High efficiency organic light-emitting diodes using CuO_x/Cu dual buffer layers*

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An organic light-emitting diode (OLED) device with high efficiency and brightness is fabricated by inserting CuO_x/Cu dual inorganic buffer layers between indium-tin-oxide (ITO) and hole-transport layer (HTL). The CuO_x/Cu buffer layer limits the operating current density obviously, while the brightness and efficiency are both enhanced greatly. The highest brightness of the optimized device is achieved to be 14 000 cd/m^2 at current efficiency of 3 cd/A and bias voltage of 15 V, which is about 50% higher than that of the compared device without CuO_x/Cu buffer layer. The highest efficiency is achieved to be 5.9 cd/A at 11.6 V with 3 400 cd/m^2, which is almost twice as high as that of the compared device.

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Since C. W. Tang and Van Slyke[1] reported their organic light-emitting diodes (OLEDs) in 1987, OLEDs have attracted much attention due to their great potential application in illumination and multi-color flat-panel displays. Tremendous efforts have been done for improving the devices performance. It's well known that the good OLEDs performance depends on balanced carry injection and excellent recombination. However, the injection of holes is easier than that of electrons, and the mobility of holes is also much higher than that of electrons. Therefore, limiting hole-injection by inorganic buffer layer is an effective way to achieve high performance, and lots of inorganic materials were introduced into OLEDs[2-9]. In this paper, dual copper oxide and copper (CuO_x/Cu) layers are introduced into OLEDs as hole-injection buffer layers. The holes injection is limited by barrier between CuO_x and Cu effectively. By optimizing the conditions, the highest brightness of the device is achieved to be 14 000 cd/m^2 at current efficiency of 3 cd/A and bias voltage of 15 V, and the highest efficiency is achieved to be 5.9 cd/A at 11.6 V with 3 400 cd/m^2.

CuO_x and Cu were introduced as dual inorganic buffer layers (DBLs) between anode and the hole-transfer layer (HTL), and two kinds of devices were fabricated as the compared device of ITO/N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (NPB) (40 nm)/tris-(8-hydroxyquinolinato)aluminum (AlQ_3) (40 nm)/LiF/Al and the sample of ITO/DBL (CuO_x/Cu)/NPB (40 nm)/AlQ_3 (40 nm)/LiF/Al.

The glass substrates coated with a 200 nm-thick ITO layer with a sheet resistance of 20 Ω^{-1} were used as the substrate. Prior to fabricating devices, the substrates were cleaned with ultra-purified water and organic solvents as routine, and then treated with an ultraviolet (UV)-ozone ambient. CuO_x layer was fabricated by sputtering with gas formed by oxygen and argon, and Cu layer was also fabricated by sputtering with pure argon. Both of them were under pressure of 2×10^{-5} Pa. Then the organic layers were deposited on the substrates by vacuum thermal evaporation respectively under pressure of about 3×10^{-3} Pa. The thickness of the inorganic layers was obtained by Ambios technology XP-2 surface profilometer, the thickness of organic layers was measured by crystal oscillator thickness meter, and the value of x in CuO_x was measured by X-ray diffraction (XRD) on a thick film.

The closely contacted Cu and CuO_x have an interesting property of rectification, which is attributed to the Schottky barrier at the interface of Cu and CuO_x, as shown in Fig.1[10]. CuO_x is a typical n-type semiconductor, and its work function is lower than that of Cu[11]. The specific difference depends on oxidization ratio, i.e., the more the oxidization, the lower the work function. Although the thickness of CuO_x is only a few nanometers, the difference of work functions still makes a barrier, and this barrier can be used to limit the hole injection.

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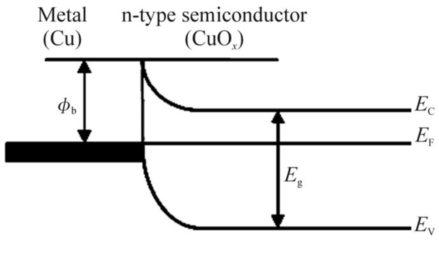
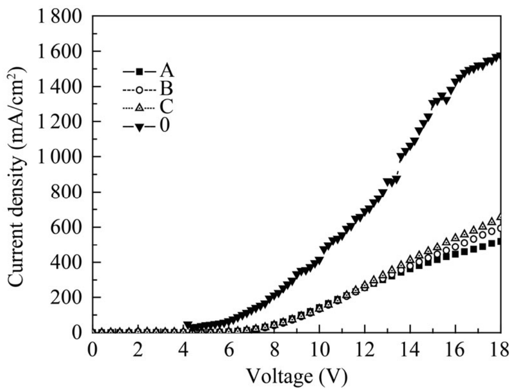


Fig.1 Schottky barrier at the interface of Cu and CuO_x

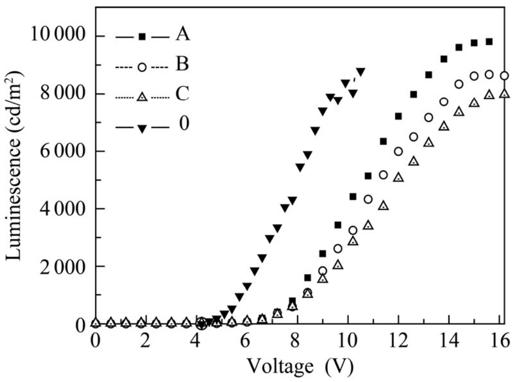
A series of devices with different oxidization ratios of CuO_x were fabricated as shown in Tab.1, and the thicknesses of CuO_x and Cu in DBL of these devices are both 4 mm. The performances of the device A, B and C are shown in Fig.2. The Fermi level of CuO_x moves to the conduction band, which leads to a higher barrier with the increase of x value. Therefore, it can be obtained from current density-voltage (*J-V*) curves shown in Fig.2(a) that the current densities of the devices with buffer layer are all decreased with the increase of x value, and all of them are much lower than that of the compared device. The luminescence-voltage (*L-V*) curves shown in Fig.2(b) and the efficiency-current density (*E-J*) curves shown in Fig.2(c) show that the operating voltages of the devices with buffer layer are all higher than that of the compared device, but the highest brightnesses and efficiencies of the device A, B and C are close to those of the compared device, and those of the device A are even a little higher than those of the compared device. It indicates that the CuO_x/Cu buffer layer can block the hole injection significantly.

Tab.1 Devices with different x values in CuO_x/Cu buffer layer

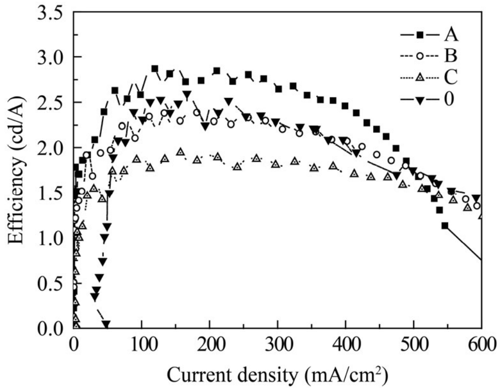
Device	Volume fraction of oxygen in sputtering gas	x in CuO_x
A	80%	~0.94
B	60%	~0.82
C	40%	~0.55
0 (Compared)	/	/



(a)



(b)



(c)

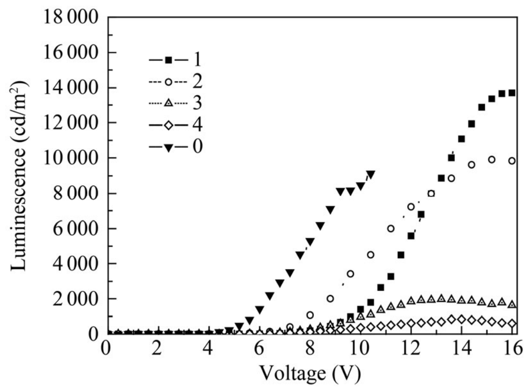
Fig.2 (a) *J-V* curves, (b) *L-V* curves and (c) *E-J* curves of devices A–C with different x values in CuO_x and the compared device

Another series of devices with different thicknesses of CuO_x and Cu were fabricated. In the process of preparation, the volume fraction of oxygen in sputtering gas is 80%, and x value in CuO_x is ~0.94. The details of the thicknesses of CuO_x and Cu in these devices are shown in Tab.2. The *L-V*, *J-V* and *E-J* curves of devices 1–4, in each of which CuO_x and Cu in buffer layer have the same thickness, are shown in Fig.3. The highest brightness of about 14 000 cd/m^2 is obtained from device 1 at 15 V with efficiency of 3 cd/A, which is 50% higher than that of the compared device. The highest efficiency of device 1 is achieved as 5.9 cd/A at 11.6 V with brightness of 3 400 cd/m^2. The highest brightness, the current density and the efficiency all decrease with the increase of CuO_x and Cu thickness in devices 1–4. As we know, the holes are injected from anode to HTL through buffer layer by tunneling effect, which provides that the buffer layer is quite thin. When the buffer layer becomes thicker and thicker, the probability of tunneling effect will decrease significantly. Then the hole injection becomes excessive blocking and leads to poor current density and luminescence.

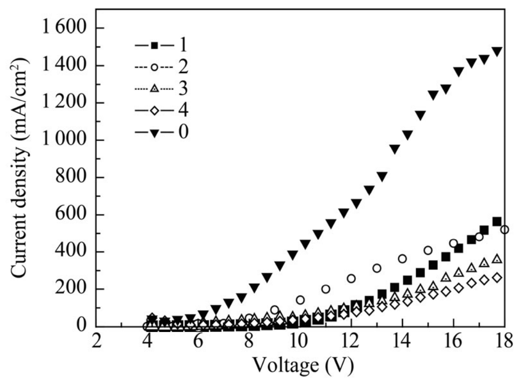
In devices A1–A3, the thickness of Cu in DBL is kept as 2 nm, and in devices B1–B3, the thickness of CuO_x in DBL is kept as 2 nm. Further, *L-V* curves and *J-V* curves of devices A1–A3 and B2–B3 are shown in Fig.4. It can be obtained from Fig.4 that the best performance is also observed from device A1 (B1), which is the same as device 1 in Fig.3. Besides that, both luminescence and current density are almost unchanged with the increase of CuO_x thickness, but those are decreased with increase of Cu thickness. It can be explained by that when the thickness of Cu increases, the space electric field near the CuO_x/Cu interface is enhanced, which leads to higher injection barrier.

Tab.2 Devices with different thicknesses of CuO_x and Cu in DBL

Device	Thickness (nm)	
	CuO_x	Cu
1(A1, B1)	2	2
2	4	4
3	8	8
4	12	12
A2	4	2
A3	8	2
B2	2	4
B3	2	6
0 (Compared)	/	/



(a)



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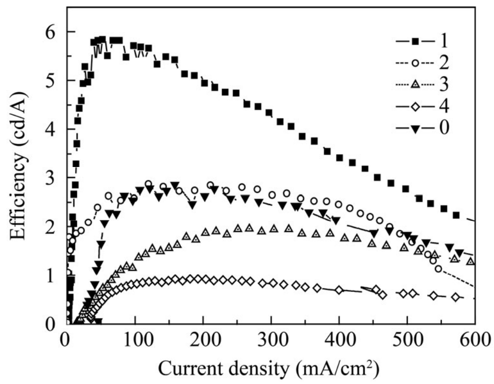
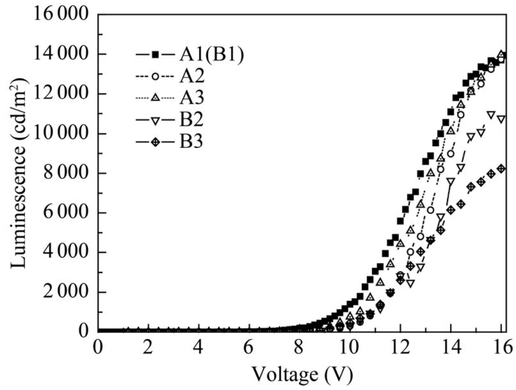
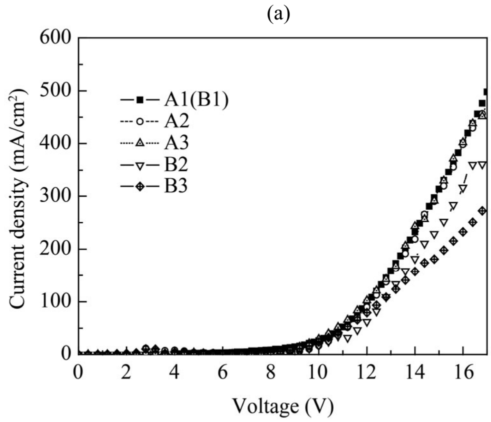


(c)

Fig.3 (a) *L-V* curves, (b) *J-V* curves and (c) *E-J* curves of devices 1–4 with different thicknesses of CuO_x and Cu



(a)



(b)

Fig.4 (a) *L-V* curves and (b) *J-V* curves of devices A1–A3 with the thickness of Cu in DBL kept as 2 nm and devices B1–B3 with the thickness of CuO_x in DBL kept as 2 nm

CuO_x/Cu dual inorganic ultra-thin layers are introduced into OLEDs as buffer layer, and a series of devices are fabricated. Both luminescence and efficiency are increased with the increase of oxidization ratio, which can be attributed to that the Fermi level of CuO_x moves close to the conduction band and leads to higher barrier with the increase of x value. The best performance is obtained from the optimized device with 2 nm-thick

$CuO_{0.94}$ and 2 nm-thick Cu dual buffer layers. The highest brightness of 14 000 cd/m^2 at current efficiency of 3 cd/A is observed at a bias of 15 V, which is about 50% higher than that of the compared device without CuO_x/Cu buffer layers. And the highest efficiency of 5.9 cd/A is achieved at 11.6 V with brightness of 3 400 cd/m^2, which is almost twice as high as that of the compared device.

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