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Surface modification and characterization of indium–tin oxide for organic light-emitting devices

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Abstract

In this work, we used different treatment methods (ultrasonic degreasing, hydrochloric acid treatment, and oxygen plasma) to modify the surfaces of indium–tin oxide (ITO) substrates for organic light-emitting devices. The surface properties of treated ITO substrates were studied by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), sheet resistance, contact angle, and surface energy measurements. Experimental results show that the ITO surface properties are closely related to the treatment methods, and the oxygen plasma is more efficient than the other treatments since it brings about smoother surfaces, lower sheet resistance, higher work function, and higher surface energy and polarity of the ITO substrate. Moreover, polymer light-emitting electrochemical cells (PLECs) with differently treated ITO substrates as device electrodes were fabricated and characterized. It is found that surface treatments of ITO substrates have a certain degree of influence upon the injection current, brightness, and efficiency, but hardly upon the turn-on voltages of current injection and light emission, which are in agreement with the measured optical energy gap of the electroluminescent polymer. The oxygen plasma treatment on the ITO substrate yields the best performance of PLECs, due to the improvement of interface formation and electrical contact of the ITO substrate with the polymer blend in the PLECs.

Keywords: Indium–tin oxide; Surface modification; Organic light-emitting device

1. Introduction

Indium–tin oxide (ITO) has attracted intensive interest in recent years because of its unique characteristics of good electrical conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates, stable chemical properties, and easy patterning ability. The thin films of ITO as transparent electrodes have already been widely applied in many optoelectronic devices, for instance, polymer light-emitting electrochemical cells (PLECs) [1–5], organic electroluminescent diodes [6–10], solar cell devices [11–13], and flat panel displays [14,15]. As a new type of organic light-emitting devices, PLECs have attracted increasing scientific and industrial interest due to their high electroluminescence efficiency, low operating voltage, and ease of fabrication since their discovery by Pei et al. in 1995 [1]. In general, a PLEC consists of a light-emitting active blend layer of conjugated luminescent polymer and solid electrolyte with supporting salt sandwiched between an ITO electrode and a metal electrode [1–5]. When a sufficiently high bias is applied to the electrodes, electrochemical doping takes place, accompanied by the redistribution of the ions in the polymer blend film. As a result, the contact at the polymer electrode interface is ohmic, the conjugated polymer is doped *p*-type near the anode and *n*-type near the cathode, respectively, and a dynamic *p*-*i*-*n* junction is created in situ. Hence, light is emitted from the intrinsic region near the center. Since the polymer blend layer is in direct contact with the ITO electrode, the surface characteristics of ITO and the properties of the interface between the polymer blend layer and the ITO electrode play an important role in the operation of PLECs.

In this paper the surface properties of treated ITO substrates were characterized by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), sheet resistance, contact

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angle, and surface energy measurements. The effects of surface modifications of the ITO substrates on the performance of PLECs were also investigated with respect to the electrical and optical characteristics of the devices.

2. Calculation of surface energy

The surface energy of a solid material is of considerable interest with regard to the prediction of its wetting and adhesion properties, not only in fundamental research, but also for many technical processes. The contact angle (θ) of a liquid on a solid is a quantitative measurement of wetting. The smaller the contact angle, the better the wetting. Contact angle is directly related to the surface energy of the solid surface (γ_S), the surface tension of the liquid surface (γ_L), and the interface energy between solid and liquid (γ_{SL}). Their relationship is given by the Young equation [16]:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}. \tag{1}$$

In order to obtain the γ_S value, γ_{SL} has to be estimated. Fowkes [17], in 1962, pioneered a surface energy component approach. The total surface energy γ is divided into two parts: a dispersive part γ^d and a polar part γ^p. The first part results from the molecular interaction due to London forces and the second is due to all the non-London forces:

$$\gamma = \gamma^d + \gamma^p. \tag{2}$$

The following relation for solid–liquid interaction is proposed:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d}. \tag{3}$$

From Young's equation (1), it follows that

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^d \gamma_L^d}. \tag{4}$$

Since only disperse interactions are taken into account, the application of the method is quite restricted.

In 1971, Wu [18] used the harmonic mean to combine the polar and dispersion components of the solid and liquid surface energies and obtained the following equation:

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} - \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}. \tag{5}$$

Combining Young equation (1) with Eq. (5), the following equation can be obtained:

$$\gamma_L(1+\cos\theta) = \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}. \tag{6}$$

Two unknowns (γ_S^d and γ_S^p), occurring in Eq. (6), can be determined from the measurements of the contact angle for the given film using two different probe liquids with known values of γ_L^d and γ_L^p.

Table 1
Probe liquids and their surface tension components

Surface tension data (mN/m)	γ_L^d	γ_L^p	γ_L
Distilled water (DW)	22.1	50.7	72.8
Methylene iodide (MI)	44.1	6.7	50.8

3. Materials and methods

3.1. Materials

Commercial ITO-coated glasses with film thickness of 180 nm and sheet resistance of 11 Ω/square were purchased from CSG Holding Co. Ltd. and cut into 3.0 × 3.0 cm^2 plates. The solvents used for cleaning ITO substrates were acetone (99.7%, from Shanghai Chem. Reagent Co.) and alcohol (99.9%, from Beijing Chem. Co.). For contact angle measurement, distilled water (DW) and methylene iodide (MI) were chosen as the probe liquids [19–23]. Both of them were reagent grade, and their surface tension and surface tension components are listed in Table 1. The organic materials poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), poly-(ethylene oxide) (PEO), and lithium trifluoromethane sulfonate ($LiCF_3SO_3$) were purchased from Sigma-Aldrich Chemical Company to fabricate the PLECs and used as received.

3.2. Surface modifications

Two different sets of processing techniques, wet and dry cleaning, were used to modify the surfaces of ITO substrates. They are

- Ultrasonic degreasing (S1)—The substrates were successively washed in an ultrasonic bath of acetone and alcohol each for 15 min, then rinsed in deionized water, and dried with nitrogen.
- Hydrochloric acid treatment (S2)—The substrates were dipped into 10% hydrochloric acid solution for 15 min at room temperature, then rinsed in deionized water, and finally dried in a flow of nitrogen.
- Oxygen plasma treatment (S3)—The substrates were exposed to oxygen plasma in a radio frequency plasma generator for 5 min at room temperature under pressure 20 Pa, plasma power 30 W, and gas flow rate 20 sccm.

Prior to surface modifications, all the ITO substrates were cleaned first by rubbing with detergent, then in an ultrasonic bath for 10 min in deionized water, and finally dried in a flow of nitrogen. In this paper, the untreated ITO is referred to as S0.

3.3. Characterization techniques

The ITO surfaces were structurally characterized by AFM with a Seiko Instruments SPA-400 in the contact mode. Measurements were achieved at room temperature in the air, using the same pyramidal Si_3N_4 tip. The surface roughness of the ITO samples was calculated with the AFM software.