Organic Electronics 13 (2012) 388–393

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Vacuum-free lamination of low work function cathode for efficient solution-processed organic light-emitting diodes

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ARTICLE INFO

Article history:
Received 30 May 2011
Received in revised form 6 November 2011
Accepted 17 November 2011
Available online 16 December 2011

Keywords:
Lamination
Polyethylene glycol
Low work function

ABSTRACT

The low work function cathode of blade-coated organic light-emitting diode is transferred from a soft polydimethylsiloxane (PDMS) mold by lamination without vacuum. The cathode is a bilayer of polyethylene glycol (PEG) (<10 nm) and Al (100 nm). A sacrificial layer of polystyrene with low Mw 1500 and melting point of 120 °C is inserted between the cathode and PDMS for the subsequent mold removal at 150 °C by melting polystyrene. Current efficiency of 3 cd/A (1.1%) and luminance of 2500 cd/m^2 are achieved for green polyfluorene fluorescent emitter. 25 cd/A (8.2%) and 3200 cd/m^2 are achieved for green phosphorescent tris[2-(*p*-tolyl)pyridine]iridium(III) (Ir(mppy)$_3$) emitter in polymer blend host. The efficiency is about 70% of the devices with thermally evaporated cathode. The turn-on voltage is about 5 V higher.

1. Introduction

One of the great advantages of organic semiconductor is the possibility to make large-area devices by solution process at low cost. The active polymer or small-molecule semiconductors can be deposited on indium-tin-oxide (ITO) glass as a large thin film by spin coating, ink-jet lamination, slot die coating, or blade coating [1,2] for organic light emitting diode (OLED) as well as solar cell. The top electrode, however, in general requires the slow vacuum evaporation which becomes the bottleneck for the high volume fabrication. Vacuum-free lamination of top metal contact for solution-processed OLED and polymer solar cell is therefore a key subject. The lamination of anode is relatively easy because many conductors with high work function are stable by itself. For example Au [3] and poly-(3,4-ethylenedioxythiophene) doped with poly-(styrenesulfonate) (PEDOT:PSS) anode [4] are printed on the active layer in inverted polymer solar cell. Cathode lamination is more challenging because of the low work function and high reactivity. In most of the high-efficiency OLED structure the cathode is on the top, and the demand on low work function is greater than solar cell. The vacuum-free cathode lamination has three requirements. (1) The resulting contact has a low enough work function for electron injection. (2) It does not depend on chemical reactions as in the common cases of evaporated LiF or CsF where the alkaline metal ions are released by reactions during vacuum deposition [5]. (3) The material should not be very sensitive to water and moisture as the case of Cs_2CO_3 [6], since it is not deposited in the high vacuum in the evaporation chamber. Printed Au has been reported as the cathode for OLED, but the high work function around

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doi:10.1016/j.orgel.2011.11.008

5.0 eV gives poor external quantum efficiency around 0.6% [7]. Mg/Ag is also printed as the cathode, the work function around 3.8 eV is still not low enough and the resulting external quantum efficiency is only 0.16% [8].

In order to realize cathode lamination for organic devices with low work function and high stability, in this work we use PEG/Al as the cathode. The HOMO level of PEG and the work function of PEG/Al measured by air photo-emission are 5.55 eV and 3.55 eV. Due to the formation of Al–O bond photovoltaic measurement shows that the work function of Al is significantly reduced by a thin layer of polyethylene glycol (PEG) on top of the active layer [9]. Performance of OLED with vacuum evaporation of Al on top of PEG suggests a work function comparable to that of Ca and LiF/Al which is about 2.9 eV [10]. Instead of evaporation we use lamination of PEG/Al, previously deposited on a soft polydimethylsiloxane (PDMS) mold, on the active layer of OLED. The PDMS layer is subsequently removed by the melting of a sacrificial polystyrene inter-layer between the cathode and the PDMS mold. The molecular weight of polystyrene is deliberately chosen to be low in order to give a low melting point which is crucial for high reproducibility and integrity of printed cathode after mold removal.

The efficiency of our OLED is much higher than the previous report on printed cathode. Multi-layers of organic semiconductors are deposited by blade coating without dissolution [1,2]. For green fluorescent device the external quantum efficiency is 1.1% with peak luminance of 2500 cd/m^2, for green phosphorescent device the quantum efficiency is 8.2% with peak luminance of 3500 cd/m^2. Because no highly reactive metals like Li, Cs, or Ca are involved, the OLED show remarkable stability in air exposure after the PDMS mold removal. All device data are taken without encapsulation, in sharp contrast to the ordinary OLED with vacuum deposited cathode. Even though Al on PDMS still requires vacuum deposition, it can be made separately with high volume in advance and will not be a limit of the OLED process throughput. With such PEG/Al lamination method OLED and organic solar cell with reasonable efficiency can be made by good reproducibility and stability entirely free of vacuum process.

2. Experimental

Before the cathode lamination the OLED is in two separate parts. One is on ITO glass substrate and the other is on elastomeric silicon rubber substrate. The ITO glass is cleaned with neutral detergent, acetone, and isopropyl alcohol, followed by ultraviolet ozone treatment for 15 min. A 500 Å layer of poly-(3,4-ethylenedioxythiophene) doped with poly-(styrenesulfonate) (PEDOT:PSS, CLEVIOS™ P VP AI4083) is spin coated at 2000 rpm on the ITO glass, then annealed at 200 °C for 15 min in air. Poly [(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(*N*-(4-sec-butylphenyl)) diphenylamine)] (TFB, American Dye Source ADS259BE) dissolved in toluene with 1 wt.% is spin coated on the PEDOT:PSS surface as the hole transport layer (HTL), then annealed at 180 °C for 40 min. TFB is finally spin-rinsed by toluene to remove the dissolvable part, whereas

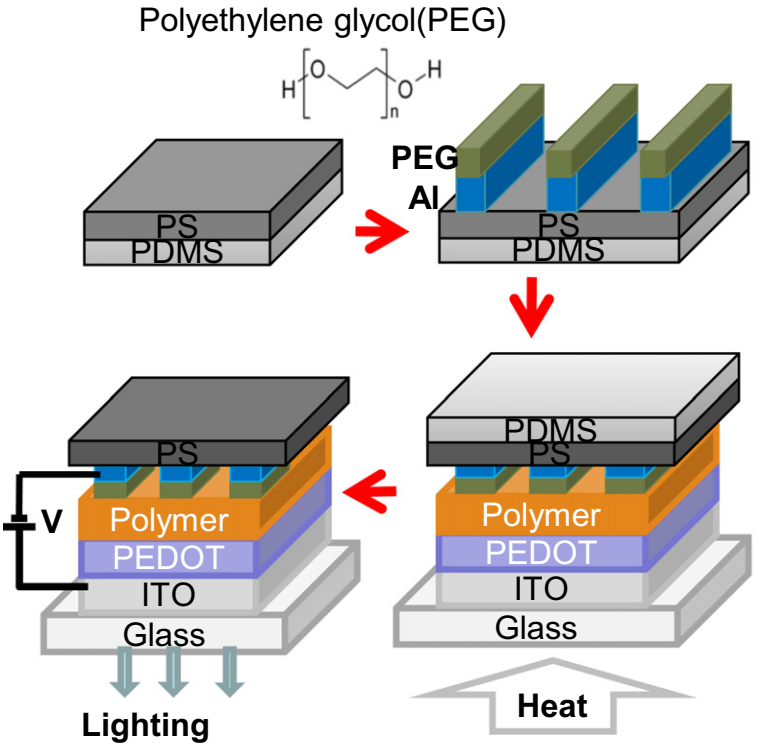

Fig. 1. The procedure of lamination process.

the remaining thickness is below 10 nm. Both green fluorescent and phosphorescent emissive layers are deposited by blade coating on TFB [11]. For fluorescence, polyfluorene derivative (Green B by Dow Chemical) dissolve in toluene with 1.2 wt.% is blade coated with 60 μm blade gap followed by spinning at 4000 rpm, resulting in 55 nm solid film. Green B film is then annealed at 130 °C for 30 min in vacuum. For phosphorescence the emission layer is a blend of tris[2-(*p*-tolyl)pyridine]iridium(III) ($Ir(mppy)_3$), *N*,*N*′-bis (3-methylphenyl)-*N*,*N*′-bis(phenyl)-benzidine (TPD), 2-(4-Biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and poly(vinylcarbazole) (PVK, Mw = 1,100,000) in the weight ratio of 6:9:24:61. The blend in chlorobenzene with 2 wt.% is blade coated with 60 μm gap followed by spinning at 5000 rpm then annealed at 80 °C for 60 min in vacuum, resulting in film thickness of 60 nm. The electron transport layer (ETL), 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBI) is dissolved in methanol with 0.5 wt.% and deposited onto the phosphorescent emissive layer by blade coating with 60 μm gap followed by spinning at 3500 rpm, resulting in 20 nm thickness. Multi-layer of organic semiconductors can be made by such blade coating method without dissolution [1,2,11]. For the elastomeric substrate, a thermally stable silicon rubber polydimethylsiloxane (PDMS, Dow Corning Sylgard 184) is used. The PDMS precursor is drop cast on the flat glass and cured at 80 °C for 1 h, resulting in rubber mold thickness of 0.6 mm. The PDMS mold is treated by oxygen plasma to make the surface hydrophilic. In order to transfer the cathode onto the other part, a sacrificial polystyrene (PS) layer is deposited by spin coating in chlorobenzene with 25 wt.% at 800 rpm on plasma-treated PDMS surface. The PS layer is annealed at 80 °C for 20 min, resulting in thickness about 1 μm. Three molecular weights Mw of 280,000, 35,000, and 1200 of polystyrene are used. Over the sacrificial polystyrene layer 1000 Å of Al is thermally evaporated under 10^{-6} torr with a rate of 2 Å/s. Finally polyethylene glycol (PEG) shown in Fig. 1 is dissolved with 0.3 wt.% in methanol then spin coated at 5000 rpm on Al, followed by annealed at 40 °C for 10 min. The PEG thickness is below 10 nm.

The transfer process of PEG/Al cathode to the other part of the device is illustrated in Fig. 1. The ITO glass part with organic film and PDMS part with PEG/Al cathode are laminated in nitrogen glove box. van der Waals force pulls them together when the two surfaces are in contact. The laminated device is then placed on a hot plate at 150 °C for 15 min without any external pressure other than gravity. The glass part is on the upper side for subsequent easy detachment of the PDMS mold from the rest of the sample.

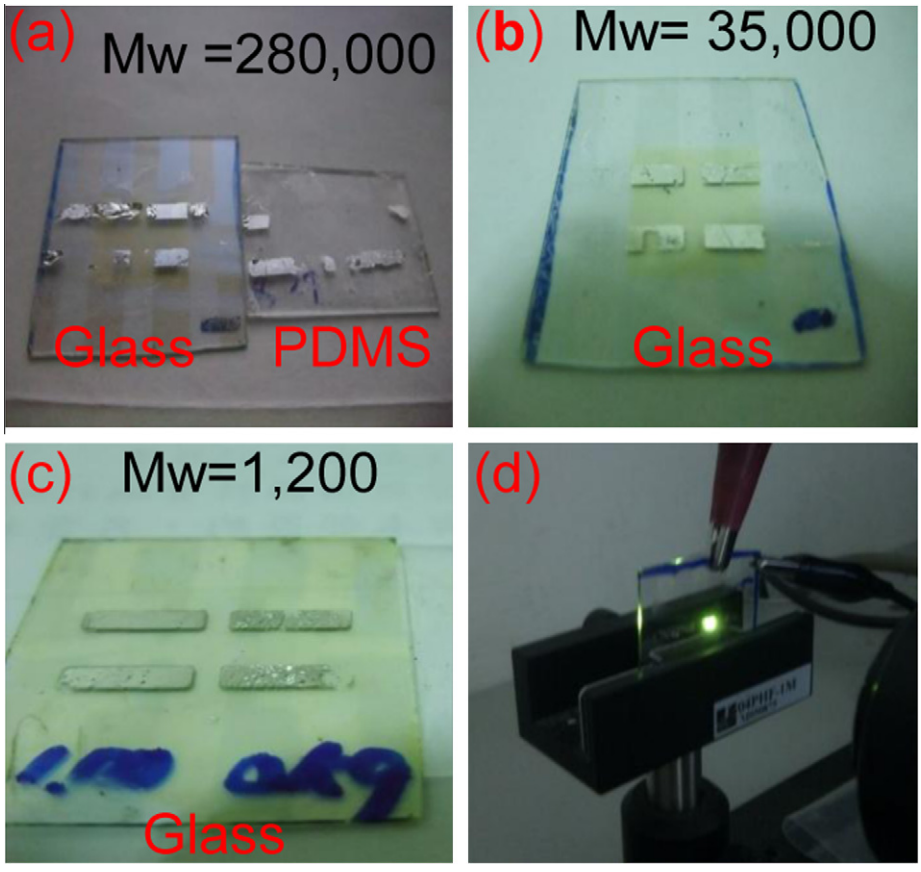

Fig. 2. The images of printed cathode on top of the emissive layer. The molecular weight (Mw) of the sacrificial PS layer is (a) 280,000, (b) 35,000, and (c) 1200. (d) The picture of a device without encapsulation under measurement.

Trapped gas bubbles between the two surfaces should be avoided in the lamination process. Baking on the hot plate not only melts the sacrificial polystyrene layer but also enhance the contact between the cathode and the organic semiconductors. Finally the PDMS substrate, now only connected to the rest of the sample by the liquid polystyrene, is peeled off to finish the device. The transferred PEG/Al pattern covers the OLED active region of 2 by 2 mm^2 and serves as connect to the ITO contact pad on the edge of the glass substrate. The device is taken out of the glove box and measured in air without encapsulation. For comparison, reference devices were fabricated with Al/PEG prepared by a regular method that PEG was spin coated on top the Green B and Al was thermally evaporated on top of PEG. PEG of standard device is made by blade coating followed by 5000 rpm using 0.3 wt.% solution in methanol on the organic surface. The standard evaporated device is encapsulated in the glove box and measured in air. The thickness of metal and organic layer was measured by surface roughness meter Kosaka ET4000. The current density–voltage (J–V) and luminance–voltage (L–V) characteristics of the devices are measured by Keithly 2400 source meter and spectrophotometer PR650.

3. Results and discussions

The molecular weight of the sacrificial PS layer between the soft PDMS mold and the evaporated PEG/Al cathode is critical to the success of metal transfer and subsequent PDMS removal from the OLED by peeling-off. For high molecular weight the melting point is so high that it is impossible to melt it without damaging the OLED underneath. The typical printed cathode on top of the active polyfluorene (PF) emissive layer is shown in Fig. 2 for various PS molecular weight (Mw). For Mw = 280,000 more than half of the metal residues on PDMS after peel-off at 150 °C as shown in Fig. 2(a). When Mw is reduced to 35,000 most of the metal can be transferred to the PF layer after peel-off at 150 °C as shown in Fig. 2(b). However the metal does not stick to the ITO contact at the edge of the glass substrate. When Mw is further reduced to 1200 the melting temperature becomes 120 °C which is below the hot plate temperature of 150 °C. As a result the metal can be transferred to not only the active layer but also the ITO contact without much remains on PDMS as shown in Fig. 2(c). It is much easier to separate the PDMS mold and the rest of the sample by applying force to the hard glass side than to the soft PDMS side. The reason is that peeling from the PDMS side will cause bending of the mold which in turn cause metal cracks. The light emission of the resulting OLED in air without encapsulation is shown in Fig. 2(d). The printed PEG/Al cathode connects the ITO contacts on the glass edge to the active region. The light is uniform indicating the good contact throughout the active region of 2 by 2 mm^2.

The energy levels of the Green B device are shown in Fig. 3. The hole can be injected from PEDOT:PSS anode to Green B highest occupied molecular orbital (HOMO) level through the TFB hole transport layer. The lowest unoccupied molecular orbital (LUMO) level of Green B is 3 eV below vacuum so a cathode with work function close to 3 eV is required for easy electron injection. Consider vacuum deposited cathodes first. Ca cathode with work function 2.9 eV gives current efficiency of 3.5 cd/A at 7 V. Evaporated PEG/Al cathode gives slightly higher efficiency of 5.4 cd/A at 6 V with Green B layer thickness of 55 nm.

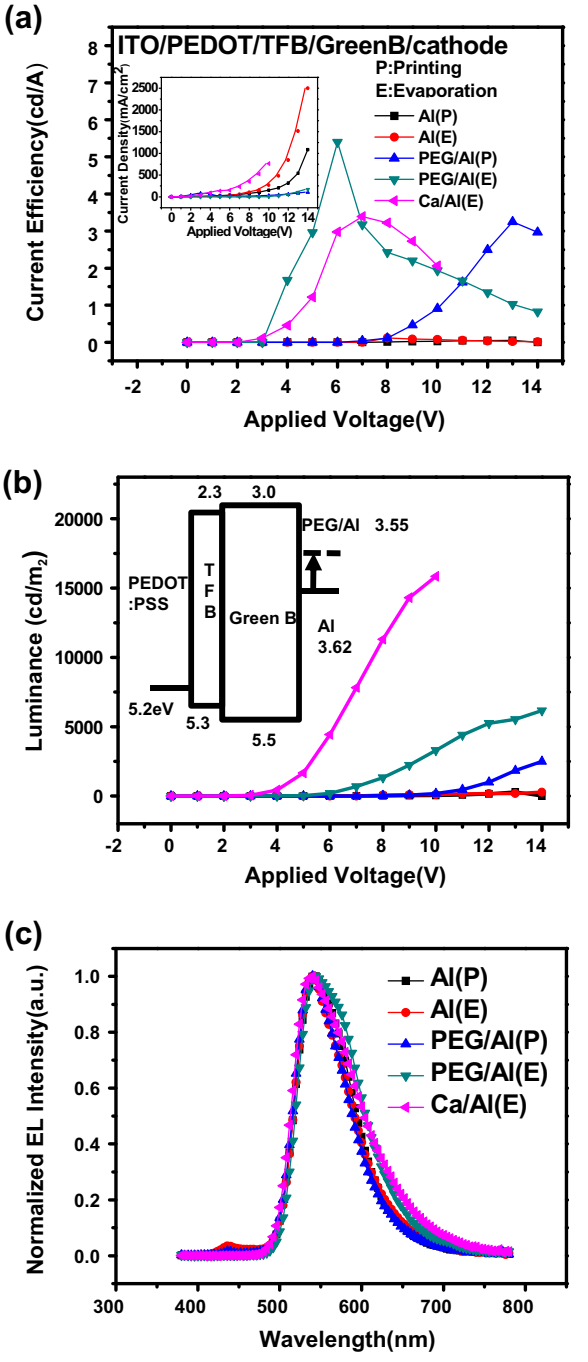

Fig. 3. The (a) efficiency, (b) luminance, and (c) electroluminance spectrum of the fluorescence OLEDs with cathodes made by lamination and evaporation. The inset of (a) and (b) shows the current density and energy level diagram of these devices.

These values are roughly the optimal performance for TFB/Green B combination. The efficiency drops to 3.2 cd/A and 1.5 cd/A when the thickness is changed to 40 nm and 75 nm respectively for evaporated PEG/Al. For devices with printed PEG/Al cathode the efficiency is 3.3 cd/A (1.1%) at 13 V with peak luminance of 2500 cd/cm^2 achieved at 14 V. Note that despite of the higher driving voltage the current efficiency of the printed devices is comparable to the evaporated devices. The increase of voltage may result from the higher work function of the printed PEG/Al cathode relative to the evaporated cathode. In evaporation process PEG is first deposited on Green B then Al is evaporated. The free Al atoms during evaporation in vacuum facilitate the chemical reaction with PEG to form Al–O bond. In contrast for lamination process PEG is spin coated on the cold Al solid film and the temperature of all the subsequent process is below 150 °C. The degree of chemical reaction is therefore expected to be much lower than the evaporated cathode. Nevertheless the overall performance of the printed OLED satisfies the preliminary requirements for some applications. Pure Al cathode is deposited for comparison. As expected the efficiency is about 100 times lower than the devices discussed above for both lamination and evaporation. The work function 4.3 eV of Al corresponds to 0.7 eV of high electron injection barrier. Such poor performance of pure Al cathode further demonstrate that the cold contact of PEG and solid Al does

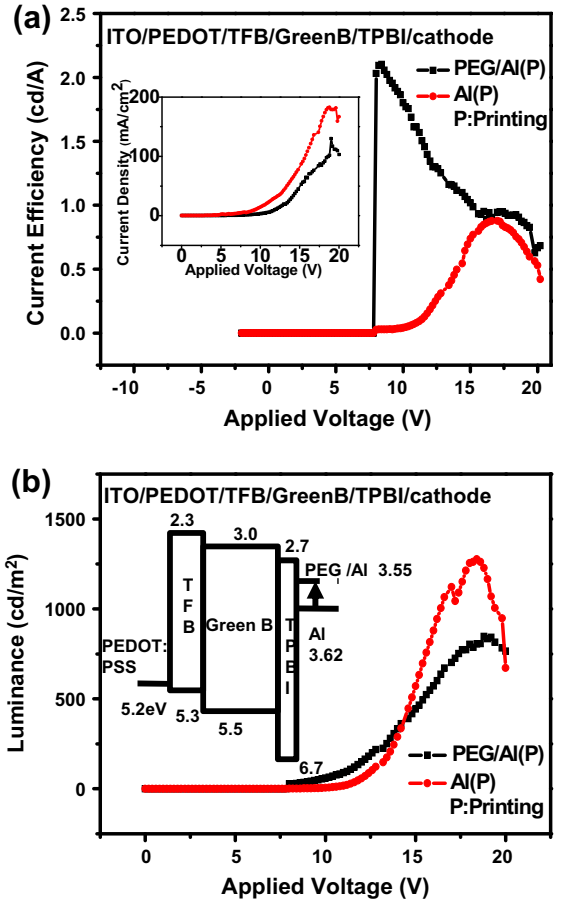

Fig. 4. The (a) efficiency and (b) luminance of fluorescence OLEDs with an electron transport layer. The cathodes are made by lamination. The inset of (a) and (b) shows the current density and energy level diagram of these devices.

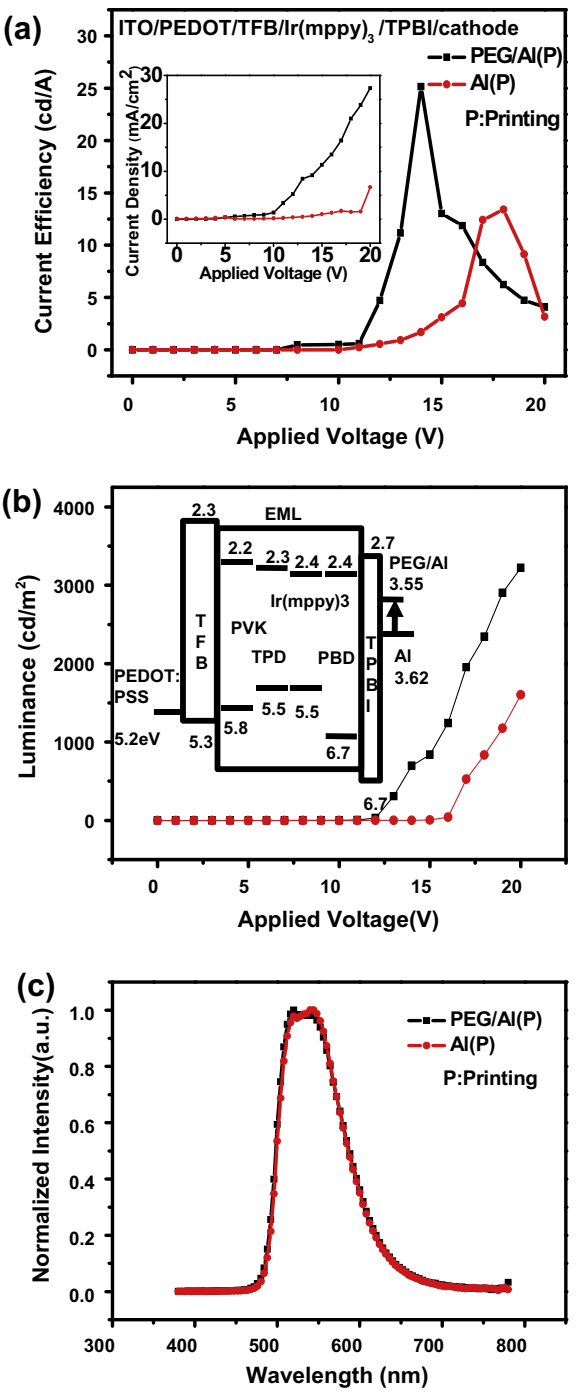

Fig. 5. The (a) efficiency, (b) luminance, and (c) spectrum of phosphorescence OLEDs. The cathodes are made by lamination. The inset of (a) and (b) shows the current density and energy level diagram of these devices.

reduce significantly the Al work function as in the case of hot contact of PEG and free Al atoms. The high driving voltage of the printed device cannot be reduced simply by decreasing the Green B thickness. The efficiency drops to 3.15 cd/A as the thickness is decreased to 40 nm, suggesting certain thickness is required for complete recombination.

An electron transport layer of TPBI is added between Green B and the cathode by blade coating [2,11] in the hope to reduce the voltage. The energy levels are shown in Fig. 4. Al evaporation on PEG is impossible for this structure because the solvent methanol of PEG will dissolve the TPBI layer. The device result for printed PEG/Al cathode on TFB/Green B/TPBI tri-layer is shown in Fig. 4. The performance is roughly the same as the devices without TPBI shown in Fig. 3. Somehow the TPBI layer does not help the electron injection from the PEG/Al cathode. The reason may be that solution-deposited TPBI has the high tendency to crystallize [11]. During the 150 °C heating for PDMS removal the TPBI molecules may aggregate and no longer form a uniform thin film to cover the entire emissive layer. Other electron transport molecules with low crystallinity may sustain the heating process and improve the driving voltage.

In addition to fluorescent OLED cathode lamination is also applied to highly efficient phosphorescent solution processed OLED. The emissive layer is a blend of PVK, TPD, PBD, and the emitter $Ir(mppy)_3$. TPD is for hole transport and PBD for electron transport in the emissive layer. TPBI electron transport layer is added by blade coating [2,11]. Such emissive layer has current efficiency about 35 cd/A for evaporated LiF/Al cathode [11]. As shown in Fig. 5 with the printed PEG/Al cathode the efficiency is 25 cd/A (8.2%) at 14 V with peak luminance of 3200 cd/m^2 at 20 V. The driving voltage is about 5 V higher than the LiF/Al cathode, however the efficiency keeps about 70% of the standard LiF/Al device. Surprisingly 13 cd/A and 1000 cd/m^2 can be reached by cathode lamination even without PEG for the phosphorescence devices. The emission spectrum shown in Fig. 5 is identical to the device with the evaporated LiF/Al device. The high efficiency of 25 cd/A by simple cathode lamination proves the feasibility of this method for real applications. As in the case of Green B, the high voltage is expected to result from the relatively high work function in comparison with LiF/Al cathode. We speculate that the work function is between 3 eV and 3.5 eV. Further photoemission study is required to confirm it.

4. Conclusion

A method for vacuum-free deposition of cathode with low work function is developed and demonstrated for solution-processed organic light-emitting diode. Current efficiencies close to the ones of vacuum deposited cathode is achieved for both fluorescent and phosphorescent OLED. The OLED shows remarkable stability without encapsulation. In particular 25 cd/A corresponding to 8.2% external quantum efficiency is realized for green phosphorescent emitter. Air-stable bilayer of PEG and Al on a soft silicon rubber is transferred onto the semiconductor layer through the melting of a polymer sacrificial layer between the cathode and rubber. Combining this cathode lamination method and multi-layer blade coating of organic semiconductors, fabrication with very low cost and high volume can be realized for both OLED and organic solar cell.

Acknowledgement

This work is supported by the Ministry of Economic Affairs of Taiwan under Contract No. 99-EC-17-A-07-S1-157.

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