Aluminum/MoO_3 anode thin films: an effective anode structure for high-performance flexible organic optoelectronics*

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Abstract: We report Al/MoO_3 thin film used as a complex anode in high-performance OLEDs. The unique efficacy of the device was found to result from the enhanced injection of holes into the commonly used hole-transporting molecules due to a large reduction in the interface dipole at the anode/organic interface. The superior optical characteristics are attributed to a strong cavity effect, Due to the ease of processing Al/MoO_3 we successfully demonstrated large-area flexible OLEDs on plastic substrates with uniform emission.

Key words: organic lighting-emitting diodes; flexible; anode
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1. Introduction

Flexible device structures are extremely promising for future applications. Over the past few years, stainless-steel foil[1], ultrathin glass sheets[2] and a variety of plastic films[3, 4] have been considered as possible substrate choices for flexible OLED displays. Stainless-steel foil has very good barrier properties but encounters difficulties with multiple bends. Ultrathin glass sheets with a reinforced molecule coating may be suitable for OLED displays with preformed, curved or conformed shapes, but have limited flexibility of use and are very brittle and difficult to handle in mass production. Highly flexible plastic substrates, e.g., polyethylene terephthalate (PET) and polyethylene naphthalate, have also been used for flexible OLEDs.

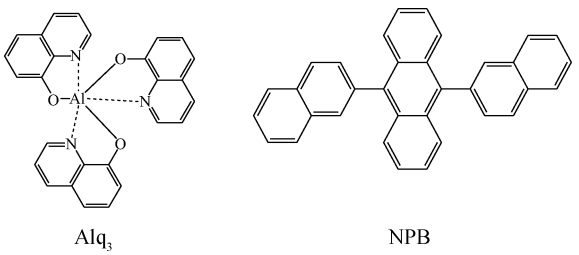
Early on, metal thin films were proposed as alternative anodes in OLEDs due to several key advantages over ITO[5]. First, the conductivity of many metals, in particular the noble metals, is nearly two orders of magnitude higher than that of ITO[6], which, as we will show, is of critical importance for large-area devices. Second, metals are easily patterned using traditional photolithography and can be deposited by using a variety of deposition techniques such as thermal evaporation, electron-beam evaporation and sputtering. Third, metals can be deposited onto large-area flexible plastic substrates using roll-to-roll processing[7]; this technique is already used in the low-cost production of thermal-control coating for windows (e.g., Pd, Pt, Au).

Despite the obvious advantages of metals, a direct drop-in replacement for ITO has yet to be demonstrated. The high reflectivity of most metals creates a strong optical microcavity between the anode and cathode. Since the reflectivity of the Al can be used to generate a strong optical cavity, the device performance can be enhanced.

In this work, we report Al thin film as a direct drop-in replacement for ITO in OLEDs. The unique combination of optical properties, high electrical conductivity, good chemical stability and ease of processing make Al/MoO_3 an interesting candidate for a new anode material in flexible OLEDs fabricated on plastic substrates.

2. Experimental details

The devices were fabricated by the thermal evaporation of the organic materials on the ITO patterned substrates. Before deposition, ITO (from CSG HOLDING CO, LTD, 20 Ω/square) was etched first, then cleaned by acetone, anhydrous ethanol, sequentially, and followed by 15 min oxygen plasma treatment. Then the substrate was transferred into a vacuum chamber for film deposition. Figure 1 shows the molecular structures of the organic materials used. The organic layers and electrode were deposited by vacuum vapor deposition at 1.0×10^{-6} Torr. The typical device structure was Al(15 nm)/MoO_3(30 nm)/NPB(60 nm)/Alq_3(65 nm)/LiF(1 nm)/Al(150 nm). Where MoO_3 is used the hole injection layer (HIL), N,N″-di(naphthalene-1-y1)-N, N″-diphenyl- benzidine(NPB) as the hole transport layer (HTL) and tris-(8-hydroxyquinoline) aluminum (Alq_3) as both an emission layer (EML) and an electron transporting layer (ETL), respectively, while LiF and Al were used as an injection layer and cathode,



Alq_3 NPB

Fig. 1. Molecular structures of main organic materials.

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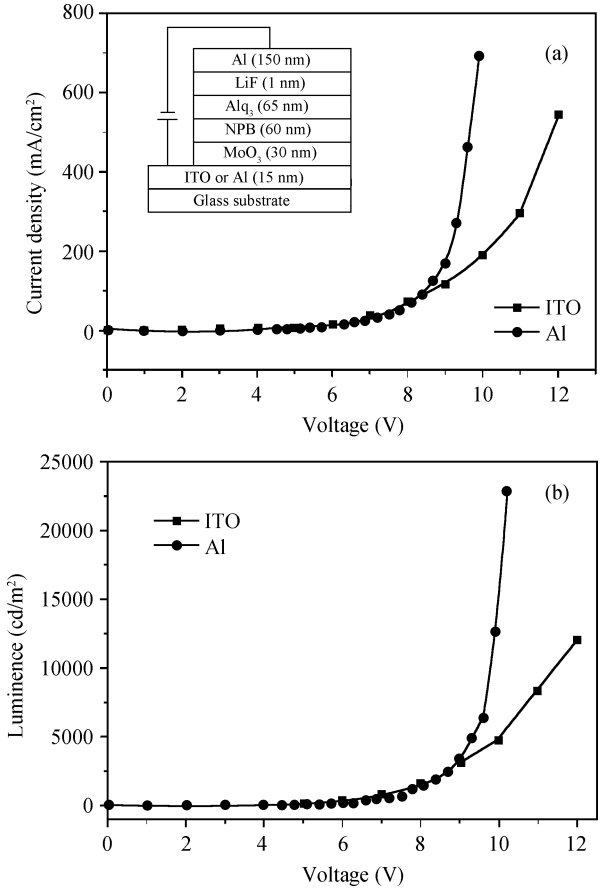

Fig. 2. Device performance characteristics of Alq_3 OLED with ITO and Al anodes. (a) Current density as a function of voltage. (b) Luminance as a function of voltage. The inset of (a) shows the device structure.

respectively.

The active area of the devices was 8×9 mm^2. The electroluminescence spectra were measured using a PR655 spectrophotometer. The luminance–current versus voltage characteristics were measured simultaneously with a Keithley 2400 voltage–current source. All measurements were carried out at room temperature under ambient conditions without encapsulation.

3. Results and discussion

Figure 2 compares the current density–voltage (J–V) and luminance characteristics of OLEDs with an Al anode in comparison to devices with a typical ITO anode. The device structure is shown in the inset of Fig. 2(a). The driving voltage at a given current density for the Al anode is found to be less than that of ITO. Figure 2(b) compares the luminescence as a function of voltage for OLEDs with Al and ITO anodes. The maximum luminance of the devices with an Al anode was 22890 cd/m^2, while for ITO it was only 12400 cd/m^2.

The unique efficacy of the device confirms that the lower barrier height and uniform morphology for MoO_3 is due to a significant reduction in the interfacial dipole at the Al/organic interface. The interaction between the oxide and the metal creates an interfacial dipole layer that modifies the work function of the pristine metal surface. This results in the organic molecules deposited on top of the oxide modified metal experiencing an effective metal work function as given by Eq. (1)[8].

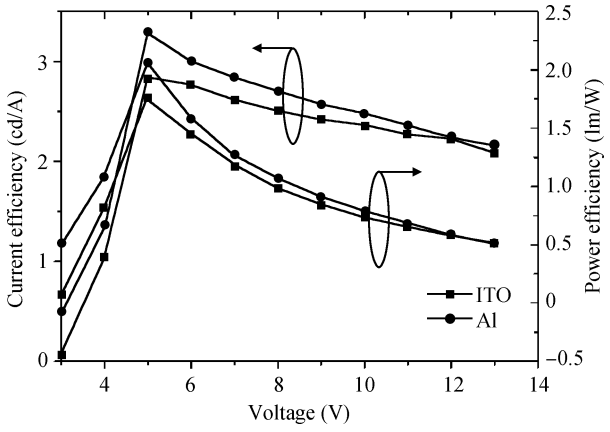

Fig. 3. Current and power efficiencies as a function of voltage characteristics of Alq_3 OLED with ITO and Al anodes.

$$\phi_{\mathrm{m,\,eff}} = \phi_{\mathrm{CNL}} + S_\phi(\phi_{\mathrm{m}} - \phi_{\mathrm{CNL}}). \tag{1}$$

Here, the interface slope parameter S_ϕ (for weakly interacting interfaces) was empirically found by Monch[9] to depend on the optical dielectric constant,

$$S_\phi = \frac{1}{1 + 0.1(\varepsilon_\infty - 1)^2}, \tag{2}$$

where ε_∞ is the optical dielectric constant (high frequency limit of the dielectric function). Monch also argued that Equation (1) should be applicable to organic semiconductors, the same as for Schottky contacts with solid xenon. A theoretical method for estimating ϕ_{CNL} for molecules has been proposed[10].

Figure 3 compares the electroluminescence (EL) efficiencies as a function of voltage for OLEDs with Al and ITO anodes. The current efficiency of the Al devices is 14% higher than that of ITO devices. Since the driving voltage of the two devices is similar, this improvement is attributed to a strong microcavity effect in the Al devices, which will be discussed in greater detail below. At high luminance (i.e., > 1000 cd/m^2) the current efficiency is 3.29 cd/A for Al. We achieved this result with only a simplified double-layer OLED structure. Clearly, the Al/MoO_3 anode structure can be used as a direct drop-in replacement for ITO.

Since Al thin films are semitransparent, an optical microcavity will be formed with the highly reflective Al cathode. Microcavity OLEDs can exhibit significantly enhanced emission along the cavity optical axis (forward direction), as well as a much narrower emission spectrum[11]. To prevent narrowing of the emission spectrum, the spectral width of the cavity resonance should be larger than the natural-emission spectrum of the emitter molecule[12]. For an optical microcavity, the spectral width of the cavity resonance is given by Eq. (3)[13].

$$\mathrm{FWHM} = \frac{\lambda_{\max}^2}{2L}\frac{1 - \sqrt{R_1 R_2}}{\pi^4\sqrt{R_1 R_2}}, \tag{3}$$

where R_1 and R_2 are the reflectivities of the mirrors and L is the effective cavity length. From Eq. (1) it is clear that a large

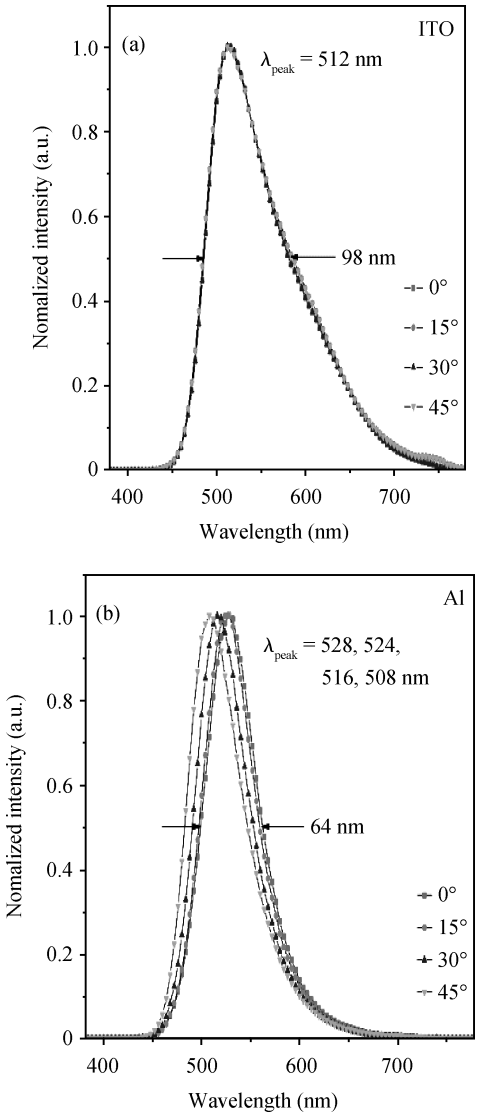

Fig. 4. Optical characteristics of Alq_3 OLEDs with and Al anodes. (a) EL spectra of ITO. (b) EL spectra of Al.

value of FWHM can be achieved by reducing the reflectivity of one of the mirrors (e.g., by using a semitransparent electrode) or by reducing the cavity length (e.g., by removing the optically thick ITO layer).

Figure 4 shows the EL spectra of Alq_3 green OLEDs with ITO and Al anodes at various emission angles under a current density of 13 mA/cm^2. Due to the microcavity effects, the Al anodes show a narrower EL spectrum with a FWHM of 64 nm in the normal direction, in comparison with that of 98 nm for the ITO anode, showing a more saturated color. In addition, as shown in Fig. 4(b), a blueshift in the spectra peak with increasing angular displacement from the normal is observed, from 528 nm as 0° to 508 nm at 45°, which confirms the strong microcavity-effect predicted by Eq. (1). What is more, the EL spectra are nearly independent of the emission angle for the ITO anode, which also confirms a strong microcavity effect.

Although the Al anode forms a strong optical microcavity, the EL intensity is still enhanced relative to ITO. The emission-enhancement factor relative to free-space emission along the optical axis of a microcavity is given by Eq. (4)[14−18].

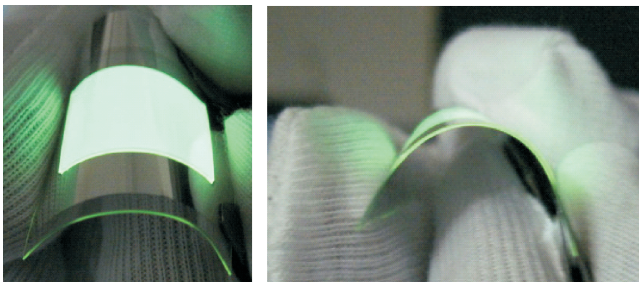

Fig. 5. Picture of operating large-area green OLEDs fabricated on flexible plastic substrate with Al anode. The size of the device is 22 × 20 mm^2.

$$G_{cav}(\lambda) = \frac{|E_2|^2}{|E_0|^2}\frac{\tau_{cav}}{\tau_0} = \left[1 - \frac{4\sqrt{R_1}\sin^2\dfrac{\phi_1 - 2kL_1}{2}}{(1+\sqrt{R_1})^2}\right] \times \frac{T_2(1+\sqrt{R_1})^2}{(1-\sqrt{R_1R_2})^2 + 4\sqrt{R_1R_2}\sin^2\dfrac{\phi_1+\phi_2-2kL}{2}} \times \frac{\tau_{cav}}{\tau_0}, \quad (4)$$

where T_2 is the transmittance of the second mirror, L_1 is the effective distance from the emission zone to the first mirror and τ_{cav} and τ_o are the radiative lifetimes in the cavity and free space, respectively. Using the above equation, Lin *et al.*[19] recently calculated a cavity-enhancement factor for microcavity OLEDs with two metal mirrors relative to a conventional OLED with an ITO anode. Based on their calculations, the Al devices with $R_1 = 0.9$ (Al cathode), $R_2 = 0.35$ and $T_2 = 0.6$ (Al anode) have an enhancement factor of 1.43 for Alq_3, consistent with the device performance (i.e., OLEDs with Al anodes had 14% higher efficiency for Alq_3). The radiative lifetime of Alq_3 in the microcavity: $\tau_{cav}/\tau_o \approx 0.9$ for Alq_3[20].

Figure 5 shows large-area (22 × 20 mm) flexible OLED on plastic using Al anodes. The device with an Al anode (Fig. 5) exhibits a significantly uniform emission. The device is free of the defects and dark spots commonly found on ITO-based devices. We have confirmed this result for multiple devices and find that the Al anode consistently yields defect-free devices on large-area substrates.

4. Conclusions

In summary, we have demonstrated the use of Al/MoO_3 as an anode in high-performance OLEDs. Combined with the enhanced EL emission as a result of a strong cavity effect, high-performance OLEDs were realized. Due to the ease of processing of Al/MoO_3 thin films we successfully demonstrated large-area flexible OLEDs on uniform plastic substrates for enabling the roll-to-roll processing of next-generation flexible organic optoelectronics for applications such as solid-state lighting.

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