Lifetime study for solution processed organic light emitting diodes

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Abstract. In this paper, blue fluorescent organic light-emitting diodes (OLED) are fabricated by solution processes. UV Ozone exposure time on the ITO surface and the thickness of the hole injection layer (HIL), electron transport layer (ETL) and electron injection layer (EIL) are modulated to study the effects on device characteristics and lifetime. ITO/MADN:13% UBD-07/Al is used as the basic structure. First, HIL (PEDOT: PSS) is added. It is found that although the hole current is increased, the device does not emit light. Secondly, ETL (TPBi) is added to facilitate the injection of electrons from cathode to EML, and in such a way, hole-electron can be recombined in EML and emit light. With an increase in the time to expose the ITO into UV Ozone from 100s and 200s to 400s, the total current of the OLED is increased, and luminance is improved, but the current efficiency is not obviously improved. Its role facilitating the electron injection is observed by adjusting the LiF thickness of EIL. In addition to increasing the hole current, the addition of PEDOT as HIL may reduce the chance of a device shorten resulting from the spikes on ITO surface, and the lifetime of the OLED with this structure is 121 min. In order to prolong device lifetime and better balance the injection quantity of electrons and holes, the structure of ETL is adjusted to be TPBi+Alq3. When TPBi+Alq3 is 10nm/15nm thick, current efficiency is 1.29 cd/A at 8V, and the lifetime is extended to 252 min.

Keywords: organic light emitting diode; solution process; blue fluorescent; hole injection layer; electron transport layer; lifetime

1. Introduction
The blue organic light-emitting diode (blue OLED) is used for full color flat-panel display and lighting. The blue emitter is used as one of three main color sources, and compared with green and red OLED, traditional blue OLED has disadvantages such as low efficiency and a short lifetime [1]. Once blue light attenuates, it is possible to cause a color shift on the whole screen, and all manufacturers are forced to study a solution to this disadvantage. In addition to a short lifetime, OLED has other...
disadvantages such as the deterioration of its organic materials resulting from water oxidation and oxygen. How to prolong the device’s lifetime is a very important research subject.

K.F. Jeltsch et al [2] fabricated OLEDs by solution process and studied the aggregation of Flrpic on PEDOT: PSS to prolong the lifetime of the OLEDs. Device structure is ITO/PEDOT: PSS/PVK: Flrpic: OXD-7/Ca/Al. During the research of blue phosphorescence OLED, Sang Kyu Jeon et al [3] inserted a host material between HTL and EML as an exciton blocking layer to prolong the lifetime by confining the recombination zone in EML. Device structure is ITO/DNTPD/BPBPA/ mCBP/mCBP: Ir(dbi)3/LG201/LiF/Al. Jang Hyuk Kwon et al [4] used Liq as EIL material for OLED and found that double electron injection layers improved current efficiency by 20% and prolonged the lifetime by 40%. Device structure is ITO/NPD/EML/Alq3:Liq/Liq/Al.

2. Experiments

| No | Anode | HIL | EML | HBL | ETL | EIL | Cathode |
|----|-------|-----|-----|-----|-----|-----|---------|
|    | ITO UV O3 | PEDOT (spin) | MADN: 13% UBD-07 (spin) | TPBi (evap.) | Alq3 (evap.) | LiF (evap.) | Al (evap.) |
| A-1 | 400s | 55 | 45 | 0 | 0 | 0 | 150 |
| A-2 | 400s | 0 | 45 | 0 | 0 | 0.8 | 150 |
| B-1 | 400s | 0 | 45 | 20 | 0 | 0.8 | 150 |
| C-1 | 100s | 0 | 45 | 20 | 0 | 0.8 | 150 |
| C-2 | 200s | 0 | 45 | 20 | 0 | 0.8 | 150 |
| C-3 | 400s | 0 | 45 | 20 | 0 | 0.8 | 150 |
| D-1 | 100s | 0 | 45 | 20 | 0 | 0.5 | 150 |
| D-2 | 100s | 0 | 45 | 20 | 0 | 0.8 | 150 |
| E-1 | 100s | 55 | 45 | 20 | 0 | 0.5 | 150 |
| E-2 | 100s | 55 | 45 | 10 | 15 | 0.5 | 150 |

The emitting layer solution was prepared in advance by mixing host material MAND: dopant UBD-07 = 8.7mg: 1.3mg, and dissolved in 1 cc chlorobenzene. In N2 glove box, 1 cc PEDOT: PSS was filtered by 0.45 μm filter, spin coated onto the ITO glass substrate at 2500 rpm for 30s, and then dried on the hot plate at 110 °C for 20min. The pre-prepared emitting layer solution was filtered by 0.2 μm filter, spin coated on PEDOT: PSS surface at 2500 rpm for 30min, and then dried on the hot plate at 110 °C for 20min [5]. After the spin-coating of EML, TPBi film was deposited by thermal evaporation, then LiF and Al also by thermal evaporation. Finally the device was sent to the glove box for packaging. The encapsulation glass was attached onto the glass substrate by UV cure adhesive, and exposed to UV-light for 170s to cure the UV adhesive. The current-voltage-luminance (I-V-L) measurement is performed by Keithley 2400 (power supply) and Photo Research PR 650 Spectra colorimeter. The L-V of OLED over time driven by a constant current source were measured by a self-designed measurement system (with photodetector, Arduino and Raspberry Pi) for lifetime measurement.

3. Results and discussion

3.1. The effects of hole injection layer (HIL)

In this section, ITO/EML (45 nm)/Al (150 nm) is used as the basic structure to explore the amount of hole injection current. The HIL is added in the device A-1, but not in the device A-2. The band diagrams are shown in Fig.1 and the structural parameters of the device are shown in Table 1. According to the luminance vs. current density shown in Fig.2, it is found that both devices A-1 and A-2 do not emit the light. Because there is about 1.7eV energy barrier between Al cathode and MAND, it may be concluded that the electrons are not injected into EML from the cathodes of A-1 and A-2. According to the I-V characteristics of device A-1 as shown in Fig.2, it can be seen that A-1 is similar to ohmic characteristics. After the insertion of the PEDOT: PSS (HIL), the hole current is increased. Due to no HIL in device A-2, during hole injection, it is required to overcome a higher energy barrier, so the cut-in voltage is higher, about 1V.
3.2. The insertion of hole blocking layer (HBL)

According to the results shown in Fig.2 that the device A-2 fails to emit the light, it may be deduced that the addition of LiF does not facilitate cathode electron injection, so ETL TPBi is inserted in the device B-2 to facilitate the electron injection. The device parameters are shown in Table 1, and the device band diagram is shown in Fig.3. The electrons injected amount is increased by the electron transporting characteristic of TPBi. The holes are confined in the emitting layer by the barrier formed from the HOMO energy level difference between EML and HBL (0.7eV) to improve the ability of electron-hole recombination opportunity to emit more light. When TPBi 20nm is inserted, the total current is decreased due to the increase in total resistance, as shown in Fig.4 (a). HBL blocks the holes, causing the hole current to decrease, but ETL TPBi 20 nm facilitates electron injection. In such a way, the recombined hole-electrons are increased to improve the luminance and efficiency of the device, as shown in Fig. 4(b). At 8V, the luminance is 221.2 cd/m², and the efficiency is 0.52 cd/A.

3.3. UV Ozone exposure time for ITO

Figure 3 shows the energy band diagram of C-1, C-2 and C-3. In this section, the time of ITO exposed to the UV Ozone is adjusted to compare the hole injection amount. With an increase in the time of exposure to the UV Ozone from 100s, 200s to 400s, the total current of the OLED is increased with the increase of ITO work function by increasing the exposure time to UV Ozone., and luminance is improved, too, as shown in Fig.5(a). But the current efficiency is not obviously improved, as shown in Fig.5(b). Furthermore, with the increase of ITO work function, the ITO-HIL-EML shared bias from applied voltage is reduced, while a partial voltage is transferred to EML-ETL-LiF-Al side which resulting in injection electrons from cathode increased. Therefore, with the increase in the ITO exposure time to UV Ozone, both the electron and hole number is increased simultaneously (and the luminance is also improved simultaneously), but the current efficiency is not obviously improved.
3.4. Adjusting the thickness of the electron injection layer (EIL, LiF)

LiF is a non-conductive material [6]. If it is too thick, the resistance of the OLED will increase, and total current will decrease. When the thickness of LiF decreases from 0.8nm to 0.5nm, the electron injection current increases, the cut-in voltage also decreases, and the luminescence and efficiency of LiF 0.5nm are better than that of LiF 0.8nm, as shown in Fig. 6.

3.5. The effects of ETL

As an energy barrier 1.5eV between the work function of Al and the LUMO of TPBi is unfavorable to the electron injection, Alq3 is inserted between TPBi and Al in the device E-2 to slightly reduce the energy barrier for electrons injected from cathode to EML (1.5eV reduced to 1.0eV). If the ETL total thickness of TPBi+Alq3 increases too much, the total resistance of the device may increase additionally which will decrease the device current. So the structure of the device E-1 is used for the device E-2, but the TPBi 20 nm is changed to TPBi/Alq3 10nm/15nm. Because in device E-2 the energy barrier for electron injection from cathode to EML increases in multi-steps (along the LUMO energy level of Alq3 and TPBi) gradually, as shown in Fig.7, more electrons could inject from cathode to EML. So the device E-2 with ETL as TPBi/Alq3 has a higher current density than device E-1, as shown in Fig.8 (a). The electron-hole recombination ratio in device E-2 is improved to enhance the luminance and efficiency. The efficiency is improved from 0.64 cd/A to 1.29 cd/A, as shown in Fig. 8 (b). As the electron injection current is relatively balanced with the hole injection current, the half-decay lifetime is prolonged from 121min to 252.2min, as shown in Fig.9. Regarding the comparison of electron mobility, the electron mobility of TPBi is about 3.3-8.0 x10^{-5} cm^2/V which is higher than Alq3 0.4-1.1x10^{-5} cm^2/Vs. However, Fig. 8(a) shows that the device E-1 has lower current density than E-2, so it is deducted that after the insert of Alq3 as part of ETL, the device lifetime is prolonged mainly because LUMO energy level of Alq3 can facilitate electron injection from cathode and reduce electron accumulation on cathode.
4. Summary
The HIL (PEDOT: PSS) is added first, and it is found that although the hole current is increased, the device does not emit light. The ETL (TPBi) is added to facilitate the electron injection from cathode to EML, and in such way, the hole-electron can recombine in EML and emit light. At 8V, the luminance is 221.2 cd/m², and the efficiency is 0.52 cd/A. By adjusting UV Ozone exposure time, the hole injection current could be controlled. When LiF thickness is reduced from 0.8 to 0.5nm, the electron injection current increases, the cut-in voltage decreases, the luminance and the efficiency (0.78 cd/A@8V) are improved. In addition to increasing the hole current, the insertion of PEDOT: PSS as HIL can reduce the chance of short circuit of the device resulting from a spike effect on the ITO surface. The lifetime of the device ITO/PEDOT: PSS/EML/TPBi/LiF/Al is 121 min. In order to better balance the electron and hole injection amount so as to prolong the device’s lifetime, the ETL structure is adjusted to be TPBi+Alq3. When TPBi/Alq3 is 10nm/15nm thick, current efficiency increases to 1.29 cd/A at 8V, and the lifetime is prolonged to 252 min. In the future, the thickness of HIL and EML will be adjusted and tried to extend the lifetime of OLEDs further more.

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