The Pennsylvania State University

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### THE FABRICATION AND ANALYSIS OF QUANTUM-DOT THIN FILM LIGHT EMITTING DIODES FOR USE IN DISPLAYS TECHNOLOGIES

A Dissertation in

Engineering Science and Mechanics

by

Shawn L. Pickering

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The dissertation of Shawn L. Pickering was reviewed and approved\* by the following:

Jian Xu Associate Professor of Engineering Science and Mechanics Adjunct Professor of Electrical Engineering Dissertation Advisor Chair of Committee

Mark Horn Associate Professor of Engineering Science and Mechanics

Sulin Zhang Assistant Professor of Engineering Science and Mechanics

Jerzy Ruzyllo Distinguished Professor of Electrical Engineering

Juddith Todd P.B. Breneman Department Head Chair Head of the Department of Engineering Science and Mechanics

\*Signatures are on file in the Graduate School

### Abstract

The quantum dot has many applications, one of which is the light emitting diode. Quantum dot light emitting diodes were fabricated for their use in display technologies. The quantum dot light emitting diodes had to be optimized to achieve maximum brightness, as well as have the ability to pattern the devices for the use of multiple color quantum dot light emitting diodes on the same substrate. After the patterning and optimization of the quantum dot light emitting diode an addressing system is needed to create a display.

In this study mist deposition patterning is used to create multiple color quantum dot light emitting diodes on a single substrate. The structure is then packaged using techniques outlined in this article to prevent oxygen and moisture damage. The brightness and spectrum of each color was then tested, and showed promising results. The multiple devices are then powered via passive matrix addressing device which utilizes a National Instruments FET switching matrix to create an array similar to a display. The results of this testing show it is possible to create a multi-colored quantum dot array using mist deposition and passive addressing.

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### **Chapter 1**

### Introduction

The advent of semiconductors created fields for computing, solar cells, and lighting. The low power consumption and high brightness has made light emitting diode (LED) research very important in creating the next generation of light emitting devices. The LED is now used as indicator lights, home lighting applications, automobile headlights, and high definition televisions [1]. The series of next generation televisions use LEDs as backlights, as the main emission source, or use organic LED (OLED) technologies as the emission source. There are specific requirements for LEDs that are used in displays, which are high brightnesses to work in pulsed modes, long lifetime of the devices, efficiency to lower power consumption, and color tunability to achieve high contrast ratios (ratio of the luminance between white and black).

The creation of a display technology that has a wide range of color contrast and can support a high pixel density is the driving force in the display industry. The display industry is moving forward because of the aforementioned characteristics and a search for the next LED that will open the door to high pixel counts and a wider/purer color range. The quantum dot LED has the possibility to include all the characteristics needed to create the next generation displays [2].

### 1.1 Importance of Research

The current display technologies on the market are limited by their design. The advent of flexible displays for cell phones, e-books, netbooks, and televisions is pushing the industry forward, but the current display technologies such as liquid crystal displays (LCDs) are incapable of moving to a flexible substrate. The need for back lighting as opposed to emissive LEDs is one reason why current technologies are in need of replacement. The power consumption of backlit displays is considerably higher than that of an emissive display that could be brighter and consume less battery life. The importance of this research revolves around the idea of creating a new generation of flat panel displays that are capable of being built on a flexible medium, achieving higher brightness, requiring less power consumption, and displaying more vibrant colors than the displays currently on the market.

### 1.2 Objectives

The objectives of this research project revolved around five areas of research including; improving general operating principles of the quantum dot light emitting diodes (QD-LED), patterning of QD films, quantum dot (QD) arrays, addressing of the QD arrays, and, multi-color quantum dot light emitting diodes. Each of the topics will have to be optimized to test the effectiveness of the QD-LED in display applications.

### 1.3 Organization of the Thesis

The thesis is divided into seven chapters. Chapter 2 discusses the background and history of current display technologies, followed by Chapter 3 an in-depth discussion of

CdSe/ZnS quantum dots. Chapter 4 is the comparison of several deposition techniques and patterning processes. The initial display testing through arrays is then discussed in Chapter 5. The culmination of the previous chapters then leads to a multicolor array which is discussing in Chapter 6. Finally, in Chapter 7 the results and findings are summarized and considerations for future work are discussed.

### **Chapter 2**

### Background

#### 2.1 Current Display Technologies

The current market for displays includes plasma displays, LCD displays, LED-LCD displays, OLED displays, digital light processing (DLP) displays, and cathode ray tube (CRT) displays. Each display has a different set of operating parameters as well as pros and cons. Some displays are incapable of being made into flat panel displays and others present problems with technical aspects like lifetime, power consumption, and color contrast. The most common of the flat panel displays would be the LCD display that is used in a wide variety of applications most notably laptop computers. The LCD monitor is capable of being made thin, portable, and can achieve brightnesses excessive of 500 cd/m<sup>2</sup>. The parameters that need to be met by these displays includes; brightness of at least 500cd/m<sup>2</sup>, a lifetime of 100,000 hours, a refresh rate of 200Hz (highest refresh rate currently is 600Hz), as well as low driving voltage [3], [4], [5].

### 2.1.1 Liquid Crystal Displays

The LCD displays use a backlight that sends white light through tri-colored pixels. The light passes through a red, green, and blue filter that changes the white light to the corresponding color, where each color filter is referred to as a sub-pixel [6]. The device structure used in an LCD display can be seen in Figure 2.1.1. The white light entering into the pixel via the backlight is polarized and matches the polarization of a polarizer on the top of the device structure. The light will then pass directly though the pixel device and be emitted in the red, green, and/or blue (RGB) colors due to the color filtering of each sub-pixel. To prevent the red, green, or blue emission a liquid crystal layer is activated that changes the polarity of the light [6]. To activate the liquid crystal beneath each color filter a silicon TFT matrix is used, which will turn on or off the liquid crystal layer. The change in polarization by the liquid crystal layer comes from a change in orientation of the liquid crystals when a voltage is applied [6].



Figure 2.1.1: The structure used in liquid crystal displays.

To change the polarization of the light an alignment plate is used, which consists of grooves which the liquid crystals anchor into, and these grooves are perpendicular on either side of the device causing the liquid crystal to be twisted on a helix of 90°. The polarized light is then superimposed onto the twisting liquid crystals which in-turn changes the polarization of the light. When a voltage is applied to the liquid crystal molecules they align parallel to the electric field, removing the twisted helix and the change in polarization [6]. This process of changing the polarization can be seen in figure 2.1.2 (a) and 2.1.2 (b). This change in polarity will prevent emission, because the change in polarity will cause the light to no longer match the polarizing layer on the top layer of the device. This means that in-order to achieve black the liquid crystal layer must be activated for each sub-pixel.



Figure 1.1.2 (a) The LCD structure when light is passing. (b) The LCD structure when light is being blocked. a: polarizer, b: glass substrate, c: transparent electrode, d: liquid crystal, e: alignment layer [6].

#### 2.1.2 Organic Light Emitting Diodes

The organic light emitting diodes (OLEDs) that are currently being used to create OLED displays are capable of achieving the needed brightnesses, color ratios, lifetimes, and refresh rates for commercially viable displays. Currently Sony, Samsung, and LG have OLED flat panel displays for sale. Despite the degradation effects and stability of both OLED and PLED materials that are used in the multi-layer devices, research and progress towards commercial products continues. The draw for commercial production being relatively low production cost, high contrast ratios (which is a ratio of brightness between the brightest and darkest colors), color saturation (the purity of the color based on its bandwidth), as well as the ability to be used in flexible and transparent device applications [7]. Sony currently offers the Cyber-shot TX100V digital camera that uses an OLED screen as the display panel of the camera as well as the XEL-1 which is an 11 inch OLED flat-panel display. According to Sony the display is capable of high contrast ratio due to the pure black, quick response time due to its emissive nature, and high brightness of vivid colors [8]. Other companies are expanding to the OLED market in phones and handheld music players as well in the form of active-matrix OLED (AMOLED) displays.

OLED devices include small-molecule and polymer-based dyes as the lightemitting layer in the device structure. There a several potential advantages to using OLED technology including: relative low cost of fabrication, active light emission as opposed to using a backlight, potential to be applied to flexible displays, transparency which allows for transparent displays, and scalability of processing [7], [9], [10]. The first OLED materials were fabricated in 1907 but it wasn't until 1987 that the first commercially viable OLED device was fabricated using the small organic molecule tris(8-hydroxyquinoline) Al (Alq<sub>3</sub>). Following this work the first polymer OLED (PLED) was created in 1990 using poly(p-phenylene vinylene) (PPV), sparking a competition between OLED and PLED over which is a more viable option for display technologies [7]. The initial devices had lifetimes of 1 minute in air and through continued work the devices improved and operated for over 20,000 hours in a pulsed mode similar to flat panel displays. This lifetime can then be improved even further through the use of packaging and sealing of the organic layers [7], [10].

The simplest design of an OLED is a fluorescent organic layer with an electrode on either side. When a voltage is applied to the electrodes, hole and electron carriers are injected into the layer containing the light emitting compound, or lumophore, and recombine to create an excited state by way of a bound electron-hole pair, or exciton, which will then create a radiative decay back to the ground state [9]. The lumophore acts as an insulator at low voltages due to intrinsic high resistivity of the organic materials. This means at high voltages the dominant conduction mechanism is space-charge-limited conduction, where the injection mechanisms are Schottky thermal emission or Fowler-Nordheim tunneling injection [7], [11]. The Schottky emission process is described by Eq. (1), where  $m^*$  is the effective mass of the carrier, k is Boltzmann's constant, T is temperature,  $\Phi_{BN}$  is the barrier height, h is Planck's constant, q is the elementary charge, and V is the applied voltage [7].

$$J = \frac{4\pi q m^* k}{h^3} T^2 \exp\left(-\frac{q \Phi_{BN}}{kT}\right) \left[\exp\left(\frac{qV}{kT}\right) - 1\right]$$
(1)

The Schottkey model uses carrier tunneling to impurities, defects, or structural disorder levels to move through the barrier. This method will not achieve the high current injection that is achieved in OLED operation; instead the Fowler-Nordheim tunneling injection process can be used to describe the current injection. The tunneling injection process can be described by Eq. (2), where  $m_0$  is the mass of a free electron [7].

$$J = \left(\frac{q^{3}V^{2}m_{0}}{8\pi h\Phi_{BN}m^{*}}\right) exp\left(\frac{4(2m^{*})^{0.5}\Phi_{BN}^{1.5}}{3\hbar qV}\right)$$
(2)

The Schottky thermal injection process is visually represented as Figure 2.1.3 (a) and the Fowler-Nordheim tunneling injection process can be seen in Figure 2.1.3 (b). The application of a high electric field at the molecule and metal interface allows for the use of the tunneling mechanism. The two charge injection methods described inject the carriers into the lumophore, which are then governed by space-charge-limited current (SCLC) when the injected current density exceeds the intrinsic charge density [7].



Figur 2.1.3: (a) Schottky thermal injection via impurity or defects. (b) Fowler-Nordheim tunneling injection by local high-electric field [7].

The injected carriers form space-charges near the organic layer and electrode interfaces because of the low carrier mobility in the organic layers. This means that the internal electric field is enhanced by space charges. Eq. (3) describes the current density

governed by the SCLC, where *J* is the current density,  $\varepsilon$  is the relative dielectric constant,  $\varepsilon_0$  is the dielectric constant, and *L* is the sample thickness [7].

$$J = \frac{9\varepsilon\varepsilon_0 \mu V^2}{8L^3} \tag{3}$$

A graphical representation of the SCLC process can be seen in Figure 2.1.4. The image depicts the overall SCLC to be a combination of the external field, the voltage over the distance, and the internal built in field which is caused by space charges [7]. The charge carriers concentrate at the metal/organic interfaces due to the low motilities. This process causes the normally insulating organic layers to become the semiconducting material that is needed for the OLED applications. The charge recombination in the lumophore layer then creates excited states which decay either radiatively or non-radiatively [7].



Figure 2.1.4: The schematic representation of SCLC inside of the organic layer in a single-layer device [7].

The charge recombination in the organic layer creates neutral excited states which are typically singlet excitons. When the singlet excitons transition back to the ground state the energy is dissipated via a photon or a phonon, there is no evidence that proves the direct recombination of the electron and the hole create light emission in the organic layers [7]. The recombination process does not necessarily create a singlet exciton it is also possible that a triplet exciton will be created. The carrier recombination creates singlet excitons and triplet excitons at a ratio of 1 to 3. The triplet exciton extinction can create phonons or more singlet and triplet excitons which create a delayed reaction of photon generation. The triplet creation limits the maximum electro-luminescence (EL) quantum efficiency to 40% [7]. The addition of carrier injection layers can improve the OLED device performance.

The purpose of the multilayer device is to confine the charge carriers inside of the emitter layer though the use of balanced carrier injection. Figure 2.1.5 shows the three commonly used and basic device structures; the single hetero-H structure (SH-H), single hetero-E structure (SH-E), and the double hetero structure (DH) [7]. The electron-transport layer (ETL) carriers the electrons to the emitter layer (EML), and the hole-transport layer (HTL) carries the holes into the EML for recombination. The SH-H and the SH-E use one of the transport layers as the light emission layer and the DH uses a separate EML from the HTL and ETL. If recombination occurs in HTL or ETL rather than the EML then it is still possible for an exciton to be produced and create a radiative recombination. This means that charge balance and mobility is an important part of charge balance in the EML [7].



Figure 2.1.5: The single hetero-H (SH-H) structure, the single hetero-E (SH-E) structure, and the double heterostrucutre (DH) device designs [7].

The DH structure has the benefit of creating a very thin layer for recombination, but also creates a problem with balancing the electron and hole injection to ensure that the recombination occurs in the correct layer. The DH structures also have a very narrow recombination region which is typically less than 10 nm from the HTL/ETL interface. With single layer devices the recombination region is 50-100 nm, which suggests a lowcarrier-capture cross section. The reason for the increased recombination is the accumulation of hole and electron carriers at the HTL/ETL interface [7].

The degradation of the OLEDs is important when considering the technological impact as well as predicting their impact on consumer products. The formation of dark spots which are non-emissive areas of the OLED is the most prominent form of degradation [7], [10]. The cause for the dark spots is delamination of the electrode metal at the organic/metal interface. The metallic delamination is caused by heating of the metal from the injected current, which is initiated by pinholes in the metal. Another cause to the dark spots would be the carbonization of the polymers. Recrystallization of polymer layers will also decrease the efficiency at which light is generated. The singlet-excitons that radiatively recombine are quenched by defects at the surface grain boundaries. The amorphous polymer layers form grain boundaries during recrystallization which occurs when its temperature reaches the glass transition temperature [7]. The glass transition temperature can be reached when phonon generation causes a buildup of heat within the layers.

There are also specific degradation characteristics found in the commonly used electron transport layer, Alq<sub>3</sub>. The Alq<sub>3</sub> layer will create charge-trapping and quenching sites as it physically ages or recrystallizes and can also change the distribution of

localized states resulting in a change of charge-transport properties [7]. In the presence of water the Alq<sub>3</sub> ligand will be replaced by the water and change the structure to be readily oxidized. The oxidation of Alq<sub>3</sub> will then create a series of quenching sites where the ligand bonding the 8-hydroxyquinoline (Hq) to the aluminum portion is separated. The Hq is further susceptible to oxidation reactions and will generate more luminescence-quenching sites [7].

Despite the degradation and lifetime constraints of the current OLED technologies research and commercialization continues. The high-speed processing as well as lost fabrication cost being the largest driving factors for commercialization. The ability to create flexible and transparent displays for heads up displays on windows and flexible computer monitors is yet another reason OLED technology continues to be researched. The processing steps and commercial possibilities are enough to create a large research basis for this technology.

### 2.2 Quantum Dots

The quantum dot (QD) was first pioneered by Louis Brus at Bell Labs and Alexander Efros in the Soviet Union for the use in solar energy conversion [12]. The advantages of surface to volume ratio were being explored in the semiconductor field and during this time it was observed that different sizes of the same material yielded different colors. This led to further research and understanding of the quantum confinement effects that take place when changing the size of a bulk semiconductor. The creation of a material capable of emitting separate wavelengths, which are size dependent, allowed for quantum dots to be used in LEDs, telecommunications, tunable lasers, quantum computing, and photovoltaics [12].

#### 2.2.1 Working Principles

The quantum dot is capable of emitting a very narrow band emission. The wavelength of the emission is dependent on the size of the quantum dot, which also dictates the bandgap. The bandgap of the quantum dot is the energy required to create an electron hole pair in the semiconductor. When energy is injected into the QD either through a photon or through an electric current an electron will be promoted to the conduction band and an electron hole pair is created. The electron hole-pair known as an exciton is bound together with electrostatic attraction. The interaction between the electron and the hole in the exciton can be compared with a hydrogen atom, which yields a Hamiltonian shown in Eq. (4), where *M* is the total mass  $M=m_e^*+m_h^*$ ,  $\mu$  is the reduced mass  $\mu = m_e^*m_h^*/(m_e^*+m_h^*)$ ,  $m_e^*$  is the effective mass of an electron, and  $m_h^*$  is the effective mass of a hole [12].

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2M} \nabla_e^2 - \frac{\hbar^2}{2M} \nabla_h^2 - \frac{e^2}{\varepsilon |r_e - r_h|} \tag{4}$$

The most probable orbit in a hydrogen atom is defined as the Bohr radius,  $a_0$ , which is similar to an exciton. A hydrogen atom being an electron bound to a nucleus of a single proton and neutron resembles the exciton. The most probable orbit of an exciton then can be related to the Bohr radius of a hydrogen atom. The Bohr radius of an exciton,  $\alpha$ , then is equivalent to the Bohr radius of a hydrogen atom that is corrected by the dielectric constant of the medium as well as the effective masses  $m_e^*$  and  $m_h^*$ , as shown in Eq. (5) [12].

$$\alpha = (\varepsilon a_0 m_e) / \mu \tag{5}$$

When the radius of the QD is less than the Bohr radius of an exciton the hydrogen model no longer applies, and the lowest energy level of the exciton is delocalized over the entire QD [13]. The exciton can be considered a free particle in a dot, where the exciton levels are given by the quantum mechanical problem of a particle in a box. The electrons and holes are now confined to the small space and the Coulomb attraction is negligible in comparison to the potential U(r) that describes a spherically symmetric well potential well of radius *r*. The Hamiltonian of the exciton can then be re-written to include the potential U(r), as shown in Eq. (6).

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2M} \nabla_e^2 - \frac{\hbar^2}{2M} \nabla_h^2 - \frac{e^2}{\varepsilon |r_e - r_h|} + U(r) \tag{6}$$

The potential U(r) describes the energy of the particle in a box where the energies of the permitted wavenumbers correspond to Eq. (7), where *n* is positive whole number,  $\mu$  is the effective mass of the particle in the box, and *r* is the radius of the quantum dot [12], [14], [15].

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2\mu r^2} - \frac{1.8e^2}{\epsilon R}$$
(7)

The lowest state allowed by this model is  $E_1$  meaning the particle cannot be sitting still because it would violate Heisenberg's uncertainty principle. The lowest energy level equation that corresponds to  $E_1$  can be seen as Eq. (8) [14], [15], [16].

$$E_{1} = \frac{\hbar^{2} \pi^{2}}{2\mu r^{2}} - \frac{1.8e^{2}}{\varepsilon R}$$
(8)

The exponential curve defines the band diagram shown in Figure 2.2.1, and furthermore the radius will affect the placement of the first energy level. As the radius decreases the value of  $E_1$  will increase causing a larger band gap for a smaller quantum dot. This equation then summarizes the bandgap of a quantum dot that has a radius smaller than the Bohr radius of an exciton in that material. As the radius of the QD becomes less and less the bandgap becomes larger and larger, and as bandgap increases the wavelength of the emission from the exciton will blue shift, or decrease. This can be shown by the relation shown in Eq. (9), where  $E_g$  is the bandgap, c is the speed of light, and  $\lambda$  is the wavelength emitted in microns [17].



Figure 2.2.1: The energy levels defined by Eq. (7) with an arbitrary r value. The  $E_n$  levels will change in distance based upon the increase or decrease of r.

The principles outlined in this section discuss the process in-which a quantum dot is capable of emitting in multiple wavelengths. Upon these principles CdSe quantum dots can be fabricated to emit in a variety of colors specifically red, green, and blue which can then be used in LEDs for display technologies. The synthesis of these dots will need to have control over the size of the dots to ensure a narrow bandwidth emission, as well as ensure a crystalline structure free of grain boundaries within each QD.

#### 2.2.2 Synthesis

The synthesis of CdSe nanocrystals uses a single crystal growth to form a colloidal suspension of the QDs referred to as the TOPO/TOP method [12], [18]. The first step in synthesis is to create a hot steric solution of CdO under argon flow at 150 °C, the argon flow will eliminate any water or oxygen from the process. Next the addition of the coordinating ligands hexylphosphonic acid (HPA) and trioctylphosphine oxide (TOPO), at elevated temperatures will generate Cd2+ in the solution. To initialize the crystal growth a solution of tri-n-octylphosphine selenide (TOPSe) is then injected into the TOPO solution and the temperature is raised to approximately 300 °C to promote high crystalline growth of the QDs. The TOPO/TOP ligands then bond to the surface of the growing nanocrystals to prevent aggregation. The following is the reaction of the process described thus far:

$$\begin{array}{c} H_{3}C \\ H_{3}C \\ H_{3}C \end{array} + \left[ CH_{3} - (CH_{2})_{7} \\ H_{3}C \\ \end{array} \right] \xrightarrow{P = Se} \xrightarrow{TOPO} CdSe + \left[ CH_{3} - (CH_{2})_{7} \\ H_{3} \\ CH_{3} \\ \end{array} \right] \xrightarrow{P = Se} \xrightarrow{TOPO} CdSe + \left[ CH_{3} - (CH_{2})_{7} \\ H_{3} \\ \end{array} \right] \xrightarrow{P = Se} \xrightarrow{TOPO} CdSe + \left[ CH_{3} - (CH_{2})_{7} \\ H_{3} \\ CH_{3} \\ \end{array} \right] \xrightarrow{P = Se} \xrightarrow{TOPO} CdSe + \left[ CH_{3} - (CH_{2})_{7} \\ H_{3} \\ CH_{3} \\ \end{array} \right]$$

As the process is taking place samples can be removed for absorption spectra measurement and the process will continue till the desired spectrum is observed [12]. After the nanocrystals have achieved the desired size, a size selective precipitation can be used to acquire a very narrow range in QD size.

The process of size-selective precipitation uses methods in which larger QDs will flocculate due to their greater attractive van der Waals forces which can then be centrifuged out of the remaining solution [19]. The dispersion then of the colloidal QDs is allowed to partially flocculate and then through centrifuging the larger QDs will be removed leaving the smaller QDs in solution. If the larger QDs are then desired the precipitate can be placed into solvent and allowed to re-disperse where the flocculation process can be repeated to further narrow the size distribution. The two methods of sizeselective precipitation are titration of a non-solvent into the dispersion or preferential evaporation of the solvent system to cause flocculation. After the size selection of the QDs it is possible to add the capping layer to the QD [19].

After the size selection process is completed the CdSe dots can be capped with the wide bandgap material ZnS [18]. To do this Diethylzinc (ZnEt2) and hexamethyldisilathiane ((TMS)2S) are used as the Zn and S precursors. The amount of precursor can be calculated by finding the ratio of the ZnS shell volume and the CdSe core volume. The amount of ZnS shell growth is less than the amount added due to incomplete reaction or precursor and loss of material to the flask walls during addition. To prepare the shell precursor the equimolar amounts of the Diethylzinc and hexamethyldisilathiane were dissolved into 2-4 mL of TOP inside of an inert glovebox. The precursor is then added to a heated reaction flask under nitrogen containing the dispersed CdSe dots in hexane. The reaction flask is heated to a temperature between 140 °C and 230 °C depending on how large the QDs are, where the larger the QD the higher the temperature. When the temperature is reached the Zn and S precursor solution is added to the vigorously stirring CdSe solution dropwise for 5-10 minutes. The solution is then reduced to a temperature of 90 °C and allowed to stir for several hours, also 5 mL of butanol is added to the solution to prevent the TOPO ligands from hardening as they cool to room temperature [18].

With the capping of the QD it is then prepared to be used in one of many applications. It is also possible to change the solution, dry them, or to change the ligand structure if needed. For this experiment the QDs are simply ready for application after capping.

### 2.3 QD-LED display vs. Current Technology

The application of the QD-LED in flat panel displays is a logical step in the progression of the technology. The QD-LEDs are capable of achieving higher brightnesses than what is actually needed for video processing, have the potential for long lifetimes, have a narrow band emission that will generate high color saturation, and due to their emissive nature will have a high contrast ratio with very pure blacks [2]. Table 2.3 lists the pros and cons of several display technologies that will be discussed in detail here.

Display		OLED/		Plasma
Technology	QD-LLD	PLED		Display
PROS:	-High Contrast	-Low Cost	-Consistent	-Emissive
	Ratio	- Flexible displays	Reproduction	-High Contrast
	-High Brightness	-High Brightness	- Easily Achieve	Ratio
	-Emissive		High Definition	-High Color Purity
	-Single Material		-Well Researched	
CONS:	-Short Device	-Short Device	-Backlight	- Prone to Image
	Lifetime	Lifetime	-Poor Contrast	Burn
	-Not Thoroughly	-Varying Emitter	Ratio	-High Power
	Researched	Materials	-High Power	Consumption
			Consumption	

 Table 2.3: The Pros and Cons of some display technologies including; QD-LED [2], [20], OLED/PLED [7], LCD
 [6], and Plasma Displays [21].

The LCD flat panel displays are backlit which wastes a greater amount of electricity than an emissive display because they have a backlight that requires energy to block the light, where emissive displays only generate light when it is needed (6). The color rendering system in an LCD also cannot achieve the colors equivalent to QD-LEDs, and this is due to the filtering of a white light to show the desired color where as the narrow emissions of the QD-LEDs presents sharper colors [2]. The chromacity coordinates of the light emitted from the QD-LEDs also falls encompasses the National Television System Committee (NTSC) standards on the Commission Internationale de l'Eclairage (CIE) chromaticity chart, meaning the colors are much richer than the current NTSC standards as shown in Figure 2.3.1 [20]. Similarly to the standard LCD display the LED-LCD flat panel display still uses a backlight but it uses LEDs as a light source making it more efficient.



Figure 2.3.1: The CIE coordinates of the QD-LEDs (white triangle) as well as the NTSC color standards (black triangle) [20].

The plasma display panel is an emissive structure similar to the QD-LED. Plasma displays have a driving system that supply voltage to an inert gas filled cell, which emits a UV light which is then absorbed by a phosphor and re-emitted as the color of the chosen cell [21]. This design would never allow for a flexible display because a rigid structure is needed to contain the inert gas within the cells. It should also be noted that considerable power is needed to energize the inert gas and cause UV emission. The final limitation is that the phosphor used in the display is incapable of reaching the wavelengths and narrow bandwidths found in QD-LEDs.

The OLED display as well as the PLED display is similar to the QD-LED display in both form and function. The operating principles of these two technologies are covered in the previous section 2.1.2. The separating factor for all three would be the lumophore layer that is used for light emission. For OLED structures a small molecule organic is used as the light emitting layer, for PLED structures a polymer chain organic structure is used, and for the QD-LED structures a layer of QDs defines the recombination regime. The components on which the devices will be compared to one another are emitter cost, manufacturing process, use in flexible displays, and emission bandwidth.

The cost of the emitter for QD-LEDs is low because the emitter is a single material that differs only by size, which means that it can be applied by the same means of solution processing and in the same solution for any desired size. The OLED material is a small molecule organic which requires a different compound for each desired wavelength. The multiple materials will have to be designed and tested, as well as deposited in the correct proportions making the cost higher [7]. The PLED material will also require separate organic polymers for each desired wavelength of the LED. The

design of the compounds will increase the price as well as the solvents in which they will be dispersed in; each polymer may require a separate solvent that when applied may damage a previously deposited film [7]. The process in which displays are made is also important to cost and reproducibility. The QD-LED emitter layer is deposited via solution processing, this means that there is no need to achieve a high vacuum which will reduce the fabrication cost [2]. The PLED is very similar to the QD-LED in the sense that it too is done through solution processing, but the OLED lumophore is deposited via thermal evaporation which requires vacuum based technologies. One of the draws to the OLED and PLED devices is the ability to be used in flexible displays [7]. This means that the entire display is built upon a flexible poly(ethylene terephthalate) (PET) rather than a solid glass substrate. The inorganic nature of the QDs makes them resilient to oxygen and moisture, but the small molecule OLEDs are very susceptible to failure when encountering oxygen and moisture which could permeate through the PET substrate [20]. Similarly to the OLED material the PLED material is also damaged upon contact with oxygen and water vapor but it is slightly more resilient because of the solution processing nature of the material [7]. Finally, the emission bandwidth of the OLED and PLED material is broad, meaning 50-100 nm, whereas the QD-LED emission is narrow, meaning less than 30 nm [7], [2]. The narrow bandwidth of the emission spectra of the QD-LED will yield a much higher color contrast ratio improving the appearance of the display to the human eye.

Based on the stated observations it can be said that the QD-LED has a very legitimate cause for research and investigation. The lower production cost, possibility for increased lifetime, the ability to be applied to flexible substrates, high color contrast ratios, and the elevated brightness are all reasons the QD-LED display has the possibility to become a viable display medium.

#### 2.4 Advances in QD-LED Display Technology

The QD-LED has advanced within the past 3 years to show its viability as a display medium. The high brightness displays, extended lifetimes, use on flexible displays, and the creation of a functioning passively addressed monochromatic display all show advances in the QD-LED field towards flat panel displays.

The brightness of the QD-LED differs for each if the QD sizes or emission wavelengths. Higher brightnesses have been achieved for the larger QDs and lower brightnesses have been achieved for the smaller QDs. The maximum luminance for the red QDs (619 nm) is 9064 cd/m<sup>2</sup>, 3700 cd/m<sup>2</sup> for the green (525 nm) device, and the blue (460 nm) device has a peak brightness of 1600 cd/m<sup>2</sup> [2], [22]. The brightnesses far exceed the video brightness of 500 cd/m<sup>2</sup> that is currently needed for a flat panel display. The ability to achieve high brightness will allow for easy to read displays in sunlight as well as the reduction of glare.

The lifetime of the QD-LED is demonstrated in Figure 2.4.1, where the brightness initiates at a value greater than 1,100 cd/m<sup>2</sup> and decays to 50% of this value after 300 hours of continuous operation [23]. The inset of Figure 2.4.1 shows an illuminated red QD-LED similar to the one used in the lifetime testing, which lacks any noticeable defects and demonstrates a uniform brightness. The cause for the degradation over the course of 300 hours would be the heat generated from nonradiative recombinations. The non-radiative recombinations generate great heat within the QD-LED which in-turn

damages the ligand structures on the surface of the QD [24]. When a ligand structure on the surface is damaged it creates a charge trapping site on the surface which will reduce the efficiency of the QD to create radiative recombinations [25]. The removal of heat from the system would be the obvious solution but to do so would require heat sinking or the removal of non-radiative recombination, which would take further research. This demonstrated lifetime is not equivalent to the 100,000 hours needed for a display but rather shows the potential to one day reach that value.



Figure 2.4.1: The lifetime of a red QD-LED under vacuum with a driving voltage of 13V. The inset shows an image of the illuminated red QD-LED [23].

The QD-LED has also been used on flexible displays, where the substrate material is PET [20]. The QD-LED has been fabricated on flexible substrates and was able to function while adjusting the radius of curvature. The maximum luminance achieved for the red QD-LED was 7070 cd/m<sup>2</sup>, 3375 cd/m<sup>2</sup> for the green QD-LED, and 1408 cd/m<sup>2</sup> for the blue QD-LED [20]. The lower maximum luminance the smaller QDs is similar to the results on glass substrates. The maximum luminance is lower for all three colors when compared to the glass substrates but the brightness achieved is still greater
than the 500  $cd/m^2$  that is needed for displays. The devices can be seen operating while the substrate is bent in Figure 2.4.2. Each of the 3 devices is being operated at its maximum luminance and showed no sign of spectral change while being bent. The ability to operate until reaching a radius of curvature of 5 mm proves the worth of flexible displays for electronic paper, newspaper replacement, and many other options.



Figure 2.4.2: The QD-LED on a flexible substrate demonstrating red (a), green (b), and blue (c) [20].

The creation of a functioning active matrix QD-LED is one of the greatest advances in QD-LED display technology. Researchers at the Samsung corporation have proven that it is possible to create a monochromatic QD-LED display shown in Figure 2.4.3 below, which depicts a tiger [26]. The display is 320x240 pixels and is built on an amorphous silicon TFT backplane. This means the display is driven using active matrix addressing rather than passive matrix addressing. It should also be noted that there is less than 5% variation in brightness across the surface of the display. The upper right inset of the image shows the screen illuminated at 500 cd/m<sup>2</sup> which is standard video brightness, and the bottom right inset shows the pixel size where the scale bar is 100 microns in length [26].



Figure 2.4.3: A 4 inch silicon TFT active matrix backplane with a 320x240 pixel array. Top right inset shows display operating at 500 cd/m<sup>2</sup> and the lower right inset shows the pixel with a scale bar of 100 microns [26].

This step in the fabrication of monochromatic QD-LED displays demonstrates the validity of the QD-LED as a display medium. There are some defects on the image found in Figure 2.4.3 but that is to be expected when attempting to spin coat an area as large as 4 inches. The use of an active matrix backplane simplifies the processing and addressing as well as removes cross talk but it also removes the ability to be put onto a flexible substrate due to the necessity of a TFT backplane. The image is also only monochromatic because the process to create a multi-color display is currently not within the means of the Samsung corporation but will be discussed within this research.

# **Chapter 3**

## The Quantum Dot LED

### 3.1 QD-LED Structure

The QD-LEDs used throughout the research described here are equivalent to the double hetero structure devices described in the OLED section 2.1.2 and seen in Figure 2.1.4. This means that the lumophore layer is between a hole transport layer and an electron transport layer. The difference between an OLED and QD-LED double hetero structure device would be that the lumophore layer in the QD-LED is made from inorganic QDs rather than an organic compound. A representation of the device structure used in this research can be seen in Figure 3.1.1. The thickness of the layers has been chosen to balance the charge injection into the QD layer to increase the amount of radiative recombination within the QD layer as opposed to one of the transport layers. The layer thicknesses have been optimized by Dr. Zhanao Tan to achieve the brightest QD-LEDs for the given structure [2]. The first layer of the device is ~30nm of poly(3,4ethylene dioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS), which helps to inject holes into the hole transport layer [2], [27]. Following the hole injection layer is the hole transport layer poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine) (poly-TPD), which is ~45nm in thickness [2]. This material was chosen for its exceptional hole transporting properties, but also because it has a strong resistance to non-polar solvents that will be applied to the surface of this layer when the QDs are deposited [23]. After the HTL is deposited the QD film is deposited onto the device structure via a solution processing method whether it be spin coating, mist deposition, inkjet printing, contact printing, or still some other form of deposition, and the thickness of the QD film depends on the diameter of the QDs. It has been experimentally proven that 2-5 monolayer thickness is optimal for achieving the highest brightnesses; hence the lumophore thickness should match this value [2], [23]. The electron transport material which consists of Alq<sub>3</sub> is then deposited to be ~30 nm thick via thermal evaporation. Finally, a bi-layer cathode of Ca/Al is deposited to be 10/150 nm thick. The calcium is used to raise the work function of the Al to meet the lowest unoccupied molecular orbital of the Alq<sub>3</sub> to increase the efficiency of the current injection [28].



Figure 3.1.1: The QD-LED structure used throughout this research, which consists of glass substrate, ITO layer, Poly-TPD, QD layer, Alq3, Ca, and Al.

It should be noted that the QD-LED is subject to the same degradation effects of the double heterostructure (DH) OLED devices concerning the HTL and ETL. Specifically, the Alq<sub>3</sub> layer which is degrades in the presence of water vapor and the presence of oxygen. One solution to this would be to remove the organic components found within the structure but to do so new inorganic options must be discovered. There is currently

research being done to replace the organic materials with inorganic compounds that would extend the lifetime of the QD-LED [29], [30].

### 3.2 Band Structure

The DH structure shown in Figure 3.1.1 correlates to a band structure that describes the QD-LED. The band structure of the device is shown in Figure 3.2.1 where the lowest unoccupied molecular orbital (LUMO) is similar to the conduction band in a semiconductor and the highest occupied molecular orbital (HOMO) is similar to the valence band.



Figure 3.2.1: The band structure of the devices used in this research [31].

The band structure shown here is based off of the structure given by Seth Coe-Sullivan et al. which incorporates the shell and ligand structure of the QD [31]. The ITO/PEDOT:PSS layer injects holes into the HOMO band of the poly-TPD material. These holes are then driven into the QD layer via the poly-TPD. There is an energy gap that is preventing the injection but due to the p-type nature of the polymer and its high mobility the barrier can be overcome. The opposite side shows the Ca/Al layer matched to the LUMO level of the Alq<sub>3</sub>, which shows that electrons can easily be transported into the Alq<sub>3</sub> layer and then into the QD layer. Once the electrons and holes reach the QD layer they will recombine and create excitons which will then radiatively recombine or non-radiatively recombine to create a photon or a phonon. As discussed in the OLED section singlet or triplet excitons could be created, though it is still uncertain whether the QD can harvest the triplet excitons or only the singlet excitons which would limit the radiative recombination rates [32]. The band structure shown in Figure 3.2.1 also assumes a single monolayer of QDs within the device. The application of multiple layers is shown in Figure 3.2.2 [31]. The example shown in Figure 3.2.2 depicts 3 layers of QDs. The core of the QD is at the center with the narrowest bandgap, then a wider bandgap material (ZnS) is placed over the shell to passivate the surface and remove any carrier traps. Then the organic ligand structures that help to separate the QDs in solution create an even larger barrier for the carriers to overcome. The electron shown in the figure will



Figure 3.2.2: When multiple QDs are placed next to each other the ligand and shell structure acts a barrier for the carriers to overcome [31].

have to overcome each barrier before it can be moved to the next QD. This hopping process requires the QD to tunnel through the energy barrier [31]. The transmission probability that a carrier will tunnel through the barrier can be given by Eq. (10) where the W is the barrier width,  $m^*$  is the effective mass of the carrier, and  $\Phi_B$  is the barrier height [33].

$$T = \exp\left(\frac{-2W\sqrt{2m^*\Phi_{\rm B}}}{\hbar}\right) \tag{10}$$

This means that for each layer of QDs there is a probability that the electron will not tunnel through to the next layer. This also means that as the number of layers increases the amount of times the electron must tunnel also increases. Hence, as the QD layers increase in thickness it is possible the electrons may never fully move through the QD layer.

The single monolayer of QDs has merit because it will require no charge loss due to tunneling, though it has been found that depositing multiple QD layers is advantageous as well [23]. When single monolayer devices are used they have increased leakage current through the QD layer without recombination. This phenomenon is due to the presence of voids, interstitial spacing, and grain boundaries within the QD layer. When the QDs are used in a monolayer fashion there is a strong recombination in the ETL which indicates poor charge recombination in the QD layer. When multiple layers are used a higher brightness can be achieved with less current leakage but the driving voltage increases. This increase in voltage is needed to account for the electrons lost to the tunneling process [23]. It should also be noted that the amount of layers used depends on the size of the quantum dot [2], [34]. The change in size of the quantum dot affects the

coverage of the film and therefore the leakage current. The thickness was optimized to balance the maximum brightness of QD-LEDs as well as the emission efficiency [2].

#### 3.3 Efficiency

The three measurements of efficiency would be the internal quantum efficiency, the external quantum efficiency, and the luminous efficiency. The internal quantum efficiency (IQE) is the efficiency defined by the numbers of photons produced within a device divided by the number of injected charge carriers [7]. The IQE,  $\eta_{IQE}$ , is defined by Eq. (11) where  $\gamma$  is the charge-balance factor,  $\eta_r$  is the efficiency of production of singlet excitons,  $\phi_f$  is the quantum efficiency of fluorescence, *J* is the circuit current, and  $J_r$  is the recombination current [7].

$$\eta_{IQE} = \gamma \eta_r \phi_f \quad Where \quad \gamma = \frac{J_r}{J}$$
 (11)

The IQE of the QD-LED is still uncertain because it is unclear whether or not the exciton harvesting of the QDs is as efficient as the OLEDs. The OLED materials are capable of catching nearly all singlet excitons as well as harvesting nearly all triplet excitons as they down grade to singlet excitons yielding a high IQE [32].

The external quantum efficiency (EQE) is defined as the number of photons that escape the device divided by the number of injected charge carriers. The main difference being between EQE and IQE being that the EQE takes into account the total internal reflection of the device. Eq. (12) describes the EQE,  $\eta_{EQE}$ , where  $\zeta$  is the multiplying factor that accounts for the refractive index of the substrate the light travels through, *n*.

$$\eta_{EQE} = \eta_{IQE} \zeta \ Where \ \zeta = \frac{1}{2n^2}$$
(12)

It should be noted that the value of the EQE will always be lower than that of the IQE because the total internal reflection will always lower the brightness [7].

The final efficiency factor is the luminous efficiency. This efficiency has a value of candela per ampere (cd/A) and describes best the efficiency of the light intensity emitted. This value is commonly used because it is a relation to the light emission and input current rather than the rate at which photons are emitted.

### 3.4 QD-LED Fabrication

The fabrication process of a QD-LED requires the deposition of multiple layers that make the double hetero structure. To visualize this process Figure 3.4.1 depicts the flowchart followed to make a QD-LED. The first step in fabrication process is to select the desired size of ITO coated glass substrate that is needed. Typically, a 2.5cm by 2.5cm substrate is sufficient, but the substrate can be larger or smaller depending on the amount of devices desired on the substrate. The ITO is then cleaned via ultrasonication and a series of solutions for 30 minutes each. The solutions used for cleaning in order are distilled water with dish detergent, distilled water, acetone, and isopropyl alcohol with the solutions being emptied and refilled halfway through each cleaning step. After the samples are cleaned the patterning and etching of the ITO takes place. The ITO is coated with photoresist in the desired pattern using standard photolithography techniques. After the photoresist is hard-baked the substrate is ready for ITO etching. The etching process is the standard procedure used by Delta Technologies, LTD, which is an ITO coated glass manufacturer and supplier [35]. Following the initial testing with patterned ITO it was shown that purchasing pre-patterned ITO yielded better results due to the elimination of over etching as well as having better defined edges. After patterning, or if pre-patterned



Figure 3.4.1: The flow chart that describes the device fabrication process for QD-LEDs.

ITO was purchased; the next step is cleaning of the substrates again. This cleaning process is the same as the first cleaning process, and is to ensure that the surface is free of photoresist and acid from the etching process. Once the sample cleaning is completed the substrates are heated to 150 °C in an oven at atmosphere to remove any residual moisture within the glass substrate. After drying the sample receives a UV-ozone treatment to enrich the negatively charged oxygen on the ITO surface, which will increase the ITO work function [2]. The UV-ozone treatment will also enhance the surface wetting of the ITO by removing carbon contaminants and modifying the surface polarity [2], [36]. Following the surface treatment of the substrate the deposition of the multiple layers is initiated.

The first layer to be deposited on the UV-ozone treated ITO is PEDOT:PSS (Manufacturer: Heraeus Clevios; Hanau, Germany; product number: PD-6002) via spin casting for 40 seconds at 2 kRPM, which generates a approximately a 30 nm coating. After the PEDOT:PSS is spun on it is oven-annealed at 150 °C for 10 minutes at atmosphere. After the oven-annealing is complete the substrate is loaded into an MBRAUN nitrogen glovebox system where the oxygen level is below 5 ppm and the water vapor is less than 1ppm. Next, the poly-TPD (Manufacturer: American Dye Source, Inc.; Baie D'Urfe, Quebec, Canada; product number: ADS254BE) is spun cast from a chlorobenzene solution onto the PEDOT:PSS layer at 2kRPM for 40 seconds, which yields approximately a 45nm thick layer. After spin casting the sample is annealed on a hot plate at 120 °C for 30 minutes to crosslink the polymer. The QD layer is then deposited onto the poly-TPD through spin casting from a toluene solution at 1kRPM for 40 seconds, or some other solution process method, and followed by a hot plate anneal at 80 °C for 30 minutes. In this research the QDs were purchased from OceanNanotech LLC, due to an NSF partnership with the company. The speed and concentration varies depending on the diameter of the QD to achieve the best thickness which was discussed in the previous section 3.2. After the annealing of the active region the substrate is placed into a thermal evaporation system to deposit the remaining layers. Alq<sub>3</sub> (Manufacturer: American Dye Source, Inc.; Baie D'Urfe, Quebec, Canada; product number: ADS061GE) is deposited via thermal evaporation at a pressure of  $3 \times 10^{-7}$  torr to achieve a thickness of 30nm. Finally, the 10nm calcium layer is then deposited through a shadow mask, followed by the 150nm aluminum layer through the same mask without breaking vacuum.

After the aluminum deposition the device is completed and ready for operation, though it has been shown that operation of the QD-LED at atmosphere will quickly degrade the Alq<sub>3</sub> layer as well as the calcium layer resulting in dark spot formation [7]. To prevent degradation a packaging process can be used to encapsulate the devices. Figure 3.4.2 depicts the device packaging process. The packaging starts with a 2.5cm by 2.5 cm glass slide with a shallow well in the center. This well is then packed and filled



Figure 3.4.2: The packaging process to encapsulate the QD-LED devices.

with calcium oxide powder. After the indent has been filled and packed with the calcium oxide a thin layer of Norland Optical Adhesive 68 (NOA68) is placed around the perimeter of the glass. The device substrate is then placed onto the glass cap so the devices are in contact with the calcium oxide powder and cured for 5 minutes under a UV lamp. After the initial curing a second layer of NOA68 is placed around the interface of the substrate and glass packaging slide, and put under the UV lamp for curing overnight.

The calcium oxide powder will absorb any residual oxygen, water vapor, or solvent from the optical adhesive, while the NOA68 forms a barrier preventing oxygen and moisture from permeating to the devices. After packaging the devices are ready for luminancevoltage testing, current-voltage testing, spectral analysis, and imaging.

## 3.5 QD-LED Results and Analysis

The tests composed on a QD-LED typically consist of testing luminance-voltage (L-V) characteristics, current-voltage (I-V) characteristics, luminance efficiency, spectrum analysis of the QD-LED, and imaging of the devices. To find the L-I-V characteristics a Keithley 4200 semiconductor parameter analyzer in conjunction with a Newport 818-SL silicon detector and a 1830-C Newport optical power meter, is used inside of an enclosed chamber. To prevent ambient light from entering the detector the testing area is enclosed within a large mesh box covered with black cloth and inside of a darkened room. The Keithley 4200 increases the voltage to the QD-LED from 0-25V increasing in increments of 0.05 V, and the Newport 818-SL silicon detector detects the light from the QD-LED and sends the signal to the 1830-C Newport optical power meter which then displays the optical power in  $\mu W$  before returning the collector voltage and current to the Keithley 4200. The Keithley 4200 then builds a list of input voltage and the resulting device current and voltage from the detector, and from this the collector voltage has the background removed. The background is found by running the Keithley 4200 without a QD-LED connected so the only light detected is the ambient light in characterization chamber. The maximum power from the power meter can then be used in conjunction with Eq. (13) to calculate the peak luminescence [37].

$$L = \frac{683*V(\lambda)*P}{A*\Omega*cos\theta} \text{ where } \Omega = 4\pi \sin^2\left(\tan^{-1}\frac{r}{R}\right)$$
(13)

In Eq. (13) *L* is luminescence,  $V(\lambda)$  is the visual function that corresponds to the light response of the eye and is specific to each wavelength (where 555nm is equal to one), *P* is the optical power, *A* is the detector area,  $\theta$  is the angle between the surface of the detector and the emission source (should be zero meaning the emitter and detector are parallel), and  $\Omega$  is the solid angle defined by *r* (the radius of the detector) and *R* (the distance from the detector to the light source) [37]. From this equation the maximum luminance can be calculated in the units cd/m<sup>2</sup> and a multiplying factor is derived from the ratio of the luminance and the base voltage. This multiplying factor is then applied to the rest of the voltage values to get the L-V curve.

The initial testing and fabrication of QD-LEDs was done with spin casting on ITO coated glass and was unpackaged. The results differ based on QD-LED area as well as layer thickness. The thickness control is crucial in fabrication as mentioned earlier. The quality of the chemicals used also is important, one example of this is the molecular weight of the poly-TPD. Higher molecular weight poly-TPD has shown the best results but is not always available meaning lower molecular weight poly-TPD has been used. This is one reason why the results differ greatly from the results reported by Dr. Zhanao Tan [2]. The results of the spin-cast QD-LED can be seen in figure 3.5.1. The L-I-V characteristics of the spin-cast QD-LED can be seen in Figure 3.5.1 (a) where the maximum luminance is shown to be 4670 cd/m<sup>2</sup>. The inset of Figure 3.5.1 (a) is the 7mm<sup>2</sup> pixel illuminated at its peak brightness. Figure 3.5.1 (b) shows the normalized spectrum of a red QD-LED measured using an Ocean Optics UV-Vis spectrometer. The spectrum shows a strong emission at 620nm which matches the manufacturers



Figure 3.5.1: The characterization results of a QD-LED where (a) depicts the L-I-V characteristics with an image of the illuminated device in the inset, (b) demonstrates the spectrum of the QD-LED device, and (c) shows the Luminous efficiency of the QD-LED.

specifications (OceanNanotech, LLC), with a full width at half maximum of 25 nm indicating a narrow bandwidth. The luminous efficiency can be seen in Figure 3.5.1 (c) which shows a maximum luminous efficiency at 1.6 cd/A.

The inset of Figure 3.5.1 (a) shows the degradation of the QD-LED when it is exposed to atmosphere. The Alq<sub>3</sub> and the calcium layers begin to oxidize and degrade the performance. To understand the degradation of  $Alq_3$  please refer to the section 2.1.2 where the mechanisms of Alq<sub>3</sub> film degradation are discussed. The calcium layer degrades as the highly reactive calcium oxidizes and forms a dielectric that no longer conducts electricity. To prevent this oxidation and degradation a packaging technique is implemented as shown in Figure 3.4.2. The results of the packaging process can be seen in Figure 3.5.2, where (a) depicts an unpackaged QD-LED and (b) shows a packaged QD-LED. From Figure 3.5.2 it can be seen that the unpackaged device (a) has many dark spots on the surface. The dark spots are sporadically spread across the surface causing a loss in brightness. The packaged device (b) shows a uniform brightness over the entire device. This has to do with the reduction of oxidation effects of the Alq<sub>3</sub> and the calcium. It should be noted the non-uniformity on the bottom portion of Figure 3.5.2 (b) is due to the movement of the sample inside the deposition tool, which causes a misalignment of the calcium and aluminum layer. This is caused when the shutter of the thermal evaporator is moved from open to close and closed to open between Ca and Aluminum depositions, which vibrates the sample holder and shifts the substrate. To solve this problem the samples are now fastened to the mask using tape to ensure there is no substrate movement.



Figure 3.5.2: QD-LED imaged without packaging (a) and with packaging (b).

The results and procedures described thus far have been a for spin-coated QD layer. To achieve a patterned RGB device spin-coating cannot be used. The spin-coating method coats the entire substrate in a uniform film which is not desired since 3 individual colors then cannot be deposited. To create a patterned tri-color array a deposition technique must be adopted that meets all the requirements that have been previously discussed for both display LEDs as well as QD-LEDs.

# Chapter 4

# **Deposition Techniques**

There are multiple modes of QD deposition that are based on solution processing techniques or physical liquid deposition. This chapter will discuss the possible deposition techniques as well as the deposition techniques used during this research. The chapter will conclude with the analysis and results of the deposition technique as well as the results for device patterning.

### 4.1 Deposition Methods

### 4.1.1 Imprint Lithography

Soft imprint lithography is a technique that can be used in the fabrication of QD-LEDs [38], [27]. Soft imprint lithography, also known as microcontact printing, uses a polydimethylsiloxane (PDMS) template to transfer the desired chemical to the substrate surface. The technique allows for highly accurate QD deposition, meaning it is possible to create a single monolayer of QDs [27]. The printing method also allows for patterning which is crucial in creating a multi-color display [27].

To create a PDMS template for the microcontact printing, first a silicon master is made using optical lithography or electron-beam lithography. This master mold is the negative image of the desired PDMS template, which is coated with PDMS and cured. The PDMS template is then peeled away from the master mask and is then used to transfer the QDs to the substrate [38]. The microcontact lithography process is depicted in Figure 4.1.1 where the PDMS is first coated over an etched silicon master mold. The next step is to coat the PDMS stamp with the aromatic organic polymer, parylene-C, via vapor deposition. After the deposition of parylene-C QDs are coated onto the PDMS stamp via spin-casting from an organic solvent. The QDs are left on the surface as the chloroform evaporates during spin-casting and the resulting film can then be transferred to the surface of the substrate via contact printing [27].



Figure 4.1.1: The microcontact printing process. The PDMS mold is created and coated with an aromatic organic polymer (parylene-C) and then coated with the QDs. The QDs are then applied to the substrate via contact printing [27].

The parylene-C is used to increase the wetting of the PDMS film. It has been proven that parylene-C decreases the contact angle of chloroform on the PDMS stamp, as well as minimizing the surface energy between the PDMS and the QD to enhance the release from the PDMS stamp [27]. This process allows for the QDs to be deposited outside of solution. This is useful for preventing damage to the layers previously deposited onto the substrate in a multi-layer design. It is also possible to achieve a small pixel size ( $<25\mu$ m) which is desirable for high definition displays. A three color device has been fabricated by a research group at the Massachusetts Institute of Technology which used QDs as the red and green lumophores and the small molecule organic TPD as the blue lumophore [27]. Figure 4.1.2 shows the RGB device that was fabricated, where the red and green strips are both 25 µm, and the brightness achieved was 100cd/m<sup>2</sup> [27].



Figure 4.1.2: Three color LED using red QDs, Green QDs, and blue emission from TPD. The maximum brightness achieved is 100cd/m<sup>2</sup> [27].

The brightness demonstrated with the microcontact printing is far less than that achieved with spin coating. This brightness does not compare to the 500 cd/m<sup>2</sup> brightness required for displays. The occurrence of defects is high when using contact printing due

to the contact nature of the process. One concern is dust or particulates on the surface of the substrate and the stamp [38]. Both need to be very clean in order to ensure that particulates are not placed on the surface during the contact process which could affect device performance. The other types of defects are from the PDMS stamp used during processing. Since the PDMS is applied to the master mold using spin coating and the surface is not smooth it is possible that the mold will not be free of defects. This defect may be an area missing PDMS which will then transfer as a blank spot onto the substrate [38]. Another concern with using PDMS masks would be the release of the QD layer. The parylene-C reduces the surface energy of the QD to increase the probability that it will release onto the surface. When compared with other materials that may create a higher surface energy between the PDMS stamp and the QD it is better to use parylene-C, since a strong interaction between the QD surface and PDMS surface would inhibit the release of the QDs [27]. Microcontact printing also requires precisely parallel surfaces, the microcontact printing was originally designed for silicon wafers where it is easy to achieve flat surfaces and then make them parallel to the stamp. The sample roughness can cause surface contact in the areas that are not supposed to come in contact, or it could cause higher pressure in one section resulting in deposition on only a portion of the sample. This dilemma will only be noticeable for the flexible substrates where the surfaces are not rigid and parallel. The final concern is deposition of large areas needed for displays. The stamp will start to exhibit inconsistencies when applied to large areas, because of the challenge in keeping the surfaces parallel, as well as defects in the PDMS stamp from attempting to spin coat a large area.

#### 4.1.2 Inkjet Printing

Inkjet printing is a physical liquid deposition via a dropwise amount of QD solution from a printing nozzle commonly used for OLED displays [36], [39]. Inkjet printing uses picoliters of an ink made of the QDs to place droplets containing the QDs onto the surface of the substrate [40]. The double heterostructure that has been previously discussed can be used in inkjet printing or the ETL and HTL layers can be replaced with a different material that will act similarly as an ETL or HTL [40], [41], [36], [39].

The inkjet deposition process utilizes a printer head filled with an ink made from chlorobenzene and the QDs. This ink is then placed dropwise onto the surface of the substrate over the HTL. Heavily used solution processing techniques such as spin coating have a 94% loss of solution that is removed from the substrate during rotation [40]. The high cost of pure QDs drives the need to reduce waste in the processing method, something that cannot be done with spin coating. The inkjet printing method uses a minimal amount of solution and places QD solution only at the desired location eliminating waste. The process of ink-jet printing can be seen in Figure 4.1.3.



Figure 4.1.3: The inkjet printing process, where a desired QD ink is deposited onto the substrate.

The printer head can be made from a modified commercially available desktop printer or it can be a specially designed printer for the purpose of inkjet printing device structures [42], [39]. The accurate placement and small drop size has led to the development of multicolor QD devices.

The work on inkjet printing demonstrates individual RGB devices as well as an integrated RGB device, made of smaller pixels. Figure 4.1.4 shows the individual RGB devices as well as the combined RGB device and its resulting spectrum from the work completed by Haverinen et al. [41]. Figure 4.1.4 (a) shows a red device made out of a series of smaller pixels, that all share a common electrode. The area of the large electrode, which encompasses the entire working area, was 14mm<sup>2</sup> and the area of the smaller sub pixel was 0.0196 mm<sup>2</sup> [41]. Figure 4.1.4 (b) and (c) show the same structure and device size except in a green and blue emission spectrum. Figure 4.1.4 (d) shows the spectrum of the RGB device and the inset is an image of the RGB device operating at 10V with a brightness of ~125cd/m<sup>2</sup>. It can be noted that the red emission is more noticeable than the green and blue emissions for the inset image; this is reflected in the spectrum. The green and blue peaks are less than half the intensity of the red emission.



Figure 4.1.4: A series of RGB devices on separate substrates and a combined RGB device. (a) Depicts the red device consisting of a series of small QD drops with a large single metal electrode. (b) Green device of similar design to (a). (c) Blue QD-LED made of smaller drops similar to (a) and (b). (d) The spectrum of a combined RGB device made of smaller pixels of all three colors, with an image of the pixel as the inset [41].

The inkjet printing process does present some defects and concerns for device fabrication. This can be seen within the red circle in Figure 4.1.4 (c) where the "L" shaped pixels are not fully complete. One possible reason for this could be clogging of the printer head. This is a common problem with inkjet printing, where the ink dries on the printer head causing the narrow hole that dispenses the ink to clog [43], [44], [39]. Other than clogging of the printer head the inkjet printing process provides other concerns as well. The droplet size directly affects the layer thickness deposited during inkjet printing [42]. The thickness of the QD layer is important in controlling the recombination of excitons in the QD layer (discussed in section 3.2 Band Structure), so the droplet size will be dictated by the desired layer thickness. One solution would be to use less ink and create small drops that generate thin QD layers but this presents a new

series of problems, such as droplet size limitations of the equipment. Another concern being that the joining of two small droplets of ink creates surface inconsistencies which will degrade the device performance [39].

A second solution to change the QD layer thickness would be to change the QD concentration of the ink. If the concentration is reduced then the resulting layers will become thinner. Unfortunately the viscosity of the ink must remain constant, because if the viscosity were to change it would affect the viscous flow of the QD droplet as well as the surface tension of the ink droplet. The surface tension must remain high enough to ensure the ink stays inside the printer nozzle without dripping out [44]. The final problem with the inkjet printing method is the resulting surface roughness, which is typically higher than that of spin coating [40]. The non-uniformity of layer thickness of the QD layer will eventually lead to the degradation of the device through localized heating and high electric currents [39]. The comparison of a spin-coated layer of poly-TPD with an inkjet printed layer of poly-TPD shows that the average roughness for spin coating was 0.51nm and the average roughness for inkjet printing was 0.97nm [40]. It should also be noted that when using inkjet printing 6 micron high features developed that could create pinhole shorts or energy barriers [41].

Despite the drawbacks and defects created by inkjet printing the reduced waste, accurate layer deposition, and small feature size still create an area of research for improving the deposition method. The advent of hybrid inkjet printing has allowed for smoother films with less pinhole defects [43]. The process combines a pinhole-free buffer polymer buffer layer with the light emitting layer to prevent defects. This process has already been explored for OLED technology and can be applied to the QD-LED devices [43].

## 4.1.3 Spray Pyrolysis

Spray pyrolysis is the act of spray deposition where the substrate is heated to remove solvent or the solvent is evaporated in transit [45], [46], [47]. Spray pyrolysis uses a solution composed of the material that is to be deposited and a solution medium in which the material will be carried to the surface of the substrate. During the deposition a reaction takes place to remove the solvent so that only the desired deposited material remains [45]. The process has several advantages for the CdSe deposition for QD-LEDs; simple operation, patternability, produces a high purity film, precision control of uniformity and stoichiometry, and continuous operation for large area coatings.

There are several different methods for spray pyrolysis that are classified by the reaction type and where the solvent is evaporated. In the first process (A) the solvent droplet resides on the surface and the solvent evaporates, this allows for a solid film to be left behind. The second process (B) the solvent is evaporated before the droplet reaches the substrate, this allows the dry solid material to impinge the surface and be deposited. The third process (C) the heating is much higher and causes the solvent to evaporate as the droplet approaches the surface, and the solid material then melts and vaporizes so that the vapor is then deposited on the substrate. The final process (D) is chemical vapor deposition where the entirety of the reaction is done in the vapor state [45]. Figure 4.1.5 depicts the experimental setup that would be used for process A, where processes B, C, and D would have a similar design but would incorporate heating the sprayed material



Figure 4.1.5: The spray pyrolysis system that is commonly used for spray coatings of particles [45].

through some means. The experimental set-up shown in Figure 4.1.5 depicts the spray solution being controlled with a needle valve to achieve the desired flow rate and then the solution is combined in the spray nozzle with the gas flow that is measured and controlled in a similar fashion. The spray nozzle then ejects the solution and medium towards the hot plate, where it is either heated in transit or the substrate is heated to create solid films [45]. The resulting films from spray deposition have varying qualities. The process can create crystalline structures if the deposition rate is slow but then it is no longer cost-effective [45]. Figure 4.1.6 (a) is a film that was deposited from a 0.07 M solution and Figure 4.1.6 (b) is a film deposited from a 1.0 M solution.



Figure 4.1.6: (a) A ZrO<sub>2</sub> film grown from a 0.001 M concentration solution. (b) A ZrO<sub>2</sub> film grown from a 1.0 M concentration solution. Where it can be seen that (a) is a more densely packed structure [48].

Some steps have been taken to improve film quality such as the inclusion of an organic polymeric precursor [48]. The fact remains that the films created from this process will be porous in nature, which can lead to increased current leakage due to the interstitial spacing [23]. The non-porous films are created with slow growth methods using low concentration solution is not cost-effective for this processing technique [45]. The high temperature that the deposition takes place at is also non-ideal for the processing of these devices. The CdSe quantum dots are contained within a non-aqueous solution such as toluene which is flammable. This means that misting and spraying a flammable substance in an oven or at a hot plate that has a temperature of approximately 275 °C which could damage the tool [45]. This increased temperature is not only

dangerous due to the carrier solution it also brings the risk of damaging the QD and organic layers that have been deposited. The ligand structure of the QD that separates the dots in solution could be burned or damaged during deposition which will create charge trapping sites where the ligands connect to the surface. It is also possible the organic poly-TPD will be damaged at such a high temperature.

#### 4.1.4 Mist Deposition

Mist deposition is a technique which incorporates many of the features of spray pyrolysis, but improves on the ability for thickness control and film growth. The mist deposition technique shows an improvement over spin-coating by allowing for thinner film thickness (below 5nm) that con not be reached by conventional means, reduction of wasted solution precursor, as well as allowing for patterning of the QD layers [49], [50], [51], [52]. The deposition takes place within a room temperature chamber at atmospheric pressure eliminating the need for vacuums that would increase the processing costs. The process is capable of coating large substrates uniformly as well as coating flexible substrates [49]. The process differs from spray coating by using a much smaller droplet size to create thinner films, as well as using an electric field to deliver the droplets to the surface as opposed to a physical acceleration [49].

Mist deposition uses a liquid precursor composed of QDs in a solution, typically toluene, which is atomized and turned into a mist to coat the samples [52]. A schematic drawing of the mist deposition tool can be seen in Figure 4.1.7 (a). The process starts in an atomizing chamber, where compressed nitrogen is blown over the top of a hose that has one end submerged in the precursor solution, which creates a mist of the precursor solution via the Ventrui effect. The shearing friction of the particle being removed from

the solution creates both positively and negatively charged droplets [52]. After the mist droplets are removed from the solution it enters into an atomizing chamber. A diagram of the atomizer can be seen in Figure 4.1.7 (b), which shows where the droplets will enter the chamber, where they will exit the chamber, and the inertial impactors as well. The atomizer is used to select the droplet size that is going to be used in the film coating [52]. The nitrogen flows into the atomizer and then flows from one chamber to the next through small holes, and in front of these holes are inertial impactors. The droplets with a greater mass will not follow the nitrogen flow around the impactor, but rather collide with it, and through this process of inertial size separation a Gaussian distribution of droplet size with a peak at 0.25  $\mu$ m can be achieved [52]. The droplets then enter into a shower head which acts to redirect the nitrogen flow into a larger area to fill the chamber. The charged droplets fill the chamber and are then acted upon by the field screen. Here the negatively charged particles are driven down onto the surface while the positively charged droplets are driven to the exhaust. The negatively charged particles then arrive at the surface with a low enough velocity that it can be said there is a negligible impact force with the surface, meaning there will be no damage to pre-deposited layers. After the droplets arrive at the surface the solvent spreads and evaporates leaving behind the QDs as a film. To decrease the rate at which the solvent evaporates hot toluene can be bubbled into the system to increase the solvent vapor pressure.



Figure 4.1.7: (a) The schematic diagram of the mist deposition tool. (b) The depiction of the inside of the atomizer used for droplet size selection.

Mist deposition does have some disadvantages as well. The process uses a precursor solution to cover a large area that is greater than the substrate. This waste makes the process nearly comparable to spin-coating [51]. The final concern with mist deposition is the creation of a micro-structure as the droplet dries. The deposition process of a solution droplet hitting the surface and evaporating is similar to the film growth

mechanisms in both spray pyrolysis and inkjet printing. It has been shown previously in this paper that a porous structure can form when using spray pyrolysis and similar microstructures can form in inkjet printed films [42]. The formation of the microstructure is evidence of mass transport due to the segregation as the solvent evaporates from the droplet [42].

## 4.2 Choosing a Deposition Technique

The deposition that was chosen for this research was the mist deposition technique. The mist deposition process presented the advantages that best suited our needs and had the least amount of disadvantages. The mist deposition technique allows for the patterning of the samples to create RGB displays, allows for control over film thickness, and has the attributes needed for future works such as larger working areas, flexible substrates and a variety of solvents and concentrations. The information provided in section 4.1 is summarized in Table 4.2 which shows the desired attributes for deposition and whether they are available. The desired deposition attributes includes: monolayer deposition and film uniformity, the ability to pattern the RGB QD layers, high processing yields to create displays quickly if commercialized, capable of performing a large-area fabrication, and the capability to be used on flexible substrates. Mist deposition meets all the desired criteria listed making it the most viable option for deposition. The mist deposition tool located in the Penn State Electrical Engineering department was used for this research.

RGB-pixel arrays of bright QD- LEDs	Monolayer deposition and uniformity	pattern capability	High processing yield	Large-area fabrication	Flexible display processing
Mist Deposition	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Spin-casting		Х	Х	$\checkmark$	$\checkmark$
Ink-jet printing	Х	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Spray Pyrolosis	Х				
Microcontact printing		$\checkmark$	Х	Х	Х

Table 4.2: A table of the desired attributes for deposition and if the process is capable.

The mist deposition tool that was used in this research was a stand-alone unit from Primaxx Inc., rather than a cluster tool that is also available. The system that was used for this research can be seen in Figure 4.2.1, where the complete mist deposition unit (a), the atomizer (b), the field screen placed inside of the cap unit (c), and the shower head (d) are all shown. The system design matches the design outlined in Figure 4.1.7 (a), where the substrate is covered with the chamber containing the field screen and the shower head. The atomizer is then attached to the chamber and a hose that delivers nitrogen (N<sub>2</sub>) is then attached to the atomizer. This hose contains a needle valve that controls the flow rate of N<sub>2</sub> into the atomizer. Between the atomizing chamber and the N<sub>2</sub> attachment is the hose that runs downward to the precursor solution. This also has a needle valve to control the flow rate of the precursor solution. The design of the atomizer is the same design depicted in Figure 4.1.7 (b), which uses inertia to separate the particle size and select the  $\sim 0.25$  micron droplets [52]. The top of the chamber shown in Figure 4.2.1 (c) shows the shower head which has a series of small holes to spread the nitrogen as well as the field screen which is located 1cm from the substrate and used to drive the droplets to the surface.



Figure 4.2.1: (a) The mist deposition system used for this research. (b) The atomizer used to select the desired droplet diameter. (c) The top half of the tool is removed and inverted to show the shower head and the field screen.

For this research it was decided that all variable parameters would be kept constant except one, which was time, for each respective QD color. The variables that can be altered for this system are the deposition time,  $N_2$  flow rate, concentration of precursor solution, and the voltage applied to the field screen. The flow rate was kept at a constant 1 mL/min to ensure that the deposition rate would be kept constant. The concentration of the precursor solution was altered for each color of QD to ensure that the same time would result in the optimal layer thickness. The effect of concentration versus thickness for mist deposited films can be seen in Figure 4.2.2 (a) [51]. The voltage across the field screen also effects the deposition rate and thickness so the bias voltage was set



Figure 4.2.2: (a) The effect that concentration has on the film thickness of Mist deposited films [51]. (b) How the intensity is effected by the deposition time. (c) The effect of deposition time on thickness as well as the effect of bias V on thickness [49].

to 8kV. Finally, the deposition time could be varied to achieve the desired thickness. Figure 4.2.2 (b) is a graph depicting the relationship between deposition time and average intensity [49]. Figure 4.2.2 (c) shows the relation between the thickness and deposition time for mist deposition process the increased deposition time allows for an increase in the amount of dots that arrive at the surface increasing the amount of QDs. As the deposition time increases so does the thickness and average intensity of the film. It is possible that the low deposition time does not create full coverage of the sample which does not occur until after 10-20 minutes. If the deposition time were to be increased even further the resulting films would be thick enough to reduce the efficiency due to the need for tunneling electrons from dot to dot transfers.

Further steps were taken to reduce the waste of the mist deposition process and to understand the resulting micro-structure. The mist deposition process uses the inertial impactors to remove the larger dots from the mist stream going into the chamber. The large droplets that impinge on the inertial impactors collect within the 3 chambers of the atomizer. The large droplets that are separated account for the bulk of the precursor solution that is being injected into the atomizer. This solution can then be removed from the atomizer and used again in the future. Currently the atomizer is cleaned between runs so that there is no contamination from one color of QDs to the next, so it is possible to first siphon off the QD solution before the next deposition. Ideally the atomizer would be used for a single material, which in our case would be QDs, and of a specific wavelength emission. This would reduce cross contamination concerns and reduce the deposition time by removing the cleaning step. It is possible to have multiple atomizers attached to
the system where the mist enters the chamber. This solution recycling will increase the product yield and decrease the waste to below that of spin coating.

The final concern with mist deposition is the process in which the QDs are left on the surface by the evaporating solution. The film structure which results in the evaporation of the carrier solvent is still unclear. The challenge lies in testing and observing a single 0.25 µm droplet as it dries. Based on the concentrations used in the experiment we know that the amount of QDs in a droplet carried by the mist deposition process is approximately five QDs, which is such a low concentration they need to be treated as discreet particles (see Appendix A for calculation and explanation) [52]. As droplets coalesce on the surface or as droplets fall onto previously deposited QDs and reabsorb them the amount of QDs will increase and are no longer discreet particles. There are a few possible outcomes for the resultant film from the mist deposition process: the concentration could be so low that the QDs are randomly distributed inside the drop as it dries [53]; the concentration is high enough that a ring is formed [54], [53], [55], [56]; or an order film could be deposited [57]. The mechanism which best describes the film deposition process is still uncertain, but atomic force microscopy can help to describe resulting film. Further testing will need to be conducted to find the resultant films and the precise film deposition process.

### 4.3 Patterning Method

### 4.3.1 Simplified Patterning

During the research project the deposition process changed to suit the needs of the experiment. Initially the patterning that was done was rudimentary and a proof of concept

rather than an accurate process. Initially the deposition process was used to create monochromatic single color devices. This process required a blanket deposition of the entire substrate and required no special patterning techniques. This was done to test devices made with mist deposition and to ensure that it was possible to create QD-LEDs using this method. This process was the same as the spin coating process discussed in section 3.4 with the exception of the spin cast QDs being replaced with mist deposited QDs. To create the first patterned display glass slides were used to cover portions of the substrate. This would create an effect similar to a shadow mask and would allow for the deposition of wide strips onto the surface. This initial patterning method is shown in Figure 4.3.1, where the ITO is covered with a mask made of glass. After the deposition over the matching ITO stripe the glass slides are moved to expose only the next ITO slide and cover the previously deposited QD layers. This process is repeated for all of the colors and then the remaining cathode can be deposited. It is also possible to spin coat the necessary PEDOT:PSS and poly-TPD prior to the QD deposition and Alq<sub>3</sub>, calcium, and aluminum after the QD deposition.



Figure 4.3.1: The process for creating rudimentary patterned devices using glass as a shadow mask to cover or expose the desired location of the QDs.

This deposition process is limited by the nature of the design which causes inherent issues. The first problem would be the limitation and restriction in the range of sizes that can be used. The glass slides are aligned to an ITO stripe by hand meaning the smaller the stripe the harder it would be to align the stripe and the mask. It is important that the deposited QD area be slightly larger than the ITO stripe to ensure that the ITO and Al are not in direct contact at the edges of the ITO stripe which could cause a short in the device. This then limits the size in which this process is realistically feasible. When aligning the glass stripes by eye to the ITO stripe the width of the ITO stripe should be no smaller than 0.5mm to ensure that the ITO and the opening are properly aligned. The gap between stripes should be slightly larger than this to ensure only the single desired ITO stripe is visible. The second flaw with this patterning method would be the amount of RGB stripes which can be deposited is limited by design. Using glass to cover the ITO stripes will mean only one stripe is coated at a time or that a large amount of glass covers would be needed to create a higher density display area. To overcome these design flaws a new patterning method had to be adopted.

#### 4.3.2 High Accuracy Patterning

Based on the previous patterning experiment a new patterning system for mist deposition was developed. The mist deposition process is capable of using masks made from Kapton films (poly(4,4'-oxydiphenylene-pyromellitimide)) to pattern the deposited films [52]. These masks align to the surface and then act as a shadow mask to prevent the mist particles from contacting the substrate in covered areas. The Kapton mask is used because it is made from a non-conducting thin sheet. A dielectric material needs to be used to prevent interference from the 8 kV electric field that is applied during the deposition process. Initially it was thought that aligning a new mask for each desired color deposition would be easiest, but the alignment of the masks proved more difficult than initially expected. The mist deposition tool currently does not have an alignment system present to facilitate mask alignment within the tool itself. This means that the alignment would have be done using an outside source such as a microscope. To simplify the process the decision was made to use a single mask for all three QD depositions rather than a separate mask for each deposition. To do this the mask is first aligned to the ITO stripes on the surface to expose the first stripe and cover the second and third stripe, and then the first color is deposited. Next, the mask would be moved along the surface to the next position where it would cover the first and third ITO stripe and expose the second ITO stripe for the second color deposition. Finally, the mask would be moved again to cover the first and second stripe and expose the third stripe for the final color deposition. The resulting experimental setup for this process is depicted in Figure 4.3.2 (a) and the process is depicted as Figure 4.3.2 (b). Figure 4.3.2 (a) shows the ideal experimental set up for adjusting the mask that is in use. The substrate is placed on a translation stage and with the mask, and placed underneath a microscope. A computer controlled stepper motor is then used to move the mask slowly and evenly on the surface to ensure that the mask is aligned to the ITO stripes. This is the ideal setup which would have required substantial adjustments to the existing tool so a separate but similar method



Figure 4.3.2: (a) The experimental set-up designed for highly accurate control of the mask for patterning. (b) The process used to deposit the RGB films needed for a display.

was used. A computer and microscope were used to examine the substrate and mask on a 3-point probe station. The probe tips from the 3-point probe were then used to push the mask in the corresponding direction. This rudimentary method required the device and probe to precisely perpendicular or a rotation in the mask would occur. Figure 4.3.2 (b) shows the process of moving the mask along the substrate surface to expose multiple strips at a time. This method allows for one mask to do a repeating RGB pattern that is needed for a three color display. This process still has limitations including mask design, alignment issues, scratching, and mask movement.

The process does allow for more control over the film deposition than the previous design but the size is still limited. The microscope is now used for alignment as well as a Kapton mask for defining the desired stripe size, but the Kapton mask has a limit to the size at which it can be manufactured. The Kapton mask will lose its structural stability if the interstitial spacing between the gaps becomes too small. As the desired stripe width decreases so will the Kapton that is used to cover the remaining two stripes. If this becomes too narrow it is no longer rigid and is no longer an effective shadow mask. The alignment of the mask to the substrate is still limited as well because of the system currently being used for alignment. For better results a suspended mask and a two axis stage with rotation would be the best method for alignment, which is similar to a mask aligner used in photolithorgraphy, but the current mist deposition tool is not capable of such movements. This means the mask must be moved along the surface, which is currently being done by hand increasing the amount of human error. The method in which the mask is moved could also possibly scratch or damage a previously deposited film. A probe tip is used to push the mask along the surface of the substrate so the tip

could potentially scratch the surface. The concern can be addressed simply by mask design, meaning a large border of the mask would be enough to prevent the probe tip from coming in contact with the working area of the device. Finally, the mask has the potential to move in transit from the alignment set up to the deposition tool. The solution here would be to include the alignment directly within the tool. This would require a mounted camera for alignment as well as modifications to the tool to allow the probe tip of the stepper motor to move the mask inside the tool.

## 4.4 Deposition Results

The first set of results are of the simplified patterning technique and the blanket deposition, which are similar and will be presented together. Following the simplified results are the high definition patterning results. The film analysis work was done mainly in part by the operators of the mist deposition tool Aditya Kshirsagar and Karthik Shanmugasundaram from the Electrical Engineering department at Penn State.

#### 4.4.1 Simplified Patterning

The results for the blanket deposition technique can be translated to both the simplified technique. The film quality of the mist deposited light emitting layer was uncertain so QDs were deposited onto glass substrates and then AFM testing was done to determine the RMS roughness of the surface. The AFM results can be seen in Figure 4.4.1 where the RMS roughness was 2.5 nm. This means the roughness differed by less than the diameter of a QD on average. There is some notable clumping in a few locations, which can be attributed to clumping during the drying process or by the random location in which the dots will land meaning some QDs could form stacks. The control of the film



Figure 4.4.1: AFM measurement of a QD film deposited on glass with an RMS roughness of 2.5nm.

deposition was also studied using transmission electron microscopy (TEM) to find the minimum thickness that could be deposited [52]. Figure 4.4.2 (a) shows a TEM image of a single monolayer of QDs deposited over a polymer, which is comparable to contact printing. Figure 4.4.2 (b) depicts a five monolayer deposition on a polymer layer, which is similar to the thickness that would be used in device fabrication. These two images show the control of the mist deposition process that can be achieved. It is possible to control monolayer depositions and as shown in Figure 4.4.2 (b) the resulting film has a relatively high packing density, meaning that gaps are not apparent in the image and the layers seem to pack tightly to one another. Though, it cannot be said that the entire film has an equivalent packing density, so some areas may be more porous than others.



Figure 4.4.2: (a) A single monolayer of QDs deposited over a polymer and analyzed using TEM. (b) A 5 monolayer film deposited over a polymer and analyzed with TEM [52].

The devices made from mist deposition displayed brightnesses below that of the spin-on technique. Figure 4.4.3 shows the brightness of a device made using mist deposition with the inset being a QD-LED operating at maximum luminance. The peak brightness, 119cd/m<sup>2</sup>, is approximately 3% of the spin cast peak brightness. The initial results are consistent showing low brightness, high turn-on voltage, and high current density. This can be attributed to the thickness and film quality of the deposited layer. If the film is thicker than what was intended, 2-3 monolayers, the turn-on voltage would

increase and the brightness would decrease, as discussed in section 3.2 [31]. This is a strong indication that the QD film is too thick and the deposition time needs to be



Figure 4.4.3: The brightness measurement of a QD-LED fabricated with mist depositions. The inset is a QD-LED operating at maximum luminance with an area of 7mm<sup>2</sup>.

changed to find a film deposition with a two monolayer thickness. It is also possible that a surface micro-structure formed during deposition and is creating holes or gaps in the film. If the film is porous it will restrict the conduction pathways for the electrons and holes to travel through limiting the device performance. These gaps and voids could also lead to an increase in crosstalk and possibly even recombination in the electron transporting layer [23]. The third possible explanation could be damage to the HTL during deposition. The poly-TPD material was chosen because it is more resilient to nonpolar solvents, but during the mist deposition process the toluene evaporates from the surface very slowly which could allow for a breakdown in the polymer layer. This could then lead to a gradient interface between the HTL and the QD layer which could cause poor hole injection into the QD layer. The devices fabricated with mist deposition showed a tendency for Alq<sub>3</sub> emission which would indicate voids, thin QD layer (or a poly-TPD/QD gradient), or partial film coverage. Figure 4.4.4 shows normalized spectrums from two separate mist deposition devices; one with a pure QD emission similar to the one depicted in the inset of Figure 4.4.3 as well as a spectrum with an Alq<sub>3</sub> emission. The reduction of Alq<sub>3</sub> emission is important for the maximization of the recombination in the QD layer. A further analysis of the mist deposition process and the resulting films is necessary in order to reach a conclusion on how to improve the recombination in the QD layer. If the resulting film is porous the actions taken to fix the problem would be much different than the actions taken to solve the problem if the QD layer is thicker or thinner than intended.



Figure 4.4.4: The spectrum of a QD-LED with no Alq<sub>3</sub> recombination and a QD-LED with some Alq<sub>3</sub> recombination.

#### 4.4.2 High Density Patterning

The high density patterning process started out with simple tests to ensure reproducibility as well as functionality, and from there a better patterning method was designed. The final goal of this patterning process is to create an alignment system within the mist deposition tool that is capable of aligning the substrate to the mask using similar alignment techniques to photolithography. This process has been discussed in section 4.3.2, where eventually it will all be computer controlled. This was not a viable option since it would require altercations to the mist deposition tool without proof of concept. Instead a manual patterning technique was done using a 3-point probe station and the probe tips would be used to align the masks, the probe station can be seen in Figure 4.4.5. The probe tips would be used to drag or push the masks on the surface of the substrate much like the computer controlled device would do. The three point probe station was located approximately twenty feet from the mist deposition tool, which is not ideal since there was a chance the mask could move during transit. To ensure that the masks did not move during transit from the probe station to the deposition tool a test would need to be conducted to measure the change in alignment after transit.



Figure 4.4.5: The three point probe station used for mask alignment in the high density patterned mist deposition process.

To test the changes in mask alignment during movement samples were patterned with photolithography to have structures that resembled the structures that would be on the mask during deposition. The photolithography mask that was chosen contained alignment marks that matched the alignment marks on the Kapton masks used in mist deposition. After the photolightography was completed and the photoresist was hard baked the samples were taken to the probe station and the alignment process was initiated. The mask could be aligned to the alignment marks and then moved from the probe station to the deposition tool and back to the probe station multiple times. Images would be taken before and after the sample movement and then the change in spacing around the alignment mark could be measured. Figure 4.4.6 shows the results from the testing, where figure (a) is the before the sample was moved and figure (b) is after it was moved. It should be noted that a single movement from the deposition tool and back did not create a noticeable change so the sample was carried from the probe station to the deposition tool and back three times. This extended movement allowed for a measureable change in the alignment. Figure 4.4.6 shows that the mask had moved six microns in



Figure 4.4.6: (a) The sample after the Kapton mask has been aligned to the photoresist marker. (b) The samples was carried to the deposition tool and back to the probe station 3 times and then the change in position was measured.

the Y direction and seven microns in the X direction, which could be attributed to a shift in position or a rotation of the mask on the surface. After moving the samples six times the length that would be required in the experiment a seven micron shift occurred which would be acceptable and within the range of error. Meaning this distance would fall within the interstitial spacing between stripes. The deposited QD films would need to extend beyond the ITO stripes to ensure proper coverage. If the QD layer does not completely cover the ITO stripe there will be a short at that particular point or a recombination in the ETL, so it is important to ensure the QD strip is wider than the ITO strip. The spacing between ITO strips would be greater than the amount the mask has shifted. This spacing will prevent the overlapping of QD layers on a QD-LED, which would cause the emission color to be changed.

The next step was to produce a series of high quality stripes in varying sizes to determine the accuracy of the process as well as the patterning ability of the mist deposition tool. This process would also allow for a repeating RGB pattern that was not feasible with the previous patterning method. Glass substrates were cleaned and prepared for deposition, and then organic light emitting polymers were deposited to test the patterning capabilities. Organic polymers were chosen because they are relatively inexpensive in comparison to QDs, provide a wide range of colors, and fluoresce well under UV light. For initial testing blue, red, and orange (BRO) fluorescent dyes were used rather than RGB since the BRO dyes were readily available. The red strip was first deposited followed by the blue strip, and then finally the orange strip was deposited. The blue and orange layers were not easily detected with the microscope used for the 3-point probe system so the second and third depositions were aligned with the red stripe as the alignment marker. This means that the red was deposited, then the mask was slid to one side to cover the red for the blue deposition, and finally the mask was moved back over the red to cover it from the opposite direction and the orange was deposited. Moving the mask greater distances allows for an increased risk of error since the mask alignment is done by hand. After deposition the films were imaged with UV illumination, and the strips were analyzed using optical microscopy. Figure 4.4.7 is images of the deposited strips under UV stimulation with stripe sizes of 1000 micron (a), 375 micron (b), and 120 micron (c). The highest density deposition was the 120 micron stripe and a 10X optical zoom image can be seen in Figure 4.4.7 (d). The brightness of each stripe is not equivalent which makes some stripes more noticeable than others. In Figure 4.4.7 the red dye is less noticeable than the blue or orange dyes due to the brightness of the film being



Figure 4.4.7: (a) Image of the 1000 micron BRO stripes under UV illumination. (b) Image of the 375 micron BRO stripes under UV illumination. (c) Image of the 120 micron BRO stripe under UV illumination. (d) A close up image of the 120 micron BRO stripes under UV illumination.

lower. The larger stripe size appears to have a higher quality of deposition since there are less defects on the surface. This is related to the Kapton mask that is used for deposition. The Kapton mask starts to lose rigidity and structural integrity when the Kapton material becomes very narrow. The Kapton used to create the narrow spacing between stripes can be easily damaged, and the result is a series of small fibers on the mask. These fibers create shadows on the surface creating a series of defects. These defects are only noticeable in the 120 micron stripe size. A possible solution would be to find a mask that better suits this process and is more rigid. The only requirement is that it must be a dielectric to ensure there are no field effects from the 8kV electric field used in the mist deposition process to drive the droplets to the surface.

A closer inspection using an optical microscope is needed to analyze the sharpness of the deposition as well as the spacing between the stripes. The 375 micron stripes as well as the 120 micron stripes are the main focus of this portion since they will generate the highest density of QD-LED. Figure 4.4.8 shows the 375 micron strips (a) and the 120 micron strips (b) under an optical microscope at 10X zoom. The images show that the line edge of the 375 micron stripe is sharper than that of the 120



Figure 4.4.8: 10X zoom optical microscope images of the 375micron (a) and 120 micron (b) stripes.

micron stripe. The edge of the 120 micron stripe is still relatively sharp and straight which indicates that the stripe could be narrower without significant distortion. It is unclear how narrow the stripe could be before defects start to occur that would prevent device fabrication. The current 120 micron stripe makes it possible to create a high density display. The ITO electrode would need to be smaller than the QD stripe to ensure that there are QDs between the ITO and the Al layer to prevent a short. The QD layers then could overlap slightly in the spacing between ITO stripes. Measurements were also taken to investigate rotation of the stripes and to determine if mask rotation could affect device fabrication. To measure rotation measurements were taken from the red stripe to the blue stripe at the top and bottom as well as measurements from the red stripe to orange stripe at the top and bottom (opposite ends of the stripes). The length of the strip and the difference in measurements could be used to determine the angle of rotation. Figure 4.4.9 shows the 375 micron stripes at the top (a) and the bottom (b) as well as the 120 micron stripe at the top (c) and bottom (d). The measurements of the gaps between stripes are shown on the image and the difference of these two numbers will be used to find the rotation along with the length of the stripe. The distances of the two stripes at the top of the deposited 375 micron stripes (a) are 115.5 microns from the blue to the red and 80.8 microns for the red to the orange. The distances at the bottom of the 375 micron stripes (b) are 158.4 microns from the blue to the red and 133.7 microns from the red stripe to the orange stripe. The difference between the blue and red stripe at the top and bottom is 42 microns and the difference for the red to orange stripe is 52.9 microns. The importance of this lies in the alignment of the stripes, meaning when the ITO width is chosen it must account for the 53 micron shift in the stripe to ensure it is within the stripe

at the top and bottom of the QD stripe. The angle of rotation can also be calculated from these measurements since we know the stripe length and the distance that the stripe shifted during alignment. Since the stripe length is much larger than the change in alignment the angle of rotation becomes very small. The blue stripe rotated 0.012° and the orange stripe rotated  $0.15^{\circ}$ , with such small angles of rotation it will be a challenge to further reduce the rotation of the mask when aligning by hand. The same calculations can be done for the 120 micron stripe, and would show that the blue stripe shifted 11.5 microns and the red stripe shifted 36.3 microns. The amount the stripe shifted is less than that of the 375 micron stripes, which could be because the mask is not being moved as far as the 375 micron stripe. Though the amount is more significant in comparison to the width of the stripe, meaning the shifted distance is 33% of the stripe width. This means that the ITO will have to be significantly smaller to fit within the stripe after rotation. Similarly the angles of rotation were calculated and the blue stripe rotation was 0.03° and the orange stripe rotation was 0.104°. The small amount of rotation needs to be corrected to ensure accurate alignment across the entire substrate and could be done with an improved mask control system. To improve the alignment system a computer controlled probe tip that pushes the mask with multiple points of contact could reduce rotation, though it is still unclear since the rotation is already quite small.



Figure 4.4.9: (a) The top of the 375 micron stripes with measurements. (b) The bottom of the 375 micron stripes with measurements shown on the image. (c) The 120 micron stripes at the top portion with the measurements shown. (d) The bottom of the 120 micron stripes with the measurements depicted.

The results from the patterning show it is a viable option for high density three color devices. The patterning method has proven it is possible to create features less than 120 microns, but a new mask material may be required to uphold structural integrity. The rotation needs to be further reduced to approach zero to ensure the QD stripe matches the ITO stripe.

# **Chapter 5**

# **LED Arrays**

The next step in the creation of a working display was the fabrication and testing of smaller arrays. A QD-LED array is a matrix of QD-LEDs that can be passively or actively addressed similarly to a fully functioning display, except the interstitial spacing is larger and the optical density does not match the density of a full display. The purpose of this step was to test the possibility of crosstalk, the driving circuit used for addressing, and the overall design of a small functioning display. First, an array size had to be chosen to accurately portray a small scale display. Then a driving system needed to be decided upon to create either a passive or actively addressed array. After this the devices could be fabricated and tested for further analysis.

## 5.1 Addressing Methods

There are two common addressing methods used in the flat panel display industry, which are passive addressing and active addressing [6]. The passively addressed displays use a series of rows and columns to create QD-LEDs at the cross points of the anode and cathode. Figure 5.1.1 shows the design of a passive matrix display, where ITO strips and aluminum strips run perpendicular to one another to create a series of cross-points with the QD film in-between them [6]. To operate the passive matrix display one strip of aluminum is grounded and one strip of ITO that is perpendicular to the aluminum strip has a voltage applied to it, where the row and column cross is the pixel that will be

illuminated. To create an illuminated pixel the applied voltage must be greater than the turn on voltage and for the pixel to remain dark the applied voltage must be below the turn on voltage. To create an image the pixels are rastered until each pixel in the array is either turned on or left off. After the passive display has rastered the entire array turning pixels on or leaving them off it has finished a frame. The frame rate is the amount of frames per second that have been rastered, which needs to be above 60Hz to ensure there



Figure 5.1.1: The depiction of a small passive addressing array where the cross points define the pixel locations [6].

is no screen flicker [58]. This design allows for the creation of a monochromatic display by varying the duty cycle of the pixel. While operating at 60 frames per second to create a very bright pixel it is turned on with every frame and similarly to create a black pixel it is left off every frame, but to create varying intensities needed to form an image with multiple shades some pixels have a separate duty cycle. By altering the duty cycle of a pixel a variety of shades can be achieved, meaning that turning a pixel on every other frame will create a dimmer pixel than one that is on every frame. The typical passive addressing scheme uses superframes which consist of four single frames. Within the superframe pixel shades can be determined by having some pixels on every frame and decreasing the number of frames it is on by one frame to create variable shades [6].

The drawbacks to the passive addressing scheme include crosstalk and bandwidth issues. Crosstalk is inevitable by design of the passive addressing architecture and will be discussed in detail in a separate section of this paper. The second drawback being the bandwidth of the pixels needs to increase as the pixel count increases. As the density of pixels increases to achieve high definition the frame rate must stay constant, meaning that the switching rate of the pixels must be increased. The display needs to switch on and off the frame at a rate of 60 times a second, so the entire frame must be alternated in 0.016 seconds, and as the definition increases so does the amount of pixels that need to be addressed in that time frame. To overcome these issues active addressing can be implemented.

The active addressing scheme uses thin film transistors (TFTs) as a switch to turn on and off the pixel [6]. Figure 5.1.2 depicts a small active matrix array that uses TFTs as the backplane for controlling the LEDs. The speed at which the switching is done is much greater than in passive displays, and it is done using the TFTs which can be considered perfect switches. The pixel holds a charge for a time longer than it takes to turn the switch on and off, which equates to the entire screen being lit at one time. The use of a perfect switch from the TFTs also reduces the crosstalk that can be found in passive displays [6].

The active addressing scheme is more expensive and more complex than the passive addressing scheme. Though it does help to prevent the problem of crosstalk the complexity of the system increases, making the driving more difficult. The active



Figure 5.1.2: A representation of an active matrix 3x3 array that is equivalent in size and shape, but uses TFTs as a means of driving the device [6].

addressing scheme was used by Samsung to create a monochromatic QD-LED display as shown in Figure 2.4.3 [26]. Because this addressing scheme requires a TFT backplane typically made from amorphous silicon the substrates need to be rigid. This means that a flexible display is not feasible unless passive addressing is used. The cost of the TFT backplane is also greater than the cost of the patterned ITO substrates that would be used in a passively addressed array. Based on the ease of device fabrication, cost, and the ability to transition to flexible substrates passive addressing was chosen for this research.

## 5.2 Array Devices

To reduce the cost of device fabrication  $Alq_3$  was initially used for the array testing. The  $Alq_3$  was more cost effective than the QDs and shows similar LV and IV characteristics. Pre-patterned ITO was purchased to ensure consistent device structure, and the devices were packaged to ensure the lifetime of the devices would be long enough for testing. The array was an 8 pixel by 8 pixel array that would equate to 64 pixels. The substrate was purchased pre-patterned ITO glass to ensure that the arrays were all consistent with one another.

The addressing system used in this experiment is a passive addressing scheme. Standard driving chips are expensive, need to be bought in bulk, and are small making the driver attachment to the sample difficult when testing multiple devices. Rather than using a commercial addressing system a driving system was designed using a switching module from National Instruments. The NI PXI-2536 is a switching matrix capable of switching 50,000 crosspoints in a second and has an 8x68 sized matrix, which means it can connect any of the 68 columns with any of the 8 rows 50,000 times a second [59]. Figure 5.2.1 (a) shows the switching matrix schematic, where the computer controls the connections, speed, and image that is desired via a LabVIEW program. The computer is connected to an NI PXI chassis that contains the switching module as well as a power source (NI PXI 4110). The switching matrix is then connected to two separate connector modules, where one module is row connections and one module is column connections. The row connector is then connected to both ground (GND) and a positive voltage, and the column connectors are connected to the aluminum and ITO stripes. Figure 5.2.1 (b) shows a schematic view of how the switching works. Each ITO and aluminum strip is part of the 68 columns and one row is an applied voltage and one row is GND. The NI PXI 2536 connects an ITO strip to the applied voltage and an Al strip to the ground to create illuminated crosspoints, so if the first column is connected to the applied voltage and the ninth row is connected to ground the first pixel will illuminate.



Figure 5.2.1: (a) A schematic of the setup used for passive display addressing. (b) A schematic view of how the matrix switching works.

The switching matrix allows the device to be operated in a line mode. This means that the first ITO strip is connected and all the desired pixels in that row are illuminated, then it disconnects the first ITO stripe and repeats for all the other ITO stripes. This is done to increase the speed at which the frames refresh, because the pixels in a row are addressed at the same time rather than rastered. So now the rastering is done by rows rather than across the entire array. This was done for simplicity of the programming as well as a reduction of the required switching speed. By switching lines rather than individual pixels the entire frame is rastered quicker than if each pixel was rastered individually.

### 5.3 Array Results

The device arrays have been tested primarily with organic materials to reduce fabrication costs. The organic light emitters such as poly[2-methoxy-5-(2'ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) or Alq<sub>3</sub> have been used because the price is much lower for testing purposes and after optimization the switch to QD-LEDs will be simple. Figure 5.3.1 (a) shows an array using only MEH-PPV as the emitter without the aid of electron transport layer. The image shows minor defects within the LED where the calcium has oxidized and created an insulating layer. The calcium was used for work function matching similarly to the Alq<sub>3</sub>. These defects would not be noticeable if it were properly packaged o prevent the oxidation process. The large defect in the bottom left corner is from the spin coating process. If there is a particle on the surface than during the spin coating a "V" structure will appear behind the particle, commonly known as a comet defect. Figure 5.3.1 (b) shows an 8x8 array using Alq<sub>3</sub> as the light emitting polymer, which also has a spin defect similar to the MEH-PPV array. The devices in Figure 5.3.1 (b) show no defects from calcium oxidation because it is packaged to prevent moisture and oxygen from damaging the calcium and organic layers. Both Figures 5.3.1 (a) and (b) were illuminated using a passive matrix display operating in line mode at 1000Hz with a driving voltage of 14V, which show a fully illuminated array. This means that the lines were scanning across the array 1000 times a second which is greater than the required 60 frames per second. To demonstrate the addressing



Figure 5.3.1: (a) A matrix consisting of MEH-PPV organic emitting layer. (b) An 8x8 array that utilizes Alq3 as the emissive layer. Both images depict a "comet" defect cause by a particle on the surface during spin coating.



Figure 5.3.2: An 8 x 8 Alq<sub>3</sub> matrix passively addressed with the National Instruments FET matrix switch module (model NI PXI-2536) to show a "PSU" crosstalk surrounding the letter should be noted.

ability of the NI PXI 2536 switching matrix the letters "PSU" were displayed on the array; this can be seen in Figure 5.3.2. The image that is being displayed by the matrix shows crosstalk surrounding the pixels that were supposed to be illuminated. The crosstalk is caused by the design of the passive matrix display, and knowing that it is a passive addressing scheme some crosstalk is to be expected as mentioned earlier in this chapter (see section 5.1). Investigation of the crosstalk for passive addressed displays shows that an equivalent circuit can be shown for the passive addressing scheme. Figure 5.3.3 (a) shows a circuit diagram of a passive display where each LED shares a common electrode with its respective row and column. Figure 5.3.3 (b) shows an equivalent circuit of the display addressing system which is centered on the pixel A1 [60]. Figure 5.3.3 (b) shows that when the LED A1 has a voltage applied to it the pixels in the same column and row (A2, A3, A4, B1, C1, and D1) are forward biased and the remaining LEDs would be reverse biased. If the LEDs being reverse biased have a large leakage current than it will allow pixels A2, A3, A4, B1, C1, and D1 to be forward biased and illuminate. The reverse leakage current occurs when a diode is reverse biased, and it should not allow any current to pass but in fact a small amount of current does in fact leak through. This means that there would be crosstalk illumination in the vertical column and horizontal row in which the illuminated pixel was being forward biased. There are three possible tests that can be done to test and confirm this phenomenon. The first test would be to power a single pixel similar to A1 and verify that the entire column and row is illuminated. The second test would be to reverse bias a pixel equivalent to A1, which should cause all the pixels to illuminate that are not in the column or row of A1. Finally, the third test would

be checking the current leakage of a QD-LED under reverse bias to see if there is a current leakage, and if it is enough to cause illumination.



Figure 5.3.3: (a) The circuit design of a 4x4 passively addressed array. (b) The equivalent circuit of a passively addressed shown in part (a).

Figure 5.3.4 shows the first test results, where the pixel in the first row and column was illuminated and the subsequent pixels were then illuminated in that row and column. The crosstalk gets weaker the further it moves from the initial pixel because the current is reduced slightly by each pixel that allows the passage of the current via reverse leakage current. This result matches the equivalent circuit design and accurately predicts the crosstalk to occur in the column and row of the illuminated pixel.



Figure 5.3.4: The pixel in the top right corner is illuminated causing the subsequent pixels in the row and column to illuminate due to the reverse leakage current.

Figure 5.3.5 shows the results for the second test, where the first pixel was reverse biased. This would cause all the pixels not in the first row or column to be forward biased and illuminate based on the equivalent circuit shown in Figure 5.3.3 (b). The result shows that no pixels in the first row or column illuminated and almost all other pixels did in fact illuminate. This result further confirms the equivalent circuit leads to a significant amount of crosstalk by design. The illumination of the surrounding pixels is limited by the amount of current that leaks through the initial diode when reverse biased, which would explain the limited brightness compared to the cross talk brightness in Figure 5.3.4. Since the arrays were made with  $Alq_3$  as the emission layer, it was still unclear if the crosstalk would occur in the QD-LEDs , to test this a Keithley 4200 semiconductor



Figure 5.3.5: The pixel in the top left corner is reverse biased causing all the pixels outside that column and row to be forward biased and illuminate.

characterization system was used to find the current vs. voltage (IV) characteristics of several QD-LEDs. By comparing the reverse leakage current and the forward bias current it is possible to tell if crosstalk would be an issue. Figure 5.3.6 shows a log plot of the IV characteristics of a QD-LED, which depicts the current density when forward biased (positive voltage) and reverse biased (negative voltage). The driving voltage for the matrix display was 14V and at this value there is a 13% difference between the forward and reverse biased currents, meaning that when the first pixel is illuminated 13% of the current applied to a reverse biased pixel will leak through and cause illumination to the surrounding pixels. In a solid-state P-N junction the depletion width acts as an insulator

when a voltage is applied with the same polarity as the depletion region, meaning when it is reverse biased significant current flow is stopped [17]. The reverse biased QD-LEDs do not have the same effect in preventing a nominal current flow when reverse biased.



Figure 5.3.6: A log plot of the current density of the device vs. the voltage showing the leakage current in the reverse bias regime.

The cause of the high reverse current leakage is thought to be caused by the interstitial spacing between the QDs [48], [61]. The gaps and voids in the film allow for a direct link between the hole transport layer and the electron transport layer which could create increased reverse leakage current as well as leakage current in forward bias that causes the Alq<sub>3</sub> layer to emit light. The creation of a more close packed system could increase the efficiency and reduce current leakage. To reduce the reverse current leakage value would reduce the light emission of the crosstalk, but to do so would require an entirely new device structure for the QD-LEDs. The crosstalk concerns shown in this study would not be an issue if active matrix displays were used in place of the passive displays because a TFT is used as a perfect switch, meaning even if there is reverse current leakage the open switch would prevent crosstalk.

# **Chapter 6**

# **Multi-color Arrays**

## 6.1 Multi-Color Array Fabrication

The main goal of this research project is the creation of a working three-color QD-LED display. The research steps taken up to this point involving device quality, QD-LED arrays, patterning, and addressing are all needed in the creation of a functioning multicolor device. The creation of a multi-color device requires the use of all the experimental procedures listed thus far. The LEDs require a high brightness and the colors will need to have similar luminescence. The devices will need to be packaged to increase the operating lifetime for testing purposes. Patterning is very important because the mist deposition is what will allow for creating strips of QDs that do not overlap the ITO strips. The addressing is also need to illuminate the separate QD-LED devices on a single substrate.

The procedure for creating a multi-color device is similar to creating a single color device up to the point where the QDs are deposited. The mist deposition process referred to as the simplified patterning method (see section 4.3.1) is then used to create strips that are deposited over an ITO stripe, and it is important that the QD stripe be no smaller than the ITO stripe. If QD layer is smaller than the ITO stripe it would allow for charge recombination in the area where the HTL and ETL are in direct contact which could cause an emission from the HTL or ETL. This makes the alignment important and

it will be crucial when scaling the device to a smaller size. The smaller the space inbetween pixels the more exact the alignment will need to be, to ensure multiple QD layers are not deposited over the same ITO stripe. Within the space between each pixel the QD colors can overlap and it will not cause a problem since that area will not be illuminated anyway.

After the QD mist deposition the samples are loaded into a nitrogen glovebox and baked at 80C on a hotplate to remove the remaining toluene similarly with the single color devices. After the solvent is removed the device fabrication continues in the same way that the single color QD devices are made (see section 3.4). The end product after packaging is then a device that has three separate colors deposited over three separate ITO strips and can be addressed similarly to that of the single color array devices.

The ideal multi-color device would consist of the primary colors of red, green, and blue. Blue QD-LEDs need to be much brighter than their red and green counterparts because the blue color has a low luminous efficacy compared to red and green [22]. As a proof of concept the three colors used in the first series of devices were red, green, and yellow. The yellow QDs have a comparable luminous efficacy to the red which will make initial testing simpler. Three devices were made that were 3x5 as a proof of concept that mist deposition is a viable method for creating multi-color arrays.

### 6.2 Multi-color Device Results

The three devices were made separately so that improvements could be made and thicknesses altered if needed in the attempt to achieve the best possible results. After fabrication the devices were photographed, the spectrums were analyzed for multiple pixels, and the brightnesses were measured for multiple pixels on each substrate. The luminescence results of the three multi-color devices were then compiled into graphs to show the brightness difference between the red, green, and yellow pixels for each device. Figure 6.2.1 (a) shows the red pixels on each device, (b) shows the yellow pixels on each device, and (c) shows the green pixels on each device, each pixel is labeled X\_Y where X denotes the device number and Y denotes the pixel number. The device number being 1 through 3 where 1 was the first device fabricated and 3 was the last device fabricated, and the pixel number is the order in which the pixels were measured on the device.



Figure 6.2.1: The brightnesses of red (a) yellow (b) and green (c) pixels on all three devices to show the device performance improvement in brightness for each device generation.

The results show that the luminescence increased with each device fabrication. This is a general indicator that the performance improved with each fabrication. The mist deposition procedure remained constant so it can be assumed that the surrounding layers
had a larger impact on the device quality. Changes in ETL thickness or HTL thickness can alter the recombination regime and could affect the brightness. The first device exhibited shorting in the pixel which led to an increased heat load and eventual damage to the device. Figure 6.2.2 shows the row of green pixels being addressed in image (a) where the first pixel is displaying a short (circled in red), where the blueish/orange color is an arc on the surface of the device. Several pixels show this shorting but the first pixel is the most dominant. After a short period of operation the heat buildup became so great that the glass substrate cracked and the device became inoperable, the cracked substrate is



Figure 6.2.2: (a) The row of green pixels operating with a short causing increased heating on the first pixel. (b) The crack in the device caused by the substrate heating from a short in the first pixel.

shown in Figure 6.2.2 (b). The shorting of the pixels is one possible reason that the first device had the worst performance. Defects in the spin coated layers could have also led to the degradation of the device performance. Figure 6.2.3 shows the device operated at 14V using passive addressing discussed in section 5.1 and section 5.2. The green row is not illuminated which could be related to the failure and cracking of the substrate. The red devices appear to be very uniform in nature but the yellow and green pixels show less

uniform devices. The green devices are very dimly lit and the yellow devices show multiple defects on the surface. This is similar to the defects seen in Figure 5.3.1 where the spin coated layers create defects that propagate through the entire device. The solution to this problem lies in the spin coating of the samples as well as the sample cleanliness.



Figure 6.2.3: The first three-color device operating as a 3x3 matrix at 14 V. Spin defects are visible on the surface and the green devices are nearly non-functioning.

The second device had no shorting in the pixels and yielded higher brightnesses as seen in Figure 6.2.1. The pixels displayed spectral data that indicates recombination in the ETL or HTL. According to the manufacturers data sheets Alq<sub>3</sub> has a wide emission spectrum with a peak at 511 nm and poly-TPD has a wide spectrum as well with a peak at 422 nm [62], [63]. The spectral data of the second device can be seen in Figure 6.2.4 (a) where the intensity is normalized to the red intensity. The yellow and green devices have a much lower intensity than the red device so the spectral data was normalized for each individual color and plotted to represent each individual device spectrum more accurately and are depicted in Figure 6.2.4 (b). From (a) we see that there is a wide emission that is in the blue and green regime that matches the emission wavelengths of the HTL and ETL, and when (b) is viewed this becomes much more apparent. The green device has such a low emission that peak becomes very flat when viewing (a) but can be seen more clearly when viewing (b). The green emission has a very wide emission peak that stretches into the red regime. This could have been caused by background or cross talk during the green pixel analysis. The emission was low enough that background noise is noticeable in the peak, and is the reason that the plot is not smooth.



Figure 6.2.4: (a) the spectral emission of a red green and yellow pixel on the second device with the intensity normalized to the red intensity. (b) The same spectral data but each intensity is normalized to itself to show to better depict the spectral range of the less intense pixels.

The emission of the green and blue wavelengths from the ETL and the HTL can be seen in Figure 6.2.5, which depicts the second device with all of the pixels illuminated. From this image it can be seen that there are minor defects in the pixels. There are some dark points with a bright crescent shape around each point, which is believed to be caused in the spin coating process (as discussed in section 5.3). The red column best depicts the variance in light emission due to the location of charge recombination. The QD-LED in the lower right corner of the red column has a bluish tint which would be caused by recombination in the poly-TPD layer. The second to last device in the red column has an altered color emission due to recombination in the Alq<sub>3</sub> layer instead of the QD layer which creates an orange/yellow emission when mixed with the red QD emission. Since this array did not show any signs of electrical arcing, device shorting, or extreme heating to the point that the glass substrate fails it is clear the ITO and Al are not in direct contact though the device performance is still greatly lacking.



Figure 6.2.5: The second 5x3 multi-color QD-LED array which depicts surface defects as well as alterations in the emission spectrum due to charge recombination in the ETL and HTL.

The third and final multi-color device demonstrated the greatest luminescence but still was plagued with the problems of the earlier devices. The best brightness measurements for each color can be seen in Figure 6.2.6, where the IV curves were all similar and depicted as the inset. The highest brightnesses achieved for the multi-color devices is shown where the yellow device had the highest brightness of 665 cd/m<sup>2</sup> and the red and green were similar in brightness at 507 cd/m<sup>2</sup> for the green pixel and 508 cd/m<sup>2</sup> for

the red pixel. This means that the brightness between brightest and dimmest pixel is 24%. These measured brightnesses are above the  $500cd/m^2$  brightness that is used in current display technology and evenly matched to ensure the color intensity is equivalent, meaning they show great potential as a display medium.



Figure 6.2.6: The brightnesses of the red, green, and yellow pixels on the third multi-color device with the red peak at 508 cd/m<sup>2</sup>, the green peak at 507 cd/m<sup>2</sup>, and the yellow peak at 665 cd/m<sup>2</sup>.

Some of the pixels on the third device had high brightnesses where others were incapable of lighting or consisted mainly of Alq<sub>3</sub> emission. This can be seen in Figure 6.2.7 where a 3x3 array is illuminated. The first row of illuminated pixels yielded the highest brightnesses for all three devices while pixels in rows two and three either did not function or exhibited ETL emission, which is most notable in the red pixels. Emission from an un-addressed pixel is visible in the column of yellow pixels which is related to the passive addressing crosstalk discussed in section 5.3. The green and red pixels displayed fewer spin coating defects, yet the uniformity of the yellow pixels is still questionable. The pixels also display an abnormal shaping which is related to the ITO etching method. The rudimentary ITO etching process allows for over-etching of the ITO stripes as well as human error in creating accurately sized devices. This leads to the rough



Figure 6.2.7: A 3x3 array of the third device operated at 14V using passive addressing.

edges presented in the devices in Figure 6.2.7. The spectrum of the first row is shown in Figure 6.2.8, and shows that the pixels had a similar intensity which is congruent with the results shown in Figure 6.2.6. The red spectrum appears to be mostly self-contained showing only the red emission from the QDs. The yellow spectrum depicts a strong emission from the QDs but also includes a peak in the green regime that matches the Alq<sub>3</sub> emission. The green device shows a very broad peak that extends to the Alq<sub>3</sub> regime as well as the red and yellow regime. After deposition the green QDs that remained in the atomizer were collected and a photoluminescence (PL) measurement was done to find the emission and added to the figure. There is a shoulder in the EL emission that matches the QD emission but the more prominent peak is closer to the Alq<sub>3</sub> peak. There is also a small emission in the red regime of the PL measurement, which is from cross contamination. The red QDs were deposited followed by yellow and then finally the

green. This allows for the red and yellow dots to contaminate the green deposition. The red and yellow dots fall into the basins within the atomizer and may not necessarily be deposited when the green mist is moving through the atomizers but was mixed into the solution that was siphoned off for PL analysis. It is possible that the green and yellow dots contaminated the green mist and could explain the broadening of the EL emission into the red and yellow regime.



Figure 6.2.8: The spectrum of the red, green, and yellow devices with the green PL fitted to the green emission to show demonstrate the emission without Alq3 emission.

Further testing of the devices and enhanced structures could lead to devices that have improved brightness and reduced emissions from the hole or electron transport layers. After the initial study of multi-color QD-LED arrays it can be said that there are four things that need to be achieved in the future for the QD-LED to become a viable option in the display industry. First, the brightness of the QD-LED needs to be improved. It is currently capable of achieving a video brightness of 500cd/m<sup>2</sup> but this value needs to be further increased to make it a sensible next generation option. Second, the emission from the ETL and HTL needs to be removed. This can be done through careful testing and analysis of the layers within the QD-LED to find the optimized layer thicknesses or new materials could be used as the HTL and ETL. Another area of improvement would be the device lifetime, since this is much lower than the 100,000 hours that is needed. The device packaging, heat dissipation, and material choices can all be altered to achieve the highest possible lifetime. Finally, the pixel density needs to be increased to match that of a display. It has already been proven that the mist deposition process is capable of patterning stripes on the order of 100 microns and that patterning them with the tool is also viable. Combining the high density patterning with the multi-color work that has been shown here to develop a high density array would allow for the fabrication of a working QD-LED display.

## Chapter 7

### **Conclusions and Future Work**

The present work demonstrates the possibility of creating multi-color QD-LED displays via mist deposition. The working mechanisms of the QD-LED have been explored and compared with the closely related OLEDs, showing that QD-LED is similar in structure to the OLED but excels in areas such as lifetime, color purity (narrow FWHM), and material properties, meaning multiple colors are derived from a single material. Light emitting devices can be fabricated via a series of solution processing techniques, but for the purposes of this research mist deposition was chosen. This deposition process was compared to various other methods and mist deposition was found to be both versatile and accurate when depositing the QDs.

The mist deposition process was thoroughly explored and parameters were chosen to create smooth films as well as thin films. Throughout the research project the mist deposition results were compared with the spin coating results, since spin coating yielded the best results. Spin-coating is not a viable option for creating three-color arrays, which is why mist deposition was still needed. The devices created via mist deposition would need a driving circuit to create either a passive or active array. The passive addressing method was chosen and a driving circuit was designed and tested. The results showed considerable cross-talk that led to an analysis of both the QD-LEDs and the circuit design. The final step was to combine the separate areas of research into a single multicolor device. The test results of the QD-LEDs helped to identify the ETL and HTL thicknesses as well as the thickness of the QD layer. The mist deposition study allowed for the best parameters to be used as well as the patterning method that was tested as a proof of concept. A 3x5 array of red, yellow, and green QD-LEDs were fabricated and tested using the passive addressing system to control each pixel individually, yielding a passively addressed multi-color 3x5 array.

The research outlined here shows the viability of both mist deposition as a multicolor QD-LED fabrication method and the QD-LED as a choice in display technologies. The brightness of the QD-LEDs is greater than video brightnesses currently used, the color contrast is exceptionally high, and the pattern-ability of the mist deposition process is capable of yielding pixels under 100 microns. The next step in this area of research to refine the process and materials and to increase the pixel density to create larger arrays that could rival other small displays.

The work outlined here culminates with the goal of creating a functioning QD-LED display, and areas of interest for improvement are pixel density, addressing, brightness, and lifetime. If the pixel density is increased along with brightness and lifetime and this is coupled with the right display driving method it could provide a greater potential as a display medium. To improve these designated areas the device structure and the patterning methods need to be taken into account.

#### 7.1 Pixel Density and Addressing

Possibly the simplest improvement to the multi-color QD-LED display research that has been done thus far would be the incorporation of the high density patterning that has been completed with organic materials discussed in section 4.4.2. The proof of concept using organic light emitting materials showed it was possible to accurately and consistently deposit a film in a desired location in the 100 micron scale. The translation from this work to a high density QD-LED display would revolve around the mist deposition of QDs over ITO strips. The deposition process could be completed using the alignment methods that are currently being used, and could accurately deposit QD strips as small as 100 microns in size. The ITO would have to be smaller than the deposited strips for reasons discussed earlier, meaning small RGB pixels aligned in a repeating pattern on the surface.

After deposition and fabrication is completed the more complicated process of addressing the strips is required. The current passive addressing device can handle a 34x34 array which is not nearly large enough to simulate a functioning display. This will be adequate for laboratory testing. This would allow for 11 red, green, and blue stripes and 33 aluminum stripes to make a 33x33 array that consists of RGB pixels. To create a passively addressed system the reverse leakage current would need to be reduced to prevent the non-addressed pixels from illuminating and causing the entire array to be illuminated. The software used in the passive addressing research would reach its limit with this device and other addressing schemes could be investigated. Display driving chips designed to handle large arrays could be used but would require mounting into an interface that would allow for simple attachment to various substrates. The lack of flexibility in the driving chips is what led to the decision of the FET switching matrix that was chosen, but the limitations were known and eventually a commercial driving circuit

would be needed. If a commercial driving circuit is matched with the work that has already been done with high density patterning a QD-LED display becomes viable.

#### 7.2 Improvement of Luminescence and Lifetime

The brightness and the lifetime could potentially be improved via the use of inorganic hole and electron transport layers. If the organic materials are removed from the device then it becomes possible to limit the degradation due to oxidation and moisture. If new materials are chosen for the electron and hole transport layers it is possible to create a completely inorganic structure with a much longer lifetime and brightness. The inorganic layers currently being tested in research are NiO for a hole transport layer and ZnO for an electron transport layer [64], [29], [30]. Switching to the new inorganic transport layers will increase the lifetime and possibly increase the brightness, which is highly desirable. Figure 7.2.1 shows the new device stack that could be used to create a new more efficient device. The NiO can be deposited onto the surface using RF magnetron sputtering with an Ar:O<sub>2</sub> plasma to sputter a Ni target, which creates a NiO. The adjustment of the oxygen concentration in the Ar:O<sub>2</sub> plasma will alter the resistivity of the NiO film [29], [30]. The ZnO film can be deposited using a spin coating technique of ZnO nanocrystals suspended in proponal [64]. The second option for ZnO layer is to create an alloy of ZnO and SnO<sub>2</sub> rather than pure ZnO. Pure ZnO layers tend to be polycrystalline or amorphous as in the case of spin on nanocrystals. A ZnO:SnO<sub>2</sub> alloy on the other hand has a root mean square roughness of less than 0.5nm making it smooth,



Figure 7.2.1: The device structure of a completely inorganic QD-LED, where the HTL is NiO rather than poly-TPD and the ETL is ZnO rather than Alq3. The replacement of the organic layers could potentially increase lifetime device lifetime.

which will reduce shorts and charge concentration [29]. This alloy can be sputtered onto the surface with minimal oxygen in the plasma gas which is favorable since increased oxygen levels can cause oxidation of the organic ligands on the QDs eventually causing sites for nonradiative recombination [29]. The work done by J.M. Caruge et. Al. shows that the sputtered films using SnO<sub>2</sub> were not amorphous, but PL testing before the ZnO:SnO<sub>2</sub> deposition compared with the PL after the deposition shows a 40% drop in intensity which is attributed to the ZnO:SnO<sub>2</sub> deposition [29].

Preliminary testing was done using the ZnO nanocrystals to test the effectiveness of the ZnO as an electron transport material. Spin coated samples as well as mist deposited samples were fabricated using poly-TPD as a hole transport layer and ZnO nanocrystals as an electron transport layer. The ZnO layer is deposited via spin coating after the QD deposition and curing. The ZnO nanocrystals are applied at 550 RPMs for 40 seconds and then cured at 80C for 30 minutes to remove any remaining solvent. The luminescence from this preliminary testing is shown in Figure 7.2.2 where the brightness of the spin coated samples, 20 minute mist deposition, and 40 minute mist depositions are shown. The ZnO ETL has a considerable effect on increasing the brightness. The spin coated sample is now exhibiting a brightness over 14,000 cd/m<sup>2</sup> which is greater than three times the brightness shown in the original testing (see Figure 3.5.2 (a)). The results from the mist deposition process are less than the spin-coated samples but are still ten times greater than the device results using Alq<sub>3</sub> that are shown in Figure 6.2.6. The 20 minute deposition brightness is considerably less than both the 40 minute mist deposition and the spin coating results. Initial thoughts were that the 20 minute deposition was creating a film that was too thin and had limited recombination sites. A 40 minute deposition was then done and it proved to have a higher brightness but the turn on voltage has increased greatly. This increase in the turn-on voltage could be related to the film



Figure 7.2.2: The brightness of samples with spin coated QDs as well as 20 minute and 40 minute mist deposited QDs. All 3 samples used poly-TPD as a hole transport layer and ZnO nanocrystals as an electron transport layer. thickness. As the thickness of the QD film increases the driving voltage required to turn-on the device increases. This can be seen when comparing the turn-on voltage for the 20 minute deposition and the 40 minute deposition. The turn-on voltage of the 20 minute run closely resembles the turn-on voltage of the spin cast device but the brightness is greatly

reduced. The similarity in turn-on voltages could mean the film thicknesses are equivalent, which would not explain the changes in brightness between the two devices. It is possible that the heating from the bubbler and the effects of the 8kV driving voltage could create a localized heating in the dot and damage the ligand or create charge trapping sites causing reduced EL intensity [25], [24]. Further testing will need to be done to determine the exact reason for changes in luminescence.

During the 40 minute deposition an 8x8 array was made using the structure that poly-TPD and ZnO was just discussed. The devices had similar brightnesses to the standard devices and showed similar results to the Alq<sub>3</sub> devices that were discussed earlier. Figure 7.2.3 shows three separate frames of the 8x8 array where the letters PSU are spelled out. The crosstalk is still present as it was with the Alq<sub>3</sub> devices but is considerably noticeable in the column on the right hand side of the device. This could be a response to packaging which was done as a precaution or it could be related to crosstalk, it is currently unclear. This is the first step in creating mist arrays that display a high brightness. Further testing will need to be done to refine the deposition process and reduce non-uniformities that can be seen in the pixels.



Figure 7.2.3: The passively addressed 8x8 arrays that show PSU. The arrays use poly-TPD as the HTL and ZnO as the ETL with a QD layer that was deposited for 40 minutes via mist deposition.

The next step in the display fabrication process is to increase the pixel density of the QD arrays. The pixel density will be scaled by doubling the pixels per row and column with each new generation. The next generation of QD-LED arrays will be 16x16 followed by 32x32 then 64x64 etc. allowing for a gradual optical density increase that will ease the transition process to a better representation of a QD-LED display. The first arrays will also be monochromatic to allow for the optimization of the patterning process, deposition time and concentration, and most importantly the display driving methodology. As the device arrays increase in pixel count a new device driver will be needed and it will have to be a fully functioning video driver commonly used in display technologies. The specific driving circuit will be need to be chosen as well as a connection system to easily attach the devices to the driver. After the completion of a functioning high pixel density monochromatic array the switch to a three-color array will be smoother. The driving circuit will be available and the patterning and deposition details will be known, which will hopefully alleviate some of the minor transition issues. The problems of crosstalk, uniformity, and increased brightness (to match that of spin coating) are all still problems which should also be addressed during the fabrication and analysis of future devices.

Based on the information listed here as well as the current work being done by Samsung and QD Vision I think it is possible that some day the technology will be available for active matrix QD-LED displays, but the passive matrix QD-LED displays is questionable mainly because of the limited research being done in this field. To become commercially viable the lifetime as well as the price of the display needs to be improved. Currently QDs are more expensive than the dyes being used in OLED displays making them not the economic decision, though if the price is reduced for QDs then the benefits would outweigh the costs.

The future work for this research should be driven towards creating a closely packed array that resembles a functioning display. The groundwork has been laid for the fabrication of a mist deposited display using passive addressing and the patterning methods described here. The addition of an inorganic ETL has already shown the potential for increasing the EL intensity well beyond the video brightness that is currently used. Further testing of the lifetime still needs to be completed to examine the changes in lifetime by using the ZnO nanocrystals in place of the Alq<sub>3</sub> layer. Based on the observations shown in this work and the future considerations outlined here it is plausible that a QD-LED display could be fabricated using the techniques and process that have been discussed.

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## **Appendix A**

## Number of QDs per Droplet Calculation

To find the number of QDs in a mist droplet first the concentration needs to be known. The concentration in mg/ml is used to ensure consistency between runs. The next step is to determine the number of atoms in a QD. This can be done by finding the diameter of the QD using Eq. (14), which is a calculation based off the empirical fitting of QD size in relation to the wavelength of the first absorption peak ( $\lambda_A$ ) [65].

$$D = (1.6122e - 9)\lambda_{A}^{4} - (2.6575e - 6)\lambda_{A}^{3} + (1.6242e - 3)\lambda_{A}^{2} - (0.4277)\lambda_{A} + (41.57)$$
(14)

To find the first Absorption peak a UV-VIS measurement was done on the QD solution to measure absorbance (A). Figure A.1 shows the Absorbance and that the first peak is at 602nm which is the value then used in Eq. (14).



Figure A.1: The Absorbance measurement for red CdSe QDs where the first absorption peak is at 602 nm.

The resulting diameter then is used to find the volume of a QD using the volume of a sphere. After the volume is found it is multiplied by the density and the molecular weight of CdSe to yield the number of moles per QD which can then be multiplied by Avogadro's number to find the number of atoms per QD. This process assumes that the ligand structure and ZnS is negligible when compared to the CdSe core.

The next step is to find the average diameter of a mist droplet which is a known constant and use this to find the volume of the droplet. The volume is then multiplied by the concentration to find the average mass of QDs in each droplet. This is then also converted to the number of CdSe atoms per droplet, in a similar fashion to finding the number of atoms per QD. The number of atoms per droplet is then divided by the number of atoms per QD to find the number of QDs per droplet to find that there are approximately 5 QDs per droplet.

## **Appendix B**

## **Symbol List**

#### **OLED**

J = Current Density  $m_e^* = \text{Electron Effective Mass}$   $m_h^* = \text{Electron Effective Mass}$  k = Boltzman Constant T = Temperature  $\Phi_{\text{BN}} = \text{Barrier Height}$  q = Elementary Charge V = Applied Voltage  $m_0 = \text{mass of free electron}$  h = Planck's Constant  $\hbar = h/2\pi$   $\varepsilon = \text{relative dielectric constant}$   $\epsilon_0 = \text{dielectric constant}$  L = Sample Thickness  $\mu = \text{reduced mass}$ 

#### **Working Principles**

- $\hat{H} = Hamiltonian$
- M =total mass
- $\mu$  = Reduced mass
- $m_e^*$  = Electron Effective Mass
- $m_h^*$  = Electron Effective Mass

 $\varepsilon$  = relative dielectric constant

- $\varepsilon_r$  = dielectric constant relative to vacuum
- $a_0$  = Bohr radius of hydrogen atom
- $\alpha$  = Bohr Radius of an exciton
- U(r) = Potential describing sphereically symmetric well
- $E_n$  = the allowed energy levels
- n =positive whole number
- r = radius of QD
- $E_g = bandgap$
- c = speed of light
- $\lambda$  = wavelength emitted in microns

#### **Band Structure**

T =tunneling probability

- W =barrier width
- m\* = effective carrier mass
- $\hbar = plancks constant$
- $\Phi B = Barrier Height$

#### **Efficiency**

- $\eta_{IQE}$  = Internal Quantum Efficiency
- $\gamma$  = charge-balance factor
- $\eta_r$  = efficiency of production of singlet excitons
- $\phi_f$  = quantum efficiency of fluorescence
- J = circuit current
- $J_r$  = recombination current
- $\eta_{EQE}$  = External Quantum Efficiency
- $\zeta$  = multiplying factor that accounts for refractive index
- n = refractive index

#### **Luminescence**

- *L* =Luminesence
- P = Optical Power
- A = Detector Area
- R = Distance between Detector and Device
- r = Detector radius
- $V(\lambda)$  = Visual Function
- $\Omega$  = Solid Angle
- $\Theta$  =Angle between detector and device surface.

#### **QD Diameter**

D= Diameter of QD

 $\lambda_A$ = First Absorption peak

## Appendix C

### **Non-Technical Abstract**

Displays and display technology are becoming a very important part of everyday life for a majority of people. People all over the world use computer screens, televisions, cell phones, digital cameras, MP3 players, and other portable devices which all contain some form of display. The display industry is creating brighter, more efficient, and higher definition displays to not only improve the viewing quality but also reduce the production cost as well as operating cost. Think of a typical LCD display that is on a laptop. If that screen can reduce the power consumption the batter life will be significantly extended and can help the company to gain a larger consumer base.

One option for next generation displays is the quantum dot (QD) display. Quantum dots are small semiconductor particles that exhibit quantum confinement, meaning when a charge is applied they can emit light. Quantum dot light emitting diodes (QD-LEDs) are made in a similar fashion to the already commercially available organic light emitting diodes, but bring various advantages of their organic counterpart. Quantum dots are inorganic which mean they are not easily affected by oxygen and water vapor, they provide a very pure color as opposed to the broad spectrum organic compounds, the various colors are made from the same material which simplifies the production process, and they can be applied to through solution processing rather than expensive vacuum depositions.

In this research the viability of a multi-color QD-LED display is explored. A method is chosen for QD deposition that will allow for patterning and parameters are selected to achieve the best results. This work describes the operating principles of the QD-LED as well as its optimization, followed by the analysis of the deposition method that will be used for fabrication. A method is designed to drive the display in a fashion that is similar to current display technology and is tested to ensure it is a viable option. Finally, multi-color devices are fabricated and tested in small arrays to show that mist deposited QD-LEDs will make a viable display medium. After analysis of the final results of the multi-color displays future considerations are made for the improvement of the device quality and the device results.

### Vita Shawn L. Pickering

#### **Degrees:**

Bachelors of Science (Applied Physics), May 2007, Lock Haven University of Pennsylvania, Lock Haven, Pennsylvania

Ph.D. (Engineering Science and Mechanics), May 2011, The Pennsylvania State University, University Park, Pennsylvania

#### **Employment Record:**

Graduate Teaching Assistant, ESM, The Pennsylvania State University, August 2007 - January 2009

Graduate Research Assistant, ESM, The Pennsylvania State University, January 2009 - January 2011

#### **Publications:**

David N. Hunter, *Shawn L. Pickering*, and Dongdong Jia. "Thin-film nanocapacitor and its characterization", Euro. J. Phys. 2006

Dongdong Jia, A. Goonewardene, C. Shaffer, *Shawn L. Pickering*, and X. J. Wang. "Behavior of TiO2 thin film in a nanocapacitor", 1<sup>st</sup> Conference on Luminescent properties of nanomaterials, Hainan, China. 2006

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Zhanao Tan, Jian Xu, Chunfeng Zhang, Ting Zhu, Fan Zhang, Brittany Hedrick, *Shawn Pickering*, Jian Wu, Huaipeng Su, Shuai Gao, Andrew Y. Wang, Brian Kimball, Jerzy Ruzyllo, Nicholas S. Dellas, Suzanne E. Mohney. "Colloidal nanocrystal-based light-emitting diodes fabricated on plastic toward flexible quantum dot optoelectronics." Journal of Applied Physics, 2009

*Shawn Pickering*, Aditya Kshirsagar, Jian Xu and Jerzy Ruzyllo. "Patterned Mist Deposition of Tri-Color CdSe/ZnS Quantum Dot Thin Films Toward RGB LED Devices." Nanotechnology, 2010 (submitted)