Inverted White OLEDs Fabricated by Full Wet-Processes

Dong-Hyun Lee, Xun Zhu, Seung Woo Seo, Ji Chang Ryu and Sung Min Cho
School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
Tel.:82-31-290-7251, E-mail: sungmcho@skku.edu

Keywords: inverted OLED, white OLED, lighting, wet process

Abstract

We report inverted white OLEDs fabricated by full wet processes. We utilized inverted structure OLEDs since the structure was better for the realization of full wet fabrication of OLEDs. It was found that the performance of inverted OLEDs is comparable to that of conventional OLEDs. In this presentation, we will discuss in detail a few important issues on the full wet fabrication of OLEDs.

1. Introduction

Vacuum-free fabrication of organic light-emitting diodes (OLEDs) [1] or organic photovoltaic (OPV) devices [2,3] has been pursued by a number of research groups. Since the OPV devices or OLEDs for lightings require large-area fabrication for commercialization, the fabrication process should be low-cost and scalable to large area. The process includes wet printings, lamination, and spray coating. Even though the active organic layers for the devices have been deposited by various solution processes such as spin coating, screen, [4,5] gravure [6] and inkjet printings, [7] the top metal electrode formed by non-vacuum processes has rarely been reported. When the top metal electrode is spray-coated with a suspension ink which is commonly composed of metal nanoparticles and organic solvents, the organic devices should be inverted devices so that the uppermost layer of the devices is water soluble PEDOT:PSS (poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate)) for protecting the active layer from organic solvents. Very recently, the spray coating of the top metal electrode has been reported for inverted OPV devices successfully. [2,3] However, the process has never been applied for the fabrication of OLEDs since the interface property is more crucial for the operation of OLEDs than OPV devices. Instead, lamination processes have been implemented for the vacuum-free fabrication of OLEDs. The most commonly utilized method was a soft contact lamination [8,9] using PDMS (poly-dimethyl siloxane). The soft contact lamination easily forms a direct and intimate contact between metal and active organic layers with the help of strong bonding force of PDMS. Direct lamination between organic layers or between metal and organic layers without PDMS has also been reported for the fabrication of OLEDs. [1,10-12] Despite the simple process, however, the direct lamination has a limitation that organics with relatively low T_g such as MEHPPV (Poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene) [10-12] and PF (poly(fluorene)) [1] are only applicable to avoid a high temperature process. Contrary to the previously reported studies, we report here the vacuum-free fabrication of PVK (polyvinyl carbazole)- based OLEDs.

Since PVK is a rigid polymer with a high glass transition temperature around 200^{o}C, it is difficult to laminate directly with organic or metal layers at near the temperature. Besides when the active organic layer is contacted with other organic or metal layers by the lamination, it is crucial for the surface roughness of laminated layers to be controlled in a few nanometer ranges since there is no protection layer on the active layer. In order to circumvent these difficulties, therefore, we have fabricated inverted bottom-emission OLEDs of which the top layer is PEDOT:PSS. With the inverted structure, the top metal anode is formed on top of PEDOT:PSS by pattern transfer at a low temperature and the PEDOT:PSS acts as a protection layer of active organic layer. A few inverted bottom-emission

OLEDs have been reported in the literature so far. [13-14] However, none of them has utilized PEDOT:PSS as a hole transport layer in their devices. Besides they also utilized sophisticated cathode structures for the efficient injection from ITO cathode, so that the inverted structures have been fabricated inevitably by all vacuum processes.

Meanwhile, the doping of an organic salt such as Bu_3NBF_4 (tetra-n-butylammonium tetrafluoroborate) has recently been reported for polymer light-emitting devices (PLEDs) to simplify the cathode structure. [15-19] The salt-doped PLEDs are known to exhibit similar characteristics of frozen-junction light-emitting electrochemical cells (LECs). [17,18] Likewise the operation of the frozen-junction LECs are insensitive to the electrode materials, [20] the salt-doped PLEDs work well with most of electrode materials without the careful consideration for work functions of the materials. Therefore, the salt-doped PLEDs show the comparable performance with the conventional PLEDs even without the electron-injecting LiF (lithium fluoride) layer. The doping of organic salt is an important technique for simplifying the device structure and fabrication process of PLEDs.

In this study, we have fabricated inverted OLEDs doped with an organic salt by all vacuum-free processes.

2. Experimental

We used poly(N-vinyl carbazole) (PVK; Mw = 1,100,000, TCI) as a host polymer for the emissive layer. A hole transporting N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1-biphenyl]-4,4'-diamine (TPD, Aldrich), an electron transporting 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD, American Dye Source), and a phosphorescent green emitter *fac*-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$, Gracel) were added in the PVK host polymer with an appropriate composition. The mixture of active organics was dissolved in chlorobenzene. As an organic salt, an appropriate amount of Bu_4NBF_4 (Aldrich) was added in the solution mixture for the single emissive layer. As the hole and electron injection materials, PEDOT: PSS (Baytron P, AI 4083) and ZnO were utilized, respectively.

The inverted bottom-emission PLEDs with ITO / ZnO / PVK+TPD+PBD+$Ir(ppy)_3$+Bu_4NBF_4 / PEDOT:PSS / Al structure were fabricated. For the devices, an electron injecting ZnO thin film was first deposited using ultrasonically pulverized mist of zinc acetylacetonate solution at the temperature of 300°C. The thickness of ZnO layer was 80 nm. An emissive polymer layer was then spin coated for 30 seconds at 1,500 rpm to have the thickness of 80 nm and subsequently baked for 30 minutes at 80°C. The weight ratio of active organics was set to PVK:PBD:TPD:$Ir(ppy)_3$ = 0.61:0.24:0.09:0.06. The emissive layer was doped with Bu_4NBF_4 at the concentration of 1.25 wt.% prior to the spin coating. On top of the emissive layer, a hole injecting PEDOT: PSS was spin coated for 30 seconds at 1,500 rpm to have the thickness of 60 nm and then baked at 80°C for 30 minutes. For some samples, 1nm thick LiF layer was thermally evaporated at 5×10^{-7} torr. For some samples, Al layer (120 nm) was formed via thermal deposition at a pressure of 5×10^{-7} torr. For vacuum-free fabrication of the devices, Al layer deposited on FEP-coated plastic substrate was transferred to PEDOT:PSS layer using a press. After the devices were fabricated, they were treated thermally and electrically for the activation of organic salt. For the activation, the devices were brought on the surface of hot plate maintained at an elevated temperature of 65°C, and then a preset voltage (12 V) was applied to the devices for a period of time (30 seconds).

All electrical measurements were performed under ambient condition. The current-voltage-luminance (I-V-L) characteristics were measured using a source measure unit (Keithley 2400) and a luminance meter (Minolta CS100).

3. Results and discussion

We have shown the fabrication method of inverted OLEDs in Fig. 1.

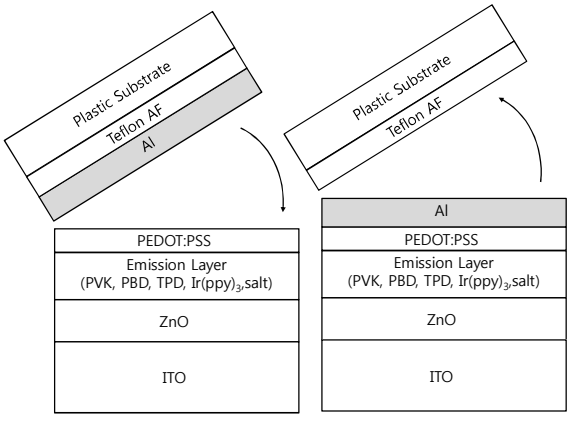

Fig.1. Schematic of vacuum-free inverted OLEDs fabrication process.

All the layers in the OLEDs were formed using wet processes except Al electrode. To complete the fabrication of OLEDs without vacuum, Al electrode was transferred to the inverted OLEDs. In the inverted OLEDs, Al electrode works as anode rather than cathode in conventional OLEDs. In the inverted structure, ZnO layer has an important role to reduce the electron injection barrier. With ZnO layer, therefore, it is expected that the turn-on and operating voltages could be reduced. We show the band alignment of the inverted device in Fig. 2 (a). As can be seen in Fig. 2 (a), it seems to be difficult to inject electrons into the emissive layer due to high energy barrier between ZnO and emissive layer. In order to investigate the electron injection from ITO cathode into the emissive layer under bias, we have first fabricated an OLED device without ZnO layer. As expected, we have failed to see emission from the device.

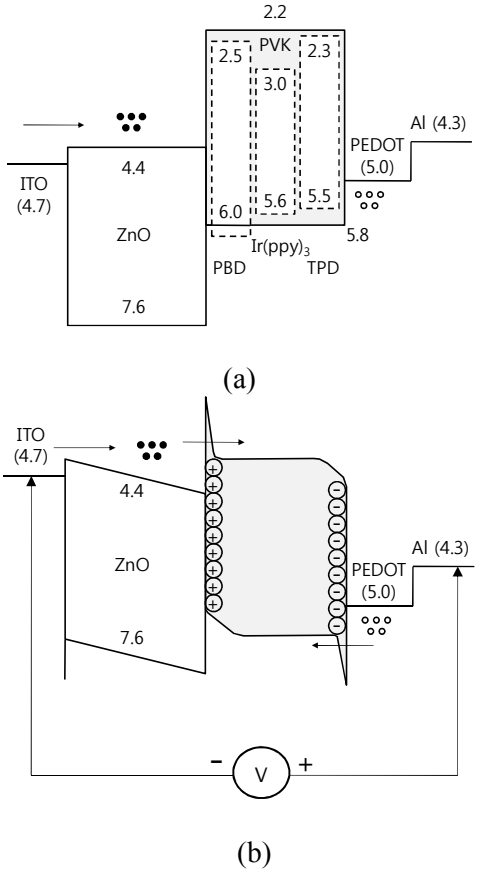

Fig. 2. Energy-level alignments for inverted OLEDs.

On the other hand, the insertion of ZnO between ITO and the emissive layer helps to inject electrons from ITO into the emissive layer. With the doping of organic salt, the barrier could be reduced significantly as shown in Fig. 2 (b). As the result, the performance of the inverted devices was enhanced remarkably as shown in Fig. 3. The maximum luminance reaches 10,000 cd/m^2 at 17 V.

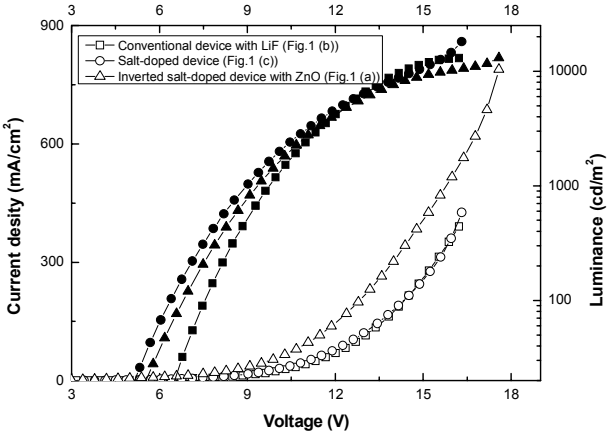

Fig. 3. Current-luminance-voltage graphs showing the relative performance of inverted devices to conventional devices.

The device with the structure of ITO/emissive layer (without salt)/PEDOT:PSS/Al does not show emission at all. The insertion of ZnO between ITO and emissive layer (without salt) produce weak emission from the device. The salt doping into the emissive layer affects the device performance more favorably than the insertion of ZnO does. With both the salt doping and ZnO insertion, the device performance was found enhanced noticeably.

Finally, we have compared the performance of the inverted salt-doped PLEDs with those of the conventional PLEDs with LiF layer and convention PLEDs with salt, as shown in Fig.3. Even though the sequence of the device is inverted, the performance of the inverted device was found comparable to that of the conventional devices. We attribute the fact to both the salt doping and the insertion of ZnO layer. We think that the inverted PLED structure can be utilized to fabricate all solution-processed polymer OLEDs or transparent polymer OLEDs.

4. Summary

We successfully fabricated inverted OLEDs using wet processes only without vacuum. In this study, we

found that the performance of inverted OLEDs was comparable to that of conventional OLEDs. We have utilized a layer of wet-processed ZnO layer and the doping of organic salt to have the full wet-processed fabrication of OLEDs possible.

Acknowledgement

This work was supported by a grant from Gyeonggi Province through the GRRC (Gyeonggi Regional Research Center) program in Sungkyunkwan University.

5. References

1. A. R. Duggal, C. M. Heller, J. J. Shiang, J. Liu and L. N. Lewis, *J. Display Technol.* **3**, p.184 (2007).
2. C. Girotto, B. P. Rand, S. Steudel, J. Genoe and P. Heremans, *Organic Electronics* **10**, p.735 (2009).
3. S. K. Hau, H.-L. Yip, K. Leong and A. K.-Y. Jen, *Organic Electronics* **10**, p.719 (2009).
4. D.-H. Lee, J. S. Choi, H. Chae, C.-H. Chung and S.M. Cho, *Displays* **29**, p.436 (2008).
5. S. E. Shaheen, R. Radspinner, N. Peyghambarian and G. E. Jabbour, *Appl. Phys. Lett.* 79, 2996 (2001).
6. P. Kopola, M. Tuomikoski, R. Suhonen and A. Maaninen, *Thin Solid Films* **517**, p.5757 (2009).
7. F. Villani, P. Vacca, G. Nenna, O. Valentino, G. Burrasca, T. Fasolino, C. Minarini and D. della Sala, *J. Phys. Chem. C* **113**, p.13398 (2009).
8. T.-W. Lee, J. Zaumseil, Z. Bao, J. W. P. Hsu and J. A. Rogers, *Proc. Natl. Acad. Sci. USA* **101**, p.429 (2004).
9. D. A. Bernards, T. Biegala, Z. A. Samuels, J. D. Slinker, G. G. Malliaras, S. Flores-Torres, H. D. Abruna and J. A. Rogers, *Appl. Phys. Lett.* **84**, p.3675 (2004).
10. T.-F. Guo, S. Pyo, S.-C. Chang and Y. Yang, *Adv. Funct. Mater.* **11**, p.339 (2001).
11. T.-F. Guo, G. He, S. Pyo and Y. Yang, *Appl. Phys. Lett.* **80**, p.4042 (2002).
12. M. Miyagawa, R. Koike, M. Takahashi, H. Bessho, S. Hibino, I. Tsuchiya, M. Harano, M. Endo and Y. Taniguchi, *Jpn. J. Appl. Phys.* **46**, p.7438 (2007).
13. T.-Y. Chu, J.-F. Chen, S.-Y. Chen, C.-J. Chen and C. H. Chen, *Appl. Phys. Lett.* **89**, p.053503 (2006).
14. S.-Y. Chen, T.-Y. Chu, J.-F. Chen, C.-Y. Su and C. H. Chen, *Appl. Phys. Lett.* **89**, p.053518 (2006).
15. C. C. Yap, M. Yahaya and M. M. Salleh, *Curr. Appl. Phys.* **8**, p.637 (2008).
16. E. A. Plummer, A. van Dijken, H. W. Hofstraat, L. D. Cola and K. Brunner, *Adv. Funct. Mater.* **15**, p.281 (2005).
17. S. S. Oh, J. H. Park, S. W. Kim and B. Park, *J. Appl. Phys.* **102**, p.74503 (2007).
18. B. Park, M. Y. Han and S. S. Oh, *Appl. Phys. Lett.* **93**, p.93302 (2008).
19. D.-H. Lee, H. Chae and S. M. Cho, *Jpn. J. Appl. Phys.* **48**, p.060204 (2009).
20. G. Yu, Y. Cao, M. Andersson, J. Gao and A. J. Heeger, *Adv. Mater.* **10**, p.385 (1998).