Fabrication and Characterization of Organic Light Emitting Devices

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Abstract

By using Indium tin oxide (ITO) as anode material and NPB and Alq3 as hole transport layer (HTL) and electron transport layer (ETL) respectively, a Organic Light Emitting Device (OLED) with emitted wavelength of (525 ± 20) nm is produced. Aluminium (Al) is used as a cathode. The calculated emission energy is 2.37 ± 0.12 eV compared to theoretically 2.8 eV from the band gap in Alq3. This shifting to lower bandgap is due to the presence of impurities in the thin film produced. This caused the panels to be highly unstable, and with a voltage above 6 V the OLED’s burnt up after a few seconds. The panels is also due to its organic compounds highly sensitive to oxidation which causes failure after only a few minutes is open air. The current-voltage and intensity-wavelength relationships is then measured and analyzed. The actual fabrication took place on Mars 27th 2015 together with my lab partners Tan Chiat Lin and Lee Zheng Kuan, Jonathan.

1. Introduction

Electroluminescence (EL) in organic materials is not a new discovery and was first demonstrated by André Bernanose at the Nancy-Université in France early as in 1953.[1]. However, due to the higher intensity and durability of LED’s, the first two-layer OLED diods was not developed before 1987 by Eastman-Kodak[2]. Since then, many different organic materials has been used for producing light emission with molecule and polymer OLED’s as the most common. In our fabrication we are making a small molecule OLED with the organometallic chelate Alq3. This is the same material as was used by Easman-Kodak in 1887[2]. OLED is being continuously enhanced, and market volume is increasing so fast that analysts forecasts that it will start competing again normal LED as early as in 2016 on the market of luminescence[5]. OLED has a many advantages over LED and traditional light bulbs like for example simpler production and thus likely cheaper production cost when production volume increases. Due to it’s thin size of less than 0.2 µm, the panels can be printed on virtually all kinds of substrates, and can even be flexible due to it’s small thickness. Some of the most promising applications of OLED is in display’s for smartphones and television. One of the main advantages is because it is more power efficient than LCD displays since there is no need for backlightening. This is because the OLED produce their own light in contrast to the crystals in LCD which need a backlighting source. This gives OLED better contrast and show’s true black when the diods is inactive. While normal LCD has a response time of about 1 ms, OLED is capable of achieving less than 0.001 ms according to manufacturer LG[8].

However, there is still a few challenges that needs to be resolved before OLED becomes mainstream industry. One of the biggest concerns is that OLED currently has a lifespan dramatically shorter than normal LED. After 1000 hours of use the luminance will be degraded with about 10 %, compared to LCD’s which has a lifetime of around 40.000 hours with minimal or none loss of luminescence. As mentioned, the organic compounds are highly sensitive to oxidation, and the panels will therefore easily get damaged in contact with water. Efficiency of blue light is also much weaker than green and red light, which is a an issue which need to be resolved for OLED to outperform regular LCD displays.

2. Theory

The theory for organic electroluminescent is quite similar to what is happening for regular LED. Instead of using a p-n doped semiconductor for creating a band gap, we use

![Figure 1: Chematic structure of light generation in a OLED.](image)
the organic materials NPB$^1$ and $Alq_3^2$ as hole transport layer (HTL) and electron transport layer (ETL) respectively.

When a potential difference is put on between the anode and cathode, where will be an electric field which draws the holes from the anode towards the cathode and the electrons vice versa, see figure 1 for drawing og the transportation of charges. When the applied voltage reaches above a certain barrier level, some of the holes will manage to get over to the ETL side where they recombine forming an exciton$^3$. This state rapidly decays into the ground state and the energy difference is mostly emitted as electromagnetic energy as described by the Planck–Einstein relation $E = \frac{hc}{\lambda}$. These states are often denoted as the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) for the organic semiconductor, and is analogous to the valence and conduction bands of inorganic semiconductors. It is important that the LUMO for the HTL is higher than the LUMO for the ETL so that the electron stay’s confined within the ETL when no voltage is applied.

Indium Tin Oxide (ITO) is used as anode material due to it’s high work function between 4.5 to 5.0 eV, which promotes injection of holes into the HOMO level of the organic layer in the HTL. ITO is also transparent for visible light, which is needed since this is where the light is emitted. The cathode on the other hand should have a low work function which promote injection of electrons into the LUMO of the organic layer. For this aluminium is used as a cathode.

3. Method

3.1. Cleaning

Due to OLED’s organic elements it is critical to remove all organic materials from the substrates so they are perfectly clean. For this the substrates is first brushed in soap before it is cleaned in an ultrasonic vibration cleaner immersed in distilled water, acetone, isopropanol (IPA) and methanol. Each of them were cleaning for 15 minutes in the ultrasonic vibration cleaner. After being dried in a oven at 80 degrees Celsius the prepares was further cleaned in a plasma cleaner. The pressure was lowered until $10^{-1}$ Pa and Argon with a flow rate of 25-27 sccm was inserted to remove excessive moisture from the ITO and improve the work function. After this the prepares was ready for OLED fabrication.

3.2. Fabrication

Using Vacuum Thermal Evaporation (VTE) the different layers of the OLED is placed on to the substrate with the already placed ITO as anode. The raw material for the different layers, aluminium, NPB and $Alq_3$ is placed in tungsten boats inside the evaporation chamber. The different substrates we prepared is placed into the sample holder in square position. The samples was already placed inside the chamber the evening before, so that the vacuum pump lower the pressure over the night. The pressure should ideally be around $10^{-4}$ Pa when the deposition is happening, to prevent collision of air molecules with flow of material for deposition. It also prevents the materials from oxidation.

To make sure the flow of coating is smooth and steady before starting depositing on to the substrate, the sample split were only opened after the flow was as desired. First the hole transport layer of NPB was deposited on top of the already existing layer of 150 nm ITO. To make sure the coating is as evenly distributed as possible, the coating speed is very low, only around 0.01 nm/s. We deposited around 9 nm of NPB, which took about 20 minutes. Afterwards we opened the boat for $Alq_3$ and repeated the process until we had 17 nm of hole transport layer. Finally on top, we deposited 100 nm of aluminium as cathode. This took quite a while, almost 2 hours.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Thickness(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Aluminium</td>
<td>100</td>
</tr>
<tr>
<td>ETL</td>
<td>$Alq_3$</td>
<td>17</td>
</tr>
<tr>
<td>HTL</td>
<td>NPB</td>
<td>9</td>
</tr>
<tr>
<td>Anode</td>
<td>ITO</td>
<td>150</td>
</tr>
<tr>
<td>Substrate</td>
<td>Glass</td>
<td></td>
</tr>
</tbody>
</table>

4. Results

Figure 3 shows the OLED panel while emitting light. Unfortunately, they didn’t last longer than 5-10 seconds before they failed.

4.1. Current-voltage relationship

Figure 4 shows the current-voltage relationship for our OLED device. As expected is the currents almost identical

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$^1$N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine
$^2$tris(8-hydroxyquinolinate)-aluminum
$^3$bound state of the electron and hole
Figure 3: Each of the substrates has four OLED elements, and in this picture one of them is lighted up. The color is yellow-green.

![Figure 3: Each of the substrates has four OLED elements, and in this picture one of them is lighted up. The color is yellow-green.](image1)

Figure 4: Current as a function of voltage for OLED thin film to 0 for low voltage, and then rises quickly when the voltage exceeds the potential barrier between the HTL and ETL layers. Above 5.5 V the panel is already saturated, so it does not make any further increase in light output by increasing the voltage, it only produces more heat and lowers the lifetime if the panel.

4.2. Intensity-wavelength relationship

![Figure 5: Intensity as a function of wavelength for OLED thinfilm](image2)

Figure 5: Intensity as a function of wavelength for OLED thinfilm

Figure 5 shows a plot of the distribution of the different frequencies in the emitted light from the OLED panel. As we can see, it is almost normal distributed around a peak at 525 nm.

5. Discussion

Since the wavelength of the emitted energy is quantified according to the the Planck–Einstein relation $E = \frac{kT}{\lambda}$ we can also use this backwards and find the supposed bandgap from the emitted light at 525 nm. By performing a Gaussian fit around the data in graph 5 we get a standard deviation of 20 nm. The emitted energy during the recombination process will therefore be $2.37 \pm 0.12 \text{ eV}$. This gives $E = 2.37 \text{ eV}$ which is surprisingly low compared to the real bandgap$^4$ of 2.8 eV for $Alq_3$ (Szu-Hung L. 2009, [7]).

One explanation for this deviation from expected energy is that most of the recombination happens in the interface between the ETL and HTL layer. This results in that some of the recombination happens in the bandgap between the HOMO level of $Alq_3$ and the LUMO level of the NPB layer and gives a different wavelength of the emitted light. With a bandgap here of 2.0 eV, this gives a wavelength of 622 nm. One other phenomena happening is that it is not only the holes that are transferred to the ETL layer, electrons also go over and get recombined with the holes in the HTL. With a bandgap of 3 eV in the NPB of the hole transport layer, the emission here corresponds to radiation with a wavelength of 414 nm. However, the amount of electrons getting all the way over is so small that this is not noticeable as we can see the wavelength-intensity graph [figure 5].

The most likely reason for for the lower energy is the fact that there is some loss of energy when the electrons returns to ground state, not all of it will be released as light of one wavelength, it might generate heat as well. This can be explained by the presence of impurities, which will lower the bandgap, and shift the emitted light to longer wavelength. This impurities is also the reason for the very short lifetime of the panels, which will be discussed next.

About half of our OLED panels were defect or stopped working only seconds after we turned on the current. This even happened when we had the panels inside the glove box$^5$. The reason for this is most likely due to contamination. Even though we cleaned the substrates very carefully in so many different ways, the environment we kept them in was never really clean. For instance the tools and multimeter we were handling the substrates with were never washed, and during the different sessions the substrates were stored without any proper sealing. We also never managed to get the pressure inside the thermal evaporation chamber as small as desired, the chamber was constantly leaking. This also caused reactions between the organic compounds and the air, and also contamination on the...

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$^4$However, this is also not exact, but in reality a gaussian distribution around a mean value

$^5$a chamber with pure nitrogen and no oxygen for preventing oxidation
substrate. Summed up, this eventually lead to short-circuit which causes the panels to burn up. Since this is all very thin and highly reactive material it is of great importance to keep the environment under control and make sure no other particles get deposited than wanted.

6. Conclusion

In this experiment we have fabricated a thin film of OLED panel using a thermal evaporation method. Using Alq₃ as electron transport layer, we get a released energy of 2.37 ± 0.12 eV during the recombination process. This is slightly lower than the bandgap of 2.37 eV for Alq₃ and is most likely caused due to loss of efficiency during the recombination process. The fabrication of OLED panels requires very clean environments and high enough vacuum under the deposition. Both of these were not very good under our experiment, and also caused most panels to fail just after we put on the current. This is something that can be improved in further experiment to make more durable and lasting OLED's.

References