High contrast ratio organic light-emitting devices based on CuPC as electron transport material

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Abstract

In this paper, a high-contrast-ratio organic light-emitting device (OLED) of high brightness is demonstrated. In this device, reflection from the cathode is reduced by inserting a copper-phthalocyanine (CuPC) layer between the emitting layer (EML) and the cathode called the Black CathodeTM technique. The absorption and the destructive interference effect caused by this layer lead to the decrease of the ambient light. With the same injection current density at 6 mA/cm², the contrast ratio of this device increases from 1.9 to 2.5 under 1000 lx illumination, when compared with a conventional device. Although the thickness of this device increases by 54.5%, its driving voltage is nearly the same as that of a conventional device. This result implies the high electron mobility in the inserted CuPC layer.
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1. Introduction

Organic light-emitting display (OLED) has attracted much attention because it exhibits the advantages of low power consumption, high brightness, high contrast, and low cost [1,2]. In a conventional OLED device, it consists of an indium-tin-oxide (ITO) anode, a p-type and an n-type organic layers, and a metal cathode. Electro-luminescence is generated from the organic layers and coupled out of the device from the ITO side. Usually, an organic material has a wide band gap and experiences little absorption in the visible range. When an OLED device is illuminated with ambient light, most of the incident photons transmit through the organic layers and are then reflected by the metal cathode to couple out of the device, as illustrated in Fig. 1. Reflection of incident ambient light also occur at each interface within the device. Such out-coupling of incident ambient light significantly decreases the contrast ratio of an OLED device and makes the outdoor application of an OLED device difficult.

Theoretically, the reflected ambient light can be eliminated with an attached film for the functions of a

quarter-wave plate and a polarizer. However, such a design would increase the cost and the complexity in manufacturing. The use of an absorptive and conductive inorganic layer inserted between the cathode and the organic layer was proposed [3,4]. Such a layer not only absorbs the incoming ambient photons, but also results in destructive interference to filter the ambient light. However, a sputtering process is usually needed for depositing such a conductive inorganic film. This process introduces damage on the organic material if the deposition rate is higher than a low value as 0.1 Å/s. Recently, a metal/organic co-deposited mixture and thermal-evaporated inorganic material were proposed and exhibited superior device performances [5,6]. In this paper we propose the use of CuPC, a widely used organic material without doping, for removing the ambient light. In our devices, although such an extra layer is inserted, the current–voltage characteristics are nearly unchanged. The maximum brightness of such a device achieves 7990 cd/m² at 8.5 V. Meanwhile, the reflectance of the whole device decreases from 70.99 to 21.5% and the contrast ratio increases from 1.9 to 2.5 under the illumination of 1000 lx. Because the material system and the fabrication procedures are identical to those of a conventional device, this technology is compatible to the existing equipment system of thin-film deposition. No further equipment modification is needed.

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Fig. 1. Ambient light reflection in an OLED device.

The experimental results and the related discussions are represented in Section 2. Conclusions are drawn in Section 3.

2. Results and discussions

CuPC was reported to have high electron mobility, about two orders of magnitude larger than that of the typically used electron transport material tris-(8-hydroxyquinoline) aluminum (Alq3). However, a certain interface modification for better electron injection from CuPC to the emitting layer (EML) needs to be made. LiF with the thickness of a few angstroms, followed by a thin aluminum layer, which is sandwiched by the emitting layer and the CuPC transport layer, is generally used for this purpose [7]. This thin metal layer in our device also plays the role of a partially reflecting mirror for the stronger destructive-interference effect.

To first understand the optical properties of CuPC, we used an n & k analyzer NKT 1512RT for measuring the refractive index and extinction coefficient [8]. The organic materials are deposited on a quartz substrate with the thickness of 50 nm. As shown in Fig. 2, CuPC exhibits a higher refractive index and a higher extinction coefficient, compared with the typical electron-transport material, Alq3. The higher refractive index is preferred in our device since it provides a reasonably large optical length in a thinner device, which is helpful for lowering the driving voltage. The refractive index (n) of Alq3 is about 1.7 in the visible range. However, that of CuPC is generally larger than two in the visible range (see Fig. 2). It has three peaks at 393, 615, and 713 nm. Although the spectral range of typical ambient light is large, we are mainly concerned with the elimination of the light around 550 nm since it is the most sensitive wavelength to the human eyes. Since the required effective optical length for the destructive interference is one-quarter wavelength of the most concerned ambient light, the thickness of the CuPC layer at 67 nm should be most effective for ambient photons at 550 nm. The extinction coefficient (k) of Alq3 is nearly zero within the visible range, while that of CuPC is always over 0.4. It has a peak around 570 nm. The strong absorption in the yellow band explains the blue color of a CuPC thin

Fig. 2. Wavelength-dependent refractive index and extinction coefficient of CuPC and Alq3.

film. With the thickness of CuPC at 67 nm, the corresponding absorption experienced by the ambient light is 61.8% at the wavelength of 550 nm. Combining the high refractive index and high absorption characteristics, simulation results showed that the reflection of the entire device at 550 nm decreased from 65 to 4% with a proper device design. It can be further reduced to be under 0.1% with anti-reflection coating at the glass/air and ITO/glass interfaces.

In all of our experiments, we used ITO glass substrate of low sheet resistivity ($10 \Omega/\text{sq}$) and flat surface roughness ($R_a < 1 \text{ nm}$). The size of active region in our test pixel was $1 \text{ cm} \times 1 \text{ cm}$. 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 $1 \times 10^{-5} \text{ Pa}$. Typically, the deposition rate was controlled at 0.1 nm/s. In our control device, we used N,N' -diphenyl- N,N' -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) as the hole-transporting material, 9-Benzo-thiazol-2-yl-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo anthracene-10-one (C545T) as the green dopant material and Alq3 as the electron transporting material. Alq3 was also used as the host material of the emitting layer. The thickness of the hole-transport layer (HTL), the emitting layer and the electron-transport layer (ETL) were 60, 20, and 30 nm, respectively. The dopant concentration of C545T in Alq3 was 1.33% in mole ratio. In our control device, LiF of 1.2 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. In the proposed device (called the black-layer device) structure, the materials and thickness of HTL, EML, and ETL are identical to those of the control device. LiF of 1.2 nm and aluminum of 6 nm in thickness

were deposited, followed by the ETL. The layers are used for interface modification and partially reflection. After the deposition of the surface modification layer, CuPC of 67 nm in thickness was thermally evaporated. Then, the other thin LiF layer with the thickness of 1.2 nm and the aluminum cathode with the thickness of 100 nm were formed. After organic and metal depositions, devices were well encapsulated in the glove box with O₂ and H₂O concentrations below 1 ppm. Device performances were characterized with Keithley 2400 for the current–voltage measurements and with SR-2 photometers for the brightness measurements. These instruments were connected to a personal computer and controlled by labview software. The setup for contrast ratio measurement was based on the flat panel display measurements (FPDM) proposed by the video electronics standard association (VESA).

Device performance comparison between the traditional device and the black-layer device is shown in Fig. 3. Here, the continuous curves with triangles and the dashed curves with circles represent the parameters of the control and the black-layer device, respectively. We can see that the current–voltage curves of the two devices are nearly the same. The only difference in device structure between the two devices is the ultra-thin surface modification layer and the CuPC layer. With the same driving current, the black-layer device does not need an extra driving voltage even though its organic material is 54.5% thicker than that of the control device. The voltage drop across the CuPC layer in the black-layer device is quite small.

At higher voltage levels, the black-layer device exhibits even higher current than the control device. Although the small difference in the *I*–*V* curves is within the range of experimental error, we can still see that the turn-on voltage

Fig. 3. Comparison of current density vs. voltage curve between the black-layer device (dashed curve with circles) and the control device (continuous curves with triangles).

Fig. 4. Comparison of luminance vs. current density curve between the black-layer device (dashed curve with circles) and the control device (continuous curves with triangles).

is below 4 V and the current density can reach 100 mA/cm² at 7.5 V in the black-layer device. The driving voltage in our black-layer device is not higher than those of other research groups.

Fig. 4 shows the luminance variations versus injected current density of the two devices for comparison. We can see that the control device has the brightness of 9610 cd/m² at 91.3 mA/cm². This result corresponds to a current efficiency of 10.52 cd/A. This is a typical value for a green-emitting device. As to the black-layer device, at 100 mA/cm², the brightness is 4410 cd/m², corresponding to the current efficiency at 4.41 cd/A, that is only 42% of the control device. The maximum brightness levels are 15,500 cd/m² for the control device and 7990 cd/m² for the black-layer device, respectively. Since the CuPC layer can absorb not only the ambient light but also the device-emitting light, the theoretical limit of current efficiency in such a black-layer device is one-half of a conventional device. Although the brightness of the black-layer device is reduced, its contrast ratio is significantly enhanced. Fig. 5 shows the pictures of the two devices under room ambient light. In the control device (part (c)), about 80% of ambient light was reflected by the aluminum cathode. In fact, this device looks yellowish because of the absorption edge of Alq₃ is extended from the UV region to the short-wavelength end of the visible range. In the black-layer device (part (b)), we can see that the device is nearly black under the ambient light. As shown in part (a), the black-layer device shows a green panel when it is turned on.

To obtain the reflection behavior of the entire device, we measured the ambient contrast ratio based on the VESA-FPDM standard. Although the calibration for the contrast ratio in such a measurement is complicated, it can

Fig. 5. Photographs of the black-layer device (parts (a) and (b)) and the control device (part (c)).

be roughly defined as:

$$\text{Contrast ratio} = \frac{\text{device luminance (on)} + \text{reflected ambient light}}{\text{device luminance (off)} + \text{reflected ambient light}} \quad (1)$$

In an OLED device, the luminance is zero when it is turned off. The measurement of the luminance was conducted with an integration sphere for collecting the output light in a dark room. We used a photometer (model SR-2) to measure the luminance from a device and the reflected ambient light. The ambient light was produced by a white-light simulator with the illumination varied from 0 to 3000 lx. Fig. 6 shows the contrast ratios of the black-layer device (dashed curve) and the control device (continuous curve) under different conditions of ambient light illumination. In this measurement, the devices were biased at 4.5 V, which corresponds to 567 cd/m² for the control device and 270 cd/m² for the black-layer one. The brightness level of the black-layer device is quite typical in display applications. With weak

Fig. 6. Contrast ratio under different conditions of ambient luminance. The continuous (dashed) curve is depicted for the control (black-layer) devices.

ambient light, the black-layer device has a significantly higher contrast ratio, compared with that of the control device, although the device luminance of the black-layer device is only 46.7% of the control device. With 1000 lx ambient light illumination, the contrast ratio of the black-layer device is 2.5, which represents a 31.6% increase, when compared with the control device. However, when the ambient light is enhanced to 3000 lx, the contrast ratio of the black-layer device is only 1.37, which stands for an improvement of only 11.3%.

Based on the results in Fig. 6, the black-layer device can be used indoors and outdoors under cloudy environments. To implement an efficient display system for the use under the direct sun, the reduction of device total reflectance by two orders of magnitude is needed. We roughly estimated that the total reflectance of the control device is about 70.99%, while that of the black-layer device is only 21.5%. Optimization of the black-layer structure and reduction of the interface reflection are needed for further decreasing the total reflectance. Since the black layer is a wavelength-sensitive material and was designed to achieve the lowest reflection around 550 nm, the ambient contributions from other wavelengths in our white-light simulator cannot be effectively suppressed. With the thickness variations of the thin aluminum and the CuPC layers, new designs for reducing the reflection in the whole visible range should be considered. Although the black layer suppresses the reflection from the cathode, reflections from the glass/air and ITO/glass interfaces still exist. Such reflections degrade the contrast ratio when the ambient light is intense. For further increasing the contrast ratio, the anti-reflection coatings on those interfaces are recommended.

3. Conclusions

We have reported a high contrast ratio OLED device with CuPC as the black-layer material. It exhibited the advantages of low-cost, simple fabrication, and low-driving voltage. Interfacial engineering was implemented for better electron injection. The current–voltage characteristics of the black-layer device were about the same as the control device.

Although the external quantum efficiency of the black-layer devices was reduced to 42% of the control device level, its contrast ratio increased from 1.9 to 2.5 at 1000 lx white-light illumination.

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