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High-performance red organic light-emitting diodes with ultrathin Cu film as anodes

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ABSTRACT

Ultrathin Copper (Cu) films are of great research interest to the transparent conductive anodes thanks to their properties of low-cost, low electrical resistivity, high transparency in the visible spectral range, and high work function. In this paper, ultrathin Cu films were thermally deposited on glass substrates as the anodes, which show low sheet resistance of and high transmittance peaking at red spectral range. Red organic light-emitting diodes (OLEDs) with 4-(dicyanomethylene)-2-*tert*-butyl-6(1,1,7,7- tetrame thyljulolidyl-9-enyl)-4H-pyran (DCJTB) as dopant were fabricated based on the Cu anodes. With the modification of MoO_3 and light enhancement of microcavity effect, the red OLED on Cu anode achieves a maximum current efficiency of 8.85 cd/A and a maximum power efficiency of 8.63 lm/W, which is superior to that on ITO glass. Moreover, oxygen-plasma treatment on the Cu anodes has been found to be able to further increase the transmittance to 75% at 624 nm, leading to high efficiency red OLEDs without MoO_3 modification. The results may pave the way towards a low-cost and tailored transparent anode for red OLEDs in practical applications such as signal lighting and therapy applications.

1. Introduction

Since organic light-emitting diodes (OLEDs) were firstly reported by Tang and Van Slyke in 1987, indium tin oxide (ITO) has become the most commonly used anode due to its unique combination of optical transparency, moderate electrical conductivity, favorable surface properties and high work function [1–4]. Indium, however, is a rare and expensive metal. The widespread use of ITO in optoelectronic devices has strained to globe indium resources. To achieve adequate conductivity of ITO [5], high temperatures of ~300 °C were required during its deposition as well as post-deposition anneal processes, which prohibits the application of flexible plastic substrates during the roll-to-roll processing. Over the past few decades, a number of alternative materials have been developed, including conductive polymers [6,7], carbon nanotubes (CNTs) [8,9], grapheme [10,11], and random networks of metallic nanowires [12]. Most of the previous studies on anode are either expensive or difficult to process. Therefore, it is highly desirable to develop new transparent electrode materials which are inexpensive and easy to process. Ultrathin metal films with Group 11 elements (gold, silver and copper) are promising alternatives to indium tin oxide (ITO) as the transparent conductive anodes for organic light emitting diodes (OLED). In these elements, copper is the cheapest. Considering the cost of device fabrication, we choose copper as the anode. In this paper, transparent and conductive ultra-thin Cu films, which show low sheet resistance of and high transmittance peaking at red spectral range, were developed as the anode of red OLEDs. With the modification of MoO_3 and light enhancement of microcavity effect, the red OLED on Cu anode achieves a maximum current efficiency of 8.85 cd/A and a maximum power efficiency of 8.63 lm/W, which is superior to that on ITO glass. Moreover, oxygen-plasma treatment on the Cu anodes has been found to be able to further increase the transmittance to 75% at 624 nm, leading to high efficiency red OLEDs without MoO_3 modification.

2. Experimental

In our experiments, the materials used include molybdenum oxide (MoO_3), N,N′-di(naphthalene-1-yl)-N,N′–diphenyl -benzidine (NPB),

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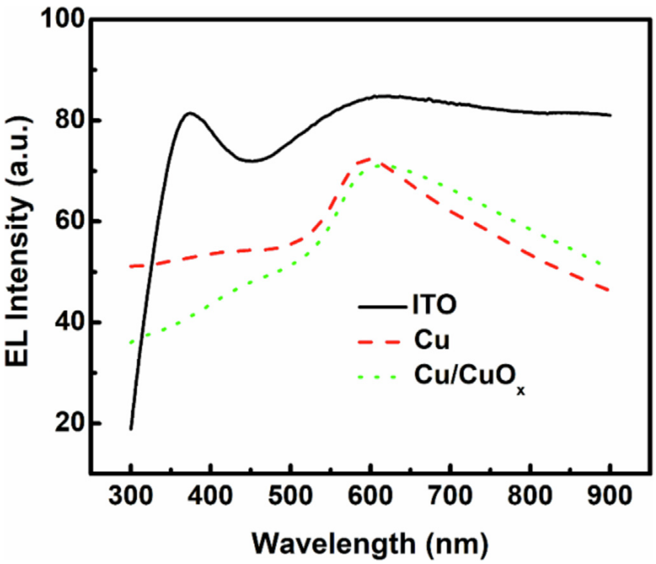

Fig. 1. Transmission spectra of ITO, Cu and Cu/CuO_x films.

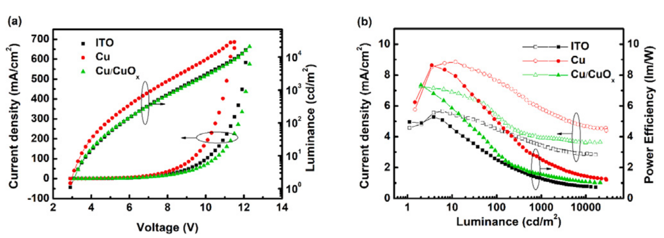

Fig. 2. Comparison of the performance of the devices with ITO, Cu, Cu/CuO_x anodes. (a) current density-voltage-luminance characteristics. (b) current efficiency-luminance and power efficiency-luminance properties characteristics.

Tris (8-hydroxyquinolinato) aluminum (Alq_3), 4-(dicyanomethylene)-2-*tert*-butyl-6(1,1,7,7- tetrame thyljulolidyl-9-enyl)-4H-pyran (DCJTB), Lithium fluoride (LiF), and Al. All the materials have the purity higher than 99% and were used without further purification. The red OLED structure used in this work was as follows. Anode/HIL/NPB (60 nm)/Alq_3:DCJTB [0.8%] (30 nm)/Alq_3 (30 nm)/LiF (1.5 nm)/Al (100 nm). The area of the light-emitting region is $4 \times 4\,mm^2$. For the control devices, commercially patterned ITO coated glass substrate with a sheet resistance of 10 Ω/□ was used as anodes. The Cu thin films with an optimized thickness of 11 nm were thermally evaporated onto the glass substrates. The Cu films were treated for an optimized time of 20 min with an oxygen-plasma to form a CuO_x film on top. Their sheet resistances measured by 4-point probe were 6.5Ω/□ and 8.4 Ω/□, respectively. Sheet resistance of the ITO, Cu and Cu/CuO_x films were measured by 4-point probe. Transmission spectra of the ITO, Cu and Cu/CuO_x films were measured by Shimadzu UV-3600 spectrophotometer. Current-brightness-voltage properties were measured by a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. Electroluminescence (EL) spectra were measured by Spectrascan PR650 spectrophotometer.

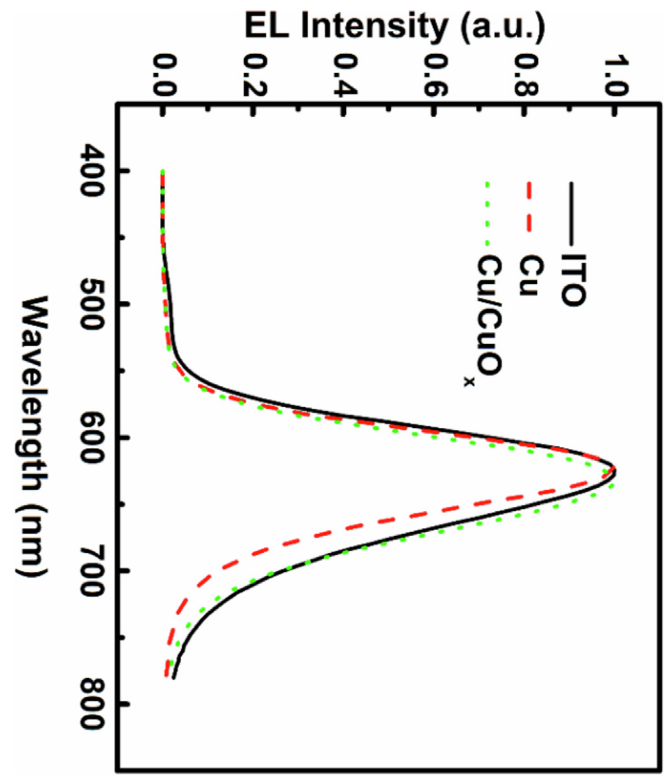

Fig. 3. EL spectra of red OLEDs with ITO, Cu and Cu/CuO_x anodes.

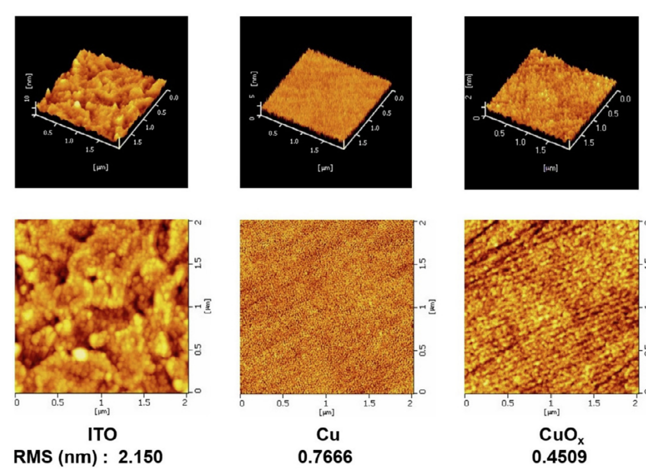

Fig. 4. AFM images and roughness of ITO, Cu and CuO_x films.

3. Results and discussion

As shown in Fig. 1, the 11 nm Cu film shows a high transmittance of 65% at 624 nm, which increased to 75% after O_2 plasma treat, thanks to the surface oxidization on top of the Cu film, while the sheet resistance increased from 6.5Ω/□ (Cu film) to 8.4Ω/□ for the Cu/CuO_x film.

Red OLEDs with Cu/MoO_3 (8 nm), Cu/CuO_x and ITO/MoO_3 (8 nm) as Anode/HIL were fabricated with the strucutre given in expreimental

Table 1
Performance summary of Devices with ITO, Cu, Cu/CuO_x anodes.

Anode	Transmittance (624 nm,%)	Sheet resistance(Ω/□)	V_{on} (V)	CE_{max} (cd/A)	PE_{max} (lm/W)
ITO	84	10.0	2.9	5.55	5.28
Cu	65	6.5	2.9	8.85	8.63
Cu/CuO_x	75	8.4	3.1	7.25	7.35

section. As depicted in Fig. 2, the performances of red OLEDs including the current density – luminance – voltage (J – L – V), current efficiency (CE) and power efficiency (PE) characteristics are compared. The key performance parameters are summarized in Table 1.

It can be seen in Fig. 2(a) that the turn-on voltages of the devices with ITO, Cu and Cu/CuO_x anodes are 2.9, 2.9 and 3.1V, respectively, exhibiting comparable turn-on voltages. The current density of the Cu/MoO_3 device is larger than those of the other two devices at the same driving voltages, which is ascribed to the lowest sheet resistance of Cu film. The CE and PE versus luminance characteristics of the three devices are shown in Fig. 2(b).

It can be clearly seen that both the devices with Cu/MoO_3 and Cu/CuO_x exhibit the obviously higher performance than that with ITO/MoO_3. For the red OLEDs on Cu/MoO_3, a maximum CE of 8.85 cd/A and maximum PE of 8.63 lm/W were achieved. For the red OLEDs on Cu/CuO_x, a maximum CE of 7.25 cd/A and maximum PE of 7.35 lm/W were achieved. That is ~59.5% and ~30.6% higher than that of ITO devices on current efficiency, respectively. The results suggest that high transmittance may not always guarantee high efficiency in red OLEDs.

Due to the similar driving voltage of the three devices, another major reason for this improvement is slightly stronger optical microcavity effect in the Cu devices than the ITO devices. Since Cu and Cu/CuO_x thin films are semitransparent, Al cathode has high reflectivity. There will be an optical microcavity between anode and cathode. Microcavity OLEDs can present essentially enhanced emission through the cavity optical axis (forward direction). Spectral narrowing is the most common phenomenon caused by microcavity effect [13]. For an optical microcavity, the spectral width of the cavity resonance can be estimated by Ref. [14],

$$\Delta\lambda = \frac{\lambda^2}{2L}\left[\frac{1-\sqrt{R_1R_2}}{\pi\sqrt[4]{R_1R_2}}\right] \quad (1)$$

where L is the effective distance of the cavity, R_1 and R_2 represent the effective reflectivity of the two reflecting mirrors. In this work, the reflectivity of Al cathode $R_1 = 0.9$ and the measured value of R_2 (the reflectivity of Cu anode) is 0.32, the spectral width is $\Delta\lambda \sim 125$ nm at $\lambda = 624$ nm. EL spectra of red OLEDs with ITO, Cu and Cu/CuO_x anodes are shown in Fig. 3.

Other than a slight red-shift (~8 nm) of the EL spectra (contrast to ITO and Cu) for Cu/CuO_x, the spectra are very similar. The full widths at half-maximum of the EL spectra are ~88 nm, ~72 nm and ~84 nm for ITO, Cu and Cu/CuO_x, respectively, which demonstrate the microcavity-effect predicted by Eq. (1). Particularly, the microcavity-effect of Cu device is a little stronger than those of other two devices. The calculated spectral width (~125 nm) is different from the experimental results in this work. It maybe because the resonance wavelength does not match the peak position of PL spectrum (DCJTB).

In order to further clarify the reasons of the three devices which have different performances, we investigated the surface morphologies of the anode films by AFM. The results are shown in Fig. 4. The mean square (RMS) of ITO, Cu and CuO_x films are 2.150 nm, 0.7666 nm and 0.4509 nm, respectively. It can be seen that the surface of CuO_x film is the smoothest among the three films, which can be attributed to the effect of oxygen-plasma treatment. The smoother anode resulted in the smoother interface between the anode and HIL, which improved the hole injection and transport, thus enhancing the device efficiency.

4. Conclusion

The high-performance red OLEDs using ultra-thin Cu films as anodes have been demonstrated. It is found that the microcavity effect and low roughness of Cu films contributes to the high performance. The easy processing of Cu films is beneficial to the mass production of OLEDs. In addition, Cu is comparatively inexpensive. It is believed that Cu provides a new avenue to a low-cost and tailored transparent anode for practical applications of red OLEDs such as signal lighting and therapy applications.

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