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High Efficiency Tandem Organic Light-Emitting Diodes with Effective Charge Generation Layer

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Abstract: By employing cesium carbonate doped tris-(8-hydroxyquinoline) aluminum/ MoO_3 as the effective charge generation layer (CGL), high efficiency two-unit series connected tandem organic light-emitting diodes were fabricated. It is found the performance of the two-unit tandem devices can be controlled by the thickness of the MoO_3 layer. The 30 nm-thick MoO_3 CGL tandem device exhibits the best device performance with the current efficiency of 14.5 cd/A, which is above 2.0 times than that of the control device over a wide range of current densities. It's suggested that the connecting layer broke down under a high current density, leading to the decrease of current efficiency. The improvement of tandem device performance is attributed to the efficient electron and hole injection from charge generation layer to two adjacent emission units.

Key words: OLEDs; charge generation layer; tandem; MoO_3 ; Cs_2CO_3

高效叠层有机电致发光器件

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摘 要: 采用 $\text{Cs}_2\text{CO}_3:\text{Alq}_3/\text{MoO}_3$ 作电荷产生层, 制备出高效双单元串联型叠层有机发光器件。双单元叠层有机发光器件发光性能受电荷产生层 MoO_3 的厚度影响很大。当 MoO_3 厚度为 30 nm 时, 叠层器件表现出最好的器件性能, 最大电流效率达到 14.5 cd/A。在相当宽的低电流密度范围内, 30 nm MoO_3 叠层器件的电流效率是对比单层器件电流效率的 2 倍以上; 但高电流密度下, 叠层器件电流效率下降较快。叠层发光器件性能的提高与中间电荷产生层向上下两个发光单元有效的电子、空穴注入有关。

关 键 词: 有机发光器件; 电荷产生层; 叠层; 三氧化钼; 碳酸铯

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1 Introduction

Rapid advances of organic light-emitting de-

vices (OLEDs) impose substantial demands in OLED structures having enhanced brightness yet without increasing driving currents^[1-2]. It is

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anticipated to provide a new approach to the design and fabrication of highly efficient OLEDs for future applications such as in televisions and illumination devices. Tandem OLEDs have drawn great attention due to their superior brightness, current efficiency, and operational lifetime compared to the conventional devices, while achieving a given luminescence level. The charge generation layers (CGLs) are required when driving tandem OLEDs, which act as the interconnecting units of bipolar charge spouting. Electrical doping in CGL has proven conspicuously effective for reducing the operating voltage of the device because of the increased conductivity and the matched energy level. Therefore, the CGLs are typically formed by combining the p-type doped organic layer and n-type doped organic layer between the emission units, such as $\text{Cs}_2\text{CO}_3:\text{Bphen}/\text{WO}_3:\text{NPB}$ ^[3], $\text{Cs}_2\text{CO}_3:\text{Bphen}/\text{WO}_3$ ^[4], $\text{CsN}_3:\text{Bphen}/\text{MoO}_3$ ^[5], $\text{Li}:\text{BCP}/\text{MoO}_3$ ^[6], $\text{Cs}:\text{Bphen}/\text{F4-TCNQ}:\text{NPD}$ ^[7], and $\text{Mg}:\text{Alq}_3/\text{V}_2\text{O}_5$ ^[8]. Generally a 2- to 3-fold increase in luminance efficiency can be achieved for tandem devices with two emitting units. Combined with the microcavity structure, a very high 5-fold efficiency enhancement can be achieved for a phosphorescent two-unit tandem device^[7].

In this letter, we consolidate both the MoO_3 hole injection layer and Cs_2CO_3 electron injection layer into the tandem CGL layers to achieve the high efficiency tandem devices. A 2-fold enhancement in luminance and current efficiency can be achieved for the two-unit tandem device compared with the control single-unit device.

2 Experiments

The ITO-coated glass substrates, with a sheet resistance of $10\ \Omega/\square$, were used. These ITO-coated glasses were washed with detergent, followed by a thorough washing with deionized water, and finally dried under a nitrogen flow before using. All series of devices were prepared

in an ultrahigh vacuum with a base pressure of 4×10^{-4} Pa. The active emission area of the device is $0.36\ \text{cm}^2$. The architecture of the tandem device used in the experiment is ITO/NPB(40 nm)/ Alq_3 (40 nm)/30% $\text{Cs}_2\text{CO}_3:\text{Alq}_3$ (20 nm)/ MoO_3 (10, 20, 30, 40 nm)/NPB(40 nm)/ Alq_3 (40 nm)/ Cs_2CO_3 (1 nm)/Al(100 nm), as shown in Fig. 1. We use 30% (mass fraction) Cs_2CO_3 doping concentration due to the enhanced electron injection and the efficient electron transport in the bulk of the $\text{Cs}_2\text{CO}_3:\text{Alq}_3$ layer^[9]. Each identical stacked element was started by the deposition of NPB, followed by an emission layer consisting of a 40 nm-thick Alq_3 . The CGL is composed by a 20 nm-thick Alq_3 layer mixed with Cs_2CO_3 in a 30% mass fraction and an amorphous MoO_3 layer (10, 20, 30, 40 nm, respectively). We use a Cs_2CO_3 -doped organic layer instead of a Li- or Cs-doped one, both of which are difficult to handle and need a special type of evaporator or dispenser set-up in the vacuum coater. The device with the structure of ITO/NPB(40 nm)/ Alq_3 (40 nm)/30% $\text{Cs}_2\text{CO}_3:\text{Alq}_3$ (20 nm)/Al(100 nm) were prepared for reference. The film thickness and vapor deposition rate were online monitored by a crystal oscillation thickness monitor (XTM/2, INFCON), which was revised by a surface profiler (XP-2, Ambios, USA). The current and the voltage were obtained from a programmable voltage-current

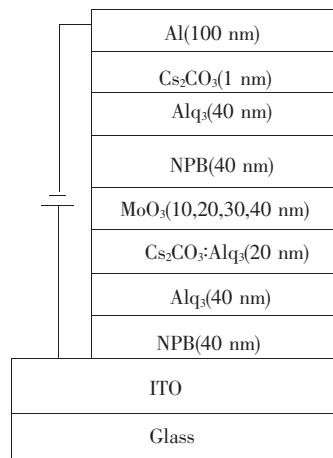


Fig. 1 Structure of the tandem device

source (2400, Keithley, USA). Luminance was measured by a brightness meter (IL1500, Beijing normal university). The devices were characterized in ambient atmosphere and room temperature without encapsulation.

3 Results and Discussion

3.1 Device performances

Fig. 2 (a) and (b) show the luminance-current density (L - J) and the current efficiency-current density (η - J) characteristics of the two-unit tandem device with 30 nm-thick MoO₃ and the control single-unit device. The luminance and the current efficiency of the two-unit device with 30 nm-thick MoO₃ are much higher than that of the control single-unit device. Obviously, this internal floating electrode can efficiently allow the electric-field assisted bipolar charge to spout toward two adjacent emitting units. However, the luminance and the current efficiency of the two-unit tandem device decrease under high current density. The details of the current efficiency enhancement characteristics of the two devices

are depicted in Fig. 2 (b). As shown, the efficiency of the tandem device maintains more than 2.0 times than that of the single-unit device in a wide range of low current densities. When the current density exceeds 110 mA/cm², the enhancement of current efficiency will fall off rapidly to 1.6 times. It is suggested that the charge generation layer broke down under high current density, leading to the decrease of device performance^[10]. In addition, it is excluded that the self-absorption of the emitted light by the underlying films influences the rapid decrease of the current efficiency in range of high current densities due to the insufficient overlap between the under layer absorption and top layer emission spectra.

3.2 Charge generation performances

To analyze the functionality of the CGL, we vary the thickness of MoO₃ components from 10 nm to 40 nm and measure the electro-optical properties of the tandem OLEDs. The L - J characteristic of the four two-unit tandem devices with different connecting layers is shown in Fig. 3 (a). The two-unit device with 30 nm-thick MoO₃ has the highest luminance among the tandem OLEDs at any given current density. This indicates that the CGL with 30 nm-thick MoO₃ has the best carrier injection capability among the four intermediate CGLs. Fig. 3 (b) shows the η - J characteristic of the four two-unit tandem devices. It is evident that only the tandem device using 30 nm MoO₃ as the connecting layer shows dramatic enhancement of current efficiency, while the efficiency of the tandem device using 10 nm MoO₃ only show a slight increase and the efficiency of the two-unit device using 40 nm MoO₃ only show a sharp decrease, respectively. It is apparent that the two-unit device with 40 nm-thick MoO₃ layer shows the lowest luminance and current efficiency due to the increase of resistance and the decrease of the transmittance of the CGL film. Furthermore, the highest luminance of the thin 10 nm-thick MoO₃ two-

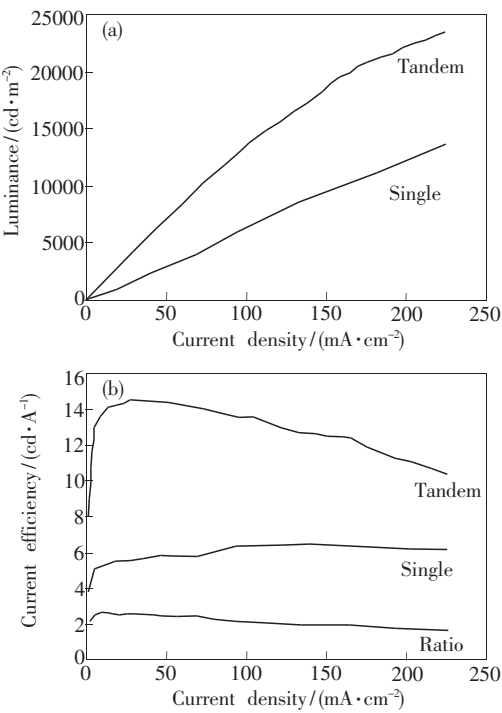


Fig. 2 (a) L - J and (b) η - J characteristics for the two-unit tandem device and the single-unit control device

unit tandem device decreases as compared to that of the single-unit control device, which may be due to the insufficient hole injection ability of the MoO₃ layer to the second emitting unit in high voltage. In addition, tandem device without depositing MoO₃ layer will perform even worse device performance than that of single-unit control device. This can be ascribed to the increase of the number of semi-conductive organic films. Details of device performance (operating voltage, luminance and η at 27.78 mA/cm²) are summarized in Table 1. As shown, the 20 nm MoO₃ tandem device has the lowest operating voltage under the same current density in four tandem devices, but its luminance is even worse than the 10 nm MoO₃ tandem device, which is related to the unbalance of hole and electron injection into the top emitting unit. Although increasing MoO₃ thickness may decrease hole injection to a certain extent, it can make the injected hole and

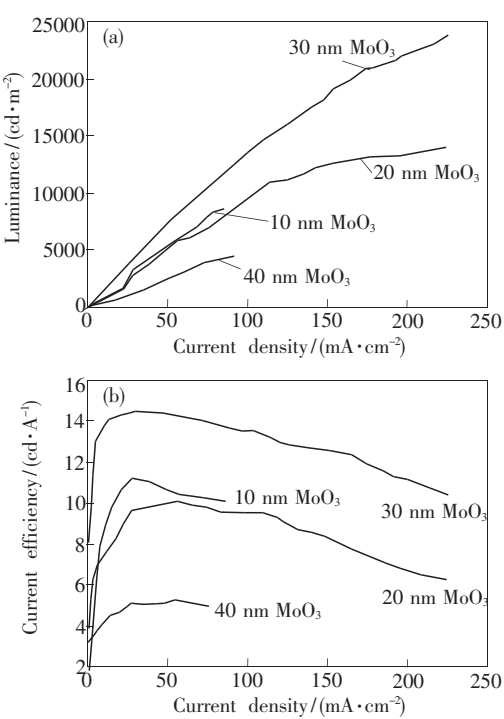


Fig. 3 (a) L - J and (b) η - J characteristics for the two-unit tandem devices with different MoO₃ thickness

Table 1 Performances of tandem devices at the current density of around 27.78 mA/cm²

Thickness of MoO ₃ /nm	Performances			
	Current density/(mA · cm ⁻²)	Voltage/V	Luminance/(cd · m ⁻²)	η /(cd · A ⁻¹)
10	27.78	38.62	3 121.5	11.24
20	27.78	27.01	2 679.6	9.65
30	27.78	31.22	4 029.9	14.51
40	27.78	43.18	1 110.3	4.00

electron charge carriers more balanced, resulting in the better device performance. This can be seen from the increased luminance and also increased operating voltage for the 30 nm MoO₃ tandem device.

3.3 Injection mechanism

It is known that the improved mechanism of MoO₃ or Cs₂CO₃ doping Alq₃ as an interfacial layer is attributed to the enhancement of carrier injection due to the reduction of hole or electron injection barrier. The UPS spectra and the energy diagram of NPD/MoO₃ and Cs₂CO₃:Alq₃ can be referred to the reports of Kröger *et al.*^[11] and Wang *et al.*^[12] in details. Our previous reports

also showed that MoO₃ and Cs₂CO₃ are superb hole-injection and electron-injection materials, which effectively enhance OLEDs performance^[9,13]. It is proposed that the improved single-layer device efficiencies relate to the enhanced hole injection at ITO/MoO₃/NPB interface, and the enhanced electron injection at the Alq₃:Cs₂CO₃/Al cathode interface in addition to the efficient electron transport in the bulk of the Cs₂CO₃:Alq₃ layer.

4 Conclusion

In summary, the two-unit tandem OLEDs based on Cs₂CO₃:Alq₃/MoO₃ as CGLs were

implemented. The 30 nm-thick MoO_3 two-unit tandem device shows the best performance, that is, the improvement of luminance and current efficiency by more than 2 times has been observed compared with those of the control single-

unit device. It is proposed that the improved efficiency of two-unit tandem device with 30 nm-thick MoO_3 CGL relates to the enhanced and balanced hole injection at the MoO_3 /NPB interface compared with those of other CGLs devices.

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