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The electro-optic performance and photovoltaic effect of organic devices based on cesium carbonate/Al/molybdenum trioxide intermediate connector

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ABSTRACT

An intermediate connector of $Cs_2CO_3/Al/MoO_3$ used in tandem organic light-emitting diodes (OLEDs) was investigated in this work. Here, an ultrathin Cs_2CO_3/Al was used as an electron-injection layer (EIL) from MoO_3 to the adjacent electron transporting layer (ETL). To verify the function of this intermediate connector, the device performances were evaluated through current density-voltage-luminance characteristics, current density-efficiency curves, and EL spectra. Additionally, the effect of photon energy on carriers behavior in the $Cs_2CO_3/Al/MoO_3$ connector is also estimated. The electrical properties and EL spectra of tandem OLEDs show that the $Cs_2CO_3/Al/MoO_3$ can function well for charge generation and transport, and the current density-voltage curves of $Cs_2CO_3/Al/MoO_3$ based special multilayer device shows the photovoltaic effect as a photovoltaic cell.

1. Introduction

Tandem organic light-emitting diodes (OLEDs) have been attracting considerable attentions to meet the demand for both long lifetime and high efficiency in the fields of lighting and display applications [1–3]. In tandem OLEDs, the intermediate connector plays a vital role in determining the device performances. The intermediate connector that connects individual electroluminescence (EL) units in series, serves as charge generation layer (CGL), in which holes and electrons are generated and transport into the adjacent hole transporting layers (HTL) and electron transporting layers (ETL) under an applied field [4]. These charges then combine with the carriers injected from electrodes in the emission layer, and finally light is emitted with the radiative recombination. Compared with single-unit OLED, tandem OLED can use a pair of hole and electron injected from the electrodes to emit multiplied amount of light. Therefore, tandem OLED can reach a high luminance of more than thousands of candelas per square meter at low current density, which is required especially for lighting, and also can alleviate the device degradation and efficiency roll-off induced by high current density [5]. Up to now, extensive efforts have been made to develop high-efficiency CGLs which could efficiently generate charge carriers for the effective exciton recombination. These CGLs typically consist of a p-n junction such as doped organic–metal (or metal oxide) bilayer structures [6], doped organic–organic bilayer structures [7–9] or metal–metal (or metal oxide) bilayer structures [10,11].

Usually, active metals (e.g., Li and Mg) [12,13] or metal compounds (Liq, Al_2O_3, Cs_2CO_3, and CsN_3, etc.) [13–15] or an ultrathin bilayer such as Liq/Al [14] and LiF/Al [3,16] onto an ETL are used as n-type materials which serve as an electron extracting layer or buffer layer in CGLs [17,18]. Recently, some groups [3,10,14,19] have designed CGLs with an ultrathin LiF or Liq layer and Al layer as an electron-injection layer (EIL) or cathode, which can achieve high-performance tandem devices. For example, Chiba et al. [3] fabricated two or three EL-unit devices by using undoped CGL structure of LiF/Al/HAT-CN_6 to realize the current efficiencies of 181 and 256 cd/A, respectively, at a luminance of 100 cd/m^2. The lifetime of single and two EL-unit devices at 50 mA/cm^2 are 98 and 190 h at degradation to 85% of their initial luminance. In this work, we propose a CGL structure of $Cs_2CO_3/Al/MoO_3$, and investigate the function of this CGL on tandem device performances. Moreover, the effect of photon energy on open circuit voltage (V_{oc}) of a special multilayer device was also studied.

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2. Experiment

Devices were grown on glass substrates precoated with a 150-nm-thick indium tin oxide (ITO). The ITO-glass substrates were cleaned by ultrasonic cleaners, dried in a closet, and treated to be nearly free from organic residuals through UV/ozone before put into the deposition chamber. All of the organic and metal films were thermally deposited onto the top of ITO substrates in succession without breaking vacuum ($\sim 2 \times 10^{-6}$ Torr). The deposition rate and layer thickness of each film were monitored by the quartz oscillating crystal situated near the substrates. The doped layer was thermally co-evaporated from individual sources with the doping ratio controlled through two quartz-crystal monitors. The compared devices with different parameters (thickness or materials) were fabricated in the same lot by changing the shadow mask. Here, *N*,*N*′-di(naphthalene-1-yl) -*N*,*N*′-diphenyl-benzidine (NPB) was used as the HTL, tris(8-hydroxyquinoline) aluminum (Alq_3) was used as the ETL, 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H, 11H-(1) benzopyropyrano(6,7,8-i,j)quinolizin-11-one (C545T)-doped Alq_3 was used for green emission, and 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7,-tetramethyl julolidyl-9-enyl)-4H-pyran (DCJTB)-doped Alq_3 for red emission.

The well-fabricated devices were transferred from the vacuum chamber into an interconnected nitrogen-filled glove box for encapsulation. Each device has an active area of 10 mm^2. All of the measurements were conducted in the ambient air at room temperature. In this work, the 300 W xenon lamp without and with filters of 300, 360, 400, 450, and 510 nm were used for supplying different photon energies. The forward bias in the current density-voltage (*J-V*) and capacitance-voltage (*C–V*) evaluations was defined as the positively applied bias on ITO electrode. The current density–voltage–luminance (*J–V–L*) characteristics and EL spectra were obtained from a computer-controlled programmable Keithley model 2400 power source with a Photo Research 655 spectrometer. The *J-V* characteristics illuminated under different photon energy conditions were measured with a programmable Keithley model 2400 power source. *C-V* curves were recorded from Keithley 4200-CVU semiconductor characterization system.

3. Results and discussion

Single-unit and tandem OLEDs with a Cs_2CO_3:Alq_3 layer of different thicknesses were fabricated to optimize the device performance. The device performance of single-unit OLEDs with a structure of ITO/NPB (40 nm)/C545T:Alq_3(1 wt%, 20 nm)/Alq_3(20 nm)/Cs_2CO_3:Alq_3(10 wt%, x nm)/Cs_2CO_3(1 nm)/Al(100 nm), (x = 10, 20, and 40 nm, marked as devices A, B, and C, respectively) are shown in Fig. 1. The performance characteristics of devices A-C are summarized in Table 1. It can be seen that the driving voltage increases with the increasing thickness of EIL. For example, to generate a current density of 1 mA/cm^2, the driving voltages of devices A-C are 3.22, 3.45, and 3.62 V, and the corresponding current efficiencies are 10.9, 11, and 9.9 cd/A, respectively.

Fig. 2 plots the performances of tandem devices D-F with a structure of ITO/NPB(40 nm)/C545T:Alq_3(1 wt%, 20 nm)/Alq_3(20 nm)/Cs_2CO_3:Alq_3(10 wt%, x nm)/Cs_2CO_3 (1 nm)/Al(1 nm)/MoO_3(5 nm)/NPB(40 nm)/C545T:Alq_3(1 wt%, 20 nm)/Alq_3(20 nm)/Cs_2CO_3:Alq_3(10 wt%, x nm)/Cs_2CO_3(1 nm)/Al(100 nm), in which the thickness of the Cs_2CO_3:Alq_3 layer are 10, 20, and 40 nm, respectively. As shown in Fig. 2, the driving voltages of devices D-F are 14.64, 15.25, and 17.06 V, the luminances are 3917, 4368, and 4469 cd/m^2, and the resulting current efficiencies are 19.58, 21.84, and 22.35 cd/A, respectively, at the current density of 20 mA/cm^2. The difference in the performance tendency for single-unit and tandem OLEDs may be due to the microcavity effect, interference of light, and so on. Considering that the demands of OLEDs are both high luminance and low driving voltage, we therefore choose a 20 nm-thick Cs_2CO_3:Alq_3 layer in tandem OLEDs for further research.

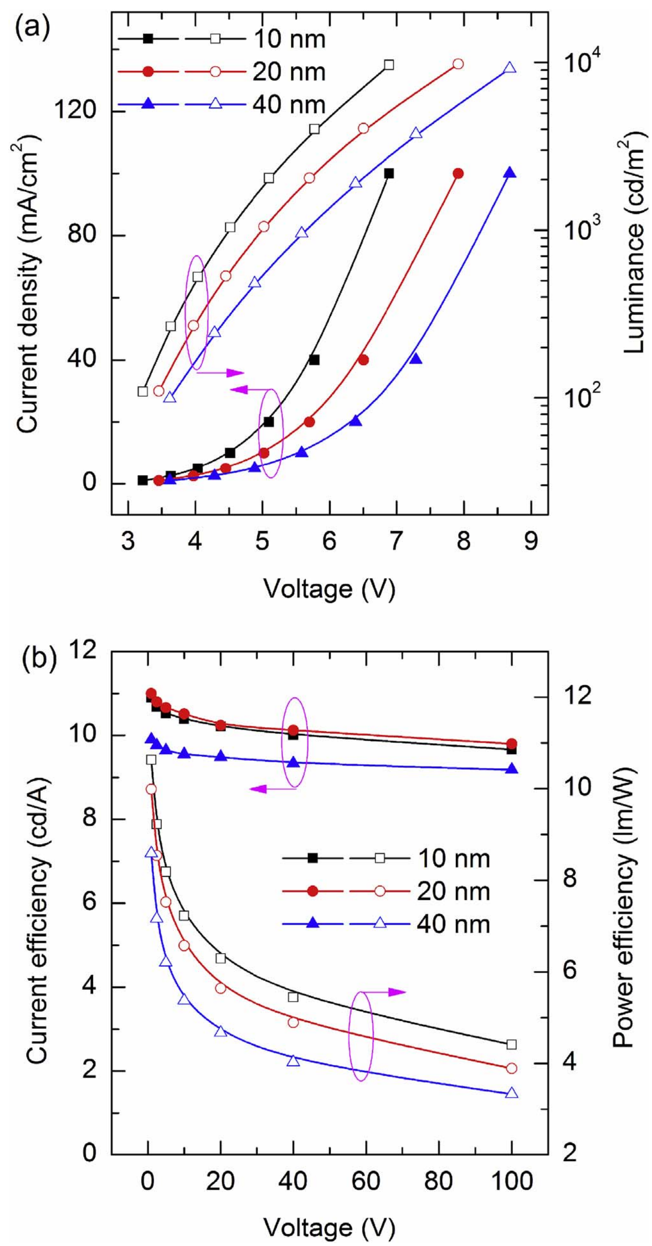

Fig. 1. The device performances of single-unit OLEDs based on the Cs_2CO_3:Alq_3 layer with a thickness of 10 nm (device A), 20 nm (device B), and 40 nm (device C).

Table 1
The performances of single-unit OLEDs based on the n-doped EIL with different thickness. V_d, L, η_c, η_p are driving voltage, luminance, current efficiency, and power efficiency, respectively. The parameters are tested at the room temperature and J = 20 mA/cm^2.

Devices	V_d (V)	L (cd/m^2)	η_c (cd/A)	η_p (lm/W)	EL peak (nm)
A	5.09	2042	10.21	6.29	524
B	5.70	2047	10.24	5.64	524
C	6.26	1901	9.51	4.77	524

To verify the function of the intermediate connector with a structure of Cs_2CO_3/Al/MoO_3, tandem devices G – J with different intermediate connectors were fabricated, and the detailed device structures are listed in Table 2. The device properties and EL spectra of these devices, together with a reference OLED with only one EL unit (device B) are depicted in Fig. 3. It is observed that the device G using Cs_2CO_3/Al/MoO_3 as intermediate connector shows the best performance,