

Effects of substrate treatment on the electroluminescence performance of flexible OLEDs [☆]

Shih-Nan Lee, Shih Feng Hsu, Shiao Wen Hwang, Chin H. Chen ^{*}

Microelectronics and Information Systems Research Center, Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan, ROC

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Abstract

Electroluminescence (EL) performance of flexible organic light-emitting device (FOLED) has been found to be highly dependent upon the morphology of the surface of the indium thin oxide (ITO)/plastic substrate as well as the patterning and processing conditions of the substrate. We will present evidence showing that luminance efficiency of FOLED can be greatly improved by pretreatment. Surface analysis of the ITO/PET by means of atomic force microscope (AFM) and optical microscope will be compared with that of the ITO/glass and the influence of flexible OLEDs substrate treatment by various methods on EL performance will also be discussed.

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1. Introduction

Since organic light-emitting diodes (OLED) have been found useful in flat panel display (FPD) applications, several novel OLED technologies such as transparent OLED (TOLED) [1,2], Stack OLED (SOLED) [3] and flexible OLED (FOLED) [4–6] have been discovered. Fabrication of a display that is conformable, wearable and still fully functional even when it is bend or flexed is the key advantages of FOLED technology as compared to the others. This is because OLED encompasses thin, amorphous solid-state films, which can be easily fabricated on any substrate, such as glass or flexible plastics and steel foil. Flexible OLEDs using plastic substrates are lighter and thinner than OLEDs

based on glass. They can be bent and twisted and are literally unbreakable.

Although flexible OLED possesses several advantages, there are still many challenges to be overcome. Two of these challenges are to enhance the efficiency and stability of devices. Through substrate pretreatment, the efficiency and stability of the devices can be enhanced. By optimizing the cleaning conditions [7], performing oxidation of the indium thin oxide (ITO) surface by O₂ plasma [8], and inserting a buffer layer or hole-injection layer [9], such as copper phthalocyanine (CuPc), between the ITO and hole transfer layer (HTL) interfaces, the energy barrier of hole-injection can be reduced and the performance of the device can be improved. In previous reports, the insertion of LiF thin film between Alq₃ and Al can effectively reduce the energy barrier of electron injection [10]. Furthermore, Zhu [11] and Zhao [12] have published thin LiF layer on the ITO anode would improve device performance, but no results about device lifetime have been reported. Due to the fact that the plastic substrates can be only operated at temperature below their T_g (glass transition temperature), the deposited ITO film is often amorphous [13] and cannot

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^{*} Corresponding author. Tel.: +886-3-5712121x59200; fax: +886-3-5737681.

E-mail address: fredchen@ic.nctu.edu.tw (C.H. Chen).

be postannealed. This results in high resistance [13], which would cause the increase of turn on voltages. In this paper we will demonstrate the application of LiF thin film on ITO/PET substrates to improve the device performance and show the influence on device lifetime.

2. Experimental

The flexible ITO substrate used is the touch panel grade PET/ITO plastic substrate, supplied by U-shine in Hsinchu of Taiwan, with resistivity of $1 \times 10^{-3} \Omega \text{cm}$. The ITO glass substrate with resistivity of $1.8 \times 10^{-4} \Omega \text{cm}$ is purchased from Merck. The sequential steps for patterning were carried out. At first step, the cleaning of ITO substrates was subsequently done with isopropanol alcohol (IPA), detergent, deionized water, and methanol in ultra-sonic bath to remove the organic contaminants that act as fatal impurities on the ITO substrates during the photolithographic patterning process.

The next step is the fabrication of patterned anode plate. First of all, the positive commercial photoresist were spin-coated on the substrate to a thickness of about $1 \mu\text{m}$. After baked, it was placed on a mask aligner and exposed to ultra-violet(UV) light for 90 s. Then it was developed in a developer for about 60 s, followed by baking process for 2 min at 75°C . Subsequently the samples were etched by 3% $\text{H}_2\text{C}_2\text{O}_4(\text{aq})$ for 2 min at bath temperature of $35\text{--}40^\circ\text{C}$. Surface analyses of the ITO substrates were performed by means of atomic force microscope (AFM) and optical microscope after wet etching. The step for pretreatment is to deposit LiF layer in different thickness, 5, 10, and 15 \AA at a deposition rate of $\sim 0.1 \text{ \AA/s}$ using ULVAC coater, or treat it with 60 sccm of O_2 plasma without LiF, and following by sequential deposition of CuPc, *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), *tris*(8-hydroxyquinolato)aluminum (Alq_3) in the $\sim 10^{-5} \text{ Pa}$ and cathode in the $\sim 10^{-4} \text{ Pa}$. The device structure is [ITO/LiF ($x \text{ \AA}$)/CuPC (150 \AA)/NPB (600 \AA)/ Alq_3 (750 \AA)/LiF (10 \AA)/Al (2000 \AA)]. The electroluminescence characteristics of OLEDs were measured with a Photo Research PR650 spectrophotometer and a programmable current source. The surface roughness and inspection measurements were performed by AFM and Olympus optical microscope, respectively. The device lifetime was measured by photodiode connected to a data acquisition instruments and computer.

3. Results and discussion

3.1. Dark spots

Compared to the traditional OLEDs, which were fabricated on glass substrate, we found the FOLEDs reveal more dark spots under the same test conditions.

This phenomenon is observed immediately after device fabrication, so the factor of O_2 and H_2O permeation is excluded. From the microscopic and macroscopic observation, we could seek the clue about why FOLEDs show more dark spots than traditional OLED. Compared with ITO/glass substrate, PET substrates show the smaller root-mean-square ($R_{\text{ms}} = 3.4 \text{ nm}$) roughness than that of glass substrates ($R_{\text{ms}} = 3.8 \text{ nm}$). The big R_{ms} value may be due to the different crystal of ITO in glass substrate. The crystal of ITO could lead to smaller resistivity than that of ITO/PET substrate. Furthermore, there was observed a spike on ITO/PET surface. Some papers have pointed out the influence of spikes on device degradation [14,15]. From the viewpoint of OLED, the spikes could be more determined than R_{ms} value on device reliability. Fig. 1(a) and (b) shows the optical microscope (OM) graphs of two ITO substrates after aluminum layer was deposited immediately in the same batch. The aluminum layer deposited on glass and PET substrates enhance the contrast for OM detection. Although the roughness of ITO on PET ($R_{\text{ms}} = 3.4 \text{ nm}$) is smaller than that on glass ($R_{\text{ms}} = 3.8 \text{ nm}$), a lot of pinholes have been found on the optical graph of aluminum on ITO/PET. By contrast, the surface of alu-

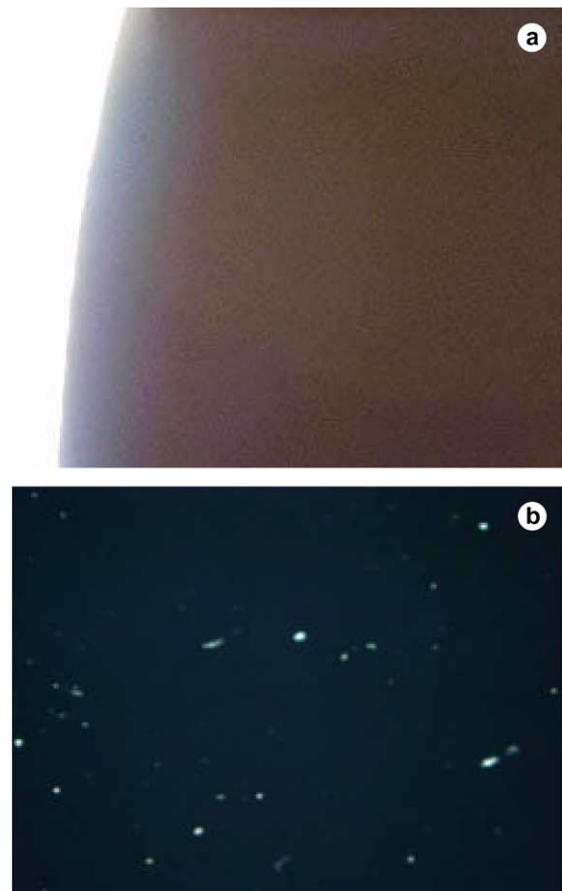


Fig. 1. (a) Microscope image ($\times 50$) of ITO/glass with Al layer. (b) Microscope image ($\times 50$) of ITO/PET with Al layer.

minimum on ITO/glass is uniform. The pinholes may result from the spike in PET substrate. In summary, the spikes of substrates and the non-uniformity of deposited films may cause the shorting of two adjacent electrodes, which subsequently result in the dark spots formation.

3.2. Pretreatment

Fig. 2(a) and (b) shows the current density and luminance vs. voltages of the FOLED devices with bare ITO or different pretreatments of the ITO. It has been reported that oxygen plasma can effectively increase the work function of ITO and improve the performance of OLED. Compare to the traditional OLED, the O₂ plasma treatment on ITO/PET does not reduce operating voltage obviously. But the operating voltages of devices with proper LiF thickness on anode are clearly reduced. Under current density of 20 mA/cm², the operating voltages of devices are 9.3, 7.9, 7.9, and 9.5 V for devices with 0.5, 1, 1.5 nm LiF, and bare ITO, respectively. The operating voltages of devices with 1 or 1.5 nm of LiF on anode are close to 7.5 V of traditional

OLED device. Similarly, the voltages required to reach a luminance of 1000 cd/m² are 9.4, 7.8, 7.8, and 9.4 V for devices with 0.5, 1, 1.5 nm, and bare ITO, respectively. As shown in Fig. 2(b), the plasma treatment does not enhance the luminance at the same operating voltages.

This enhancement of carrier-injection is due to the tunneling junction [16,17] caused by inserting a thin insulating layer between ITO and HTL. The energy level of LiF is at around 12 eV, which is an insulator [11]. By adding an ultra-thin layer of LiF between ITO and CuPc, the hole-injection can be enhanced by means of tunneling junction. Hence, the operating voltages can be reduced. By increasing the LiF thickness, the effect of carrier tunneling will decrease, therefore, leading to a weaker carrier-injection process and higher operating voltages.

Fig. 3 shows the power efficiency vs. current density of devices with bare ITO and with different thickness of LiF on the ITO. The graph clearly shows that the power efficiency of the device is improved by adding at least 1 nm of LiF. Furthermore, the power efficiency of the device with plasma treatment is worse than that of bare ITO. This is due to that the plasma treatment only reduces the hole-injection barrier, but does not increase the hole-electron balance. Otherwise, as 1 nm LiF layer was inserted between ITO and CuPC, not only the voltage was reduced, but also the brightness could be enhanced. Due to the lower hole-injection barrier and better hole-electron balance than those of devices without LiF layer, the power efficiency was improved. Therefore, the performances of FOLEDs using ITO/PET substrate with unfavorable electronic properties could be dramatically improved by LiF pretreatment.

Fig. 4 exhibits the lifetime curves of devices with and without LiF in glove box. Excluding the extrinsic factor, such as the attack of O₂ and H₂O, the graph indicates that the device with LiF is more stable than the device

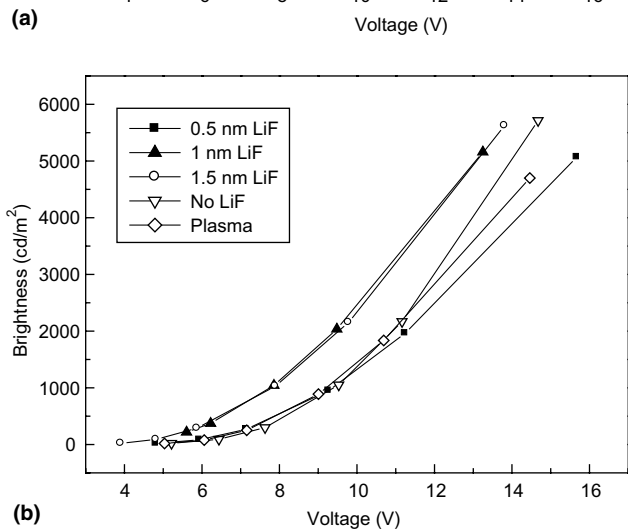
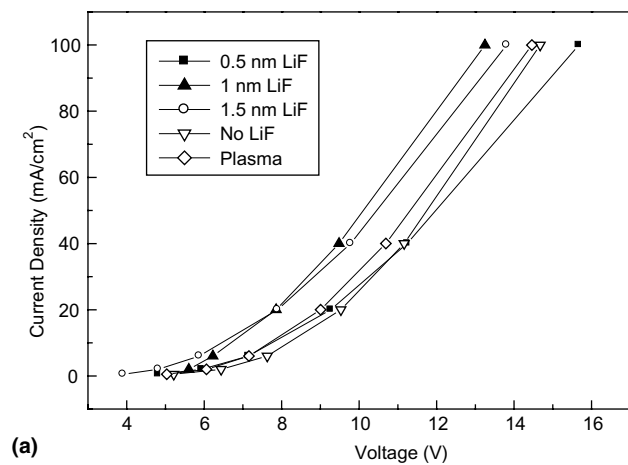


Fig. 2. (a) Current vs. voltage graph of various LiF thickness. (b) Brightness vs. voltage graph of various LiF thickness.

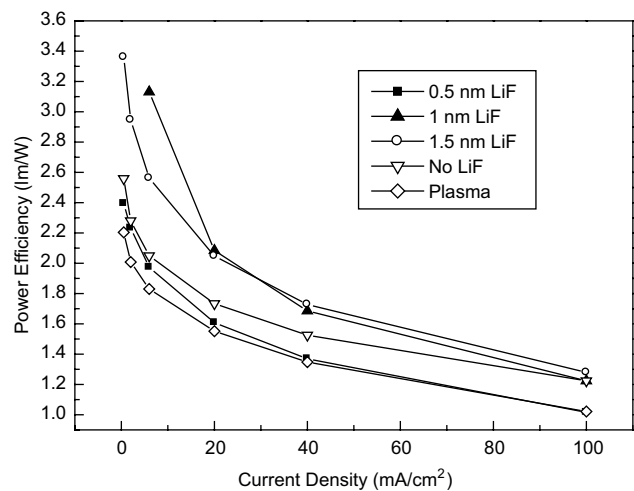


Fig. 3. Power efficiency vs. current density graph of various LiF thicknesses.

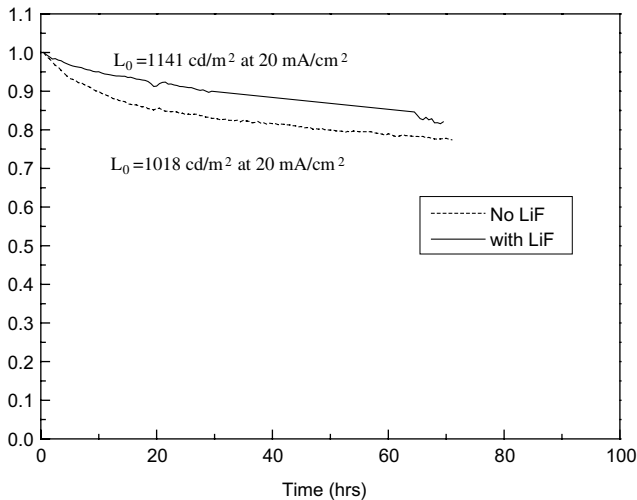


Fig. 4. Device lifetime comparison between device with LiF and device without.

without LiF. Further investigation is needed to elucidate detailed mechanism.

4. Conclusion

From the AFM analysis, although the grains of ITO on glass substrate result in the big Rms value, the local spike on ITO/PET substrate can affect the uniformity of deposited films. The spike and the non-uniform of deposited films may cause more dark spots in FOLEDs than in traditional OLED. In addition, by inserting LiF layer between ITO and CuPc interface, the device operating voltage was reduced, and luminance efficiency was increased. The performances of FOLEDs using PET substrate with unfavorable electronic properties of ITO could be dramatically improved by LiF pretreatment. The lifetime test also indicates that the device with LiF is more stable than the device without.

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References

- [1] G. Gu, V. Bulović, P.E. Burrows, S.R. Forrest, M.E. Thompson, *Appl. Phys. Lett.* 68 (1996) 2606.
- [2] V. Bulović, G. Gu, P.E. Burrows, M.E. Thompson, S.R. Forrest, *Nature* 380 (1996) 29.
- [3] P.E. Burrows, V. Khalfin, G. Gu, S.R. Forrest, *Appl. Phys. Lett.* 73 (1998) 435.
- [4] A.N. Krasnova, *Appl. Phys. Lett.* 80 (2002) 3853.
- [5] Z. Chen, B. Cotterell, W. Wang, *Eng. Fract. Mech.* 69 (2002) 597.
- [6] A.B. Chwang, M.A. Rothman, S.Y. Mao, R.H. Hewitt, M.S. Weaver, J.A. Silvernail, K. Rajan, M. Hack, J.J. Brown, X. Chu, L. Moro, T. Krajewski, N. Rutherford, *Appl. Phys. Lett.* 83 (2003) 413.
- [7] Th. Kugler, A. Johansson, I. Dalsseg, U. Gelius, W.R. Salaneck, *Synthetic Met.* 91 (1997) 143.
- [8] D. Lu, Y. Wu, J. Guo, G. Lu, Y. Wang, J. Shen, *Mater. Sci. Eng.* B97 (2003) 141.
- [9] S.A. VanSlyke, C.H. Chen, C.W. Tang, *Appl. Phys. Lett.* 69 (1996) 2160.
- [10] L.S. Hung, C.W. Tang, M.G. Mason, *Appl. Phys. Lett.* 70 (1997) 152.
- [11] F. Zhu, B. Low, K. Zhang, S. Chua, *Appl. Phys. Lett.* 79 (2001) 1205.
- [12] Y. Zhao, S.Y. Liu, J.Y. Hou, *Thin Solid Films* 397 (2001) 208.
- [13] D.C. Paine, T. Whitson, D. Janiac, R. Beresford, C.O. Yang, B. Lewis, *J. Appl. Phys.* 85 (1999) 8445.
- [14] Y.H. Tak, K.B. Kim, H.G. Park, K.H. Lee, J.R. Lee, *Thin Solid Films* 411 (2002) 12.
- [15] J. McElvain, H. Antoniadis, M.R. Hueschen, J.N. Miller, D.M. Roitman, J.R. Sheats, R.L. Moon, *J. Appl. Phys.* 80 (1996) 6002.
- [16] X.M. Ding, L.H. Hung, L.F. Cheng, Z.B. Deng, X.Y. Hou, C.S. Lee, S.T. Lee, *Appl. Phys. Lett.* 76 (2000) 2704.
- [17] Y.E. Kim, H. Park, J.J. Kim, *Appl. Phys. Lett.* 69 (1996) 599.