

# Electron Injection Enhancement by Diamond-Like Carbon Film in Polymer Electroluminescence Devices \*

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**Abstract :** A diamond-like carbon (DLC) film is deposited as an electron injection layer between the polymer light-emitting layer (MEH-PPV) and aluminum (Al) cathode electrode in polymer electroluminescence devices (PLEDs) using a radio frequency plasma deposition system. The source material of the DLC is *n*-butylamine. The devices consist of indium tin oxide (ITO)/MEH-PPV/DLC/Al. Electron injection properties are investigated through *F*-*V* characteristics, and the mechanism of electron injection enhancement due to a thin DLC layer has been studied. It is found that: (1) a DLC layer thinner than 1.0 nm leads to a higher turn-on voltage and decreased electroluminescent (EL) efficiency; (2) a 5.0 nm DLC layer significantly enhances the electron injection and results in the lowest turn-on voltage and the highest EL efficiency; (3) DLC layer that exceeds 5.0 nm results in poor device performance; and (4) EL emission can hardly be detected when the layer exceeds 10.0 nm. The properties of ITO/MEH-PPV/DLC/Al and ITO/MEH-PPV/LiF/Al are investigated comparatively.

**Key words :** diamond-like carbon; polymer electroluminescence device; electron injection enhancement

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## 1 Introduction

The interfaces between metals and organic semiconductors play an important role in the physics of polymer light emitting diodes (PLEDs). In addition, the asymmetry in the work function of the two electrodes is responsible for the PLEDs' rectifying behavior and governs the injection of carriers into the polymer<sup>[1]</sup>. In order to fabricate efficient devices and to minimize injection barriers low work function cathodes and high work function anodes are desirable. "Ideal" electrode materials have been difficult to obtain, however, as has the incorporation of injecting interlayers at enhanced carrier injection. For example, although indium tin oxide (ITO) is the most widely used anode because of its

transparency and low resistivity, the additional insertion of a hole injecting layer, such as poly-ethylenedioxythiophene/poly-styrene sulphonic acid (PEDOT:PSS), has been shown to improve the performance of LEDs substantially<sup>[2~5]</sup>.

In ITO/MEH-PPV/Al, where the anodic barrier is already low, a major improvement in efficiency and lifetime is achieved by increasing the electron current since electrons typically have lower mobility than holes. Injection can be enhanced by using low work function cathodes such as calcium or magnesium. These are not ideal, however, because they are reactive. Recently, improved performance and stability have been obtained by inserting a thin insulating film of lithium fluoride (LiF) or diamond-like carbon (DLC) between the more stable cathodic metal (such as Al) and the polymer

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emitter. This has been shown to improve electron injection significantly<sup>[6-9]</sup>. The mechanism behind this enhancement is not fully understood. Possible candidates include tunneling<sup>[7]</sup>, longer electron attenuation length<sup>[10]</sup>, quenching of interfacial reactions with the metal electrode<sup>[11]</sup>, reduction of the barrier height to electron injection<sup>[6,11-14]</sup>, and dissociation of the LiF to form a low work function contact<sup>[11]</sup>.

We report the excellent EL performance of devices containing an Al/DLC cathode structure. The thickness of the DLC layer we adopted varies within the range of 0 ~ 10.0 nm. The presence of an ultrathin DLC layer of 1.0 nm between the MEH-PPV and Al leads to a poorer EL performance than that in a device without DLC. When the thickness of the buffer layer is further increased, however, the current injection gradually improves. A device with a 5.0 nm thick DLC layer exhibits excellent EL characteristics. A significantly reduced turn-on voltage, brightness of 15800 cd/m<sup>2</sup>, and EL efficiency of 4.3 cd/A, are achieved. We tentatively ascribe the dependence of device performance on the DLC thickness to the effect of electron tunneling through the DLC layers.

## 2 Experiment

ITO-coated glass with a sheet resistance of 20  $\Omega$  was used for the device fabrication. The routine cleaning procedure included sonication in detergent, rinsing in de-ionized water, and a final UV ozone treatment to remove the remaining organic materials. During the fabrication process, a quartz-oscillator thickness monitor was used to detect the deposition rate. A multilayer structure of ITO/MEH-PPV/DLC/Al was sequentially deposited on the cleaned ITO substrate.

The DLC films were prepared<sup>[15]</sup> in a capacitive couple radio frequency plasma system with a stainless reactor and were deposited onto MEH-PPV thin film. The source material of the DLC film was *n*-butylamine. The organic precursor vapor was carried into the reactor by pure hydrogen. In the process of deposition, the carrying gas flow rate was 50 mL/min; the pressure of the chamber was maintained at 266 Pa; the apparent radio frequency power was 150 ~ 300 W. Raman spectroscopy analysis shows that this film has a diamond-like struc-

ture. The Al cathodes were evaporated subsequently at 0.2 nm/s through a shadow mask. The thickness of the DLC and polymer films was measured using an oscillating crystal monitor. The active area of the pixels was 10 mm<sup>2</sup>. All the fabrication and measurement processes were performed in a nitrogen glove box, and the completed LEDs were encapsulated using an epoxy resin.

Luminance-current-voltage (*L-I-V*) characteristics were recorded simultaneously by combining the spectrometer with a programmable voltage-current source Keithley Sorce 2400.

## 3 Results and discussion

Current-voltage (*I-V*) and luminance-voltage (*L-V*) characteristics of devices with an Al/DLC cathode with different DLC layer thicknesses are shown in Figs. 1 and 2, respectively. The *I-V* curve of an ITO/MEH-PPV/DLC/Al exhibits a typical rectifying junction behavior. Similar rectifying *I-V* characteristics have also been observed from ITO/MEH-PPV/Al. With a 1.0 nm DLC layer inserted between the PPV and Al, both *I-V* and *L-V* curves are shifted towards higher voltage region as compared with the device without DLC. With a 0 ~ 1.0 nm DLC layer inserted between the PPV and Al, the *I-V* characteristics indicate a relatively large series resistance  $R_s$  compared to the device without DLC, basically due to nonoptimized sample preparation procedures (including the Al deposition). We note that the devices with a 0 ~ 1.0 nm DLC layer inserted between the PPV and Al can limit the electrical-to-optical conversion efficiency since a portion of the applied voltage will be dropped across the resistance. However, with further increasing of the DLC layer thickness, the current injection of the device is gradually enhanced. We ascribe the improvements in charge injection to one of two possible effects. The barrier between the cathode Fermi level and the organic HOMO may be lowered by decreasing either the metal work function or the interfacial gap states in the organic film, which may be eliminated. In other words, the series resistance  $R_s$  in the ITO/MEH-PPV/DLC/Al is reduced greatly, probably due to *n*-butylamine molecular permeation of the pores, forming a better contact between the Al and inner surface of the MEH-PPV.

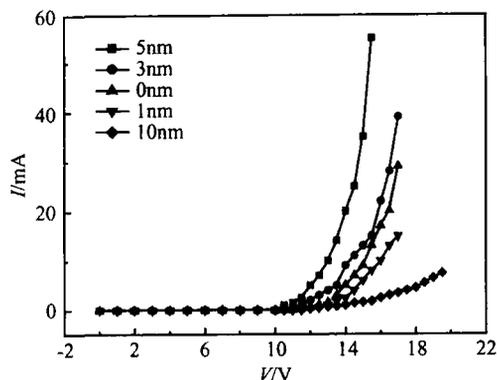


Fig. 1  $I$ - $V$  characteristics of devices with different DLC layer thicknesses

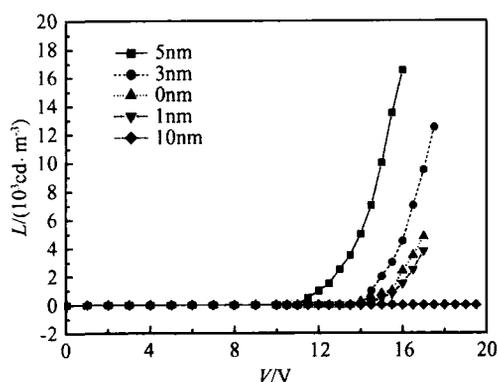


Fig. 2  $L$ - $V$  characteristics of devices with different DLC layer thicknesses

A DLC layer thickness of over 5.0nm shifts the  $I$ - $V$  and  $L$ - $V$  curves back to the higher voltage region. EL emission can hardly be detected when the layer exceeds 10.0nm. This indicates that whether the EL performance, can be greatly improved or not by using an Al/DLC cathode structure strongly depends on the thickness of the DLC layer.

The curves of EL efficiency versus the bias voltage for the devices are shown in Fig. 3. The device without DLC exhibits poor EL performance and the highest efficiency is only about 2.7cd/A. Among the devices we fabricated, that with 5.0nm-thick DLC gives the highest EL efficiency of 4.3cd/A, which is comparable to that of the OLED with an Al/LiF or Ag/LiF cathode reported by Brown *et al.*<sup>[8]</sup> and Wang *et al.*<sup>[9]</sup>. It is interesting to note that the EL efficiency of the device with 1.0nm-thick DLC is lower than that of the device without DLC. This is different from the case using

Al/LiF as the cathode in OLEDs<sup>[8]</sup>, but it is the same as the case using Ag/LiF as the cathode in OLEDs<sup>[9]</sup>.

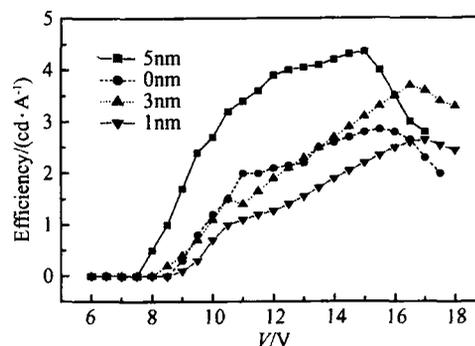


Fig. 3 Electroluminescent efficiency versus voltage curves with different DLC thicknesses

The turn-on voltage as a function of DLC thickness is measured. It is found that the turn-on voltages for the devices with DLC layer thicknesses of 0, 1.0, and 3.0nm are 11.9, 12.5, and 11.7V, respectively. This means that inserting a DLC layer thinner than 1.0nm between the MEH-PPV and Al would lead to a turn-on voltage higher than that of the device without DLC. It is also evident that the device with 5.0nm-thick DLC demonstrates the lowest turn-on voltage of 10.0V. The optimal thickness of DLC layer for the LEDs with the Al/DLC cathodes is 5.0nm.

In contrast, first, the turn-on voltages of ITO/MEH-PPV/DLC(LiF)/Al with the same LiF and DCL thickness are measured. It is found that the turn-on voltages for the device with a DLC layer thickness of 5.0nm is almost same as that for the device with a LiF layer thickness of 1.0nm, and the EL efficiencies of two devices have the same level; second, the optimal thickness of LiF in small molecule OLEDs with Al cathodes previously reported is around 0.5nm<sup>[8]</sup>. With Al used as the cathode, a LiF layer thinner than 1.0nm would significantly improve the EL efficiency; when the LiF thickness is increased beyond 1.0nm, the EL efficiency drops rapidly. However, the optimal thickness of LiF in small molecule OLEDs with Ag cathode reported by Wang *et al.*<sup>[9]</sup> is around 3.0nm. With Ag used as the cathode, the influence of LiF layer thickness on EL efficiency is different from the case using Al/LiF as the cathode in OLEDs<sup>[8]</sup>. In the experi-

ments, the EL performance of the PLEDs with an Al/DLC cathode structure can be significantly improved by using a 5.0nm-thick buffer layer of DLC, much thicker than that for the Al/LiF cathode structure, and the influence of the thickness of DLC layer on EL efficiency of the PLEDs with an Al/DLC cathode structure is different from the case using Al/LiF as the cathode in OLEDs and the same as the case using Ag/LiF as the cathode in OLEDs.

## 4 Summary

A DLC film is deposited as an electron injection layer between the MEH-PPV and Al cathode electrode in PLEDs using a radio frequency plasma deposition system. For ITO/MEH-PPV/DLC/Al, the efficiency of electron injection from the cathode is strongly dependent on the thickness of the DLC buffer layer. In contrast, the turn-on voltages of ITO/MEH-PPV/DLC(LiF)/Al with the same LiF and DCL thickness are measured. It is found that the turn-on voltage for the device with a DLC layer thickness of 5.0nm is almost same as that for the device with a LiF layer thickness of 1.0nm, and the EL efficiencies of the two devices have the same level.

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## 聚合物电致发光器件中用类金刚石碳膜增强电子注入<sup>\*</sup>

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**摘要:** 用正丁胺作碳源,采用射频辉光等离子系统制备类金刚石碳膜(DLC),沉积在聚合物发光器件中的发光层(MEH-PPV)和铝(Al)阴极间作电子注入层.制备了结构为ITO/MEH-PPV/DLC/Al的不同DLC厚度的器件,测量了器件的*I-V*特性、亮度及效率,研究了DLC层对器件电子注入性能影响的机制.结果表明:当DLC厚度小于1.0nm时,其器件有较ITO/MEH-PPV/Al高的启动电压和低的发光效率;当DLC厚度在1.0~5.0nm之间时,器件的性能随着DLC厚度增加而变好;当DLC厚度为5.0nm时,器件具有最低的启动电压与最高的发光效率;当DLC厚度继续增加时,器件的性能随着DLC厚度增加而变差.并对ITO/MEH-PPV/DLC/Al和ITO/MEH-PPV/LiF/Al的器件性能进行了比较研究.

**关键词:** 类金刚石碳膜; 聚合物发光器件; 电子注入增强

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