region of the electromagnetic spectrum. The spectra of devices E-F are also centered near 520 nm. There is not a major shift in the spectrum of the devices due to the addition of the TPBI buffer layer.

Figure 3-10: Normalized emission spectra versus wavelength for devices A-G.
A comparison of the device characteristics with and without the TPBI buffer layer is summarized in Table 3-2, Table 3-3, and Table 3-4; at different current densities. It is seen that there is actually degradation in the device performance when the thickness of the TPBI buffer layer is 100Å. As the thickness of the layer is increased to 200Å and 400Å, there is a substantial increase in the luminance, luminous efficiency and external quantum efficiency of the OLEDs.

The improvement in the luminance, Luminous efficiency and the EQE at a current density of 1mA/cm² is tabulated in Table 3-2.

<table>
<thead>
<tr>
<th>Device</th>
<th>Buffer Layer</th>
<th>Cd/m²</th>
<th>Cd/A</th>
<th>%EQE</th>
<th>% Improvement in Cd/m²</th>
<th>% Improvement in Cd/A</th>
<th>% Improvement in EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td></td>
<td>28.4</td>
<td>2.554</td>
<td>0.842</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>24.5</td>
<td>2.395</td>
<td>0.786</td>
<td>-13.73</td>
<td>-6.22</td>
<td>-7.12</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>47.7</td>
<td>2.981</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>200</td>
<td>49.3</td>
<td>3.06</td>
<td>0.994</td>
<td>3.35</td>
<td>2.65</td>
<td>1.4</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>46.4</td>
<td>3.39</td>
<td>1.074</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>400</td>
<td>53.5</td>
<td>3.657</td>
<td>1.16</td>
<td>15.3</td>
<td>10.8</td>
<td>8.411</td>
</tr>
</tbody>
</table>

Table 3-2: Comparison of figure of merit for Devices with and without the buffer TPBI layer at a current density of 1mA/cm². (Devices B, C and D do not have the buffer layer and devices E, F and G have the buffer layer)
The improvement in the luminance, Luminous efficiency and the EQE at a current density of 10mA/cm$^2$ is tabulated in Table 3-3.

<table>
<thead>
<tr>
<th>Device</th>
<th>Buffer Layer TPBI (Å)</th>
<th>Cd/m$^2$</th>
<th>Cd/A</th>
<th>%EQE</th>
<th>% Improvement in Cd/m$^2$</th>
<th>% Improvement in Cd/A</th>
<th>% Improvement in EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>309</td>
<td>2.67</td>
<td>0.883</td>
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<td></td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>265</td>
<td>2.479</td>
<td>0.826</td>
<td>-14.23</td>
<td>-7.15</td>
<td>-6.45</td>
</tr>
<tr>
<td>C</td>
<td>319</td>
<td>3.147</td>
<td>1.022</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>200</td>
<td>355</td>
<td>3.488</td>
<td>1.105</td>
<td>11.28</td>
<td>10.8</td>
<td>8.12</td>
</tr>
<tr>
<td>D</td>
<td>333</td>
<td>3.081</td>
<td>1.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>400</td>
<td>405</td>
<td>3.783</td>
<td>1.2</td>
<td>21.62</td>
<td>22.7</td>
<td>18.81</td>
</tr>
</tbody>
</table>

Table 3-3: Comparison of the figure of merit for Devices with and without the buffer TPBI layer at a current density of 10mA/cm$^2$. (Devices B, C and D do not have the buffer layer and devices E, F and G have the buffer layer)
The improvement in the luminance, Luminous efficiency and the EQE at a current density of 80mA/cm$^2$ is tabulated in Table 3-4.

<table>
<thead>
<tr>
<th>Device</th>
<th>Buffer Layer TPBI (Å)</th>
<th>Cd/m$^2$</th>
<th>Cd/A</th>
<th>%EQE</th>
<th>% Improvement in Cd/m$^2$</th>
<th>% Improvement in Cd/A</th>
<th>% Improvement in EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2280</td>
<td>2.82</td>
<td>0.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>2260</td>
<td>2.64</td>
<td>0.88</td>
<td>-0.877</td>
<td>-6.17</td>
<td>-5.26</td>
</tr>
<tr>
<td>C</td>
<td>2760</td>
<td>3.217</td>
<td>1.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>200</td>
<td>2840</td>
<td>3.29</td>
<td>1.08</td>
<td>2.89</td>
<td>2.30</td>
<td>0.46</td>
</tr>
<tr>
<td>D</td>
<td>3190</td>
<td>3.702</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>400</td>
<td>3340</td>
<td>4.07</td>
<td>1.29</td>
<td>4.72</td>
<td>10.2</td>
<td>10.14</td>
</tr>
</tbody>
</table>

Table 3-4: Comparison of the figure of merit of Devices with and without the buffer TPBI layer at a current density of 80mA/cm$^2$. (Devices B, C and D do not have the buffer layer & devices E, F and G have the buffer layer)

From the tables above it is clearly seen that Device E, with a very thin layer of TPBI has a degraded performance in comparison with Device B. This is because of the dominating effect of leakage of holes and quenching at the NPB/Alq$_3$ interface owing to the very thin TPBI layer. As the thickness of the buffer TPBI layer is increased, the performance of the devices is found to improve which is evident for devices E and F.
3.5.2 Devices with constant electron transport layer thickness

In order to show that the displacement of the recombination zone form the NPB/Alq₃ interface, causes an improvement in the EQE of the devices another set of devices were fabricated. The set of devices was fabricated with a constant electron transport layer thickness. The electron transport layer consisted of both Alq₃ and TPBI.

Simulation results by M. A. Webster et al. [66] have shown that as the thickness of the Alq₃ layer is increased in a bilayer device the EQE of the device improves. They have also shown that there is an optimum thickness of the Alq₃ layer after which the EQE of the devices starts to decrease. This optimum thickness was shown to be 800Å. Thus we have chosen the thickness of the Electron transport layer as 800Å.

The second set of devices was fabricated with the structure shown in Table 3-5.

<table>
<thead>
<tr>
<th>Device</th>
<th>HAT-CN (Å)</th>
<th>NPB (Å)</th>
<th>Alq (Å)</th>
<th>TPBI (Å)</th>
<th>LiF (Å)</th>
<th>Al (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>100</td>
<td>500</td>
<td>800</td>
<td>0</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>I</td>
<td>100</td>
<td>500</td>
<td>100</td>
<td>700</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>J</td>
<td>100</td>
<td>500</td>
<td>200</td>
<td>600</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>K</td>
<td>100</td>
<td>500</td>
<td>300</td>
<td>500</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>L</td>
<td>100</td>
<td>500</td>
<td>400</td>
<td>400</td>
<td>5</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 3-5: Layer thickness configurations for devices (H-L) of structure

ITO/HAT-CN/NPB/Alq₃ (800Å – xÅ)/TPBI (xÅ)/LiF/Al OLEDs

The devices were fabricated, encapsulated and tested in the same manner as that of the device A-G. Device H, having only Alq₃ layer is the control device for this set of devices. The rest of the
devices, (namely I – L) were fabricated with increasing thicknesses of the buffer TPBI layer. Figure 3-11 shows the EQE vs current density plot for devices H- L. It is seen that devices I – L having a buffer layer of TPBI have a better EQE when compared to the control device H. In device I, the Alq3 layer is just 100Å, resulting in the recombination zone at the Alq3/TPBI being very close to the NPB/Alq3 interface. As the NPB/Alq3 interface is prone to quenching as discussed earlier, this causes a loss in EQE resulting in a marginal improvement in the EQE. In device J, when the Alq3 layer thickness is increased to 200Å, an improvement in the EQE of the device is seen. Similar results are also seen for Device K and L. In device L, when the Alq3 layer is 400Å, a maximum improvement of 15% in the EQE is found, thus showing that the pushing away of the recombination zone from the NPB/Alq3 interface improves the EQE of the device.

Figure 3-12 shows the current efficiency versus current density plot for devices H-L. Similar results as seen from the EQE plots are seen here. The current efficiency of the device is seen to improve as the recombination zone is pushed away from the quenching prone NPB/Alq3 interface. A marginal improvement in the current efficiency is seen for device I and a maximum improvement of 15% is seen for device L when the recombination zone is moved 400Å away from the NPB/Alq3 interface. The plot of luminance versus current density is shown in Figure 3-14. The luminance also shows a similar behavior as that of the EQE and current efficiency plots. The current density versus the driving voltage plots for the devices H-L is shown in Figure 3-13. This figure shows that, similar to the results obtained from devices A-G, the addition in the driving voltage gradually reduces as the current density increases and becomes almost nil for a current density in excess of 10mA/cm2. This again shows that, at current densities less than 10mA/cm2, there is an increase in the internal electric field in the Alq3 layer causing an addition
to the driving voltage. The effect of the addition in the driving voltage can also be seen in Figure 3-16. At a current density of 80mA/cm², the plot is seen to be linear showing that there is no change in the electric field and thus proving that the electric field is independent of the thickness of the emission layer.

Figure 3-11: Current density versus External Quantum Efficiency for Devices H-L
Figure 3-12: Current density versus current efficiency plot for Devices H-L
Figure 3-13: Current density versus driving voltage plot for Devices H-L
Table 3-6 summarizes the characteristics of the best performing devices at various current densities. It is seen that, as the Alq₃/TPBI interface is pushed away from the NPB/Alq₃ interface, the performance of the devices improve significantly.
The spectra of the devices H-L are shown in Figure 3-15. It is seen that the spectra is centered near 520nm, corresponding to a green wavelength of the visible electromagnetic spectrum. Also the addition of the buffer TPBI layer does not lead to a significant variation in the spectra of the devices.

Figure 3-15: Emission spectra of Devices H-L. Plot of normalized intensity (a.u) versus wavelength (nm)
At a current density of 0.03mA/cm$^2$, Device K showed the best improvement

<table>
<thead>
<tr>
<th>Device</th>
<th>Cd/m²</th>
<th>Cd/A</th>
<th>%EQE</th>
<th>% Improvement in Cd/m²</th>
<th>% Improvement in Cd/A</th>
<th>% Improvement in EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.823</td>
<td>2.904</td>
<td>0.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.28</td>
<td>3.867</td>
<td>1.215</td>
<td>55.55</td>
<td>33.16</td>
<td>22.28</td>
</tr>
</tbody>
</table>

At a current density of 10mA/cm$^2$, Device L showed the best improvement

<table>
<thead>
<tr>
<th>Device</th>
<th>Cd/m²</th>
<th>Cd/A</th>
<th>%EQE</th>
<th>% Improvement in Cd/m²</th>
<th>% Improvement in Cd/A</th>
<th>% Improvement in EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>355</td>
<td>3.158</td>
<td>1.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>535</td>
<td>3.617</td>
<td>1.16</td>
<td>50.70</td>
<td>14.53</td>
<td>14.28</td>
</tr>
</tbody>
</table>

At a current density of 80mA/cm$^2$, Device L showed the best improvement

<table>
<thead>
<tr>
<th>Device</th>
<th>Cd/m²</th>
<th>Cd/A</th>
<th>%EQE</th>
<th>% Improvement in Cd/m²</th>
<th>% Improvement in Cd/A</th>
<th>% Improvement in EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2870</td>
<td>3.693</td>
<td>1.169</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>3340</td>
<td>4.073</td>
<td>1.292</td>
<td>16.376</td>
<td>10.02</td>
<td>10.52</td>
</tr>
</tbody>
</table>

Table 3-6: Characteristics of the best performing Alq3/TPBI devices at various current densities
Improvement in luminance, current efficiency and EQE is shown in Table 3-6. It is seen that at a current density of 0.03mA/cm$^2$ Device K, with a TPBI layer of 300Å shows the highest improvement in the luminance, current efficiency and EQE when compared to Device H, with only an Alq$_3$ of 800Å. As the current density is increased Device L is seen show the highest improvement in the luminance, current efficiency and EQE compared to Device H, showing that movement of the recombination zone away from the NPB/Alq$_3$ interface causes the devices to perform better.

Figure 3-16: Plot of driving voltage of devices versus total thickness of the electron transport layer at current densities of 1, 10 and 80mA/cm$^2$. Devices shown here consist of the reference device with an Alq$_3$ layer only and devices with both Alq$_3$ layer and TPBI as electron transport layer with constant thickness (800Å).
From Figure 3-16, it is seen that as the thickness of the electron transport layer increases the driving voltage is found to increase. The plot for the devices having only Alq₃ as the electron transport layer is seen to be linear, hence showing that the internal electric field in the Alq₃ layer is independent of its thickness, as reported by Yamada et al. and Martin et al. [42], [44], [65]. When the TPBI buffer layer is added to the Alq₃ layer, there is a steep increase in the operating voltage at a current density of 1mA/cm² showing that there is a change in the internal electric field across the electron transport layer. This steep rise is seen to gradually reduce as the current density is increased to 10mA/cm² and is found to become very negligible at a high current density of 80mA/cm², where a linear behavior is recorded. This shows that there is no change in the internal electric field across the electron transport layer at high current densities.

In summary, we have improved the efficiency of bi-layer devices by the addition of the TPBI buffer layer. The improvement is achieved by a combined action of hole blocking nature of TPBI and the displacement of the recombination zone from the NPB/Alq₃ interface. The improvement achieved is significant at lower current densities when compared to higher current densities. We have also achieved a gradual reduction in the addition to the driving voltage of the device as the current density increases. Finally, we have also shown that the displacement of the recombination zone from the NPB/Alq₃ interface causes a large improvement in the performance of the devices.
Chapter 4 Conclusions

4.1 Conclusions

In this thesis the concept of ‘hole confinement’ has been used to improve the luminance and efficiencies of both green and blue inverted OLEDs and conventional green OLEDs. BCP and TPBI have been used as the hole confining materials in inverted and conventional OLEDs, respectively.

The mobility of holes in the HTL is higher than the mobility of electrons in the ETL which leads to a mismatch in balance of the carriers (holes travelling faster and leaking to the cathode). This imbalance causes a decrease in the carrier recombination probability, which in turn decreases the luminance and efficiency of the devices. The hole confining concept suggested by K. Garre [23], consists in the addition of a hole confining layer to help in slowing down hole motion leading to their confinement in the desired region, thus achieving a better balance of holes and electrons within the device. This better balance improves the probability of carrier recombination and emission resulting in improvement in device efficiency.

BCP is an excellent hole blocking material owing to its deep HOMO level. It offers a barrier for hole transport compared to Alq3. BCP was used as the hole confining layer in inverted green and blue emitting OLEDs in this thesis. The BCP layer is used on either side of the Alq3 layer. A thin layer before the Alq3 layer to slow down the flow of holes into the emitting layer and a thicker layer after the Alq3 layer to confine the holes in the emitting layer and to prevent their leakage. More specifically, the structures of the new inverted OLEDs are Al/LiF/BCP/Alq3/BCP/TPD/Al and Al/LiF/BCP/TPD/BCP/Al for green and blue emitting devices, respectively. The devices
fabricated using the above structure exhibited significant improvements in efficiency and luminance compared to the devices without the hole confining layer. For a green light emitting inverted OLED a hole confining layer consisting of 21 Å and 148 Å of BCP, respectively, showed an improvement of 14.31% in its luminance. Similarly for a blue emitting inverted OLED with a hole confining layer consisting of 28 Å and 147 Å of BCP, respectively, showed an improvement of 13.3% in its luminance.

Hence, we have shown that the addition of BCP as a hole blocking layer to the inverted OLEDs (green and blue) causes an improvement in the performance of the OLEDs. Also, the addition of BCP caused an increase in the driving voltage of the devices owing to the nonlinear electric field across the BCP layer [41].

TPBI is also an excellent hole blocking material. The mobility of electrons in TPBI is of the order of mobility of holes in Alq$_3$ [55]. TPBI layer was used a hole confining buffer layer in conventional green emitting OLEDs. These green emitting OLEDs were fabricated at Universal Display Corporation R&D laboratories. A set of devices with varying thickness of the hole confining buffer layer of TPBI were fabricated with the following structure: ITO/HAT-CN/NPB/Alq$_3$/LiF/Al and the effects were studied.

The addition of the hole confining buffer layer of TPBI caused an increase in the operating voltage at low current densities such as 1mA/cm$^2$, which gradually reduced with the increase in current density and showed a linear behavior at higher current densities such as 80mA/cm$^2$. This showed that the change in the internal electric field across the electron transport layer gradually reduced as the current density went up and became a constant.
For a 200Å thick hole confining buffer layer of TPBI, the peak improvement in luminance and luminous efficiency was found to be around 11% and 5% at a current density of 10mA/cm² and 1mA/cm², respectively. Similarly improvements in the external quantum efficiency were 10% and 4%, respectively, at the above mentioned current densities. For a 400Å thick hole confining buffer layer of TPBI, the peak improvement in luminance and luminous efficiency was found to be around 22% and 15% at a current density of 10mA/cm² and 1mA/cm², respectively. Similarly improvements in the external quantum efficiency were 18% and 8%, respectively, at the above mentioned current densities. As the thickness of the TPBI layer was increased the performance of the devices improved due to better confinement and reduction in the leakage of holes and reduction in the quenching at the NPB/Alq₃ interface. The improvement in the efficiency is attributed to the displacement of the recombination zone from the NPB/Alq₃ interface.

Another set of devices were fabricated with TPBI and Alq₃ as electron transport layers while maintain the combined thickness of the electron transport layer a constant at 800Å. These devices had the following structure ITO/HAT-CN/NPB/Alq₃ (800Å – xÅ)/TPBI (xÅ)/LiF/Al, where x denotes the thickness of the TPBI layer, which was varied from 700Å to 400Å at intervals of 100Å and then to 0Å. These devices also demonstrated an improvement in the efficiency and luminance. The highest reported improvement in luminance and luminous efficiency was found to be 56% and 33% at a current density of 0.03mA/cm², respectively, for the device with 500Å thick TPBI layer. At higher current densities of 10mA/cm² and 80mA/cm² the improvements in luminance and luminous efficiency was found to be 51% and 16% and 15% and 10 %, respectively.

In conclusion, we have shown that the addition of the hole confining buffer layer of TPBI causes an improvement in the performance of the devices due to its hole blocking nature and the
displacement of the recombination zone away from the NPB/Alq$_3$ interface. The use of hole confining layer also causes a gradual reduction in the operating voltage of the devices as the current density increases.

### 4.2 Suggestions for future Work

Efficiencies and lifetime improvements are two key issues widely addressed in the OLED market. We have shown how the efficiency of inverted and conventional OLEDs can be improved significantly based on the concept of hole confinement. Further, the thickness of these hole confining layers for the inverted OLEDs can be optimized. The inverted OLEDs made in our lab were not encapsulated and hence a rapid degradation in their luminescence was observed with time. The OLED performance was found to degrade severely when the organics are exposed to atmospheric oxygen and moisture [67]. Encapsulation carried out in a nitrogen or argon ambience would help improving the lifetime of these OLEDs. A simple encapsulation procedure would be to place the device in a plastic/glass cap filled with desiccants. The cap can then flipped over and bound to the OLED using UV epoxy. The epoxy can then be cured by shining UV light. We believe the encapsulation process would improve the lifetime of the OLEDs fabricated in our lab.

Further, previous students in our lab have predicted that an Al/LaS bilayer cathode will improve the efficiency of OLEDs due to the low work function of the LaS [23], [27]. The LaS is deposited by pulsed laser deposition at the Wright Patterson Air Force Base, as the bottom cathode and inverted OLEDs can be fabricated on top of them. A simple structure of the OLED would be Al/LaS/BCP/Alq$_3$/TPD/Ag-Al. A thin layer of Ag or Al can be used as the top electrode so as to obtain emission. Further improvements in the performance of these inverted
OLEDs can be done by the implementation of the hole confining concept and their thickness can also be optimized.

Finally, if the Kodak Research Labs or Universal Display Corporation R&D labs are accessible to future students in our lab, co evaporated hole blocking layers could be investigated for the inverted OLEDs. Also, other hole confining materials such as BPhen, BALq, Hexaphenylbenzene, Tetr phenyl napthalene could be used.
References


Appendix

This appendix gives a brief description of the procedures for the operation and maintenance of our vacuum chamber and the nitrogen glove box. Section A & B describe the operation and regeneration procedure of the vacuum chamber and nitrogen glove box, respectively.

A) Operation and Regeneration of the Vacuum Chamber

As discussed earlier in Chapter 2, the deposition of organic and metallic thin films is done in the vacuum chamber pumped down to a base pressure of $10^{-6}$ Torr.

A.1 Procedure for pumping down vacuum

A combination of a mechanical and cryo pump is used to pump down the vacuum in the chamber. A schematic showing the various valves and connection is shown in Fig. A.1. Initially the chamber is pumped down using the mechanical pump through the mechanical roughing valve till a base pressure of 100 microns. Once it is reached the system is switched over to the cryo by opening the high vacuum valve and the mechanical pump is switched off. The chamber is pumped down by the cryo until it reaches a pressure of $10^{-6}$ Torr. The chamber can now be used for thin film deposition.

A.2 Regeneration of the vacuum chamber

With repeated deposition in the chamber, the cryo pump gets saturated and the base pressure of $10^{-6}$ Torr becomes difficult to achieve. Hence the chamber needs to be regenerated for efficient use. It is best to regenerate the chamber after the fabrication of about 4-5 OLEDs, typically a
period of 10-15 days. Regeneration is a process by which nitrogen gas is fed into the cryo pump so as to remove the impurities formed on the inner wall. These are the following steps for the regeneration of the chamber.

![Diagram of vacuum chamber](image)

**Figure. A.1: Schematic of the vacuum chamber used for the deposition of thin films**

1) First, the high vacuum valve is closed and the cryo pump is switched off and allowed to warm up to room temperature. This takes approximately 4 -5 hours. The power supply to the cryo pump, compressor and the main cabinet is also switched off.

2) Once it warms up the power supply to the main cabinet is switched on and the toggle switch is set to read the cryo pressure.
3) Nitrogen is then fed into the cryo pump using the cryo vent valve until a pop sound is heard indicating that the pump is filled after which the vent valve is closed.

4) Then the mechanical pump is switched on and connected to the cryo using the cryo rough valve. In order to prevent the oil from the mechanical pump to leak into the valves a liquid nitrogen trap is formed so as to condense the oil vapors.

5) When the pressure reaches 100 mTorr, the cryo rough valve is closed and nitrogen is again fed and this cycle is repeated for 4-5 times.

6) At the end of the cycle, the cryo and the compressor are powered back on and left to cool to about 15 Kelvin. This cooling down takes approximately 2-3 hours.

**B) Operation and regeneration of the Glove box**

The fabricated OLEDs are stored in a nitrogen glove box in order to protect them from being exposed to atmospheric moisture and oxygen. A low moisture content and humidity is maintained in the glove box.

**B.1 Operation of the glove box**

The schematic of the nitrogen glove box is shown in Fig. B.1. It consists of two chambers, chamber A which houses the devices and chemicals that need to be stored and chamber B which is used for loading and unloading materials. Chamber A is never exposed to air and is always filled with inert nitrogen gas while chamber B is isolated during normal operation and is pumped using a mechanical pump when required. While loading and unloading materials chamber B is also pumped with inert nitrogen gas so as to maintain both chambers A and B in the same condition.
The following are the steps for loading materials into the chamber:

1) During normal working conditions chamber B is isolated from the mechanical pump due to the closure of valve C.

2) Valve D is opened to feed nitrogen into chamber B until the pressure reaches atmospheric pressure after which valve D is closed.

3) Now valve B is opened to load devices into chamber B and closed once thereafter.

4) Chamber B is pumped down to vacuum by opening valve C.
5) Once chamber B is under vacuum steps 1 and 2 are repeated and valve AB is opened so as to transfer the materials/devices into chamber A from B. The valve AB is closed once the transfer is complete.

6) Valve C is opened again and vacuum is pumped into chamber B.

The following are the steps to remove materials/devices from the glove box

1) Steps 1 and 2 are repeated and then valve AB is opened to transfer materials/devices that have to be taken out from chamber A to B.

2) Valve B is opened and the materials/devices are taken out after which valve C is opened to pump the chamber B back into vacuum.

**B.2 Regeneration of the glove box**

There is a filter present through which the nitrogen in the glove is circulated. This filters out the moisture from the nitrogen gas. For efficient operation of the glove box the filter has to be regenerated periodically. This regeneration process consists of two parts namely, heating of the filter and then purging of the chamber with the regenerating gas to remove impurities trapped in the filter. The procedure is as follows:

1) The chamber A is filled with nitrogen gas completely until the gloves pop out and then the nitrogen gas is pumped out using the pedal switch. This cycle is repeated for 4-5 times after which the regenerating cylinder is opened.

2) Switch 1 is then kept in the OFF position and the chamber is isolated from the filter by closing the two black valves.
3) Switch 1 is then turned to ‘REGENERATE’ position which initiates the regeneration process by heating up the filter which takes 3 hours.

4) Once the heat cycle ends the purge cycle begins which takes about 7 hours.

5) The regeneration process is completed after this and the switch 1 is turned to the ‘CIRCULATE’ position and the two black valves are opened to start the circulation of gas into the glove box.