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A hybrid encapsulation of organic light-emitting devices

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Abstract
A novel hybrid encapsulation for organic light-emitting devices was investigated. The hybrid encapsulation consisted of films of polyimide, titanium nitride and stainless-steel foil, and was found to greatly enhance the lifetime of the devices in air. Through optical measurements of the preservation of calcium films encapsulated with a glass cap and in hybrid encapsulation, it was found that the water and oxygen permeation rates of the hybrid encapsulation were of the same order of magnitude as that of the glass cap encapsulation. More importantly, the hybrid encapsulation is ultra-thin and flexible, making it suitable for the encapsulation of flexible organic light-emitting devices.

1. Introduction

Since the development of organic light-emitting diodes (OLEDs) operating at reasonably low voltages, organic electronics have attracted great interest due to the lower cost and new potential niches, like large-area flat displays [1, 2]. However, the short lifetime is still a critical factor. Many mechanisms have been proposed for the decay in luminance, but the dominant degradation mechanism is agreed to be the exposure of the organic–cathode interface to atmospheric oxygen and water [3, 4]. This leads to the oxidation and delamination of the metallic cathode [5]. In order to isolate OLEDs from atmospheric oxygen and water, encapsulation of OLEDs is a key technology, which is necessary to extend the lifetime. The typical encapsulation for OLEDs based on glass substrates uses a glass or metal cap with a desiccant inside [6]. Although this encapsulation is simple and quite efficient, it cannot be applied to flexible OLEDs (FOLEDs), which are built on a flexible plastic substrate. For FOLEDs, thin film encapsulation methods consisting of multi-layer barrier coatings directly deposited on the FOLEDs have been recently reported [7–15]. These encapsulations with multi-layer barrier coatings are effective in protecting the FOLED from water and oxygen, but the process of deposition of these multi-layer barrier coatings is very complicated because many organic and inorganic layers are involved in thin film encapsulations.

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In this study, a hybrid encapsulation for both OLEDs and FOLEDs was investigated, which consists of polyimide (PI), titanium nitride (TiN) and stainless-steel foil. To demonstrate the effect of this hybrid encapsulation, OLEDs based on glass substrates were fabricated with tris(8-hydroxyquinoline) aluminium (Alq) without encapsulation, with the glass cap and with hybrid encapsulation, respectively. The OLED with the hybrid encapsulation had a long operational lifetime after being exposed to atmospheric oxygen and moisture. In order to evaluate the impermeability of the hybrid encapsulation, the calcium film was encapsulated to estimate the permeability of oxygen and water with the glass cap and with the hybrid encapsulation method. By measuring the optical reflectivity of the Ca film [16], it was found that the permeability of oxygen and water in the hybrid encapsulation method is of the same order of magnitude as that with the glass cap. Furthermore, due to the stainless steel foil's thickness, which is hundreds of micrometres, the hybrid encapsulation is flexible enough to be applied to FOLEDs.

2. Experiment

Figure 1 shows a schematic diagram of the OLED with the hybrid encapsulation. The following process was used to fabricate the OLED. Indium-tin oxide (ITO)-coated glass substrates with a surface resistance of 10–20 $\Omega\,sq^{-1}$ were cleaned in ultrasonic baths of acetone and methanol. N,N′-diphenyl-N, N′-bis(1,1′-biphenyl)-4,4′-diamine (NPB) was the

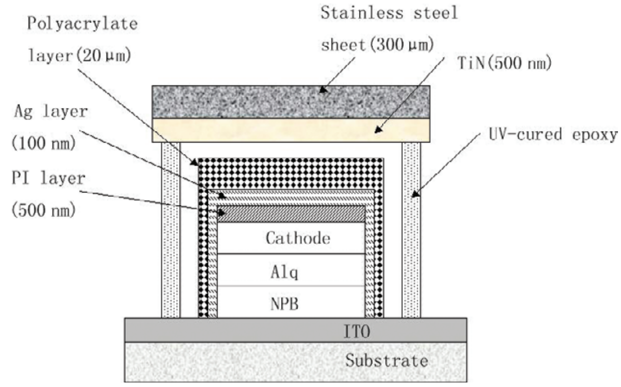

Figure 1. Schematic diagram of the OLED with hybrid encapsulation.
(This figure is in colour only in the electronic version)

hole transporting layer and Alq was the emitting layer. The cathode was an alloy or mixture of magnesium and silver with a ratio of 10 : 1. The layers of NPB, Alq and metallic cathode were all deposited by vacuum deposition (below 10^{-3} Pa). The process of the hybrid encapsulation was as follows: under a base chamber pressure below 10^{-3} Pa, the layer of PI was deposited onto the metallic cathode with a thickness of 500 nm, and a 100 nm layer of Ag was deposited above the layer of PI. Subsequently, the device was transferred to a nitrogen glove box, and a layer of acrylic monomer was spin-coated on the Ag layer of the device at 3000 rpm for 30 s. After photopolymerization of the acrylic monomer, the thickness of the polyacrylate layer was about 20 μm. Polymerization was initiated using a high-pressure mercury (Hg) lamp with an intensity of 7 mW cm^{-2} (at 366 nm). Finally, a TiN-coated stainless-steel foil was used to seal the device outside. The TiN film was 500 nm thick and the stainless-steel foil was 300 μm thick. A thin bead of epoxy adhesive was applied from a syringe around the edge of the device and between the substrate and the TiN-coated stainless-steel foil.

3. Results and discussion

In order to evaluate the effect of the hybrid encapsulation, OLEDs without encapsulation, with the hybrid encapsulation and with the glass cap were fabricated to compare their luminescence and the degradation of their emission efficiency. Figures 2(*a*) and (*b*) show the current–voltage (I–V) and luminance–voltage (L–V) characteristics to compare the electrical and emissive behaviour of the devices without encapsulation, with hybrid encapsulation and with glass cap encapsulation. As shown in figures 2(*a*) and (*b*), no notable difference in L–V or I–V behaviour was found among these three cases. The operational lifetimes of the fabricated devices were measured from the initial luminance of about 610 cd m^{-2} to half of the initial value at a constant dc current. For comparison, the lifetimes of devices without encapsulation, with hybrid encapsulation and with glass cap encapsulation were investigated, as shown in figure 2(*c*). The device without encapsulation had a very short lifetime of about 2.5 h in ambient conditions. This was because the reactive metal (metallic cathode) and organic layers are susceptible to moisture and oxygen, so the device could not withstand the ambient conditions for long. The lifetimes of the devices with hybrid encapsulation and glass cap encapsulation were about 64 h and 61 h, respectively, as shown in figure 2(*c*). This shows that both these methods of encapsulation could effectively protect devices from moisture and oxygen, and prolong the operational lifetime of devices. Of course, in addition to encapsulation, the lifetime of OLEDs could be affected by many factors such as the structure of the OLED, substrate treatment (especially for substrate coated ITO), doping in the hole transport layer or emission layer and so on. In our experiment, however, the equipment and atmosphere for fabrication of the OLEDs were limited, so the lifetime of OLEDs with glass cap encapsulation would be shorter than the reported one.

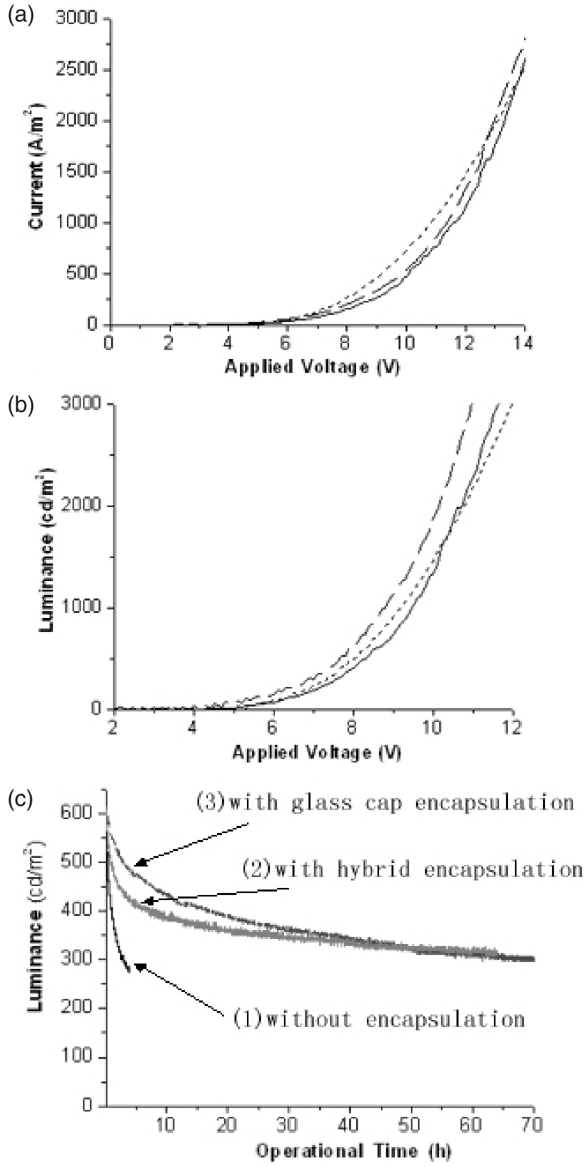

Figure 2. (*a*) and (*b*) show the I–V and L–V characteristics of OLEDs without encapsulation (· · · · · ·), with hybrid encapsulation (- - - -) and with glass cap encapsulation (——); (*c*) shows the operational lifetime of OLEDs (1) without encapsulation, (2) with hybrid encapsulation and (3) with glass cap encapsulation.

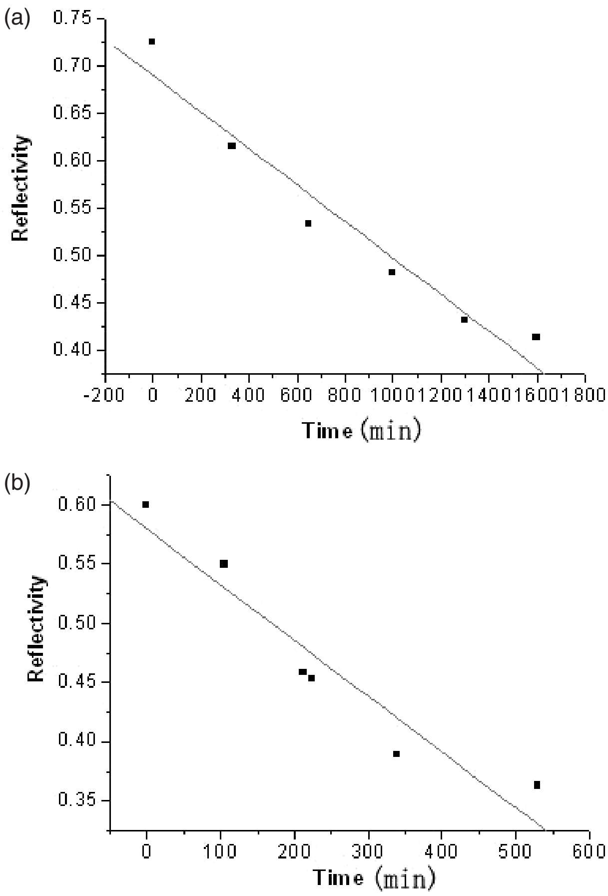

Figure 3. Decrease in optical reflectivity of the calcium film with time: (*a*) shows the calcium film with glass cap encapsulation and (*b*) shows the calcium film with hybrid encapsulation.

In order to accurately evaluate the quality of the glass cap and hybrid encapsulation, we used a calcium testing method to compare the permeation rate of oxygen and moisture for both types of encapsulations [16–19]. The test was based on the observation of optical transmission (reflectivity) of a thin film of calcium, which is easily oxidized by water and oxygen. In our experiment, a film of calcium with a thickness of 100 nm was encapsulated using glass encapsulation and hybrid encapsulation, respectively. After the encapsulation the calcium film was exposed to air, and we simultaneously measured the decrease of optical reflectivity of the calcium film with time due to the oxidation of calcium caused by permeation of water and oxygen. Figures 3(*a*) and (*b*) show the change in optical reflectivity of the Ca film with time with glass cap and hybrid encapsulations, respectively. Because the decrease in optical reflectivity of the Ca film results from the oxidation of the Ca film by the permeating water and oxygen, we assume that the derivative of the optical reflectivity of the Ca film is proportional to the permeation rate of oxygen and water, shown as follows:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = KV_\mathrm{p}, \qquad (1)$$

where R is the optical reflectivity, K is a constant, V_p is the permeation rate of oxygen and water, and t is the time. For simplicity, the linear relation between the optical reflectivity R of the Ca film and time t is assumed to be

$$R = A + Bt \qquad (2)$$

where A and B are constant. From equations (1) and (2), we can obtain

$$\frac{\mathrm{d}R}{\mathrm{d}t} = B = KV_\mathrm{p}.$$

Using equation (2) to fit the data in figures 3(*a*) and (*b*), we get

$$B_\mathrm{g} = KV_\mathrm{g\text{–}p} = -0.0116, \qquad (3)$$

$$B_\mathrm{h} = KV_\mathrm{h\text{–}p} = -0.0283, \qquad (4)$$

where B_g and B_h are the slopes in figures 3(*a*) and (*b*), respectively. $V_\mathrm{g\text{–}p}$ and $V_\mathrm{h\text{–}p}$ are the permeation rates of oxygen and water with the glass cap and hybrid encapsulation, respectively. From equations (3) and (4), we can get $V_\mathrm{h\text{–}p}/V_\mathrm{g\text{–}p} \approx 2.44$. This shows that the permeation rates of oxygen and water by hybrid encapsulation is of the same order of magnitude as that by glass cap encapsulation. The hybrid encapsulation presented in this paper is lightweight and ultra-thin in contrast to the glass cap encapsulation, and the process of fabrication of the hybrid encapsulation is simple and stable.

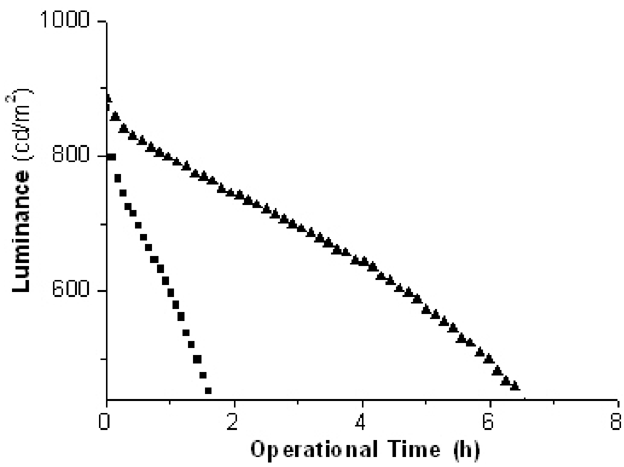

Figure 4. Operational lifetime of FOLEDs on a PET substrate without encapsulation (■) and with hybrid encapsulation (▲).

The most important advantage of the hybrid encapsulation is its flexibility. Because the stainless-steel foil is only 300 μm thick, it bends easily. Figure 4 shows the ageing characteristics of FOLEDs on a polyethylene terephthalate (PET) substrate. The lifetime of FOLEDs without encapsulation is about 1.6 h and the operational lifetime of FOLEDs with hybrid encapsulation is increased to 6.5 h. The results show that the hybrid encapsulation is suitable for the FOLEDs and can be effective in prolonging the operational lifetime of the device.

4. Conclusion

In summary, a hybrid encapsulation for OLEDs was demonstrated. This encapsulation method was found to effectively enhance the lifetime of OLEDs on a glass substrate and FOLEDs on a PET substrate. Although the lifetime of devices with the hybrid encapsulation was short owing to the limited experimental conditions, the hybrid encapsulation is lightweight, ultra-thin and flexible compared with glass cap encapsulation. Furthermore a Ca test proved that the water and oxygen permeation rates of the hybrid encapsulation were of the same order of magnitude as that of glass cap encapsulation, which shows the application potential of this hybrid encapsulation.

Acknowledgments

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