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Oxygen plasma treatment effects of indium-tin oxide in organic light-emitting devices

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Abstract

The effects of oxygen plasma treatment on the surface properties of indium-tin oxide (ITO) substrates and its aging were investigated by X-ray photoelectron spectroscopy (XPS), contact angle, surface energy and polarity measurements. Experimental results demonstrate that the oxygen plasma treatment improves the stoichiometry of the surface and enhances the ITO wetting, so as to improve the surface properties of ITO substrates, due to the introduction of oxygen and the partial removal of hydrocarbon contaminants from the ITO surfaces. With the increment of aging time, however, the improved ITO surface properties are observed to tend to decay. Furthermore, the aging effect of treated ITO substrates on the performance of organic light-emitting devices (LEDs) was studied with respect to the driving voltage, brightness and efficiency. It is found that the device performance is subjected to the ITO surface properties and the ITO substrates aged for various times result in significant differences in electrical and optical characteristics which become worse as the aging time increases. The results indicate that the performance of organic LEDs is closely related to the surface properties of ITO substrates and the interface characteristics of ITO/organic layer.

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Keywords: Indium-tin oxide; Oxygen plasma treatment; Surface property; Organic light-emitting devices

1. Introduction

Indium-tin oxide (ITO) is an n-type, highly degenerate, wide-bandgap semiconductor with an optical bandgap of more than 3.4 eV [1,2]. Due to its high transparency in the visible light region, low electric resistivity, excellent adhesion to the substrate, chemical stability, and ease of patterning and preparation, ITO thin films have already been widely applied in optoelectronic devices such as transparent electrodes for light-emitting devices (LEDs) [3–8], solar cells [9–11] and flat panel displays (FPDs) [12,13]. In general, a typical organic LED consists of one or more layers of organic fluorescent materials sandwiched between an ITO anode and a metal cathode [3–8]. Since the organic thin film is in direct contact with the ITO anode, the electroluminescent characteristics of the organic LED are greatly influenced by the surface properties of the ITO. Many previous researchers have reported and suggested that modifying the surface properties of the ITO is a crucial step for the fabrication of the high performance organic LEDs. Up to now, a variety of methods have been developed in the preparation of ITO surfaces for organic LEDs. They include gas plasma [14–16], ultraviolet-ozone cleaning [18,19], mechanical polishing [15,20], wet treatment [15,20], annealing process [21–23], and coating treatment with self-assembled monolayers [24,25]. Among them, oxygen plasma was considered as a promising treatment because it results in the highest work function, the lowest sheet resistance, and the smoothest surface [15].

In the present study, oxygen plasma treatment was carried out on the ITO substrates for organic LEDs. The effects of oxygen plasma treatment on the surface properties of ITO substrates and its aging were investigated by

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X-ray photoelectron spectroscopy (XPS), contact angle, surface energy and polarity measurements. In addition, we studied the aging effect of treated ITO substrates on the device performance of organic LEDs, in terms of the electrical and optical characteristics of the devices.

2. Experimental details

2.1. Surface modification

Commercial ITO-coated glasses with film thickness and sheet resistance of 150 nm and 30 Ω/square, respectively, were used and cut into $20 \times 20\,mm^2$ plates in this experiment. Prior to their use, the ITO substrates were routinely cleaned by rubbing in a detergent, rinsing in deionized water, successive ultrasonification with acetone and isopropanol each for 10 min, and finally dried in a flow of nitrogen. Then, the ITO substrates were transferred into the vacuum chamber for oxygen plasma treatment. The substrates were exposed to the oxygen plasma in a home-built radio frequency (RF) plasma etcher (SPD-400, 13.56 MHz) for 3 min at a RF power of 30 W and maintained about 30 °C. The pressure of the chamber base level and the flow rate of the oxygen were 16 Pa and 20 ml/min, respectively.

2.2. Characterization methods

The XPS measurements of the ITO substrates were carried out in a VG ESCALAB MK II spectrometer, using a monochromatic Al Kα ($h\nu = 1486.6$ eV) as X-ray source. The vacuum in the analysis chamber was maintained at approximately 10^{-8} Pa or lower. All binding energies were referenced to the binding energy of the carbon C 1s peak at 285.0 eV. The elemental composition of the films was calculated using

$$[X] = \left(\frac{A_X}{S_X}\right) \Big/ \sum_{i=1}^{N}\left(\frac{A_X}{S_X}\right), \tag{1}$$

where [X] is the content of element X, A_X the area under the peak of element X in the spectrum, and S_X is the sensitivity factor [26].

The contact angle measurements were performed using a JY-82 type contact angle goniometer by the sessile drop technique [27–31] at 20 °C in an environmental chamber. A substrate was placed on the sample stage of the goniometer, and a micro-syringe was used to deposit a liquid drop of 2–3 μl on the surface of the substrate. The steady-state contact angle was recorded within 30 s after the formation of the sessile drop. Five readings were taken, and the average was reported unless otherwise indicated. Distilled water (DW) and methylene iodide (MI) (from Beijing Chem. Co.) were chosen as the contact liquids [27–31]. Both liquids were reagent grade, and their surface tension and surface tension components are listed in Table 1.

The surface energy (γ_S) and polarity (χ_p) were calculated from the measured contact angles (θ) using the geometric-mean approach [27,28,31]:

$$(1+\cos\theta)\cdot\gamma_L = 2\left(\gamma_S^p\cdot\gamma_L^p\right)^{1/2} + 2\left(\gamma_S^d\cdot\gamma_L^d\right)^{1/2}, \tag{2}$$

$$\chi_p = \gamma_S^p/\gamma_S. \tag{3}$$

Here $\gamma_L = \gamma_L^p + \gamma_L^d$, $\gamma_S = \gamma_S^p + \gamma_S^d$; γ_L is the surface tension of the contact liquid; γ_S is the surface energy of the solid; superscripts p and d refer to the polar and dispersion components of the surface tension of the contact liquid and/or the surface energy of the solid, respectively.

Table 1
Contact liquids and their surface tension components

Surface tension data (mN/m)	γ_L^p	γ_L^d	γ_L
Distilled water (DW)	51.0	21.8	72.8
Methylene iodide (MI)	2.3	48.5	50.8

In addition, for investigating the changes in surface properties of treated ITO substrates with aging time, both chemical composition and contact angle were measured at 0, 2, 9, 21 and 48 h after the oxygen plasma treatment, respectively. During the measurements period, the ITO substrates were stored in a desiccator at a pressure of 30 Pa.

2.3. Devices fabrication

In order to study the aging effect of oxygen plasma-treated ITO substrates on the device performance, single-layer structure organic LEDs were fabricated using the ITO samples aged for various times as hole-injecting electrodes. Poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, purchased from Sigma-Aldrich Chem. Co. and used as received) was used as light-emitting material. About 100 nm thick emitting layers were obtained by spin-coating MEH-PPV from a chloroform solution at a concentration of 6 mg/ml, using a KW-4A spin-coater. After that, the organic films on the ITO substrates were heat-treated in a vacuum oven at 60 °C for 2 h. The bilayer cathode consists of a magnesium layer (60 nm) overcoated with an aluminum layer (200 nm), thermally evaporated at around 5×10^{-5} Pa (area about $3 \times 3\,mm^2$) and evaporation rates of 0.1–0.5 nm/s. In forward bias, the ITO substrate was wired as the anode. The current–voltage–brightness characteristics of the non-encapsulated devices were measured with a source measure unit (Keithley-238) and a luminance meter (Photo-2000Z). All measurements were carried out in ambient air at room temperature.

3. Results and discussion

3.1. Oxygen plasma treatment effect on the surface properties of ITO

Investigation of the chemical composition of the ITO surfaces was carried out by XPS, and Fig. 1 presents the