Improved hole-injection contact for top-emitting polymeric diodes

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In this letter, an efficient hole-injection contact was achieved for the top-emitting polymeric light-emitting diodes (PLEDs). The anode has a structure of metal/molybdenum oxide/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). It has been found that hole injection was significantly improved by inserting a thin layer of MoO_3 between aluminum and PEDOT:PSS. An ultraviolet photoelectron spectroscopy (UPS) was used to investigate the change of work function, and photovoltaic measurement confirmed that the improved hole injection is due to the reduction of barrier height, resulted from the addition of transition metal oxide. PEDOT:PSS layer was found necessary in anode structure to further enhance the hole injection and electroluminance efficiency. A peak power efficiency of 11.42 lm/W was achieved at current density of 1.2 mA/cm^2 for the white emission top-emitting PLEDs. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2731684]

With potential applications in display and solid-state lighting, organic/polymeric light-emitting diodes (OLEDs/PLEDs) have recently attracted considerable attention due to rapidly improving efficiency and performance.[1–6] Two major device structures, bottom emitting and top emitting, have been demonstrated. Compared to conventional bottom-emitting OLEDs/PLEDs, top-emitting organic light-emitting diodes have the structural advantage of higher aperture ratio for display application.[7–10] Typically, a top-emitting OLED/PLED consists of a reflective metal anode, an organic light-emitting layer, and a transparent cathode. The physical properties of anode and cathode, such as work function, charge injection, and reflectivity, significantly determine the device performance in top-emitting OLEDs/PLEDs. High work function metals, such as nickel (Ni) or gold (Au), have been widely used as anode; however, an additional hole-transport layer is usually required to improve the device performance. This approach is convenient and efficient for OLEDs, in which multiple layers of thin films can be easily deposited on top of each other. However, it is inapplicable in top-emission PLEDs because of the difficulty to process multiple layers.

Transition metal oxides, such as molybdenum oxide (MoO_3), tungsten oxide (WO_3), and vanadium oxide (V_2O_5), were used in tandem OLEDs as the charge generation layer[11,12] and also as the charge injection layer in bottom emissive OLEDs.[13,14] These applications suggest that transition metal oxides could be used as an effective hole-injection layer in top emissive PLEDs/OLEDs. On the other hand, it has been reported that poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer can effectively improve the hole injection in polyfluorene-based PLEDs.[15–17] In this letter, we demonstrated an anode structure of aluminum (Al)/MoO_3/PEDOT:PSS, showing an excellent capability of hole injection in top-emitting PLEDs. Our optimum top-emitting PLEDs can achieve a high power efficiency of 11.42 lm/W at a low current density of 1.2 mA/cm^2. Moreover, a series similar anode structure was also found applicable in top-emitting PLEDs, such as silver (Ag)/MoO_3/PEDOT:PSS or Al/V_2O_5/PEDOT:PSS. Therefore, this kind of anode structure, metal/transition metal oxide/PEDOT:PSS, can provide a general and convenient method for obtaining an efficient hole-injection contact in top-emitting PLEDs.

To investigate the improvement of hole injection, we examine the current density-voltage-luminance (*J-V-L*) characteristics of devices and work function of anode by using UPS. The investigation of thickness dependence by photo-current measurement showed that there is a range of MoO_3 thickness for the optimum device performance. The surface of anode was confirmed by atomic force microscopy (AFM) to provide the evidence of morphology and roughness.

The devices in this work have a structure of anode/LEP/cathode, where the light-emitting polymer (LEP) is a blended polymer consisting of poly(9,9-dioctylfluorene) (PFO) and 0.2 wt % rubrene dissolved in *p*-xylene. From our previous works, PLEDs using this blended polymer can achieve rather high efficiency.[18] For comparison, different types of bottom electrodes were used: Al, Al/PEDOT:PSS, and Al/MoO_3/PEDOT:PSS. Al(100 nm) and MoO_3 are evaporated on the precleaned glass substrates under the vacuum pressure of about 1×10^{-6} Torr. PEDOT:PSS was then spun coated and baked at 120 °C for 30 min in the air. For the cathode, a spin coated cesium carbonate (Cs_2CO_3) layer was used to improve the electron injection before the cathode was depos-
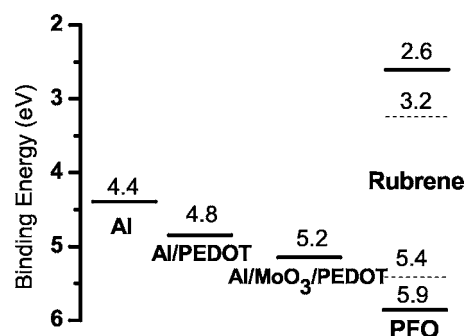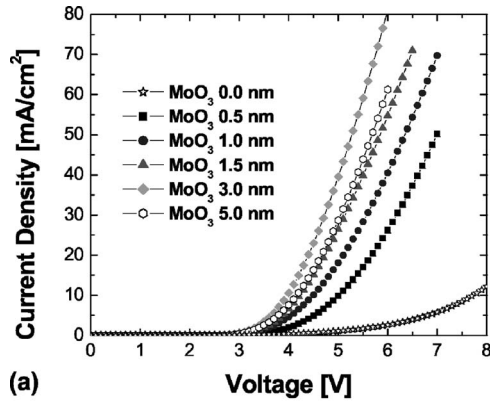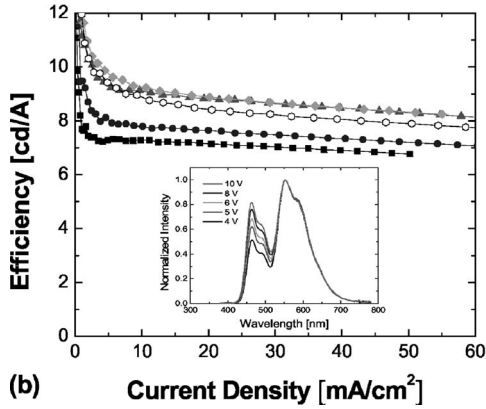

FIG. 1. Work function of different types of anode structure and energy-level diagram for the PLEDs components.

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FIG. 2. (a) *J-V* characteristics and (b) efficiency as a function of current density for top-emission devices with different MoO$_3$ thicknesses. The structure of top-emitting PLEDs: Al(100 nm)/MoO$_3$(X nm)/PEDOT:PSS (25 nm)/LEP(80 nm)/Cs$_2$CO$_3$/Ca(10 nm)/Ag(10 nm), X from 0 to 120 nm. The inset of (b) shows EL spectra of devices under different biases.

ited. The details of solution process of LEP and Cs$_2$CO$_3$ can be found elsewhere.[18] Finally, the semitransparent cathode, calcium (Ca: 10 nm) and silver (Ag: 10 nm), was thermally evaporated on top of the emission layer under a vacuum of $\sim 1 \times 10^{-6}$ Torr. The electrical properties of devices were characterized by a Keithley 2400 source meter and the electroluminance (EL) spectra were measured by SpectraScan PR-650 spectrometer. The work function of anode was measured by UPS. The photocurrent of devices was measured under illumination from a ThermoOriel 150 W solar simulator with AM1.5G filters.[19] An AFM was used to investigate the surface morphology of anode.

A desired hole-injection contact should provide a good energy-level alignment with the adjacent active emission layer. An effective way to provide this information is to examine the work function of anode structure. Figure 1 shows the work function of various anode structures measured by UPS and energy level of the other layers. The structure of Al/MoO$_3$/PEDOT:PSS shows a higher work function, 5.2 eV with a thickness of 3 nm MoO$_3$ layer, than bare Al(4.4 eV) and Al/PEDOT:PSS(4.8 eV). The work function of Al/MoO$_3$ cannot be obtained here because an unexpected secondary electron edge appeared at low binding energy, which makes the work function hard to be determined. It might result from the high roughness of MoO$_3$ thin film on Al surface, and we will discuss it later. However, comparing the change of work function, the insertion of thin MoO$_3$ layer should be responsible for the rising of work function from 4.8 to 5.2 eV.
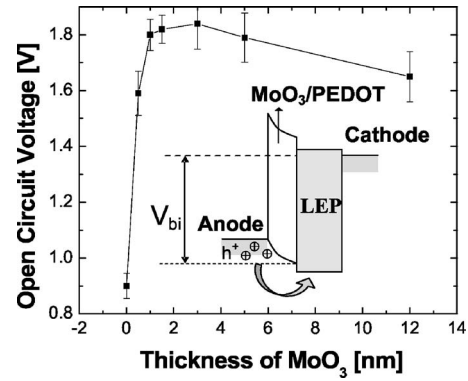

FIG. 3. Open circuit voltage as a function of MoO$_3$ thickness. The inset shows a schematic diagram to explain the reduction of barrier height for hole injection with a MoO$_3$ layer in the anode structure.

Although the structure of Al/MoO$_3$/PEDOT:PSS shows a good capability to be the anode from the information of work function, to realize the role of this anode structure employed in working devices, a series of top-emitting PLEDs was fabricated with different thicknesses of MoO$_3$ layer. In Fig. 2(a), the *J-V* characteristics of devices showed much improvement with the addition layer of MoO$_3$ in anode structure. The current density initially increased as the increasing of MoO$_3$ thickness, and reached a maximum value at the MoO$_3$ thickness of 3 nm. The current density then decreased with further increased MoO$_3$ thickness. At the optimal thickness of 3 nm, a peak luminance efficiency of 11.64 cd/A was obtained at a low current density of 1.2 mA/cm^2 with the Commission International de L'Eclairage (CIE) coordinates of (x=0.35, y=0.43). The turn-on voltage for this device was also dramatically reduced to 2.7 V. This performance is much better than devices using Al/PEDOT:PSS as anode (turn on voltage of 4.2 V). To achieve high luminance efficiency, it is insufficient to have good charge injection; charge balance also plays an important part in device performance. In Fig. 2(b), the thickness dependence on luminance efficiency shows the same trend as *J-V* characteristics, indicating that the addition of MoO$_3$ layer also improves the charge balance, and thus enhances the luminance efficiency. The inset of Fig. 2(b) reveals the bias dependence on eleectroluminace characteristics of top-emitting PLEDs. As expected in polymer blended system, the blue emission peaks increase as the bias increases, resulting the blueshift in color presence.

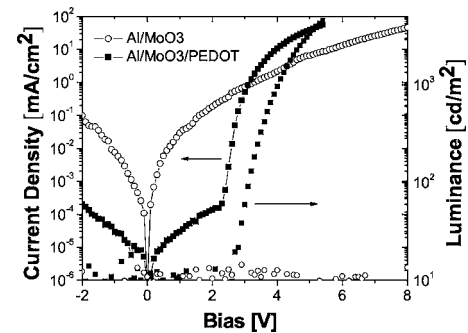To further study the actual role of MoO$_3$ layer in enhancing the device performance, a photovoltaic experiment was

FIG. 4. *J-V-L* characteristics of devices with and without PEDOT:PSS layer in anode structure.

conducted to measure the open circuit voltage (V_{oc}). Similar to electroabsorption measurement,[20] photovoltaic measurement provides information about work function shift of electrode.[3] In this measurement, photocurrents of the devices were measured when the devices were subjected to a simulated solar lamp with fixed brightness and spectrum. Figure 3 shows the MoO_3 thickness dependence on V_{oc} in our experiment. An obvious increasing of V_{oc} is found between devices with and without MoO_3 layer, and V_{oc} reaches a maximum value at MoO_3 thickness of 3 nm. The V_{oc} then decreases slightly when the thickness continuously increases.

The thickness of the MoO_3 layer was varied without changing any other layers in this experiment. Therefore, if one ignores the effect of interface dipole, since it is the same for all devices, the change in V_{oc} should reflect the change in built-in potential between the cathode and the anode. In other words, we can observe the shift of the work function for the anode when the MoO_3 thickness is changed. The inset of Fig. 3 can be used to explain this concept. The increase in V_{bi} suggests that the work function of the anode is increased as well. As a result, the energy barrier for hole injection could be lowered with the introduction of MoO_3. Although introducing a MoO_3 layer can effectively lower the barrier energy for hole injection, thicker layer of it may introduce series resistance into the device structure, resulting in lower V_{oc} and efficiency after an optimal thickness, as shown in Fig. 3. The nature of interface between MoO_3 and Al is still unclear. An earlier study[21] indicated that an Ohmic contact may be formed between MoO_3 and Al due to charge tunneling through the thin depletion region at the interface.

An interesting question is that why a PEDOT:PSS layer should be necessary in the structure of anode. Figure 4 shows the different J-V-L characteristics of devices with and without PEDOT:PSS layer. Two obvious changes arise in devices with PEDOT:PSS coating anode: leakage current dramatically reduces at low bias voltage, while hole injection significantly increases under higher bias voltage. Devices with PEDOT:PSS layer show an obvious turn-on effect around bias of 2.7 V, while the other one does not have this characteristic, and the light output is also found dramatically diminished. Previous study for the role of PEDOT:PSS layer in polyfluorene-based LEDs (Refs. 15–17) reported that an Ohmic contact was formed between PEDOT:PSS and PFO due to the electron trap at the interface, increasing the electric field at the anode and consequently improving the hole injection and cause the switching (turn-on) effect. The surface morphology measured by AFM showed that a thickness of 3 nm MoO_3 layer may not cover the whole surface of Al layer; instead, lots of "nanoislands" formed (not shown here) and exposure part of the Al surface. Therefore, the LEP layer might directly contact with Al surface without the layer of PEDOT:PSS; moreover, the surface roughness becomes much poor (rms: 7.67 nm) compared with device with PEDOT:PSS layer (rms: 3.42 nm), raising the possibility of pinhole existence in the following LEP layer, which could be the main reason for high current leakage at low bias voltage. In this condition, the rough active polymer layer will have the chances to contact with Al and MoO_3, resulting in exciton quenching and poor electroluminance. Therefore, the presence of PEDOT:PSS layer with MoO_3 layer can further enhance the hole injection, smooth the mechanical contact of LEP, and improve the EL efficiency. As a result, with the combination of Al/MoO_3 and PEDOT:PSS layers, a nearly Ohmic hole-injection contact for top-emitting PLEDs can be formed in this case.

In summary, we reported an improved hole-injection contact, Al/MoO_3/PEDOT, in white top-emitting PLEDs. Similar anode structures of metal/transition oxide/PEDOT:PSS were also found effectively when employed in top-emitting PLEDs. UPS measurements confirmed the rising of work function resulted from an additional MoO_3 layer in the anode structure. A luminance efficiency of 11.64 cd/A was achieved at a low current density of 1.2 mA/cm². The results of the photovoltaic experiment showed that the addition of MoO_3 layer can effectively lower the barrier height for hole injection, and there is an optimal thickness for the metal oxides layer. PEDOT:PSS layer plays an important role in the anode structure, improving not only hole injection but also mechanical contact for active polymer layer and EL efficiency.

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