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Influence of plasma treatment of ITO surface on the growth and properties of hole transport layer and the device performance of OLEDs

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Abstract

Surface energy of indium tin oxide (ITO) surfaces treated by different plasmas, including argon (Ar–P), hydrogen (H_2–P), carbon tetrafluoride (CF_4–P), and oxygen (O_2–P), was measured and analyzed. The initial growth mode of hole transport layers (HTLs) was investigated by atomic force microscope observation of thermally deposited 2 nm thick *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) on the plasma treated ITO surfaces. The results show that different plasma treatments of ITO influence the growth of HTLs in significantly different ways through the modification of surface energy, especially the polar component. The O_2–P and CF_4–P were found to be most effective in enhancing surface polarity through decontamination and increased dipoles, leading to more uniform and denser nucleation of NPB on the treated ITO surfaces. It was further found that increased density of nucleation sites resulted in a decreased driving voltage of OLEDs. Under the same fabricating conditions, a lowest driving voltage of 4.1 V was measured at a luminance of 200 cd/m^2 for the samples treated in CF_4–P, followed by the samples treated in O_2–P (5.6 V), Ar–P (6.4 V), as-clean (7.0 V) and H_2–P (7.2 V) plasma, respectively. The mechanisms behind the improved performance were proposed and discussed.

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Keywords: Plasma; Indium tin oxide; Morphology; OLEDs; Surface treatment; Surface energy

1. Introduction

Indium tin oxide (ITO) is commonly used as an anode in organic light emitting diodes (OLEDs) due to its high conductivity, transparency in visible wavelength range, wide energy band gap and relatively high work function. OLED devices with

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as-deposited ITO, however, were found to have many problems, such as shorting, unstable I–V characteristics and indium penetration into organic layers after device operation, causing degradation in device performance [1]. To mitigate these problems, various surface treatment processes using UV ozone [2,3], gas plasma [4–6], acids [7,8], hydrogen peroxide [9], and electrochemistry [10] have been adopted to modify the ITO surface properties such as work function, surface roughness, surface energy, carrier concentration and mobility, and surface sheet resistance. Among these methods, the oxidative treatments (e.g., oxygen plasma and UV ozone) were found to be most effective in improving OLED device performance in terms of driving voltage, luminance efficiency, and stability [4,8,11,12]. The work function hypothesis is often used to explain the mechanism behind, in particular to explain the reduced device driving voltage [13–17].

Besides the work function, other surface properties were also found to play an important role in influencing the device performance [5,18,19]. It was reported that the increased surface energy would provide a better adhesion of the polymer layer and reduce the interfacial tension between polymer and substrate [6]. This would lead to an improved charge carrier injection through the interface, and thereby the OLED performance due to the better electronic contact between the two materials. Other experimental results [10,20] showed that the devices fabricated on ITO substrates with similar work functions but different surface morphologies (e.g., roughness) exhibited markedly different performance. Chen et al. recently reported their experimental results using different hole injection layers (HILs) with different levels of high occupied molecular orbital (HOMO), and concluded that the energy barrier difference between the ITO/HIL interface was not the main factor in determining the hole injection efficiency from the ITO anode to HIL [21]. Instead, they proposed that the morphology of HIL and therefore the contact of HIL/HTL would play a decisive role in the device performance.

Another point to note is that the increased work function due to plasma treatment decays over time and returns to its original value within hours [22–24]. The ultimate cause of this erratic increase of work function is yet to be understood. Possible explanations include the diffusion of high concentration oxygen on ITO surface into the ITO bulk [25] and/or adsorption of ambient carbon during handling [26,27]. It is reasonable to deduce that if the increase of ITO work function induced by oxygen plasma treatment is the governing factor, the improvements of OLED performance would be diminished correspondingly with the decay of ITO work function. However, there has been no such report on device instability attributed to the oxygen plasma treatment. In other words, no close correlation has been found between the work function and the device stability [11,28].

Therefore, more experimental work is needed to understand the mechanisms behind the improved device performance by surface treatments. This work was aimed to study the effects of gas plasma treatment on ITO surface and the correlated dependence of device performance. Four different types of plasmas, namely, hydrogen (H_2–P), argon (Ar–P), oxygen (O_2–P), and carbon tetrafluoride (CF_4–P) were used in this work. Ultra thin HTLs of N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) were deposited on the ITO samples plasma treated, respectively. The surface polarity of ITO, morphology of NPB, and the performance of OLEDs made thereof were characterized. The results showed that ITO surface polarity controls the nucleation and the initial growth of HTL. The morphology of initially formed HTL on ITO surface is closely influenced by the gas plasma used via the change of surface energy, especially the polar component. The samples with highly uniform HTLs on ITO surfaces treated by O_2–P and CF_4–P were observed to have the best improvements in OLED performance. The results suggest that the performance enhancement is the consequence of the high quality interface between ITO surface and HTL.

2. Experiment

The ITO-coated glass (Präzisions Glas and Optik GmbH) with an initial sheet resistance of 10 Ω/□ was used as the substrate for surface characterizations and also for device fabrication. After a routine cleaning process, involving a sequence of sonication in detergent solution, ethanol and de-ionized (DI) water, the ITO glass samples were transferred into a parallel plate type plasma system (MARCH PX-1000) for plasma treatment at room temperature using Ar, H_2, CF_4, and O_2, respectively. In the plasma chamber, two electrode plates were fixed with a distance of 10 mm, and the samples were placed on the bottom plate. The plasma treatment was carried out for 3 min at an rf (13.56 MHz) power of 600 W, where process pressure was main-