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Efficient electron injection from bilayer cathode with aluminum as cathode

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Abstract

A new bilayer cathode has been developed for varieties of RGB emitting polymers to form an effective electron injector. An effective electron injection from high work function metal, such as Al cathode can be realized by incorporation of a thin layer of amino-ended alkyl-substituted polyfluorene copolymer and corresponding ammonium salt-cationic polyelectrolyte between metal cathode and emitting layer. The performance of polymer light emitting-diodes (PLEDs) fabricated with such bilayer cathodes can be enhanced to the levels comparable or even higher than that obtained by using Ca and Ba as the cathode (for red QE=2-3%, for green 5-8%, for blue 1-2% respectively). The new electron-injection layer can be processed from environment-friendly solvents such as alcohol or water in which most of light-emitting polymers are insoluble. The mechanism of lowering the barrier height for electron injection from Al is discussed based on I-V characteristics, build-in potential, and X-ray diffraction data.

Keywords: electroluminescent, polyelectrolyte, polymer light-emitting diode, Schottky barrier, metal/semiconductor interfaces

1. Introduction

Electroluminescent (EL) conjugated polymers have attracted intense research interests due to their potential application as active semiconductors in large-area flat-panel displays. [1] Since their first demonstration from poly (*p*-phenylene vinylene) (PPV), [2] persistent endeavors have been bought out to improve device performance and tune the emitting spectra covering the whole visible spectra to meet the practical needs. [3-4] Balanced charge carrier injection and transport are essential to achieve efficient, low operating voltage and long life PLEDs. Since most of conjugated EL polymers are p-type semiconductors, electron injection and its transport are limited by the low electron affinity and low electron mobility. As a result, it is desired to use low work function metals such as alkali metal or alkaline-earth metals as cathode although these metals are susceptible to degradation upon air and water vapor atmosphere. Over the past years, great efforts have been made to develop a new type of electron injection cathode with high environmental stability and high efficiency. Hung et al. [5] first discovered that effective electron injection electrode could be constructed by the incorporation of a thin layer of dielectric metal fluorides, such as LiF, between high-work function metal Al and Alq_3. [6] It is approved that metal fluoride/Al cathode is equally effective in PLEDs. [7] Later, Li et al. reported that an effective electron injection can be achieved by the insertion of an ultrathin aluminum oxide between the Al and emitting layer. [8] It was shown by Uniax group that the insertion of organic surfactant molecules between Al and EL polymer could improve device performance up to the level obtained by low-work function metal cathodes. [9]

In this paper, we report an efficient electron injection from a new bilayer cathode which consists of aminoalkyl-substituted polyfluorene copolymer or its quaternized salt which can be spin-coated from alcohol or water solution on top of an emissive layer in combination with subsequent thermal deposition of high-work function metal, such as Al. This new type of bilayer cathode significantly enhances electron injection for varieties of red, green and blue EL polymers, resulting in high efficiency PLEDs, which are comparable to that of using low work function metals, such as Ca and Ba as cathode.

2. Experimental

The synthesis of the alternating copolymers poly [(9, 9-bis (3'-(N, N-dimethylamino) propyl)-2, 7-fluorene) -alt-2, 7- (9, 9–dioctylfluorene)] ($PF\text{-}NR_2$) and their quaternized salt ($PF\text{-}N{+}R_3$) are described elsewhere. [10] MEH-PPV and P-PPV were prepared according to a well-known procedure. [11] The fabrication of PLEDs with soluble PPV derivative, MEH-PPV, and P-PPV as an electroluminescent layer follows standard process, as described in [10]. A thin $PF\text{-}NR_2$ film of 3 or 20nm was deposited subsequently on top of emitting layer by spin

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coating from 0.04% or 0.2% methanol solution with a few drops of acetic acid. The thickness of PF-NR_2 layer was determined by Surface Profiler (Alfa Step-500, Tencor). Finally, 200nm-thick aluminum is evaporated with shadow mask to form the top electrode at a base pressure of 2×10^{-4}Pa. Except the spin coating of PEDOT layer, all the processes were carried out in a controlled atmosphere of nitrogen dry-box (Vacuum Atmosphere Co.) with less than 1 ppm oxygen and moisture. For blue light-emitting PFO, a 40nm-thick poly (N-vinylcarbazole) (PVK) was spin-coated on the top of PEDOT layer to facilitate holes injection from anode. In order to avoid a contamination of volatile low work function metal during Al cathode deposition on top of PF-NR_2 layer, an evaporation chamber was thoroughly cleaned down by long time baking at a high temperature and in a high vacuum ($<1\times10^{-4}$ Pa) before Al deposition. Control device from corresponding EL polymer without a PF-NR_2 layer was always placed side by side with EL polymer/PF-NR_2 devices in order to check the contamination. The current-voltage-luminance (I-L-V) characteristic was measured by a Keithley 236 source-measurement unit and a calibrated silicon photodiode. The luminance was calibrated by a PR-705 SpectraScan spectrophotometer (Photo Research) and the external EL quantum efficiency (QE) was collected by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere).

3. Results and discussion

Figure 1a shows a typical J-V characteristic and light output of ITO/PEDOT/MEH-PPV/PF-NR_2(3nm)/Al at bias from -7 to +7V. Upon the application of a voltage between the ITO and the Al contact, an orange light was observed only when the ITO was wired to the positive terminal. The rectification ratio was greater than 5800 for ±7V, and the emission intensity exceeded 3330 cd/m^2 at 7 V. Figure 1b shows the luminance, and external quantum efficiency (QE) as a function of bias for ITO/PEDOT/MEH-PPV/PF-NR_2/Al device. A control device without PF-NR_2 layer (ITO/PEDOT/MEH-PPV/Al) fabricated in exactly the same Al deposition conditions with the same batch of MEH-PPV was shown for comparison (Fig. 1b). As can be seen from Fig. 1b, the external QE of MEH-PPV LED devices fabricated with Al as the cathode is generally less than 0.07% with a luminance of 100cd/m^2 at 7.0V, which is consistent with an earlier report on PLEDs with the high work function Al cathode. [12] For the device with a bilayer cathode with a thin layer (ca. 3nm) of PF-NR_2 inserted between MEH-PPV and Al, the operation voltage at 100cd/m^2 decreased to 3.2V. The maximal external quantum and luminous efficiency reached 1.85% and 1.58cd/A respectively, with a luminance of 2000cd/m^2 at 5.5V. Device performance with Ba/al cathode is also shown in Fig. 1b for comparison. It indicates that bilayer device shows similar device parameters as that with Ba/Al device, although it shows slightly lower efficiency at low operating voltage. Since PEDOT/MEH-PPV/Al is hole-dominated devices, any enhancement in electron injection will certainly reflected in the improvement of device performance. In this case, we conclude that with the incorporation of PF-NR_2/Al bilayer cathode, more efficient electron injection was achieved resulting in more balanced current between holes and electrons. Table 1 compares the performance of MEH-PPV devices with PF-NR_2/Al bilayer cathode in comparison with the controlled devices with Al and Ba/Al cathodes fabricated from the same batch of MEH-PPV at current density around 30mA/cm^2. It is obvious that the PF-NR_2/Al can reach the levels comparable to that obtained by using low work function metal like Ba, Ca as the cathode without significant rise of operating voltage.

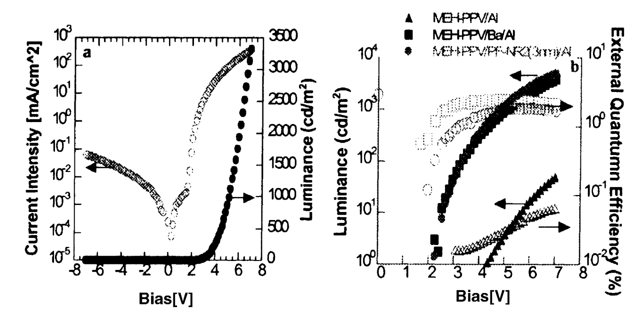

Fig. 1 (a) I-L-V characteristic of ITO/PEDOT/MEHPPV/ PF-NR_2/Al at -7-+7V bias, (b) L-V, QE-V characteristics of MEH-PPV devices with Al, Ba/ Al and PF-NR_2(3nm)/Al cathodes

Similar improvements were observed for other EL polymers of different band gap with a PF-NR_2/Al bilayer cathode. As shown in Fig. 2a, for blue emitting PFO polymer with a thin PF-NR_2/Al cathode, the current increase pattern change dramatically and tend to be similar to that of device with Ba/Al as cathode, indicating enhanced electron injection. As a result, device with a 20nm-PF-NR_2 layer shows an external quantum efficiency of 1.59% at a current density of 30.0mA/cm^2, compared to 0.03% at similar current density for a plain Al device (Table 1). When this bilayer cathode applied to green-emitting poly [2-(4-(3',7'-dimethyloctyloxy) -phenyl) -p-phenylenevinylene] (P-PPV), the external quantum efficiency of 7.42% and luminous efficiency of 22.6 cd/A with a luminance of 7927cd/m^2 have been reached at a current density of 35.1mA/cm^2, a little bit higher than that with a low-work function Ba/Al cathode (6.71%, 20.46cd/A, Table 1). Table 1 also compares the device performance for P-PPV and PFO with Al, Ba/Al and bilayer PF-NR_2/Al cathodes at current density around 30mA/cm^2.