Low Power-Consumption and Long Lifetime OLED with a High Tg n-type Organic Transport Material

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ABSTRACT

In this paper, we demonstrated an organic light emitting device (OLED) of low driving voltage, high current efficiency and long lifetime by using an n-type organic material as the electron transport layer (ETL). Such a layer is composed of a large alkali metal, i.e. Cesium (Cs), doped into the organic material. Cs atom is heavy and hard to diffuse into the emitting layer (EML) material that decreases the metal quenching and increase the operation lifetime. 2,9-dimethyl-4,7-diphenyl 1,10- phenanthrolin (BCP) and 2,5-diaryl-1,3,4-oxadiazoles (OXD) were used as the host organic material. OXD is thermally stable and exhibits a high glass transition temperature (Tg) of 147 ^{o}C that can further increase the operation lifetime. The resistivity of those doped materials is about $3x10^{5}$ Ω-cm that is two orders of magnitude lower than the resistivity of the pure organic materials. Compared with the conventional LiF/Al device, about two-volt reduction in driving voltage was observed. Current efficiency is also increased due to better carrier balance. Operation lifetimes of metal dopant devices are longer than that of the conventional device especially by using OXD as the host of the ETL.

Keywords: OLED, conductivity, ETL.

1. INTRODUCTION

OLED is one of the most promising candidates for the next generation display technologies since it exhibits advantages such as self emissive, wide-view-angle, flexible-substrate-capability and potentially low cost [1], [2]. For recent years, OLED technologies also show a remarkable progress in material and device for improving the efficiency and the stability [3], [4].

However, because of the wide bandgap of the organic material, the carrier concentration of such a material is quite low [5]. Carrier mobility is limited by the amorphous structure that is about six to eight orders of magnitude lower than that in semiconductor. Hence, the resistivity of organic material is quite high. As compared with typical semiconductor LED, the driving voltage of OLED device is three to four times larger although the semiconductor LED is much thicker than OLED device. Hence, to lower down the driving voltage of such a device and increase the power efficiency is one of the most important issues in OLED device development.

In order to improve the electrical injection ability, a thin low work function metal (like Li, Na, K, Cs, Ca, Mg) or metal compound (like LiF and Li_2O) was used to insert between the cathode and electron transport material [6], [7]. Metal alloy composed of the low work function and typical cathode materials (like Mg:Ag and Li:Al) are also developed. With those technologies, the driving voltage of typical OLED devices can be much decreased [8], [9]. An

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alternative approach was proposed to solve the electron injection and transport problem at the same time. To dope the low work function metal materials into organic materials may yield an improvement in voltage reduction and form an ohmic contact between the cathode and organic material while it is usually a shottky barrier in this interface [10],[11]. Besides, the free electrons of the metal ions in ETL may help to transport the electrons and hence increases the carrier concentration. However, not all of the organic materials can be used for the host for such kind of technology. An organic material would have a proper molecule structure that is suitable for the diffusion of the metal ion. The energy level of such an organic material also has strong influence on the activation of the metal ion. By the way, it must exhibit basic electron transport property. Unfortunately, only some materials with low Tg can be used to fulfill those requirements [12],[13]. The low Tg materials are easily to crystallize under high temperature or high current injection. Hence it may arise some lifetime issue.

Here, we propose to use 2,5-diaryl-1,3,4-oxadiazoles (OXD), as the host of the metal dopant. Compared with the typically used material, 2,9-dimethyl-4,7-diphenyl 1,10- phenanthrolin (BCP), such a OXD derivative layer exhibits a high Tg of 147 ^{o}C that is much higher than Tg of BCP, 83 ^{o}C. Molecular structures of OXD and BCP are shown in Fig. 1.The metal dopant material we used is Cesium (Cs). Such an atom exhibits a low work function and easily releases an electron. It also has a large atomic number. That means such an atom is large and more difficult to diffuse as compared with the smaller atoms like lithium or Calcium [14], [15]. It can greatly improve the operation lifetime. To further investigate the electrical property of the n-doping layer, we fabricated a series of electron-only device with different metal contact and found that the material can form ohmic contact in all our trials. In a conventional OLED device, ETL is followed by a thin LiF as an electron injection layer and an Al cathode since it exhibits a suitable wourk-function. It serves as the function for reflecting light and coupled out from the ITO anode side. Among the metal materials, silver (Ag) exhibits the highest conductivity and lowest absorption in visible range. It was chosen as the cathode material in our metal dopant devices. By increasing the metal dopant concentration, the conductivity increases rapidly, saturates and then decreases. The first increase is caused by the carrier concentration increase. However, carrier transport in such a material is dominated by hopping process assisted by electrical field. Further increase in Cs atom does not increase the hopping ability. On the other hand, further increase in concentration means too many “free” electrons in this material that impedes the hopping process. The lowest resistivity we achieved was 3.14*10^{5} and 3.24*10^{5} Ω-cm for the Cs:BCP and Cs:OXD systems, respectively.

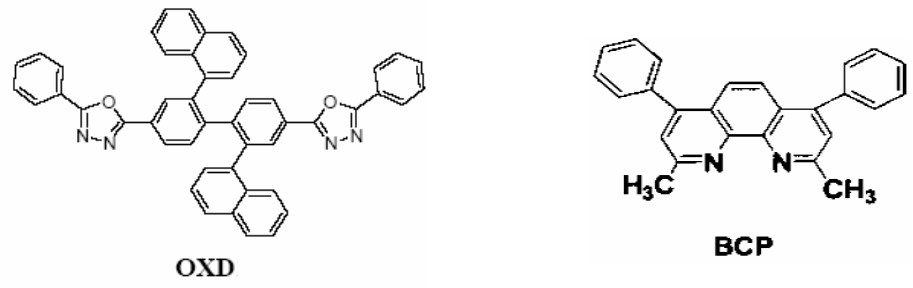


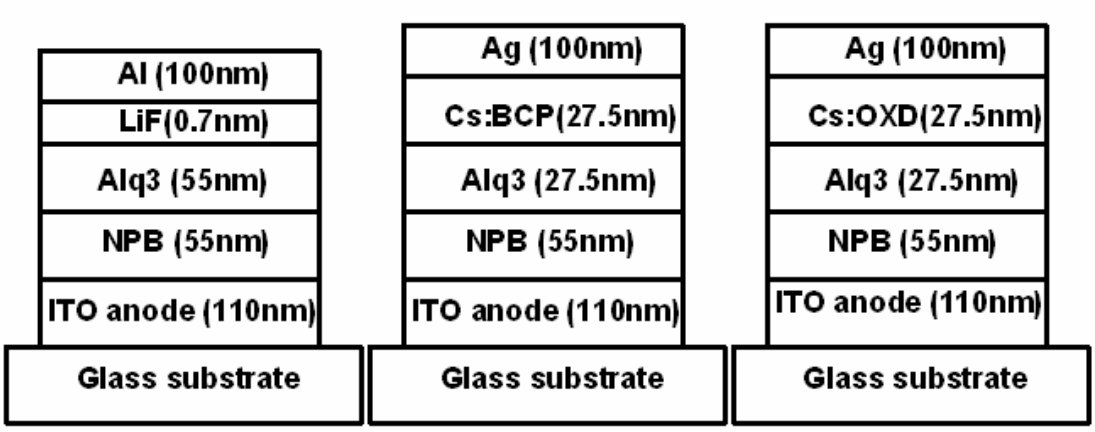
Fig. 1 Molecular structures of OXD and BCP

By using Cs:BCP and Cs:OXD as the ETL, we fabricated OLED devices and it has a 1.8 and 2.3 V reduction in driving voltage as compared with a conventional LiF/Al device. Hole transport layer (HTL) material usually exhibits higher mobility and higher conductivity than that of the ETL. That results in the carrier imbalanced in such a device. We also found that in our metal dopant devices, the higher current efficiency is obtained with a lower driving voltage device. That indicates the carrier is more balanced in such a device. Lifetime experiments were also conducted for studying the reliability issue. It is found the Cs:BCP device has a 70% longer lifetime than that of a

conventional device. Luminance of the Cs:OXD device is increased rather than decreased within three hours under a high brightness value, i.e. 10000cd/m^2. We attribute it to the high Tg of the host material and high efficiency of such a device.

2. EXPERIMENTS

In all of our experiments, we used ITO glass substrate of low sheet resistivity (10 Ohm/sqr) and flat surface roughness (Ra<1 nm). The size of active region in our test pixel was 0.5 cm x 0.5 cm. Before organic deposition, O_2 plasma treatment was used to clean the ITO surface and increase the ITO work function. All the deposition process was carried in a batch-type multi-source chamber. The base pressure was about $1x10^{-7}$ torr. Typically, the deposition rate was controlled at 0.1 nm/sec. In our control devices, we used N,N'-diphenyl-N,N'-bis(1-napthyl)-1,1'-biphenyl-4,4'-diamine (NPB) as the hole transporting layer (HTL) material and tris-(8-hydroxyquinoline) aluminum (Alq3) as the emitting layer (EML) material. In our control device, Alq3 is also used as the ETL material. LiF of 0.7 nm in thickness was used for more efficient electron injection between the ETL and the aluminum cathode. The thickness of the aluminum cathode was 100 nm. For the metal dopant devices, Cs:BCP and Cs:OXD with the concentration of 1:9 and 1:5 were used as the ETL materials, respectively. The Ag cathode with the thickness of 100 nm was then evaporated. The thickness of the HTL, EML and ETL were 45, 27.5, and 27.5 nm, respectively. Device structures are shown in Fig. 2. After organic and metal depositions, devices were well encapsulated in the glove box with O_2 and H_2O concentrations below 1 ppm. Device performances were characterized with Keithley 2400 for the current-voltage measurements and with PR705 photometers for the brightness measurements. These instruments were connected to a personal computer and controlled by labview software.



Device A Device B Device C

Fig. 2 Device structures of a convnetional device and two metal dopant devices

3. RESULTS AND DISCUSSIONS

Fig. 3 shows the current-voltage characteristics of different samples. Sample A is our control device and exhibits

lowest current density under the same driving voltage among all the samples. Compared the I-V characteristics between devices A and B, which have similar device structures except the EML and the cathode materials, we can see that the driving voltage has a 1.8 V reduction in device B, which has the Cs:BCP metal dopant as the ETL. Replace the metal dopnat material from Cs:BCP to Cs:OXD, a 0.5 Volt further reduction in driving voltage is obtained. Although the conductivity of Cs:BCP is slightly higher than that of Cs:OXD, the driving voltage is smaller in device C, which has the Cs:OXD as its ETL material. The LUMO levels of BCP, OXD and Alq3 are 1.8, 2.17 and 3.7 eV, respectively. We can see that the difference between BCP/Alq is higher than that of OXD/Alq. Further phonons would be released when carriers transport from ETL to EML in BCP/Alq device. That attributes to the higher driving voltage. However, further experiments will be conducted to prove this assumption

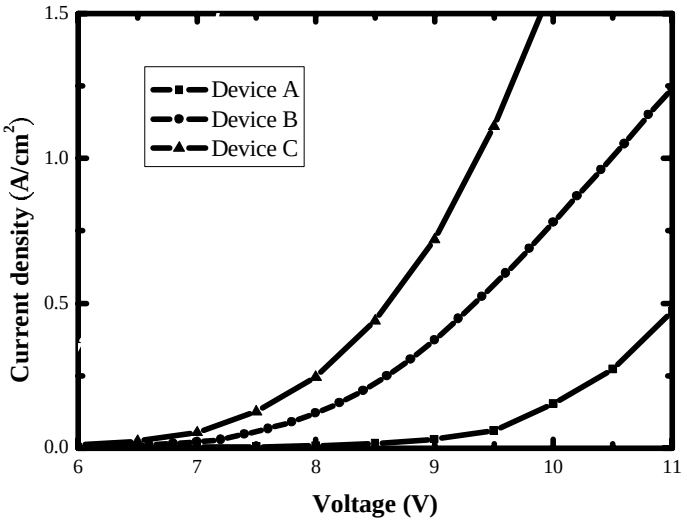


Fig. 3 Comparison of current density versus voltage curves.

Figure 4 shows dependence between luminance and injection current density. The slope of B-I curves corresponds to current efficiency (cd/A). Since there are many metal atoms (or ions) inside the metal dopant ETL, the strong absorption within this layer is one of the major concern for such a technique. We can see that in Fig. 4 the devices B and C also

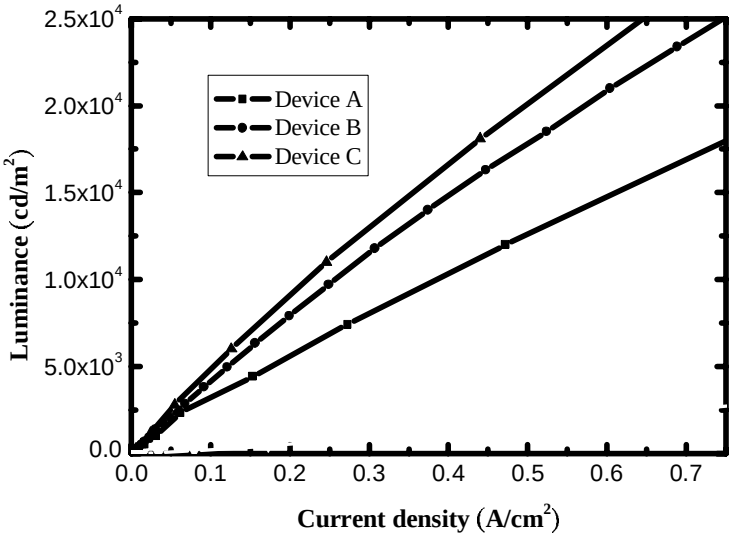


Fig. 4 Comparison of brightness versus current curves.

have higher brightness than device A under the same current density. We did not observe the metal atom (or metal ion) quench effect in our devices with the EML thickness of 25 nm. On the other hand, we can see that the current efficiency is higher in the metal dopant devices. In OLED devices, hole mobility of HTL is usually much higher than electron mobility of ETL. Hence, the conductivity of HTL is much higher than that of ETL. When a voltage is applied on the device, voltage drop is mainly on the ETL. At the same time, there are more holes than electrons near the emission center. That means the carrier is not balanced in this interface. That results in low current efficiency and shorter lifetime. Here, the use of metal dopant ETL increases the carrier concentration and conductivity. It also helps to balance the electrons and holes distribution near the interface. Not only the driving voltage is decreased, current efficiency is also increased in our metal dopant case, especially in the Cs:OXD case.

Interference effect due to different refractive index and extinction coefficient values among the Alq3, Cs:BCP and Cs:OXD may account for the current efficiency. However, as shown in Fig. 5, we can see that the spectrums of these three devices are identical. We did not see any spectrum shift due to the interference effect. We also found similar results that the metal dopant layer exhibits a lower refractive index and absorption concentration as mentioned in ref. 9.

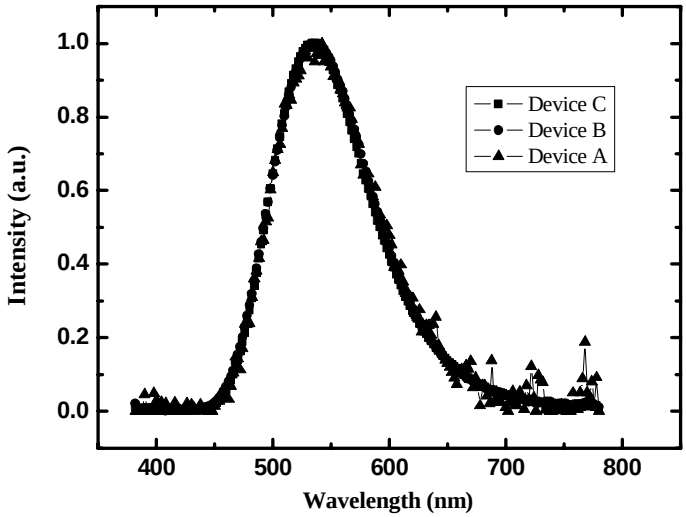


Fig. 5 Spectrum of different samples.

Fig. 6 shows the results of the acceleration lifetime test. The initial brightness of this test is set at 10000cd/m^2 under DC constant current driving. Under this condition the temperature of the glass side is around 40 ℃ hence the temperature at the device side and inside the device may be much higher than this temperature. We can see that our control device, device A, has shortest lifetime. The half lifetime can be estimated under such a high brightness is 14.5 hours by extrapolating the data. Device B exhibits a half-life of 24 hours although the Tg of the metal dopant host is low. We attribute this to the higher power efficiency of the metal dopant devices. Due to less heat generated, the degradation speed is also slow down. For the device C, Cs:OXD case, we can see that operation lifetime is as high as 42 hours that is 75% and 189% longer than those in Cs:BCP and control devices. That results from the high Tg characteristics of OXD and high efficiency in such a device.

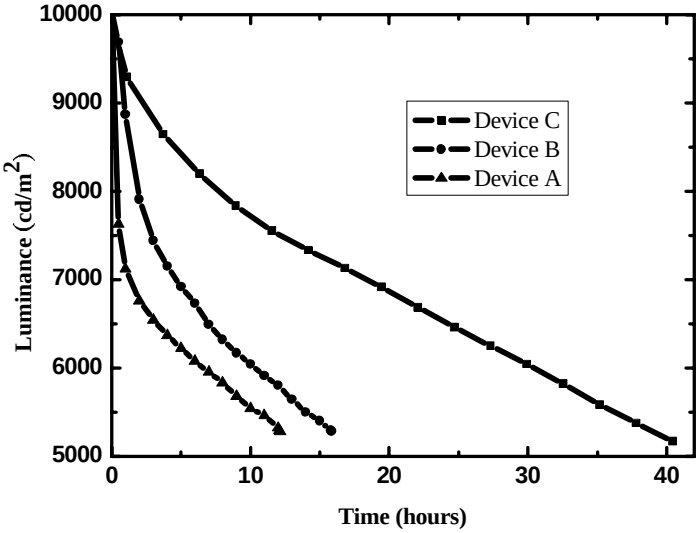


Fig. 6 Accelerated lifetime test of devices.

4. SUMMARY

In summary, we have shown device performance of an OLED with metal dopant technique that can effectively increases the carrier concentration of the ETL and decreases the driving voltage of a device. The interface between the ETL and cathode is also modified that results in an ohmic contact rather than a schottky barrier regardless the cathode materials due to the alkali metal dopant. In our devices, Ag is used as the cathode electrode for lower ohmic loss and less optical absorption. We choose cesium doped into BCP and OXD as the ETL material. The heavy alkali metal atom decreases the effects of metal ion diffusion from the ETL to EML and inhibits the quenching effects after long-term operation as compared with the use of the light alkali metal, lithium. It hence increases the operation lifetime. For devices with metal ETL, not only the driving voltage is decreased, higher current efficiency is also achieved due to better charge balance. A 70% increase in lifetime was observed in our Cs:BCP device even the Tg of the BCP is low. The increasing lifetime suggested that Cs did not diffuse into emission layer and the devise is stable. Replacing BCP by the high Tg organic material (OXD), the driving voltage, current efficiency, power efficiency and lifetime all increase due to the thermally stable and good energy alignment with EML.

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