Fabrication and encapsulation of polymer light emitting diodes

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Fabrication and Encapsulation of Polymer Light Emitting Diodes

by

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Chairperson of Polymer Science and Engineering
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ABSTRACT

Organic Light Emitting Diodes (OLEDs) are promising techniques for next generation flat panel displays, due to their thin-film form, low power consumption, wide viewing angle, and the ability of flexibility. A polymer top-emitting diode was developed to integrate with the TFT backplane on the silicon wafer and flexible steel substrate. Different combinations of anode and cathode were tried in order to reach high efficiency. A device with platinum anode and calcium/indium tin oxide cathode has been demonstrated the promising characteristics. The conventional encapsulation with glass lid does effectively prevent moisture and oxygen. Furthermore, a hermetrical encapsulation has to be developed for the flexible devices in the future.
CHAPTER 1

INTRODUCTION TO ORGANIC LIGHT EMITTING DIODES

1.1 Overview

Organic Light Emitting Diodes (OLEDs) include both small-molecular and polymer-based devices, which are known as a promising display technology nowadays. The inherent thin-film structure of OLEDs make them attractive for flat panel displays. Compared with the currently dominant liquid crystal display technology (LCD), OLEDs have many potential advantages. The manufacturing process is low cost and easy. Due to their basic properties as active light emitters, OLEDs are more competitive than LCD which needs the polarizing filters requiring a back light. OLEDs also have the developing ability toward to flexibility application.

1.2 Historical Development

The first OLED based on single crystal of anthracene was fabricated in 1963, but it was not a thin film device and required a very high operating voltage. [1] In 1987, Tang and Van Slyke of Kodak developed the first multi-layer structure and demonstrated the high efficiency and low voltage (~10V) of thin film (~100nm) OLEDs which were a p-type, hole-transporting molecular film of aromatic diamine and an emitting layer of the n-type, electron-transporting tris(8-hydroxyquinoline) aluminum (Alq3) between the ITO anode and a low work-function alloy of magnesium as the electron-injecting cathode, shown in figure 1.1(a). [2,3] The 1990 paper by Friend et al. of Cambridge University described the first polymer OLED (PLED) based on the conjugated polymer
polyparaphenylenevinylene (PPV) which was a single-layer device structure, shown in figure 1.1(b). [4] PPV is insoluble in common solvents; therefore, a soluble precursor polymer is first prepared, and then a film is spun from solution which is thermally converted to the conjugated form. [5,6] Cambridge Display Technology was founded in 1992 to promote the commercial development of PLEDs. In 1991, Heeger and co-workers at the University of California at Santa Barbara announced the application of a soluble derivative of PPV, poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene] or MEH-PPV. [7] Heeger founded UNIAX Corporation in 1990 and UNIAX was acquired by DuPont in 2000. It was established to optimize the manufacturing process for the commercialization of PLED devices.

**Figure 1.1.** (a) First practical thin-film electroluminescent device; (b) First polymer-based organic light emitting diode.

### 1.3 Device Structure and Operation of OLEDs

The basic structure of a typical dc-biased bi-layer OLED is shown in figure 1.2. The first layer above the glass substrate is a hole-injecting electrode which is typically a
high work function and transparent material, indium tin oxide (ITO); therefore, emission from the organic can escape the device. The layer deposited on the anode would generally be a good hole transport material, providing the hole transport layer (HTL). Similarly, the organic layer in contact with the cathode would be the electron transporting layer (ETL). The electron-injecting electrode is typically a low-to-medium work-function metal.

In the basic operating mode of an OLED, when a voltage is applied across the electrodes, holes are injected from the anode and electrons from the metal cathode. Electrons and holes migrate through the transport layer and then meet in the emitter layer. They move toward the interface under the influence of the applied field and recombine to form excitons which prefer to form in the emissive layer. These excitons then emit light which can escape through the transparent side.

![Diagram of a bi-layer OLED structure](image)

**Figure 1.2. Basic structure of a bi-layer OLED**
Applied forward bias, the electronic energy diagram for a bi-layer OLED device is illustrated in figure 1.3. HOMO and LUMO are the respective highest occupied and lowest unoccupied molecular orbitals of the organics. The work-function, \( \Phi \), is shown with reference to the vacuum potential. Organic materials tend to possess low electron affinities; therefore, conjugated semiconductors exhibit hole-transporting properties. The electron affinity (EA) of a semiconducting organic is equivalent to the conduction band or \( \pi^* \) state density (or LUMO). Also, the valence band or \( \pi \) state density (or HOMO) corresponds to the ionization potential (IP) of the material. A theoretical study by Friend et al. indicates that there is no band bending at the junction between semiconducting polymers. [8] The barrier comes from the interface of electrodes and transport layers. Charge transport is carried out by hopping along \( \pi \) orbitals under the applied field and is tunneling through the electrode-organic interface barrier (Shottky barrier).

![Figure 1.3. Schematic energy level diagram of an OLED](image-url)
1.4 Materials for OLEDs and PLEDs

1.4.1 Anode and cathode materials

As mentioned above, the anode is usually made by a high work-function metal such as transparent ITO and the cathode is a low work-function metal. ITO is a non-stoichiometric mixture of In, In₂O, InO, In₂O₃, Sn, SnO, and SnO₂. The work-function of ITO films is around 4.5 eV. With increasing the oxygen content, the surface can be modified more conductive and has the electric work-function up to 5.1 eV. For a reverse top emission OLED, different high work-function metals can be chosen, such as Pt. only if they could strongly enhance hole injection. Low work-function metals, such as Li, Ca, Ba, and Mg₀.₉Ag₀.₁, can be deposited either by thermal or e-beam evaporation. Al or ITO is often used as an additional protective layer over the low work-function layer.

<table>
<thead>
<tr>
<th>Element</th>
<th>Work-function (eV)</th>
<th>Element</th>
<th>Work-function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>5.56</td>
<td>Mg</td>
<td>3.66</td>
</tr>
<tr>
<td>Ni</td>
<td>5.12</td>
<td>La</td>
<td>3.50</td>
</tr>
<tr>
<td>Au</td>
<td>5.10</td>
<td>Li</td>
<td>2.90</td>
</tr>
<tr>
<td>Si</td>
<td>4.85</td>
<td>Ca</td>
<td>2.87</td>
</tr>
<tr>
<td>Sn</td>
<td>4.42</td>
<td>Na</td>
<td>2.75</td>
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<td>Ti</td>
<td>4.33</td>
<td>Ba</td>
<td>2.70</td>
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<td>Zn</td>
<td>4.33</td>
<td>Sm</td>
<td>2.70</td>
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<tr>
<td>Al</td>
<td>4.28</td>
<td>Sr</td>
<td>2.59</td>
</tr>
<tr>
<td>Ag</td>
<td>4.26</td>
<td>Eu</td>
<td>2.50</td>
</tr>
<tr>
<td>Cd</td>
<td>4.22</td>
<td>K</td>
<td>2.30</td>
</tr>
<tr>
<td>Ga</td>
<td>4.20</td>
<td>Rb</td>
<td>2.16</td>
</tr>
<tr>
<td>In</td>
<td>4.12</td>
<td>Cs</td>
<td>2.14</td>
</tr>
</tbody>
</table>

1.4.2 Small molecular materials

Copper phthalocyanine (CuPc), N, N'-diphenyl-N', N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), and N, N'-diphenyl-N', N'-bis(1-naphthylphenyl)-1,1'-
biphenyl-4,4’-diamine (NPB) are widely used as a HTL. However, CuPc may either inhibit hole injection or enhance it due to the other layers in the OLED. The glass transition temperature of TPD is $65^\circ$C that will cause recrystallization and make OLEDs fail. Compared to TPD, NPB is modified by naphthylphenyls which makes it have a higher glass transition temperature. Alq$_3$ is a green emitter and an electron transport layer, which is used extensively in OLEDs. 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1.3.4-oxadiazole (PBD) is also used as an ETL between the cathode and emitting layer, but it is non- emissive. The structures of these small molecular organics are shown in figure 1.4.

1.4.3 Polymer materials

Poly(3,4-ethylene dioxy-2,4-thiophene)-polystyrene sulfonate (PEDOT-PSS) is water-based which is commonly deposited on ITO as a HTL in PLEDs or can be used as a transparent anode. [11] PEDOT/PSS has a high work function (5.0 eV) and a $\pi-\pi^*$ electronic bandgap of 1.6~1.7 eV, which allows holes to be injected easily. Polyaniline (PANI) is another doped conducting polymer which is also water-based and transparent. The first all plastic PLED was constructed on the top of PANI anode. [12] Most conjugated polymers have semiconductor band gaps of 1.5~3.0 eV, which means that they are able to emit visible light. PPV has an energy gap between $\pi$ and $\pi^*$ states of about 2.5 eV, and produces yellow-green luminescence in a band below this energy. [6] Its various derivatives and block copolymers which are soluble have drawn more attention than any other conjugated polymers. [13] Another class of conjugated polymer is poly(1,4-phenylene) (PPP) which has wide bandgaps and allows emission of blue light.
However, most PPPs are insoluble and intractable. The structures of those conjugated polymers are shown in figure 1.5.

![Molecular structure of π-conjugated small molecules](image-url)

Figure 1.4. Molecular structure of π-conjugated small molecules
Figure 1.5. Molecular structure of π-conjugated polymers
CHAPTER 2

FABRICATION OF POLYMER LIGHT EMITTING DIODES

2.1 Overview

Conjugated polymers have been applied to a range of semiconductor devices because of its thin film property. [18] Particularly, polymer light emitting diodes are attractive to commercial markets. PLEDs offer the low-cost manufacturing by using solution process, instead of using expensive vapor deposition. Solution-processing of polymers provides new ways to deposit thin film over large areas by spin-coating or doctor blade techniques. It also offers a new method for color patterning, ink-jet printing, which is developed to place separate pixels of red, green, and blue emitting polymers onto the substrate. [19] Moreover, color and emission efficiency can be fine-tuned by manipulating their chemical structures.

Here, the polymer based top-emitting OLED is chosen as our research goal because of easy processing and low cost. Another advantage is to integrate with a TFT backplane. Because OLEDs are current-driven devices, it is important to provide a constant and uniform drive current. It might sacrifice the aperture ratio if three or more TFTs are used within each pixel to maintain the driving current. The circuit and backplane designs are the other part of our projects which can be referred to those publications in our laboratory. [20,21] However, top-emitting OLEDs have been demonstrated less efficient than bottom-emitting ones. Improving the efficiency of top-emitting OLED is a challenge for this project. [22]
2.2 Experimental Procedures

The fabrication of PLED is involved with several semiconducting processes in our laboratory, including metal deposition, photoresist coating, development, exposure, and wet etching. Moreover, all works are done in the clean room here. The OLEDs were constructed on different substrates, including 5 inch silicon wafer with 20,000 Å thick layer of thermally grown SiO₂, stainless steel foil, and quartz wafer.

2.2.1 Anode deposition and patterning

Different high work-function materials are chosen as the anode depending on types of OLED. In most cases, transparent ITO is the anode for bottom-emitting OLED. Those anode depositions are processed by using rf magnetron sputtering (Kurt J. Lesker system) in our laboratory. For top-emitting OLED, we choose different combinations of high work-function metals to achieve efficient hole injection, such as Al/Ni/ITO, Al/Ni, Ni and Platinum (Pt). [23,24] Those materials will be deposited on top of the silicon wafers or steel foils either by sputter or e-beam evaporation. In order to pattern the anodes, lift-off resist (LOR 10B, MicroChem) and a following photoresist (AZ MiR 703 Photoresist) are coated sequentially on the substrates before the metal deposition and then soft-baked on the hot plate. After exposure, the wafers are developed (AZ 300MIF Developer) to get those patterns. When finished the metal deposition, a lift-off process is carried out in EBR PG solution (Positive Radiation Resist Edge Bead Remover, MicroChem), which is placed in an ultrasonic bath. Afterwards, wafers are cleaned by several washes of de-ionized water (DIW) and rinsed by isopropanol (IPA). Following the same procedures as described, the anode of bottom-emitting OLED is sputtered-ITO.
(Plasmaterials) which is 10% SnO₂ and 90% In₂O₃ by weight with 99.99% purity. After lift-off process, a post-deposition annealing is performed at 300 °C for 30 minutes. Prior to the next step, the ITO surface must be cleaned and exposed to an oxygen plasma or ultraviolet (UV) ozone. [25-27] The oxygen plasma treatment increases the work function of ITO and removes contaminants, thus enhancing the hole injection. Table 2 indicates the thickness of different anode combinations measured by alpha-stepper 200 (TENCOR Instrument).

<table>
<thead>
<tr>
<th>Anode</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al / Ni / ITO</td>
<td>1500 Å / 500 Å / 1000 Å</td>
</tr>
<tr>
<td>Al / Ni</td>
<td>2500 Å / 500 Å</td>
</tr>
<tr>
<td>Ni</td>
<td>3000 Å</td>
</tr>
<tr>
<td>Ti / Pt</td>
<td>2000 Å / 1000 Å</td>
</tr>
<tr>
<td>ITO</td>
<td>3000 Å</td>
</tr>
</tbody>
</table>

2.2.1 Silicon oxide deposition and patterning

Silicon oxide (SiO₂) defines the active areas of the device and prevents short-circuits when contact is made to the electrodes. The first layer of SiO₂ is deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) at 300°C and the thickness is around 1500 Å. A following second layer of SiO₂ is coated with spin-on glass (SOG 211, Honeywell). SOG is spun and baked at 300°C for 1 hour on the hot plate. The 3000 Å thick SOG film served as a planarization and insulating layer. The use of PECVD oxide is for compensating the insufficient quality of SOG. After depositing the SiO₂ layer, adhesion promoter, HMDS, and photoresist are spun and soft-baked for next lithography
step to get the contact holes which are etched by buffered HF solution, 6 parts of ammonium fluoride (NH₄F) and 1 part of hydrofluoric acid (HF).

\[
\text{SiO}_2(s) + 6\text{HF}_{(aq)} \rightarrow \text{H}_2(g) + \text{SiF}_6(g) + 2\text{H}_2\text{O}(g)
\]

2.2.3 Surface treatment by oxygen plasma

Prior to spin-casting of the polymer films, the surface of silicon oxide should be modified by oxygen plasma in order to make the surface more hydrophilic and contact with the following layer of water-based PEDOT. In order to prevent the anode damage, oxygen plasma treatment is operated at low power (100 W) in the reactive ion etching (RIE) mode.

2.2.4 Spin casting of polymers

PEDOT/PSS (Baytron P VP AI 4083, H.C. Starck) and PPV type material (COVION) are spun on top of the insulating layer sequentially. PPV is suggested to be dissolved in dry toluene (water<50ppm). ~5g/L. under inert atmosphere. [28] The concentration of PEDOT/PSS is 1.3 to 1.7wt% and its resistivity is 500 to 5000 Ω-cm. The PEDOT/PSS dispersion is recommended to be filtered by 0.45 μm Millex PVDf-Filter (Millipore). [29] The PEDOT/PSS layer allows efficient hole injection and helps smoothing the rough surface of anode. [30] By following each spin-casting of the polymers, a drying process has to be performed in order to drive the solvent away. PEDOT/PSS is baked at 120 °C for 10 minutes on the hot plate in the ambient atmosphere. PPV is recommended to be coated in the inert atmosphere and not to be heated up. However, we can not process it without a glove box. A substitute way is
chosen to spin in the air and leave it in the vacuum oven at room temperature for several hours. The thickness of PEDOT and PPV are 800 Å and 600 Å respectively.

2.2.5 Cathode deposition

For a top-emitting PLED, the semi-transparent or transparent cathode is required. Usually, the cathode consists of two different metals. One is the low work-function metal (Ca, Ba, Li, Mg…etc.), which is in contact with the light emitting layer and enhance the electron injection. The other layer plays a role of carrying the current and capping the low work-function metal as a protective layer (ITO or IZO). The cathode of our PLEDs consists of a thin layer of Ca and a transparent layer of ITO. Without breaking vacuum, Ca is thermal evaporated in the sputter vacuum system with a rate of 2.2 Å/s and a thickness of 100 Å. A following ITO film is then deposited by low-power rf sputtering at room temperature in order to reduce the ion bombardment upon the surface of PPV. [31,32] The thickness of ITO is around 1500 Å. On the other hand, a thin layer of Ca and another Al film are thermal evaporated for the cathode of bottom-emitting PLED.
Figure 2.1. Process flow of PLED fabrication
2.3 PLED on Flexible Steel Substrate

One advantage of OLEDs is the solid state nature and OLEDs have been fabricated on plastic or thin-glass substrates as flexible displays. It is possible for flexible substrates to fabricate displays by a roll-to-roll process, which can produce the devices 10-100 times higher than normal processing and reduce the cost for mass production. Thin steel foil is another appropriate candidate to be the flexible OLED substrate. [33-35] It has high mechanical strength, light weight, and thermal stability. Except for light weight, the plastic substrate is limited by its high gas permeability and low processing temperature. Using a thin stainless steel substrate has a great potential to integrate the thin-film transistors (TFT) and OLED because the fabrication of TFT on plastics has demonstrated difficult due to the processing temperature. [36] Also, the opaque steel substrate can prevent the water and gas penetration that will seriously damage the lifetime of OLED. Therefore, to integrate both TFT and OLED on flexible steel substrate is our ultimate research goal here.

The most important aspect of processing steel substrate is surface preparation. Since the surface of steel foil is rugged, the surface needs to be polished to achieve a low surface roughness. A rough surface will lead to disastrous defects through breaks or shorts of the deposited thin films. Several surface conditionings are required before fabrication, including cleaning, polishing, and passivation coating of the substrate. Those works are referred to previous research work of Dr. Afentakis in our laboratory. [37] Type-304 stainless steel and Kovar® stainless steel are the best results in hand. Before fabricating PLEDs on steel foils, insulating layers are deposited on top of steel foils, in order to planarize the surface. The fabrication of OLED on steel foil is the same with
those procedures on the silicon wafer. Successful working OLEDs were fabricated, 3 cm×2 cm seven-segment display, on type 304 steel foil with peak luminance values in the region of 5~6 cd/m². Figure 2.2 (c) shows a non-encapsulated PLED on the steel foil. A lot of dark spots appeared in the emitting areas. There were also some shorts outside the emitting areas. It is crucial for the flexible steel substrate to have a smooth surface and a good passivation layer because the roughness will cause further hillocks which will break down due to electrical charging.

![Figure 2.2](image)

Figure 2.2. (a) and (b) Seven segment display fabricated on thin stainless steel foil (c) non-encapsulated OLEDs on a steel foil flexed by a hand
those procedures on the silicon wafer. Successful working OLEDs were fabricated, 3 cm × 2 cm seven-segment display, on type 304 steel foil with peak luminance values in the region of 5–6 cd/m². Figure 2.2 (c) shows a non-encapsulated PLED on the steel foil. A lot of dark spots appeared in the emitting areas. There were also some shorts outside the emitting areas. It is crucial for the flexible steel substrate to have a smooth surface and a good passivation layer because the roughness will cause further hillocks which will breakdown due to electrical charging.

Figure 2.2. (a) and (b) Seven segment display fabricated on thin stainless steel foil (c) non-encapsulated OLEDs on a steel foil flexed by a hand
2.4 Results

In Top-emitting PLED, it is essential to have a more reflective anode for achieving high luminance efficiency, and a transparent or semitransparent cathode for top surface emission. For our PLED structure, the efficiency is mostly determined by the performance of electrodes. The PLED characteristics are decided by current-voltage curve, luminescence, and electroluminescence spectrum. The current-voltage (I-V) characteristics of the devices are measured by using a semiconductor parameter analyzer (Hewlett-Packard 4145B), and the brightness is determined by a luminance meter (Minolta, LS-100).

Figure 2.3 shows the significance of different ITO thickness on top of device. After encapsulation, the I-V curves were similar with each other. It meant that the cathodes, Al/1000 Å ITO and Al/2000 Å ITO, provided almost the same electron injection, and the operating voltage of PLED showed no significant dependence on thickness. However, from I-V-B curves, PLED with 1000 Å ITO could reach the brightness to 5.2 cd/m$^2$, but PLED with 2000 Å ITO only reached 4.4 cd/m$^2$. Although a thicker layer of ITO can provide higher conductivity and better protection, it will sacrifice the brightness due to the lower transmittance. Moreover, a thicker ITO film will result in stress accumulation which will make a fraction of devices fail due to crazing of the film. Therefore, optimizing the quality and thickness of ITO to make it transparent and efficient is the main issue for top-emitting PLED. Finally, a 1500 Å thick ITO is determined.
Figure 2.3. (a) Significance of cathodic ITO thickness (b) I-V-B curves of aluminum-based diode (ITO~1000 Å) (c) I-V-B curves of aluminum-based diode (ITO~2000 Å)

For the cathode of OLED, single layer of metal film can not provide efficient electron injection, which will result in high driving voltage. Therefore, double-layer cathode is introduced to minimize injection barriers. In the bottom-emitting OLED, the use of a cathode consisting of a thin LiF layer and a thick Al overlayer produced an excellent electron-injecting contact. [38,39] The results were even better than those with a conventional Mg:Ag alloy contact. Friend et al. reported a comparison of different cathode combination, including Al, LiF/Al, Ca/Al, and LiF/Ca/Al. [40] It turned out that LiF Ca/Al had the highest brightness and LiF/Al had the maximum efficiency.
According to previous research, different double-layer cathodes are considered in our top-emitting PLEDs. As for the high reactivity of low work-function metal, Al is our first trial to be the interlayer between active polymer layer and ITO film because Al is not as reactive as Mg and Ca. Using a thin Al layer and ITO, we couldn’t have a lower threshold voltage below 10 V. The driving voltage is around 10.8 V in the figure 2.4 (a) and the device still can not emit bright light because the current density is quite low. Hence, a lower work-function of Ca is chosen to be the interlayer. In the figure 2.4 (b), Ca did help a lot in electron injection and decrease the driving voltage to 8.1 V. Hence, the turn-on voltage strongly depends on the electron injecting contact. Also, the sheet resistance of double-layer cathode is another indicator to show the efficiency of electron injection. Usually, the sheet resistance of Ca/ITO cathode is as low as 300 Ω/□. If the sheet resistance is higher than 900Ω/□, a driving voltage higher than 15 V is expected. The quality of ITO film is crucial to the value of sheet resistance. ITO is sputtered under low rf power and the uniformity of film is sometimes variable. Therefore, controlling the deposition of ITO film is another important issue.

Furthermore, the light turn-on voltage is 13.3 V for the Al/ITO cathode and 6.6 V for the Ca/ITO cathode. The Ca/ITO PLED consumes less power but emits more light, and works much more efficiently than the Al/ITO PLED. For a dual-layered PEDOT/PPV device, hole is the majority carrier. Inside this particular combination of polymers, holes move much faster than electrons. Thus, the electron injection governs the performance of the device. That explains why the Ca/ITO PLED performs better than Al/ITO PLED. In most cases, the current turn-on voltage can be reduced by improving
the electron injection. Al has the theoretical work-function of 4.3 eV, and Ca has the work-function of 2.8 eV. The electrons would absolutely have problems on overcoming the energy barrier at polymer/Al interface and finally give rise to an insufficient injection.

Figure 2.4 (c) presents the electroluminescence spectra of PLED based on Al/ITO cathode and Ca/ITO cathode, and both of them have NiO$_2$ anodes. The luminescence with arbitrary unit was collected at the peak wavelength of the electroluminescent spectrum by Cary Eclipse fluorescence spectrophotometer. The peak wavelength is 550 nm for Al/ITO cathode and 600 nm for Ca/ITO cathode respectively. A red-shifted spectrum was observed for the Ca/ITO PLED. This shift might be caused by the re-locating of the recombination plane. An advanced study needs to be done for clarifying this phenomenon. The whole research refers to a recent presentation in the conference.

![Electroluminescence vs Bias Voltages and Current Density vs Bias Voltages chart](chart.png)
Figure 2.4. EL and I-V characteristics of PLED (a) with Al/ITO cathode (b) with Ca/ITO cathode and (c) electroluminescence spectra of PLED based on Al/ITO cathode and Ca ITO cathode.
For top-emitting PLEDs, the transparent ITO anode has been replaced by the other high work-function metals, such as Ni and Pt. In figure 2.5, a PLED based on Pt anode and Ca/ITO cathode has a current turn-on voltage of 5.0 V, which is 3.03 V less than the PLED with Al/Ni anode and Ca/ITO cathode. When adopting an Al/Ni anode, it essentially becomes Al/NiO₂ because of the O₂ plasma treatment before the spin-casting of polymers. [23] It has been proved that NiO₂ has the work-function of 5.0 eV which is approximately as high as that of ITO. However, Pt has a better smooth surface after the whole fabrication processing and it is resistive to chemicals. This advantage can make the anode surface get rid of being attacked. Pt has a work-function as high as 5.5 eV and is also found to have a hole injection efficiency comparable to ITO. A PLED with Pt anode and Ca/ITO cathode has higher current density than the other PLEDs. Thus, the higher brightness is expected.
Figure 2.5. I-V curves of PLEDs with various anode/cathode combinations.
CHAPTER 3

ENCAPSULATION OF POLYMER LIGHT EMITTING DIODES

3.1 Overview

The degradation of PLEDs has been attributed to various mechanisms. Research has been done to identify the causes of degradation, which is the major factor in shortening the lifetime of PLEDs. Cathode oxidation and cathode delamination were shown to be responsible for the growth of non-emissive spots on the emitting device area. When a PLED is operated under ambient atmosphere, black spots formation leads to complete device degradation within a few hours. The major suspected reasons behind the formation of black spots and rapid device degradation are three external factors: dust particles deposited during the fabrication process, pollution by water vapor, and pollution by oxygen. It is believed that an effective encapsulation technique absolutely can help in prolonging the device lifetime. [42]

3.2 Conventional Encapsulation Process

Development of a long-lifetime OLED poses the challenges, preventing moisture and oxygen diffusion into the display area from the top substrate and the sealant. There are two main encapsulation techniques: (i) seal inside a protective sheath. (ii) simply add a coating layer to the device. In most cases, OLED has either a glass or stainless steel lid which is glued on top of the display to keep the water out. Figure 3.1 shows the encapsulation of rigid OLED structure patented by Pioneer. Desiccant is incorporated to absorb moisture or vapor from the chemical reaction.
3.2.1 Evaluation of sealants

For a given distribution of dust particles and a given concentration of the polluting agent, water is a thousand times more destructive than oxygen at room temperature. The reactive low work-function metals are unstable and can delaminate when exposed to water. [43,44] Therefore, we face a difficulty in choosing an appropriate adhesive with good physical properties, preventing the moisture diffusion. Different sealants were tested in the humidity oven in order to figure out the water vapor absorption and diffusion coefficient. Sample preparation was achieved by mold casting. The PTFE release agent (Miller-Stephenson, MS-122DF) was sprayed on the microscope slides and mold in order to have a completely separate casting sample. Adhesives were dispensed in the mold and cured two minutes for each side of microscope slide. Then, a post-curing at 70 °C was carried out in the oven for 10 minutes. Those cured samples were placed in the environmental chamber which was under 85 °C and 85% relative humidity, and tested for several days. Thermogravimetric analyzer (Hi-Res TGA 2950, TA Instruments) was used to measure the weight loss and the water content. The bulk
diffusion coefficient of the adhesive is calculated from the equation shown below. [45]

When the TGA curve reached equilibrium, half-time \((t_{1/2})\) was determined.

\[
D = \frac{0.04939(t^2)}{t_{1/2}}
\]

Figure 3.2 shows the curves of G3PS2 (National Chemicals & Starch) which we are currently using. After placed in the environmental chamber for 4 days, the curves didn’t change a lot for the equilibrium part. Among those testing adhesives, it is also the one which absorbs less moisture. The physical properties of different adhesives are shown in the table 3 for comparison. After one-week test, only four adhesives had the moisture absorption below 1% and they all had higher viscosity than the others. For bulk diffusion coefficient, almost adhesives have the order of \(10^{-8}\). Except for UV-9000, it reached the equilibrium quickly, and thus it has a shorter lifetime. Actually, interfacial diffusion is a more major factor than bulk diffusion. Moisture will prefer to diffuse through the way with less barrier. The diffusion happened between the interface might be faster than the diffusion through material itself. That is related to the adhesion issue of adhesive and substrate.
Figure 3.2. TGA curves of adhesive (G3PS2) tested in 85°C /85%RH environmental chamber for different days

Figure 3.3. TGA curves of adhesives tested in 85°C 85%RH environmental chamber for a week
<table>
<thead>
<tr>
<th>Company</th>
<th>Product code</th>
<th>Density (g/cm³)</th>
<th>Viscosity (poise)</th>
<th>$D$ (cm²/s)</th>
<th>Absorption%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAGASE</td>
<td>XNR5516</td>
<td>1.41</td>
<td>1260</td>
<td>$3.8 \times 10^{-8}$</td>
<td>0.50%</td>
</tr>
<tr>
<td>National Chemicals &amp; Starch</td>
<td>G3PS#1</td>
<td>1.74</td>
<td>442</td>
<td>$2.6 \times 10^{-8}$</td>
<td>0.53%</td>
</tr>
<tr>
<td></td>
<td>G3PS#2</td>
<td>1.51</td>
<td>307.2</td>
<td>$3.6 \times 10^{-8}$</td>
<td>0.25%</td>
</tr>
<tr>
<td>Emerson Cumming</td>
<td>Eccobond UV-9000</td>
<td>1.03</td>
<td>300</td>
<td>$1.0 \times 10^{-7}$</td>
<td>0.77%</td>
</tr>
<tr>
<td>Loctite</td>
<td>LOC3525</td>
<td>1.11</td>
<td>~95</td>
<td>$2.0 \times 10^{-8}$</td>
<td>1.68%</td>
</tr>
<tr>
<td></td>
<td>LOC352</td>
<td>1.11</td>
<td>140</td>
<td>$3.1 \times 10^{-8}$</td>
<td>2.60%</td>
</tr>
<tr>
<td></td>
<td>LOC3492</td>
<td>1.03</td>
<td>5</td>
<td>$1.8 \times 10^{-8}$</td>
<td>1.50%</td>
</tr>
<tr>
<td>3M</td>
<td>LC1211</td>
<td>1.14</td>
<td>~155</td>
<td>$3.4 \times 10^{-8}$</td>
<td>1.75%</td>
</tr>
<tr>
<td>Star Technology</td>
<td>UVA4103</td>
<td>1.13</td>
<td>~10</td>
<td>$4.8 \times 10^{-8}$</td>
<td>5.12%</td>
</tr>
<tr>
<td>DYMAX</td>
<td>621</td>
<td>1.06</td>
<td>~7.5</td>
<td>$2.4 \times 10^{-8}$</td>
<td>2.19%</td>
</tr>
<tr>
<td></td>
<td>6-621</td>
<td>1.07</td>
<td>~7.5</td>
<td>$3.6 \times 10^{-8}$</td>
<td>2.67%</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>1.07</td>
<td>~5.0</td>
<td>$1.5 \times 10^{-8}$</td>
<td>1.50%</td>
</tr>
<tr>
<td>Heigl Technology</td>
<td>MP53021</td>
<td>1.00</td>
<td>7.5</td>
<td>$2.8 \times 10^{-8}$</td>
<td>2.30%</td>
</tr>
<tr>
<td></td>
<td>MP53037</td>
<td>1.10</td>
<td>25</td>
<td>$3.4 \times 10^{-8}$</td>
<td>1.92%</td>
</tr>
<tr>
<td>Chemence</td>
<td>UV02</td>
<td>1.09</td>
<td>26~38</td>
<td>$1.2 \times 10^{-8}$</td>
<td>2.96%</td>
</tr>
<tr>
<td></td>
<td>UV50</td>
<td>1.09</td>
<td>55~75</td>
<td>$1.2 \times 10^{-8}$</td>
<td>3.40%</td>
</tr>
<tr>
<td></td>
<td>UV70</td>
<td>1.08</td>
<td>9~18</td>
<td>$2.0 \times 10^{-8}$</td>
<td>1.08%</td>
</tr>
</tbody>
</table>
3.2.2 Experimental setup

In order to encapsulate our device in the environment of free moisture and oxygen, packaging in the glove box is applied to improve the efficiency of PLED. UV-cured resins (acrylic or epoxy) are used to seal the leak between glass cap and substrate. An automatic dispenser, Asymtek (Automove® 402 Dispensing System), is installed to help the encapsulation process. Asymtek is equipped with a control software, vacuum system, a touch sensor, and automatic dispenser. Through the computer control panel, we can easily fix the position at which the adhesive can be dispensed precisely. Also, we can control the amount of the sealant and the width of the bead. This experiment should be performed inside a glove box which has nitrogen flowing to keep the whole chamber under positive pressure of nitrogen all the time, and the pump system will keep the moisture and oxygen concentration at the low level. By using conventional encapsulation, adhesive should be dispensed on a piece of 0.7 mm thick glass before encapsulation. Then, the device and glass cover lid will be placed in the load lock to be pumped down and transferred into the main chamber. After placing the lid on top of the device, whole device will be sealed in a nitrogen box, and then removed from the glove box. A complete encapsulation is performed under the UV lamp (Zeta® 7411 UV Flood Curing System, Loctite®) in the ambient atmosphere. The majority of the whole encapsulation process is to prevent the moisture existing in the device and to make the dry nitrogen full of the space between cathode and glass lid. Figure 3.4 (a) illustrates the main idea of encapsulation.
Figure 3.4. (a) The structure of encapsulated device (b) a complete scheme of glass encapsulated PLED (c) encapsulated PLED in the ambient atmosphere with LCD monitor as a background
Figure 3.4. (a) The structure of encapsulated device (b) a complete scheme of glass encapsulated PLED (c) encapsulated PLED in the ambient atmosphere with LCD monitor as a background
3.3 Thin Film Encapsulation Techniques and Applications

For flexible OLEDs, it is difficult to employ the conventional encapsulation techniques because of the rigidity of the glass lid. Therefore, a variety of laminated barrier coated polymers and monolithic thin films are applied to the encapsulation of flexible OLEDs in figure 3.5. [46] Especially, thin film encapsulation has great potential which allows flexible OLED display applications to become feasible. Universal display corporation and Vitex systems proposed the thin film encapsulated flexible OLED displays which are hermetically sealed with an optically transmissive multilayer barrier coating (Barix™ Encapsulation). [47] This multilayer barrier coating is a structure of alternative inorganic and organic layers. The inorganic layer works as the water diffusion barrier, while the organic layer functions as a planarization layer which is a new smooth surface to deposit the next organic layer on. The Barix™ Encapsulation process includes deposition of Al₂O₃ layers (reactively sputtered by an energetic plasma), and polyacrylate layers (flash evaporation of the monomer followed by UV curing). [48] Similarly, Yoshida et al. used a multi-layer barrier approach by spin coating a UV curable resin onto a plastic substrate to planarize the surface, and then deposited a SiON moisture barrier film and repeated the resin/SiON layers. [49] Another promising technique to deposit layers with good step coverage is plasma enhanced chemical vapor deposition (PECVD). However, single layers of PECVD silicon nitride have been demonstrated that the water permeability is generally too high because of pinholes. [50] Therefore, a novel multilayer stack of silicon nitride – silicon oxide – silicon nitride – silicon oxide – silicon nitride (NONON) was proposed by Philips research laboratories as thin film encapsulation. [51] To minimize the possible plasma-induced damage, plasma-enhanced atomic layer
deposition (PEALD) is an attractive technique for depositing oxide films ($\text{Al}_2\text{O}_3$:N) at low temperature by using a pulsed plasma with a short pulse time. [52] Yamashita et al. reported another encapsulation method by using thermal chemical vapor deposition polymer films (TCVDPF). They used poly-p-xylylene (PPX) and/or poly-2-chloro-p-xylylene (PCPX) films to encapsulate OLEDs with a dry process at room temperature. [53] Thermal evaporation was also demonstrated as a way to form the passivation layers. High-density polyethylene was used as the insulating layer in combination with an Al-Li layer. [54] All those approaches try to meet the OLED permeation requirements of water vapor transmission rate (WVTR) for $1\times10^{-6}$ g/m²/day and oxygen transmission rate (OTR) for $10^{-5}$-$10^{-3}$ cm³/m²/day.

The most common way to measure WVTR and OTR of the barrier film is employed the MOCON™ measurement. A variety of ASTM standards are used in measuring the transmission rate, including D1434 and D3985 for gases, and E96 and F1294 for water vapor. However, there is a minimum measurement for this commercial system which is limited to rates in the range of $5\times10^{-3}$ g/m²/day for water vapor. Also, if samples would like to be tested under high temperature and high humidity, they have to be sent back to MOCON laboratory because the service is not installed in commercial instrument. Therefore, the other approach is known as calcium test. [55,56] The permeation rate is calculated from the degradation of a calcium layer. [57] There are the important chemical reactions of calcium with air existing shown below. An obvious optical change will be observed easily from metallic color to transparent.
\[ 2\text{Ca} + \text{O}_2 \rightarrow 2\text{CaO} \]

\[ \text{Ca} + \text{H}_2\text{O} \rightarrow \text{CaO} + \text{H}_2 \]

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]

Using the calcium test, a transmission rate of \(3 \times 10^{-7} \text{ g/m}^2/\text{day}\) for \(\text{H}_2\text{O}\) through barrier films can be measured.

Figure 3.5. Schemes of OLED encapsulation structures: (a) a flexible polymer lid with barrier film (b) barrier thin films deposited on the device
3.4 Results

Conventional encapsulation is a promising way to seal the whole OLED device and isolate it from exposure to moisture or oxygen. The electrical characteristics did not show a big difference after one-month testing in the figure 3.6 (b). Current density dropped from 29.6 mA/cm² to 25.4 mA/cm². However, the brightness decays and the black spots increase with time. For our process, it’s difficult to incorporate desiccant onto the glass cover lid. What we can do is keep the whole device to be encapsulated in the glove box with positive pressure of N\textsubscript{2} or Ar. This type of conventional encapsulation is made for measurement of PLEDs on top of silicon wafer, however, that is not a flexible encapsulation process. For a flexible steel substrate, the encapsulated glass lid is better to be replaced by a flexible polymer lid which is coated with another barrier film. However, we still face another problem in choosing the adhesives and barrier films, and both of them have to be compatible. That is the other issue related to the mechanical property of bending and the adhesion of interface.

As mentioned above, thin film encapsulation is another potential method for the flexible PLEDs in the future. Through multilayer deposition of organic or inorganic materials, the encapsulation can be done in a thin-film form that will match the criterion of light weight. However, the processing temperature compatibility and stress accumulation need to be overcome after several depositions.
Figure 3.6. (a) Encapsulated PLED device with Al/Ni anode and Ca/ITO cathode emitted light at 10 V under the room light on (b) time dependence of encapsulated PLED with Al/Ni anode and Ca/ITO cathode.
Figure 3.6. (a) Encapsulated PLED device with Al/Ni anode and Ca/ITO cathode emitted light at 10 V under the room light on (b) time dependence of encapsulated PLED with Al/Ni anode and Ca/ITO cathode.
CHAPTER 4
CONCLUSIONS

Top-emitting PLEDs with Pt anode and Ca/ITO cathode show promising characteristics and is going to be integrated onto poly-silicon TFTs backplanes. In order to integrate the TFTs and PLEDs, the driving voltage of PLEDs is better to be as low as 5 V. Now, we can reach light turn-on voltage of 6.6 V and current turn-on voltage of 8.03 V. Even we could have the light emitting with room light on, but we still observed the formation of dark spots under microscope, shown in figure 4.1 (b). It is believed that the sputtering damage to the polymer does dominate in fabricating top-emitting diodes. Tuning the conditions of ITO is the first priority, including the lower rf power, ITO target position, deposition rate, small amount of O₂, and sheet resistance.

Another important aspect is to build up a better injection contact. The overall efficiency of PLEDs is determined by the injection of electrons and holes at the respective metal-polymer interfaces. We do prove that Pt and Ca are excellent materials for anode and cathode. The efficiency of PLEDs strongly depends on the balanced injection of electrons and holes. PEDOT/PSS is lightly p-type doped by the PSS that makes the hole injection easier. Many publications have shown that the PPV/Ca interface is nearly barrier-less. The work-function of Ca is 2.8 eV which is close to the electron affinity of PPV (2.7 eV) and the barrier for electron injection is small. Ca diffuses into the near surface region and donates electrons to the π-system. The interfacial region between the Ca contact and the polymer has an approximate scale in the range of 20 to 50 Å. Ca forms an ionic charge-transfer complex with the surface layers of the PPV, which n-
dopes the polymer. [30,58] Once the ohmic contact has been established, the electron injection will reach the saturated point. Then, there will be little effect to change the cathode metal to lower work-function than Ca.

Except for tuning conditions and selecting materials, fabrication processing is another issue to improve our device quality. In the future, all the processing will be carried out in the glove box and the vacuum deposition system. This will help to solve some affects from the environment and make the fabrication more progressive.

Figure 4.1 (a) An encapsulated-PLED with Pt anode and Ca/ITO cathode emitted light under room light on (b) dark spots formed in the emitting areas
dopes the polymer. [30.58] Once the ohmic contact has been established, the electron injection will reach the saturated point. Then, there will be little effect to change the cathode metal to lower work-function than Ca.

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Figure 4.1 (a) An encapsulated-PLED with Pt anode and Ca/ITO cathode emitted light under room light on (b) dark spots formed in the emitting areas
REFERENCES


Curriculum Vita

Profile

Yu-Lin Chang was born in Kaohsiung, Taiwan (1976). She had undergraduate studies in Chemical Engineering at National Taiwan University, Taipei, Taiwan (2000). In the summer of 2003, she entered the Department of Chemical Engineering at Lehigh University in Bethlehem and joined the Display Research Lab in the Department of Electrical Engineering. Graduate studies focus on polymer science, including fabrication and encapsulation of polymer light emitting diodes.

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END OF TITLE