



Letter

Solvent treatment as an efficient anode modification method to improve device performance of polymer light-emitting diodes



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ARTICLE INFO

Article history:

Received 7 September 2012

Received in revised form 17 November 2012

Accepted 23 November 2012

Available online 14 December 2012

Keywords:

Organic light emitting diodes

Surface engineering

Solvent treatment

Hole injection barrier

Work function

ABSTRACT

Solvent treatment was discovered as an efficient anode modification approach to improve the performance of polymer light-emitting diodes. By simply spin-coating several drops of the polar solvent on top of the PEDOT:PSS hole injection layer, the maximum luminance efficiency was increased by as much as 83% without sacrificing the operation voltage. The combination effects of the reduced work function and the lowered resistivity of PEDOT:PSS film, decreased the hole leakage current, leading to a more balanced charge density inside the emission layer, thereby enhancing the device performance.

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1. Introduction

It is well known that high performance and good stability of Organic Light Emitting Diodes (OLEDs) strongly depend on the balanced charge densities inside the device achieved by the efficient bipolar carrier injections [1–4]. Since the charge injection is determined by the injection barrier at the organic/metal interface, it is essential to minimize the barrier by seeking the electrodes with work functions matching the electron affinity and ionization potentials of the organic layer [3–5]. At the anode side, Indium Tin Oxide (ITO) is widely used as the transparent conductor [6,7]. However, the ITO's work function of around 4.4–4.7 eV is not high enough to match the HOMO (highest occupied molecule orbital) level of the organic

emission layer which is generally in the range of 5.0–6.0 eV below the vacuum level [8–11]. In order to improve hole injection, a hole injection layer (HIL) is introduced on top of the ITO [12–14]. The most successful HIL in the application of polymer OLED (PLED) is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). With PEDOT:PSS as HIL, the PLED devices show significantly improved performance in terms of efficiency, brightness, and lifetime, etc. [15–17].

With efficient HIL, for most PLED devices, the hole possesses a smaller injection barrier at the anode side compared to the electron at the cathode side [18,19], inducing extra holes into the emission layer. Furthermore, the hole mobility of some widely-used conjugated light emitting polymers is much higher than the electron mobility, resulting in a recombination zone close to the cathode which is not a preferable location [20,21]. Recently, a lot of works have been carried out to reduce the hole leakage to the cathode, and move the recombination zone away from the cathode [22–27].

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In our early contribution, we demonstrated that by spin-coating the solvents on top of the light emitting layer, an interface dipole layer formed at the organic/metal interface lifts the vacuum level on the metal side, reducing the electron injection barrier, thereby leading to better device performance [28]. Herein, we discovered that spin-coating the polar solvents, such as methanol and ethanol, on top of the PEDOT:PSS HIL layer, could also attain the highly improved device performance. After the solvent treatment, the maximum luminance efficiency is increased by as large as 83% without sacrificing the operation voltage. The significant performance improvement is attributed to the considerably lowered hole-current which is mainly induced by the reduction of the work function of the PEDOT:PSS HIL layer. The reduced work function, confirmed by Kelvin Probe Force Microscopy, gave rise to a larger hole injection barrier which prevented excessive holes into the emission layer, thereby balancing the hole and electron current. In addition, the solvent treatment modified the PEDOT:PSS surface composition and morphology, increasing the conductivity of the film. The increased conductivity helped stabilize the device operation voltage, and reduced the Joule heating.

2. Experiments

The bi-layer PLEDs were fabricated using a conjugated polymer poly[2-(4-(3',7'-dimethyloctyloxy)-phenyl)-p-phenylenevinylene] (P-PPV) purchased from Canton OLEDing Optoelectric Materials Co. Ltd, in the device architecture of ITO/PEDOT:PSS(45 nm)/P-PPV(80 nm)/Ba(4 nm)/Al(120 nm). The hole injection layer PEDOT:PSS is Clevisos™ P Al 4083 from H.C. Starck GmbH. All chemicals and materials were purchased and used as received. Before making the light emitting devices, the ITO substrates were thoroughly cleaned in sequence in ultrasonic bath of acetone, isopropyl alcohol, detergent, de-ionized water, isopropyl alcohol, and went through O₂ plasma for 20 min. A thin layer of PEDOT:PSS was spin-casted in air followed by 10 min baking at 200 °C in nitrogen. To treat the PEDOT:PSS surface with solvent, 60 μL of the selected solvent were spin-coated on top of the PEDOT:PSS layer with the spinning speed of 2000 rpm for 1 min inside a nitrogen filled glove box. All the solvents are high purity grade (>99.8%) from Sigma–Aldrich. Immediately after the solvent spin-coating, without any further treatment, an 80 nm thick P-PPV layer was spin-casted from *p*-xylene solution. The device was completed by thermally evaporating the metal cathode of 4 nm Ba followed by 120 nm Al in the vacuum under a pressure of 3×10^{-4} Pa.

After the device structure and fabrication process had been optimized, the data reproducibility had been examined by repeating the experiments eight times. In each experiment run, there were five devices, of which one was control device without any solvent treatment, two were devices with methanol treatment, and two were devices with ethanol treatment. A total of eight control devices, sixteen methanol treated devices, and sixteen ethanol treated devices have been fabricated and characterized. In the publication, we chose a set of devices in

the same run whose maximum luminous efficiency (LE_{\max}) was most close to the average value.

Samples for UV–visible absorption spectrum measurements were prepared by spin-coating PEDOT:PSS on wet-cleaned and UV-treated quartz substrates. The J – V – L characteristics were obtained using a Keithley 236 source meter and a silicon photodiode calibrated by a Chroma Meter CS-200 (Konica Minolta). The absorption spectra measurements were carried out with a HP 8453E UV–visible Spectrophotometer. The AFM images were acquired using a DI NS4 AFM (Veeco) while the thickness of the films was measured by a Dektak 150 surface profiler.

Following the Ohm's law, the resistivity was determined by the I – V sweeps on PEDOT:PSS devices. To measure the resistivity along the vertical direction, the vertical cell structure of ITO/PEDOT:PSS/Au was adopted. To obtain the resistivity along the lateral direction, the surface cell structure was used, in which a 30 μm wide channel was formed by laser ablation on the ITO substrate with PEDOT:PSS film subsequently spin-coated on top.

XPS was performed at room temperature and pressures of less than 10^{-9} mbar, using Mg K α radiation (1253.6 eV) with the energy resolution of 0.48 eV. The power of the X-ray source was 75 W (15 kV at 5 mA) while the energy pass was set at 160 eV for all the experiments. The X-ray survey spectra were recorded in the 0–1110 eV binding energy region. Narrow scans of C 1s, O 1s, N 1s, S 2p, Na 1s, In 3d, Sn 3d were obtained at 40 eV pass energy.

Samples for Kelvin Probe Force Microscopy (KPFM) measurements were prepared by spin-coating PEDOT:PSS on ITO substrate in air followed by 10 min baking at 200 °C in nitrogen, and spin-coating respective solvent on top of the PEDOT:PSS film in a customized glove-box. The Ag paste was used to connect the test surface and the sample stage. The KPFM measurements were performed with both tapping mode and lift mode on Bruker's Dimension Icon scanning probe microscope. MESP probes (cobalt-chromium coating, Bruker) were used throughout the measurements. The contact potential difference (CPD) images were obtained on a $5 \mu\text{m} \times 5 \mu\text{m}$ area, over which the averaged CPD values are used.

3. Results and discussions

To demonstrate the solvent treatment, two polar solvents: methanol and ethanol, were selected as the representative solvents. The devices' current density (J)-bias (V)-luminance (L) characteristics and the luminous efficiency's (LE) dependence on the current density, are illustrated in Fig. 1a and b. Without solvent treatment, the device exhibits a maximum LE of 13.3 cd A^{-1} , and a threshold voltage (V_{on}) of 3.0 V. At the current density of 35 mA cm^{-2} , the operation voltage is 5.0 V with a luminance of $5.2 \times 10^3 \text{ cd m}^{-2}$ (Table 1). After ethanol treatment, the maximum LE reaches 24.3 cd A^{-1} , and the threshold voltage lowers to 2.75 V. At the current density of 35 mA cm^{-2} , the operation voltage reduces to 4.75 V, while the brightness increases to $8.3 \times 10^3 \text{ cd m}^{-2}$ (Table 1). The device treated with methanol shows similar performance enhancement. The enhancements of the max-

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