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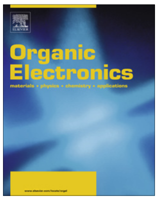

Improved efficiency of indium-tin-oxide-free flexible organic light-emitting devices

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ABSTRACT

An indium-tin-oxide (ITO)-free flexible organic light-emitting device (OLED) with improved efficiency has been demonstrated by employing a template stripping process to create an ultrasmooth PEDOT: PSS anode on a photopolymer substrate. The device performance has been improved owing to lowered surface roughness of the PEDOT: PSS anode. A 38% enhancement in efficiency has been obtained. The ITO-free OLEDs on the polymer substrate have shown flexibility, and the device is free of cracks and dark spots under small bending radius. Moreover, the elimination of the H_2SO_4 residues on the surface of the H_2SO_4-treated PEDOT: PSS by the template stripping has demonstrated its beneficial effect on the device stability.

1. Introduction

The rapid development of organic light-emitting devices (OLEDs) in recent years makes them increasingly competitive in flat-panel display and solid-state lighting applications [1–9]. In particular, the flexibility of the OLEDs becomes a very attractive feature and has potential applications in flexible devices due to the sufficient ductibility of the organic materials. Indium tin oxide (ITO) is currently dominant transparent anode in OLEDs, due to its high optical transparency in most of the visible range, high electrical conductivity and high work function. However, ITO presents several key drawbacks, such as its high cost due to the scarcity of indium, its relatively high refractive index ($n_{ITO} \sim 2.0$), which induce power lost to the total internal reflection at the ITO/glass and ITO/organic interfaces [10] and its poor mechanical robust, which is unsuitable for applications in flexible devices [11]. There are several emerging materials that have shown promise for the replacement of ITO films, for example, metal grid [12], conducting polymer [12–17], carbon nanotube [18], graphene [19], and metal nanowire [20]. Among them, conducting polymer, particularly, poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) has been attracted much attention for organic optoelectronic devices, because it enables cost-effective flexible devices as well as roll-to-roll mass production [21]. Several methods have been reported to enhance the conductivity of PEDOT: PSS [11–16]. The treatment method of dropping H_2SO_4 solutions on the dried PEDOT: PSS films had been employed to obtain high conductivity [15]. Unfortunately, the dropped H_2SO_4 will increase the surface roughness of the spin-coated PEDOT: PSS, and as well as results in a residue of the H_2SO_4 on the PEDOT: PSS surface, which is adverse to the device performance.

In this letter, we have demonstrated a flexible ITO-free OLED with ultrasmooth PEDOT: PSS anode by template

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stripping process [22–26] combined with the treatment method of dropping H_2SO_4. Compared to as-deposited PEDOT: PSS film on glass substrate, the template-stripped PEDOT: PSS film on polymer substrate has shown superiority on both conductivity and surface morphology. Its maximum current efficiency is 6.21 ± 0.43 cd/A, which corresponds to a 38% enhancement compared to that on the glass substrate. This improvement is obviously originated from hole-injection enhancement as a result of lowered surface roughness, and higher conductivity of PEDOT: PSS anode. The OLEDs based on the template-stripped PEDOT: PSS anodes on the polymer substrate have shown excellent flexibility, the devices are free of cracks and dark spots under a very small bending radius. In addition, the template stripping technique exhibits its effect on eliminating the H_2SO_4 residues on the anode surface, which is beneficial to the device stability.

2. Experimental details

2.1. Fabrication of PEDOT: PSS film on a flexible substrate

PEDOT: PSS aqueous solution (Clevios PH 1000) was purchased from Heraeus Clevios GmbH. The PEDOT: PSS films were prepared by spin coating the PEDOT: PSS aqueous solution on glass substrates at 2000 rpm for 30 s. The glass substrates were pre-cleaned with acetone, alcohol, and deionized water. The PEDOT: PSS films were dried at 120 °C on a hot plate for 15 min. The H_2SO_4 treatment was performed by dropping 100 μL H_2SO_4 (1 mol/L) solution on a PEDOT: PSS film on a hot plate at 160 °C. The films dried after about 5 min. They were cooled down to room temperature, and then were rinsed with deionized water. Finally, the polymer films were dried at 160 °C for about 5 min again. The thickness of PEDOT: PSS is decreased from 105.3 nm to 60.4 nm after the H_2SO_4 treatment. Then, a photopolymer (NOA63, Norland) film was spin coated onto the PEDOT: PSS film for 20 s at 1000 rpm and exposed to an ultraviolet light source for 5 min. The power of the light source is 125 W. At last, the cured photopolymer film can be peeled off as shown in Fig. 1(a). The photopolymer film has better adhesion with PEDOT: PSS than that with glass substrate, so that the PEDOT: PSS film can be peeled off with photopolymer and the flexible substrate with PEDOT: PSS was obtained. The thickness and refractive index of cured photopolymer substrate are around 400 μm and 1.56, respectively. Although the as-deposited PEDOT: PSS has a rough surface after H_2SO_4 treatment, the smoothness of the opposite interface is near that of the glass substrate. The surface morphology of peeled-off PEDOT: PSS will be almost identical with that of the glass surface. The surface morphology of both spin-coated PEDOT: PSS film on glass substrates and template-stripped PEDOT: PSS film on photopolymer substrates were measured by atomic force microscopy (AFM, iCON, Veeko). The sheet resistance and transmittance spectra of the PEDOT: PSS film were measured by a 4-point probe (ST-21H, 4probes Tech.) and a UV–Vis spectrophotometer (UV-2550, SHIMADZU Co., Inc., Japan), respectively.

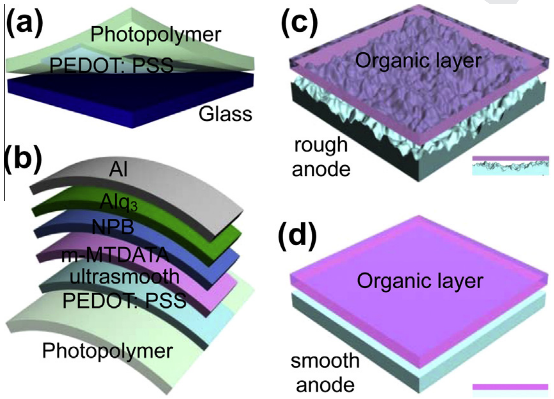

Fig. 1. Schematic of the template stripping process (a), structure of the flexible OLEDs (b), and the schematic for the contact area at the interface between the anode and the organic layer for the rough (c) and smooth (d) anode.

2.2. Fabrication and characterization of OLEDs

The OLEDs with the as-deposited PEDOT: PSS anode on glass substrates and ultrasmooth template-stripped PEDOT: PSS anode on photopolymer substrates were both fabricated. After the fabrication of the PEDOT: PSS anode, the glass and polymer substrate were put into thermal evaporation chamber. Then the organic layers and top contact were deposited layer by layer at a rate of 1 Å s^{-1} and at a base pressure of 5×10^{-4} Pa. 4,4′,4″-tris (3-methylphenyl-phe-nylamino) triphenylamine (m-MTDATA) and N,N′-diphenyl-N,N′-bis (1,1′-biphenyl)-4, 4′-diamine (NPB) were used as hole-injecting and transporting layers respectively. Tris-(8-hydroxyquinoline) aluminum (Alq_3) was used as emitting and electron-transporting layer. A 100-nm thick Al film was used as top cathode. LiF was inserted into the cathode and organic layers to enhance the electron injection. The detailed structure of OLED is PEDOT: PSS/m-MTDATA (30 nm)/NPB (20 nm)/Alq_3 (50 nm)/LiF (1 nm)/Al (100 nm) and shown in Fig. 1(b). A hole-only device with the structure of PEDOT: PSS/m-MTDATA (30 nm)/NPB (70 nm)/Al (100 nm) was also fabricated to investigate the effect of the ultrasmooth template-stripped PEDOT: PSS anode on the hole injection. Here, the active area of the device is 2×2 mm^2. The voltage–luminance and voltage–current density characteristics of the devices were measured by Keithley 2400 programmable voltage–current source and photo research PR-655 spectrophotometer. All of the measurements were conducted in air at room temperature.

3. Results and discussion

The surface morphology and conductivity of electrode plays a fundamental role in the behavior of OLEDs. The surface morphology of the bottom electrode will affect its contact area with the deposited organic layer as shown in Fig. 1(c) and (d). Generally, organic molecules are in form of large clusters when they deposited on an electrode by thermal evaporation, and they can not fill the depression of the rough electrode surface. Therefore, the contact

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