Experimental Study of Chemical Reaction between LiF and Polyflourene Interface During Sputtering ITO Cathode for Top Emission PLED Devices

C.W. Teng¹, C.C. Lee¹, K.C. Liu^{1,2}, W.T. Liu³, C.C. Chen³, Y.R. Peng³, L.C. Chen³

¹Institute of Electro-Optical Engineering, Chang Gung University, Taiwan

²Correspondence to this author: TEL: +886-3-2118800 ext: 3152 E-mail: jacobliu@mail.cgu.edu.tw

³DELTA OPTOELECTRONICS, Taiwan, Tel: 03-563-0727, Fax: 03-563-0723

1. Introduction

Recently, the organic LED attracts great attention due to many superior features including simple structure, high performance, etc [1]. In terms of applications, top emission structure will be the better candidate for the next generation display [2~3]. The transparent conductive oxide (TCO) is usually employed as the cathode, especially ITO. However, the high work function of ITO will create the high electron injection barrier. In order to improve the electron injection behavior, a thin LiF layer is inserted between cathode and organic layer. Up to now, it is an effective method to reduce the electron injection barrier [4]. Unfortunately, some reports found the Li diffusion into organic layer caused device performance degradation [5]. In top emission process, ITO transparent cathode sputter onto the LiF thin layer. Usually, ITO needs to deposit at higher temperature (>300°C) to obtain lower resistivity. Nevertheless, the higher substrate deposited temperature, the worse Li diffusing problem. Therefore, these two contradiction problems have to be cautiously considered during transparent ITO cathode formation. In this work, we have done systematical experiments to find an appropriate process for the best device performance.

2. Experiment

The devices are made of following structure of glass/ITO(230nm)/PEDOT(70nm)/PF(70m)/LiF(1.5nm)/ITO(120nm). The ITO coated glass substrates were cleaned by using commercial cleaning procedures. Thereafter, samples were via O_2 plasma treatment. The organic layers were spun on the ITO glass, and LiF interlayer was deposited by thermal evaporation. ITO cathode was deposited by sputtering of dc power 50 W under the working pressure of 5 mtorr. The devices were heated at different temperature and different layers shown in Table 1. XPS analysis was processed with the configuration of glass/PF(70nm)/LiF(3nm) that attached to the PERKIN-ELMER 5400 system.

3. Results and discussion

Fig.1. shows the double logarithm of current density-voltage curve. According to other investigations [6~7], in low operating voltage region, due to the traps in organic will capture the carriers that resulted in the current is non-sensitive to the applied voltage. In high operating voltage region, the expression can be derived to $J \propto V^{m+1}$, m+1 is the value of slope in logJ-logV curve. In this region, the traps are approximately filled; we observe that m+1

raises steeply (compared to low applied voltage). The value of m corresponds to the trap concentration and characteristic trap energy level. The value of m raises, the trap concentration reduces, and characteristic trap energy level increases, correlate to each other. At the same operating region (no matter in low or high operating voltage), the RT device always shows the highest m than that of the other two devices. Hence, the trap concentration of RT device is the lowest and easily filled up resulted in increasing rapidly of current in high applied voltage region. When increasing the ITO deposition temperature, the slope is reduced. It means the higher deposition temperature of ITO cathode leads to the more trap density that gives rise to the higher turn-on voltage. Compared to the variation of slope, we can observe that the increasing of trap density by improperly substrate temperature. The similar physical phenomenon also can be explained through the optical performance. Fig.2. shows the electroluminance of devices; the result can be found that the reduction of light intensity by increasing the substrate temperature during ITO cathode deposition. According to the literatures [5], the Li diffused into organic layer to form non-radiative recombination centers and the centers quenched the light that caused degrading the optical performance of devices. To find out the critical process factor, the experiments with or without heated LiF layer are systematically studied. Fig.3. shows the J-V characteristic of different heating process. The RT device (S1) is for a reference device. We can observe that device S5 exhibits the similar characteristic to device S1. It represents that the heating process with only organic layer does not introduce the excess traps. Then device S4 is used to compare with device S1, the resistivity of ITO cathode of these two samples are the same (deposited at RT). But, the electrical characteristic of device S4 is more like device S3. It means that the resistivity of cathode does not dominate the electrical characteristic. In device S6, it can be found that the trap concentration increased significantly. To analyze S4 and S6 process conditions, the heating process with LiF plays a main role of the traps produced in devices. Fig.4. shows the electroluminance of different heating processes in different layers. The heating process only with organic layer exhibits almost the same EL as the non-heating device. On the other hand, the heating process involved the LiF layer clearly shows the detrimental optical characteristic. The result of XPS analysis is consisted with both optical and electrical characteristics shown in Fig.5. (a) (b) shows the core-level spectra of F 1s and Li 1s measured on the organic side of the interface. The binding energy of

Li 1s and F 1s do not shift as increasing temperature, but the intensity increased as raising temperature; the atomic concentration ratio of Li 1s, and F 1s are listed in Table.2. We observed that the concentration of Li and F increases in organic layer which produce traps as raising temperature. In optical behavior, the higher concentration of Li will increase the amount of non-radiative centers. From reducing the value of m, this indicates higher trap density causing the more injection carriers captured. In this reason,

Table.1. The configuration of top emission device, and the position of heating process. All heating processes were taken for 25 min.

	Heating Process (°C)			The factors of influence devices		<i>m+1</i> sequence <i>Voltage region</i>	
N.O	PF	LiF	Cathode ITO	Cathode resistivity difference	Trap From LiF	low	high
S 1			RT			1	1
S2			60	\checkmark	\checkmark	3	3
S 3			100	\checkmark	\checkmark	4	4
S 4		100			\checkmark	5	5
S5	100					2	2
S 6	Devi	ce heati	ng at 100	\checkmark	\checkmark	6	6

Note: 1. " \checkmark " is defined that the factor influence devices indeed.

2. The sequence of m+1 is defined from "1" (highest) to "6" (lowest).



Fig.1. Current-voltage of top emission devices with different ITO cathode deposition temperature. L means the slope operated under low bias and H is the slope operated under high bias.



Fig.4. Electroluminance of top emission devices with heating process in different layer.



Fig.2. Electroluminance of top emission device with different ITO deposition temperature.



the turn-on voltage raises shown in the insert figure of Fig.1.

Conclusion

In summary, if LiF serves the electron injection layer, the deposition temperature of ITO cathode has to keep lower to avoid the Li and F diffused. For top emission structure using LiF/TCO as cathode, the lower risistivity TCO materials deposited at room temperature has to be incorporated in the fabrication process.

Reference

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Table.2. XPS data taken from a multilayer of Glass/PF (70nm) /LiF(3nm).

	Atomic concentration (%)				
Element	Glass/PF/LiF (RT)	Glass/PF/LiF (60°C)			
Li 1s	2.83	6.92			
F 1s	10.33	17.05			



Fig.3. Electrical characteristics of top emission devices with heating process in different layer. L means the slope of device operated under low bias and H is the slope operated under high bias.



Figure.5. XPS core-level spectra recorded on the organic side with (a) Li 1s and (b) F 1s. The insertion is the schematic diagram of the measured position.