Thin Film Encapsulation of Light-Emitting Diodes with Photopolymerized Polyacrylate and Silver Films *

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A thin film encapsulation of organic light-emitting diodes (OLEDs) is investigated with a multi-layer stack of polyacrylate-Ag-polyacrylate-Ag-polyacrylate-Ag-polyacrylate (PAPAPAP). It is shown that the fabrication of polyacrylate films by a wet process does not affect the electroluminescent (EL) characteristics of the devices and polyacrylate films together with the silver layers can perform to minimize oxygen and water diffusion into the organic light-emitting device. The structure of polyacrylate(20 μm)-Ag(200 nm)-polyacrylate(20 μm)-Ag(200 nm)-polyacrylate(20 μm)-Ag(200 nm)-polyacrylate(20 μm) is demonstrated to enhance dramatically the lifetime of OLEDs.

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Since the development of organic light-emitting diodes (OLEDs) operating at reasonably low voltages, organic electronics has attracted great interest due to lower costs and new potential applications, such as large-area flat displays.[1−3] However, short lifetime is still a critical factor. There have been many proposed mechanisms for the decay in luminance, but the dominant degradation mechanism is consistently known as the exposure of the organic-cathode interface to atmospheric oxygen and water.[4,5] This leads to the oxidation and delamination of the metallic cathode.[6] In order to isolate OLEDs from atmospheric oxygen and water, encapsulation of OLEDs is a key technology necessarily to extend the lifetime. The typical encapsulation for OLEDs based on glass substrates uses a glass or metal cap with a desiccant inside.[7] Although this encapsulation is simple and quite efficient, it is heavy and cannot be bent, thus severely limiting the applications of OLEDs, and it cannot be applied to flexible organic light-emitting diodes (FOLEDs), which are built on a flexible plastic substrate. For thin, light and flexible encapsulation of OLEDs, many thin film encapsulation methods have been developed recently.[8−15] Researchers[8−10] have reported a thin film encapsulation technique for OLEDs named as Barix^{TM}, which is based on the flash evaporation and sputtering deposition process. Lifka *et al.*[11] and Assche *et al.*[12] show the thin film encapsulation based on the plasma enhanced chemical vapour deposition. Although these encapsulations are quite effective to prevent the devices from the water and oxygen, the encapsulation process is also quite complicated. In this study, a thin film encapsulation for OLEDs is developed with a novel multi-layer stack of polyacrylate–Ag–polyacrylate–Ag–polyacrylate–Ag–polyacrylate (PAPAPAP).

The polyacrylate film was fabricated by spin-coating, and the Ag film was deposited by thermal evaporation, so the encapsulation with the stack of PAPAPAP is quite easy to be carried out. The lifetime of OLEDs with the encapsulation with the stack of PAPAPAP was greatly prolonged in air.

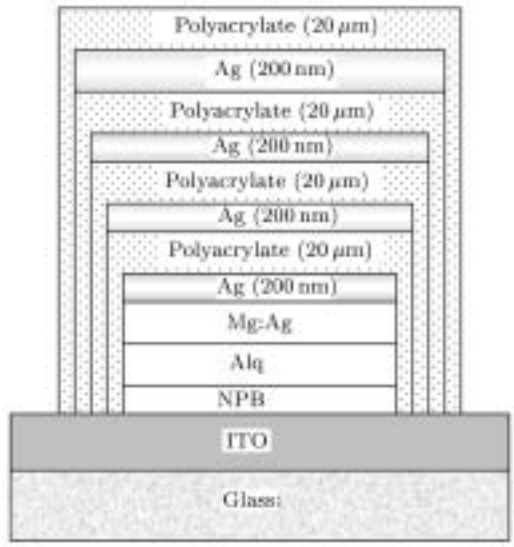

Fig. 1. Schematic diagram of the OLED with encapsulation of a PAPAPAP stack.

Figure 1 shows a schematic diagram of the OLEDs with the stack encapsulation. The following process was used to fabricate the devices. Indium-tin-oxide

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(ITO)-coated glass substrates with a surface resistance of 10–20Ω/sq were cleaned in ultrasonic baths of acetone and methanol. N,N-diphenyl-N,N-bis (1,1-biphenyl)-4,4′-diamine (NPB) was the hole transporting layer and tris(8-hydroxyquinoline) aluminium (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). Light cure adhesive (Loctite 352), which was monomers of acrylic acid and methacrylate ester, was purchased by Loctite Co., Ltd. The process of the stack encapsulation was as follows: step 1, under a base chamber pressure below 10^{-3} Pa, the layer of Ag was deposited onto the metallic cathode with a thickness of 200 nm; step 2, the device was transferred to a nitrogen glove box, and a layer of monomers of acrylic acid and methacrylate ester was spin-coated on the Ag layer of the device at 3000 rpm for 30 s. After photopolymerization of the monomers, the polyacrylate layer was formed with thickness of about 20 μm. Polymerization was initiated using a high-pressure mercury (Hg) lamp with intensity of 7 mW/cm^2 at 366 nm. Then steps 1 and 2 were repeated four times. At last, the multi-layer stack of encapsulation is polyacrylate–Ag–polyacrylate–Ag–polyacrylate–Ag–polyacrylate.

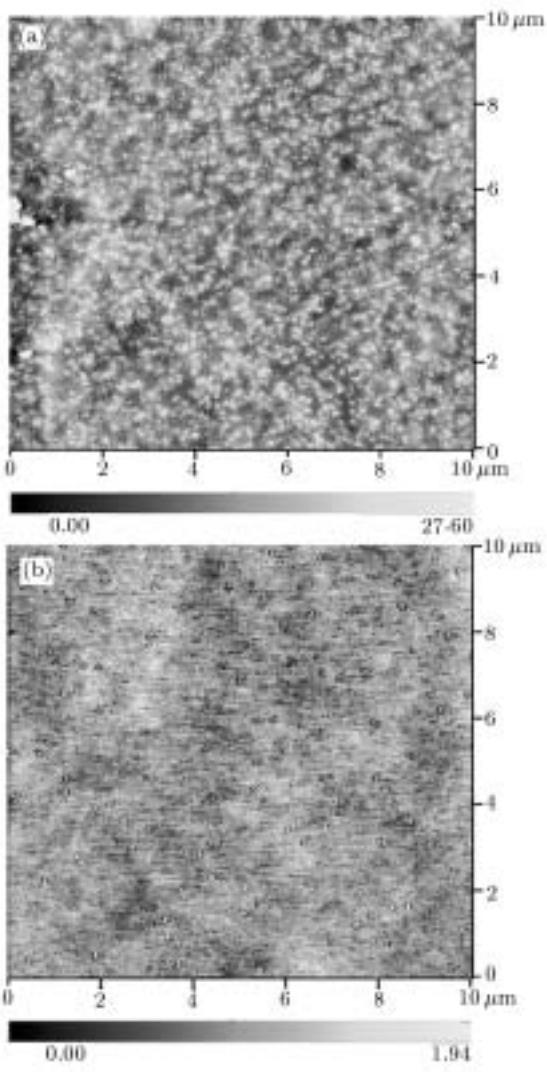

Fig. 2. AFM images of surfaces of (a) the PET substrate (rms roughness 3.963 nm) and (b) the polyacrylate film (rms roughness 0.2599 nm) by the spin-coating method.

Morphology of the polyacrylate film by spin coating has been investigated. It is clear that a smooth surface of polyacrylate film is quite necessary for the PAPAPAP stack. Figures 2(a) and 2(b) show the surface morphology of a commercially available polyethylene terphthalate (PET) substrate and the polyacrylate film on PET by spin coating, respectively. It is obvious that the surface of PET is somehow rough, and there are some spikes higher than tens of nanometres observed in Fig. 2(a). A thin film of the acrylic monomer was spin-coated on the PET at 3000 rpm for 30 s, and was immediately cured to yield a highly cross-linked polyacrylate film. The surface morphology of the thin polyacrylate film was shown in Fig. 2(b). It was found that the fabrication and curing of the liquid monomer resulted in a flexible and smooth polymer film, which is non-conformal to the substrate. In Fig. 2, the rms surface roughness of PET is 3.963 nm, but rms roughness of the thin polyacrylate film on PET is 0.2599 nm. This indicates that the formed polyacrylate film is quite smooth. The water permeation rate of the highly cross-linked polyacrylate film is quite high and is tens of g/m^2 per day,[16] so we adopted the stack of polyacrylate films and inorganic films to encapsulate the OLEDs, and Ag was chosen to form the inorganic films owing to its easy fabrication by thermal evaporation.

In order to evaluate the effect of the stack encapsulation with polyacrylate films and Ag films, OLEDs without encapsulation, with encapsulation of a polyacrylate–Ag–polyacrylate (PAP) stack and with encapsulation of a PAPAPAP stack were fabricated to compare their luminescence and degradation of emission efficiency, respectively. Figures 3(a) and 3(b) show the current–voltage (I–V) and luminance–voltage (L–V) characteristics to compare the electrical and emissive behaviour of different devices. As shown in Figs. 3(a) and 3(b), no notable difference in the L–V or I–V behaviour was found among these three devices. These show that when the photopolymerizable blend is cured to form the polyacrylate film, both the light-emitting material and the metallic cathode were slightly affected by photopolymerization, and encapsulation process did not change the electrical and the emission properties of OLEDs.

The operational lifetimes of the fabricated devices

were measured from the initial luminance of about 1000 cd/m^2 to half of the initial value at a constant dc current. For comparison, the lifetimes of devices without encapsulation, with encapsulation of the PAP stack and with encapsulation of the PAPAPAPA stack were investigated, as shown in Fig. 4. The device without encapsulation has a very short lifetime of about 2.5 h under ambient conditions. This is 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 a long time. The lifetimes of the devices with encapsulation of the PAP stack and with encapsulation of the PAPAPAP stack were about 24.5 hours and 107 hours respectively, as shown in Fig. 4. This shows that encapsulations with stack of polyacrylate films and Ag films could be effective to protect the devices from the moisture and oxygen, and to prolong the operational lifetime of the devices. The lifetime of OLEDs with encapsulation of the PAPAPAP stack was almost 43 times longer than the bare device, and four times longer than the device with encapsulation of the PAP stack. Assuming that the operational lifetime is inversely proportional to the initial luminance,[17] the lifetime of OLEDs with encapsulation of the PAPAPAP stack was larger than 1000 h at 100 cd/m^2.

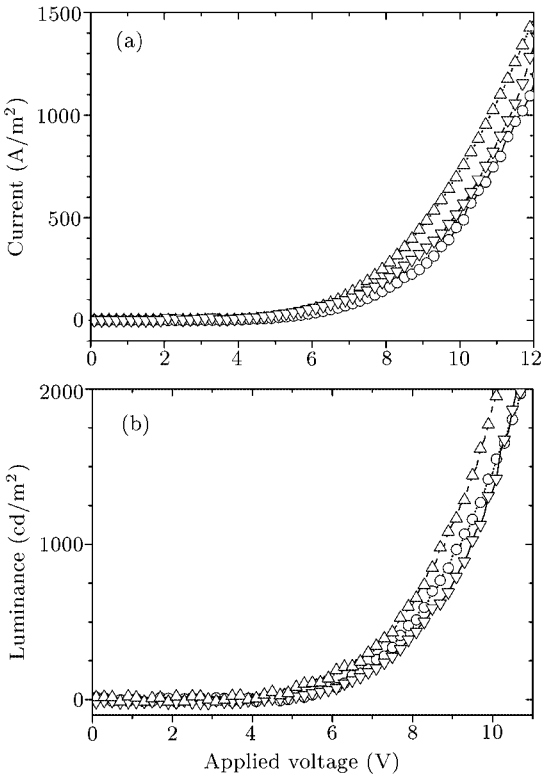

Fig. 3. (a) I–V and (b) L–V characteristics of OLEDs without encapsulation (down-triangles), with encapsulation of PAP stack (up-triangles), and with encapsulation of PAPAPAP (circles).

As is well known, in addition to encapsulation, the lifetime of OLEDs could be affected by many factors such as the structure of OLEDs, substrate treatment (especially for the ITO coated substrate), doping in hole transport layer or emission layer and so on.[18,19] In our experiment, the structure of OLEDs was ITO/NPB/Alq/Mg:Ag, and the operational lifetime of this OLED with encapsulation of the PAPAPAP stack was larger than 1000 h, which was comparable with that of the OLED based on the similar structure with the glass cap encapsulation.[20] More importantly, the encapsulation of the PAPAPAP stack is flexible, quite light and thin, and is suitable for flexible OLEDs. Because the total thickness of encapsulation is often less than 100 μm, the PAPAPAP stack can also be used as the pre-encapsulation layers for the glass cap encapsulation for more longevity of OLEDs based on glass substrates.

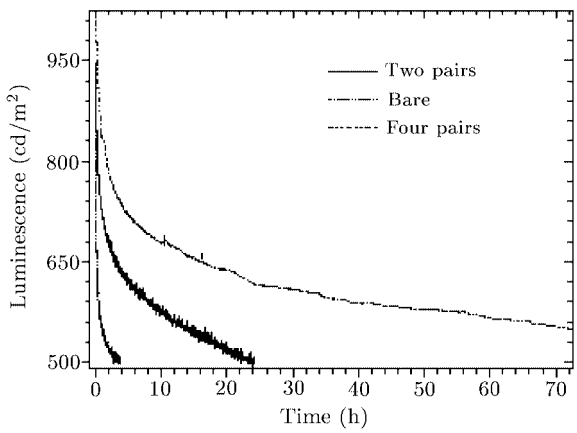

Fig. 4. Operational lifetime of OLEDs (1) without encapsulation, (2) with encapsulation of the PAP stack, and (3) with encapsulation of the PAPAPAP stack.

In conclusion, we have demonstrated a thin film encapsulation with a PAPAPAP stack for OLEDs, and have shown the fabrication of polyacrylate films by spin-coating. It is found that the encapsulation of the PAPAPAP stack is efficient in protecting OLEDs from the water and oxygen and is helpful to prolong its operational lifetime. The lifetime of OLEDs with encapsulation of the PAPAPAP stack was 43 times longer than the bare device. More importantly, the encapsulation layer of the PAPAPAP stack was lightweight, thin and flexible, which has potential applications in encapsulation for flexible OLEDs or as pre-encapsulation for conventional OLEDs.

References

[1] Tang C W and van Slyke S A 1987 *Appl. Phys. Lett.* **51** 913

[2] Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackey K, Friend R H, Burns P L and Holmes A B 1990

Nature **347** 539
[3] Wu Z X, Wang L D and Qiu Y 2004 *Chin. Phys. Lett.* **21** 1370
[4] Aziz H, Popovic Z, Tripp C P, Hu N, Hor A and Xu G 1998 *Appl. Phys. Lett.* **72** 2642
[5] Lin K K, Chua S J and Lim S F 2001 *J. Appl. Phys.* **90** 976
[6] Liew Y F, Aziz H, Hu N X, Hu H, Chan H, Xu G and Popovic Z 2000 *Appl. Phys. Lett.* **77** 2650
[7] Burrows P E, Bulovic V, Forrest S R, Sapochak L S, McCarty D M and Thompson M E 1994 *Appl. Phys. Lett.* **63** 2922
[8] Weaver M S, Michalski L A, Rajan K, Rothman M A, Silvernail J A, Burrows P E, Graff G L, Gross M E. Martin P E, Hall M, Mast E, Bonham C, Bennett W and Zumhoff M 2000 *Appl. Phys. Lett.* **81** 2929
[9] Chwang A B, Rothman M A, Mao S Y, Hewitt R H, Weaver M S, Silvernail J A, Rajan K, Hack M, Brown J J, Chu X, Moro L, Krajewski T and Rutherford N 2003 *Appl. Phys. Lett.* **83** 413
[10] Burrows P E, Graff G L, Gross M E. Martin P M, Shi M K, Hall M, Mast E, Bonham C, Bennett W and Sullivan M B 2001 *Displays* **22** 65
[11] Lifka H, van Esch H A, Rosink J J W M 2004 *Proc. SID: 2004 International Symposium* vol XXXV p 1384
[12] Assche F J H V, Vangheluwe R T, Maes J W C, Mischke W S, Bijker M D, Dings F C, Evers M F J, Kessels W M M, van de Sanden M C M 2004 *Proc. SID: 2004 International Symposium* vol XXXV p 695
[13] Kwon S H, Paik S Y, Kwon O J and Yoo J S 2001 *Appl. Phys. Lett.* **79** 4450
[14] Zyung T H, Hwang D H and Jung S D 2000 *United States Patent* (No 6150187)
[15] Affinito J D, Eufinger S, Gross M E, Graff G L and Martin P M 1997 *Thin Solid Films* **308** 19
[16] Kim G H, Oh J, Yang Y S, Do L and Suh K S 2004 *Polymer* **45** 1879
[17] Kwon R C, Nugent M R, Michalski L, Ngo T, Rajan K, Tung Y J, Weaver M S, Zhou T X, Thompson M E, Forrest S R and Brown J J 2002 *Appl. Phys. Lett.* **81** 162
[18] Shia J and Tang C W 1997 *Appl. Phys. Lett.* **70** 1665
[19] Popovic Z D, Xie S, Hu N, Hor A, Fork D, Anderson G and Tripp C 2000 *Thin Solid Films* **363** 6
[20] Burros P E, Bulovic V, Forrest S R, Sapochak L S, McCarty D M and Thompson M E 1994 *Appl. Phys. Lett.* **65** 2922