Ether solvent treatment to improve the device performance of the organic light emitting diodes with aluminum cathode

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ABSTRACT

By treating the organic/metal interface between the light emission layer and the cathode with ether solvent, the device performance of the organic light-emitting diodes with aluminum cathode is significantly improved. The maximum luminous efficiency is not only more than thirty times higher than that of the device without any ether solvent treatment, but also higher than the device with regular low work function metal cathode, such as Ba/Al. The enhanced efficiency results from the reduction of electron injection barrier, which is confirmed by the photovoltaic measurements. X-ray photoelectron spectroscopy study reveals that the formation of a carbide-like layer by the reaction between the thermally evaporated aluminum and the ethylene oxide functional group, $-CH_2CH_2O-$, helps the electron injection.

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1. Introduction

Organic light-emitting diodes (OLEDs) are "dual-injection" light emission devices whose performance strongly depends on the balanced charge densities inside the device achieved by the efficient bipolar carrier injection [1–3]. Since most organic light-emitting materials have low LUMO (lowest unoccupied molecular orbital) level, the injection of electrons from the cathode is extremely critical to balance the charges. Reducing the electron injection barrier by modifying the organic/metal interface, such as the deposition of low work-function metals [4,5], alkaline halides and alkali-earth halides [6], metallic compounds [7,8], water/alcohol soluble polymers like conjugated polyelectrolytes or their neutral precursor [9–12], non-conjugated interlayer materials like polyethylene imine (PEI) [13,14], and even solvents [15,16], has been proved to be an effective approach.

Recently, surfactants have emerged as another group of promising electron injection layer (EIL) materials for OLEDs. By blending ionic surfactants into the electroluminescent (EL) layer [17], or inserting a thin layer of ionomers or organic salts containing lithium or sodium at the interface of cathode [18,19], the EL efficiency of OLEDs with the high work function Al cathode can reach or exceed that of the devices with conventional Ca/Al or LiF/Al

cathode. Deng et al. [20] and Niu et al. [21] showed that highly efficient OLEDs were achieved by blending polyethylene glycol (PEG) into the EL layer or by casting a buffer layer of nonionic PEG-based surfactants on the EL layer with Al cathode. They found that the surfactants with a general chemical formula of $C_mH_{2m+1}(OC_kH_{2k})_n(OH)$ provide similar performance enhancement. Based on the photovoltaic measurement and the X-ray photoelectron spectroscopy (XPS), it's believed that the thermally deposited Al reacts with the ethylene oxide functional groups, $-CH_2CH_2O-$ in PEG-based surfactants, to form a thin carbide-like (negative carbon) layer. The carbide-like thin layer is essential to the formation of the interfacial dipoles to reduce the electron injection barrier [22,23]. However, PEG is an intrinsically neutral and insulating polymer. The increasing thickness of PEG in PEG/Al cathodes eventually decreases the overall device performance because of the increased cathode resistance. As a result, the PEG thickness has to be carefully controlled [24].

Since the critical functional group in the PEG-based surfactants is $-CH_2CH_2O-$, any chemical with the ethylene oxide function structure should react with Al and produce the carbide-like/Al complex layer to reduce the electron injection barrier. In our contribution, we replace PEG with the ethylene glycol monoethyl ether (EE) solvent as the EIL layer. By spin-coating EE onto the surface of the organic layer before the deposition of the metal layer, the device performance is significantly enhanced. The luminous efficiency is increased as large as 32% compared to that of the device with low work function Ba/Al cathode, and more than 30

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times higher than the device with high work function Al cathode. The XPS study reveals that the thermally evaporated Al oxidizes the residual ether solvent, introducing a carbide-like (negative carbon) layer at the organic/metal interface which helps the electron injection. Ether solvent treatment not only extends the understandings on the solvent EIL, but also provides a cost-effective approach to enhance the OLED performance without any worry on EIL thickness control compared to PEG EIL.

2. Experiments

The ITO glass substrates are purchased from the China Southern Glass Holding Corp. The PEDOT:PSS (Clevios P VP AI4083) are purchased from H.C. Starck GmbH. Poly[2-(4-(30,70-dime-thyloctylo xy)-phenyl)-p-phenylenevinylene] (P-PPV) is from Canton OLedking Optoelectric Materials Co. Ltd. All the solvents used in the study are purchased from Aldrich. All chemicals and materials are purchased and used as received unless otherwise noted.

Before making the organic light emitting devices, the ITO substrates with a sheet resistance of 17 $\Omega/\square$ were thoroughly cleaned in sequence in ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, isopropyl alcohol, followed by O_2 plasma for 20 min. A thin layer of PEDOT:PSS was spin-coated in air followed by 10 mins' baking at 200 °C in nitrogen. After PEDOT:PSS annealing, a 75 nm thick P-PPV layer was spin-casted from p-xylene solution. To treat the organic/metal interface by solvent, 60 μL of the ether solvent was spin-coated on top of the P-PPV layer with the spinning speed of 2000 rpm for 1 min. The cathode was formed by evaporating a 120 nm thick Al through a shadow mask in vacuum with a base pressure of 1×10^{-4} Pa.

The thickness of the organic films was determined by a Dektak 150 surface profiler. The current density(J)–bias(V)–luminance(L) characteristics were measured using a Keithley 236 source meter and a silicon photodiode that was calibrated by a Konica Minolta Chroma Meter CS-200. The photovoltaic measurements were performed on a Keithley 2400 source meter and an Air Mass 1.5 Global (AM 1.5 G) solar simulator (SAN-EI Electric, XES-40S1 150 W, AAA class, Japan).

Four different samples were made for XPS measurements. The sample configurations are ITO/P-PPV, ITO/P-PPV/Al (3 nm), ITO/P-PPV/EE treated, and ITO/P-PPV/EE treated/Al (3 nm). To prepare the samples, P-PPV was first spin-coated on the cleaned ITO substrate following the procedure described earlier. The EE solvent treatment followed the same process aforementioned. The aluminum was deposited in vacuum with a base pressure of 1×10^{-4} Pa. XPS analyses were performed on a Kratos Analytical Axis Ultra DLD X-ray Photoelectron Spectroscopy with a monochromatic Al Kα (1486.6 eV) X-ray source. All recorded peaks were corrected for electrostatic effects by setting the C–C component of the C 1s peak to 284.6 eV. The base pressure in the XPS analysis chamber was about 5×10^{-9} Torr. The probing depth of XPS was around 5–8 nm. The KP5050 (KP Technology, England) in a glove-box filled with nitrogen was used for all the surface potential measurements.

3. Results and discussion

To study the effect of the ether solvents on OLEDs, the green light-emitting conjugated polymer P-PPV was chosen as the light emitting layer. The chemical structures of P-PPV and the ether solvents are shown in Fig. 1. Three types of devices were fabricated. Device A: ITO/PEDOT:PSS (45 nm)/P-PPV (75 nm)/Ba (4 nm)/Al (120 nm) device as the standard reference device; Device B: ITO/PEDOT:PSS/P-PPV/Al device without any ether solvent treatment as the reference Al device; Device C: the P-PPV layer was spin-coated with ethylene glycol monoethyl ether solvent before the Al deposition. The J–V–L characteristics, and the luminous efficiency's (LE) dependence on the current density are illustrated in Fig. 2a and b, respectively. The performance data are summarized in Table 1. Compared with the standard Ba/Al Device A, which has the peak LE of 14.8 cd A^{-1}, and the maximum brightness of 47,067 cd m^{-2}, the reference Al Device B has the maximum LE of 0.6 cd A^{-1}, and the maximum brightness of 2921 cd m^{-2}. The significantly low device performance of Device B suggests that the high work function of Al makes the electron injection very difficult. After modifying the P-PPV/Al interface by EE, the peak LE is increased to 19.5 cd A^{-1} with a maximum brightness of 56,274 cd m^{-2}. Even at high working brightness of 3000 cd m^{-2}, Device C exhibits a LE of 19.0 cd A^{-1}, which is 40% higher than the standard Ba/Al device.

Based on past investigations, the device performance improvement can be attributed to the reduction of the electron injection barrier which helps electron injection and makes electron and hole density balanced inside the emission layer [15,24]. Photovoltaic measurements were carried out on the devices to verify the increase of the built-in potential due to the decrease of the electron injection barrier under the white-light illumination (100 mW cm^{-2}). As showed in Fig. 3 the open-circuit voltage (V_{OC}) of the standard Ba/Al Device A is 1.35 V. Replacing Ba/Al with Al lowers the V_{OC} to only 0.85 V. After EE solvent modification at the organic/metal interface, the V_{OC} recovers to 1.65 V. The enhancement of V_{OC} from 0.85 to 1.65 V confirms that the electron injection barrier is substantially lowered at the organic/metal interface after the solvent interface modification.

Two possible mechanisms for electron injection barrier reduction are proposed. First, the polar ether solvent molecules are self-assembled on the organic layer, and strong dipoles are formed to lift the work function of Al cathode [25–27]. Second, the residual ether reacts with aluminum during the metal deposition, and the product contributes to the efficient electron injection [23–28]. Kelvin Probe was used to measure the surface potential of the P-PPV film before and after EE treatment to detect if a dipole layer was formed by the ether solvent molecules [29,30]. Before EE treatment, the contact potential difference (CPD) between the KP tip and the P-PPV surface is 0.47 V. After EE treatment, the CPD becomes 0.55 V. The difference of 0.08 V shows that a weak dipole layer is formed by the ether solvent on the P-PPV film surface. As demonstrated in the photovoltaic experiments, the built-in potential is increased by 0.8 V after the EE solvent treatment. Therefore, the weak dipole layer cannot account for all the electron injection barrier's reduction.

If the residual ether reacts with aluminum, the compositional differences at the organic/metal interface can be characterized by XPS measurements [22,23,28]. Four samples were measured: (a) ITO/P-PPV; (b) ITO/P-PPV/Al (3 nm); (c) ITO/P-PPV/EE treated; and (d) ITO/P-PPV/EE treated/Al (3 nm). The deconvoluted and normalized C 1s core level spectra are illustrated in Fig. 4. The deconvolutions of spectra are based on the minimum Gaussian peaks to make the best fit after the background subtraction [31]. For P-PPV film without any solvent treatment in Fig. 4a, there are three peaks at binding energy 284.5, 285.9 and 288.4 eV. Among the peaks, the main peak (Peak 2) at 284.5 eV is associated with hydrocarbon atoms (C–C and C–H) [32]. After the pristine P-PPV film is treated with EE solvent, the intensity of Peak 3 at 285.9 eV increases (Fig. 4b), showing that more C–O bonds are introduced by EE solvent. Since Peak 4 is associated with the carbon atoms in a highly oxidative environment, such as those in the carboxylate ester groups [33–35], the intensity enhancement of Peak 4 is attributed to the oxidization of the polymer film by aluminum. After the pristine P-PPV film was treated by EE solvent followed by Al evaporation, a new Peak 1 at 283.5 eV is observed in Fig. 4d. It has been