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Improving the stability of organic light-emitting devices using a solution-processed hole-injecting layer

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ABSTRACT

The stability of organic light-emitting devices with a spin-coated film of 4,4′,4″-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA) as hole-injection layer (HIL) was investigated. The lifetime of this device is increased to 40 900 h (with an initial luminance of 100 cd/m^2), which is 2.7 times as large as that of the control device with a vacuum-deposited film of m-MTDATA as HIL. A significant feature with this method is that the performance and the operational stability of the device with spin-coated HIL are little attenuated by the rough substrate coated by the indium-tin oxide film. The surface morphology of the solution-processed m-MTDATA thin film is quite even and uniform, and it acts as a smoothing layer in the device, which leads to the stability enhancement of the device.

1. Introduction

The operational stability is a critical factor for the commercialization of the organic light-emitting diode (OLED) in flat panel displays and lighting. There have been considerable research efforts to improve their operational stability [1–4]. For small molecule-based OLEDs, several causes for its degradation have been suggested, such as, crystallization of organic thin films [5,6], electrochemical reactions at the electrode/organic interface [7], migration of metal species [8], quenching by tris(8-hydroxyquinolinato) aluminum (Alq_3) cations [9,10] and the local decomposition of the electrode/organic interface [11–13]. In this paper, we focus on the stability of the anode/organic interface, which is an important factor to obtain long-life devices as it determines charge injection into the devices [13–16].

Indium-tin oxide (ITO) films are widely used as anode because of its good conductivity, transparency, and high work function. Surface morphology of ITO film is an important factor for the stability and efficiency of OLEDs. In small molecular devices, all the functional organic layers (about 100 nm) are deposited on ITO, thus surface morphology of an ITO can be directly transferred to them [16,17]. It has been found that the large surface roughness of an ITO substrate induces layer unevenness for the vacuum deposited organic layers [16,17]. Therefore, the rough surface of an ITO can have a negative effect on the operational stability of the device [16]. In practice, the roughness can be reduced by incorporating a polymeric smoothing layer, such as parylene and poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) [18–20]. However, ITO corrosion by the acidic PSS, and the following indium diffusion into the organic layers has been reported to be an important cause to the poor electroluminescent durability of devices made of PEDOT:PSS [21].

In this paper, we introduce a hole-injection layer (HIL) using spin-coated 4,4′,4″-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA) as a smoothing layer. The surface morphology of the spin-coated HIL after thermal annealing is much smoother than that of the vacuum-deposited HIL, which substaintially reduces the device leakage current, and thus enhances the lifetimes of the devices with spin-coated HILs. We attribute this improvement to the ability of the spin-coated m-MTDATA films to improve the surface of the ITO, which in turn reduce the possibility of getting shorts through the thin molecular films.

2. Experimental

Two types of ITO substrates with different surface morphology were selected as the anode to compare their effect on the stability of the devices. The two types of ITO were both purchased from Shenzhen Nanbo Display Technology Co., Ltd. of China. ITO_S and ITO_R have smooth and rough surface morphology (details are given below), respectively. Using these ITO substrates, we fabricated four kinds of devices as follows:

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Device A: ITO_S/m-$MTDATA_{VD}$/NPB/Alq_3/LiF/Al;
Device B: ITO_S/m-$MTDATA_{SC}$/NPB/Alq_3/LiF/Al;
Device C: ITO_R/m-$MTDATA_{VD}$/NPB/Alq_3/LiF/Al;
Device D: ITO_R/m-$MTDATA_{SC}$/NPB/Alq_3/LiF/Al.

In the devices, *N,N*′-di(naphth-1-yl)-*N,N*′-diphenyl-benzidine (10 nm) is used as the hole-transport layer (HTL), Alq_3 (60 nm) is used as the emitting layer as well as the electron-transport layer. LiF (0.5 nm)/Al (100 nm) is used as the bilayer cathode. These layers were deposited by thermal evaporation in a vacuum chamber at a pressure of 5×10^{-6} Torr. The film with m-MTDATA is used as HIL, which was fabricated on the two kinds of ITO substrates by either spin-coating or vacuum deposition. Devices A and C are the control OLEDs, in which the film of m-MTDATA was prepared by vacuum deposition (m-$MTDATA_{VD}$). In devices B and D, the films of m-MTDATA were fabricated by spin-coating (m-$MTDATA_{SC}$).

In our experiment, the chlorobenzene solution containing 15 mg/ml of m-MTDATA was prepared first, then it was spin-coated on patterned ITO glass substrates. After this step, the samples were dried in an oven for 3 h at 70 °C. The thickness of these spin-coated films was approximately 50 nm. The devices were then encapsulated under a nitrogen atmosphere (O_2 and H_2O levels less than 2 ppm) with epoxy and glass lids. Finally, the devices were tested in the ambient environment.

The thickness of the organic films by vacuum deposition and spin-coating on the ITO substrates was measured by an ellipsometer. The surface morphology of the ITO and the organic thin films was examined by atomic force microscope (AFM). Electroluminescence characteristics of the devices were measured using a Keithley 2602 source-measure unit. Operational stability measurements of the encapsulated devices were performed using a constant DC current. All measurements were carried out at ambient temperature.

3. Results and discussion

Since the roughness of the ITO is often a critical parameter for the performance of OLEDs, we examined the surface morphology of the ITO film using AFM. Fig. 1 shows the surface morphology images (5 μm × 5 μm) of the cleaned ITO electrode. As seen in Fig. 1(b), the grainy structure of the surface is clearly recognizable. The R_{rms} (root-mean-square roughness) of the ITO_R is 9.6 nm, and the R_{pv} (peak-to-valley roughness) reaches 69.4 nm. The island structures with lateral extensions of about 0.1–0.5 μm on the surface can be seen in Fig. 1(b). In contrast, the R_{rms} of the ITO_S (Fig. 1(a)) is only 1.3 nm, and the R_{pv} is 13.4 nm. The detailed surface characteristics of ITO electrodes are listed in Table 1.

Table 1
Surface roughness of ITO substrates and the organic thin films, average rough R_a, root-mean-square roughness R_{rms} and peak-to-valley roughness R_{pv}.

Sample	Thickness (nm)	R_a (nm)	R_{rms} (nm)	R_{pv} (nm)
ITO_S	100	1.1	1.3	13.4
ITO_R	100	7.8	9.6	69.4
ITO_S/m-$MDTATA_{VD}$	100/50	1.2	1.5	16.2
ITO_S/m-$MDTATA_{SC}$	100/50	0.2	0.2	2.3
ITO_R/m-$MDTATA_{VD}$	100/50	6.1	7.5	52.9
ITO_R/m-$MDTATA_{SC}$	100/50	0.6	0.8	8.0

Fig. 2 shows the current density–voltage, luminance–voltage and efficiency–current density characteristics of devices A–D. As seen in Fig. 2(a), the device C has a higher current density compared to devices A, B and D. Especially, there is a large leakage current at voltages well before the appearance of luminance. Similar phenomena had been found by other authors [20,22]. This suggests that the "island"-like surface of the ITO_R works as a current injection center [16]. Because the rough surface morphology of the ITO was directly transferred to the organic layer [16,17], the local electric field concentrated on certain points. This concentration of the electric field is the main cause of the leakage current [16,17,20,22]. In Fig. 2(b), little difference on luminance–voltage characteristics was found in device A (smooth ITO, vacuum deposited) and device B (smooth ITO, spin-coated) with m-MTDATA as HIL. But device B shows the highest current–efficiency of 6.15 cd/A among devices A–D, which is shown in Fig. 2(c). The detailed characteristics of the devices are listed in Table 2.

Fig. 3 shows the operational stability of devices A–D, which was measured under the condition of constant current density (35.7 mA/cm^2) and at ambient temperature. The gradual degradation is frequently disrupted by a sudden drop in the luminance of device C (rough ITO, vacuum deposited), which then recovers gradually. The sudden luminance-drop indicates the formation of a short in the device. However, most of the shorts do not last for a long time, the luminance of the device C can return to normal through the "self-healing" or "repair" process [22,23]. Parallel to the decay of the luminance, an increase of non-emissive area in device C was observed, which was also reported by Forrest and co-workers [12]. The non-emissive regions were not caused by O_2 or H_2O, but by the shorts that eventually results in the failure of device C. In contrast, the dark spots (non-emissive regions) were not observed in other devices.

The half lifetimes of the devices could be extrapolated by fitting the measured decay curves with a stretched exponential decay

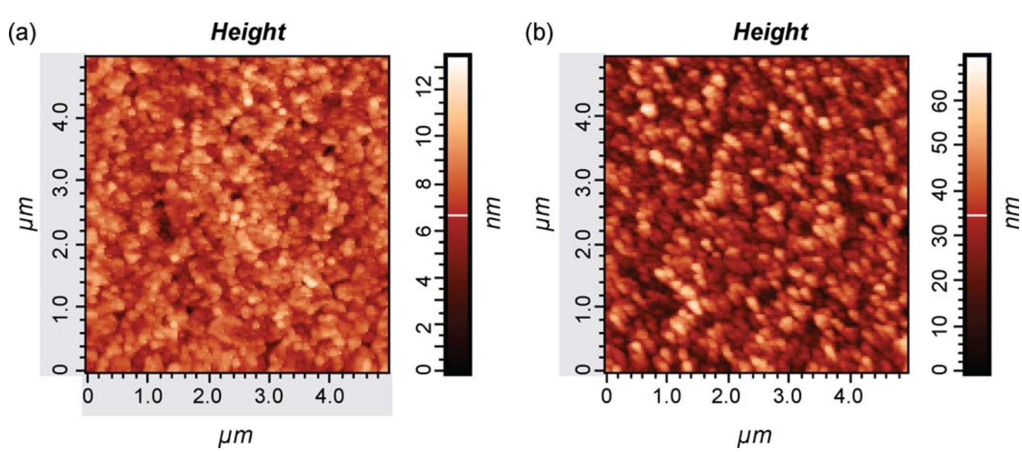

Fig. 1. AFM images (5 μm × 5 μm) of the cleaned ITO electrode: (a) ITO_S (the ITO with relatively smooth surface) and (b) ITO_R (the ITO with rough surface).