

Effect of polymer-insulating nanolayers on electron injection in polymer light-emitting diodes

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We report the effect of polymer-insulating nanolayers on electron injection in the polymer light-emitting diodes (PLEDs) in which a hole is the major charge carrier. Several different polymer nanolayers with varying dielectric constants were placed between the emitting layer and the aluminum cathode, and their influence on the device performance was investigated. The device with a nanolayer of lower dielectric constant demonstrated higher luminescence quantum efficiency. In particular, when a ~ 10 -nm-thick polystyrene layer was employed, the device gave approximately two orders of magnitude higher external quantum efficiency than that of the one without an insulating nanolayer. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667014]

Light-emitting diodes (LEDs) based on conjugated polymers have attracted much attention because of their potential applicability to flat, large area displays which can be operated at a relatively low driving voltage.^{1,2} One of the most important current challenges in the field of polymer LEDs (PLEDs) is to achieve balanced charge carrier injection that is essential for high light-output as well as for high efficiency. For this purpose, many an electron-injecting or transporting material has been employed in PLEDs.^{3–5}

Aluminum (Al) is inexpensive and easy to use for the cathode of PLEDs but electron injection in the devices with Al cathode has proved more difficult to occur than hole injection, resulting in unbalanced charge injection. It is necessary to use a low work function metal such as calcium (Ca) to reduce electron injection barrier for a higher efficiency.^{2,6} Such metals, however, are so susceptible to moisture and oxygen that the resulting devices suffer from poor environmental stability. Various methods have been tried to achieve balanced injection of holes and electrons without using low work function metals. Postdeposition annealing has been tried above the glass transition temperature (T_g) of emitting polymer;⁴ it greatly enhanced the luminance and the electroluminescence (EL) quantum efficiency by modifying the polymer/metal electrode interfaces. Another method is to introduce an *n*-type material with high electron affinity for the purpose of lowering the electron injecting barrier at the polymer/cathode interface.^{3,7,8}

An interface modification layer of inorganic insulating material such as lithium fluoride has been introduced between the Al cathode and emitting layer to minimize the electron injection barrier.^{9–11} The underlying mechanism of the enhanced electron injection, however, is not completely

understood yet. An insulating polymer film formed by the Langmuir–Blodgett technique and thin enough to allow electron tunneling has also been used as the insulating layer, and the quantum efficiency of the device was increased by four times with the turn-on threshold voltage almost unchanged.¹²

In this work, we employed three kinds of polymer thin films that are capable of electron tunneling and are of different dielectric constants [$\sigma_{\text{polystyrene}}$ (2.5) $< \sigma_{\text{poly(methylmethacrylate)}}$ (3.0) $< \sigma_{\text{polyethylene oxide}}$ (4.0)] as the insulating layer. We investigated how the dielectric property of the insulating layer influences the lowering of the effective barrier height for electron injection to the emitting layer of poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV).

We used polystyrene (PS, Aldrich Chem., M_w : 280 000), poly(methylmethacrylate) (PMMA, M_w : 120 000), and polyethylene oxide (PEO, M_w : 30 000) as the insulating layer. PS and PMMA are soluble in dimethyl formamide and PEO is soluble in acetonitrile. We prepared several kinds of polymer light-emitting devices composed of the MEH-PPV emitting layer and one of the above polymer insulating layers to investigate the effect of the insulating layer on electron injection to the device. ITO-coated glass substrates were subjected to a wet cleaning process and treated by oxygen-plasma prior to use.¹³ A 100-nm-thick MEH-PPV layer was spin-cast from the chlorobenzene solution on the ITO substrate. And then, one of the polymer insulating materials was also spin-cast from the solution with a ~ 10 nm thickness on top of the emitting layer, followed by the thermal evaporation of Al cathode in vacuum to complete the device preparation.

Figure 1 shows the current–voltage (I – V) characteristics of the devices prepared. We observed a dramatic current density increase at the same bias voltage when a PS nanolayer was inserted between the emitting layer and the Al

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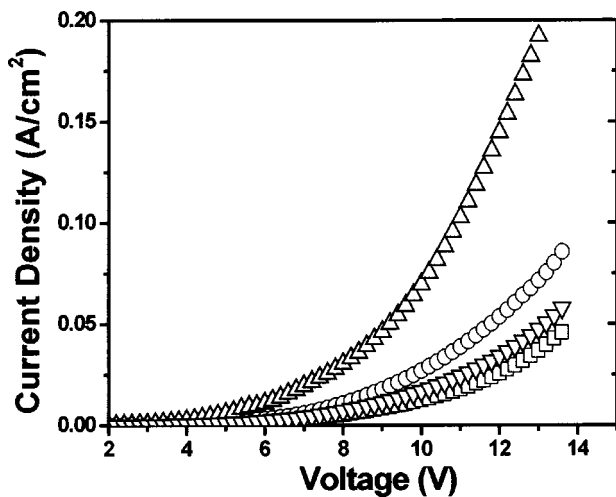


FIG. 1. Current density vs voltage characteristics for the EL devices of the ITO/MEH-PPV/AI (\square), ITO/MEH-PPV/PEO/AI (∇), ITO/MEH-PPV/PMMA/AI (\circ), and ITO/MEH-PPV/PS/AI (\triangle) structures.

cathode. All three devices with polymer insulating nanolayers showed increased current density, however, the influence of the nanolayer varied with its dielectric constant: A nanolayer with lower dielectric constant further increased the current density. Generally, in the devices with Al cathode, the observed current is mainly contributed by the hole current because the energy barrier to electron injection is much higher than that to hole injection in those devices.¹⁴ So the enhanced current density indicates that the insulating nanolayers facilitate the electron injection.

The energy band model can explain the facilitated electron injection in the devices with insulating nanolayers. Figure 2 illustrates the band gap structures of the devices consisting of two polymer layers between anode and cathode, where layers 1 and 2 represent the emitting (MEH-PPV) and the thin insulating layers (PS, PMMA, or PEO), respectively. If the potential V is applied between the two electrodes, the

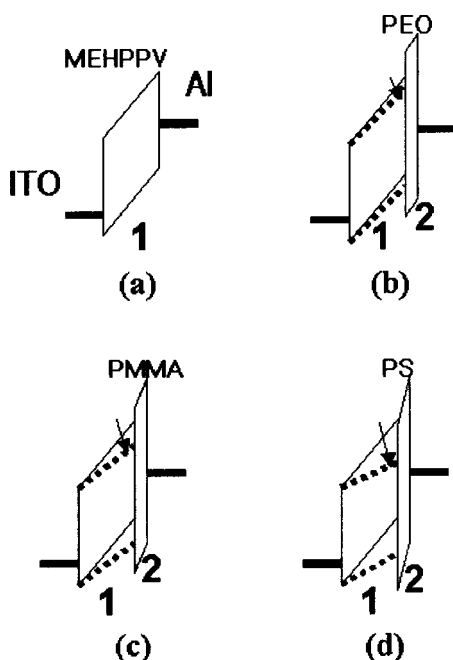


FIG. 2. A schematic representation of the charge injection barrier lowering for positively biased sandwich devices of the ITO/MEH-PPV/insulating nanolayer/Al structure. Nos. 1 and 2 denote MEH-PPV and insulating nanolayer, respectively.

potential drop in each layer at the steady state can be expressed as follows:¹²

$$V_1 = \frac{(\epsilon_2/d_2)V - \sigma}{\epsilon_1/d_1 + \epsilon_2/d_2}, \quad V_2 = \frac{(\epsilon_1/d_1)V + \sigma}{\epsilon_1/d_1 + \epsilon_2/d_2}, \quad V_1 + V_2 = V, \quad (1)$$

where ϵ_i is the dielectric constant, d_i the thickness of the i th layer, and σ the accumulated charge density, respectively. This relationship states that the overall potential drop (V) across the device is distributed to each layer and the potential drop in the emitting layer (V_1) can be controlled by changing the layer thicknesses and dielectric constants. By lowering V_1 , the slope of band bending in the emitting layer will be lowered and the electron tunneling probability will increase, thus we can achieve a reduced effective energy barrier to electron injection to the device.

When the cathode is in direct contact with the emitting layer [Fig. 2(a)], the energy barrier to the electron injection is determined as the difference between the lowest unoccupied molecular orbital level of the emitting layer and the work function of the cathode. However, when an insulating layer is inserted between the cathode and the emitting layer, the barrier height becomes dependent on the thickness and the dielectric constant of the insulating layer. The effect of the thickness of a polymeric insulating layer has been systematically investigated by Kim's group.¹² It has been also reported that the inorganic insulating materials, such as Al_2O_3 (Refs. 15 and 16) and LiF,^{17,18} which are present at the emitting polymer/metal interface and of the thickness of tunneling range, facilitate the electron injection.

In the present device system, the potential drop in the MEH-PPV emitting layer was varied by employing the polymeric insulating layers with different dielectric constants. When PS was inserted as a thin insulating layer, the potential drop in the emitting layer and the effective barrier height for electron injection to the device must be smaller than the case when PMMA or PEO was inserted. The use of a polystyrene layer in LEDs has been examined by several authors^{19–21} but it has been employed for other purposes. The arrows in Fig. 2 indicate the change in energy band bending due to the lowering of potential drop in the emitting layer.

The optical outputs of the devices with various insulating layers were shown in Fig. 3(a). As is typical of PLEDs, the emission intensity increases with increasing electron current for all the devices. The luminescence quantum efficiency was, however, strongly influenced by the dielectric constant of the insulating layer employed as shown in the inset of Fig. 3(b). We obtained the maximum external quantum efficiency of 0.15% (photons/electrons) when PS was used as the insulating layer. This is ~ 50 times higher value than that of the MEH-PPV device without an insulating layer. The insulating layer also affected the turn-on threshold voltage. Because the thicknesses of the insulating layers in the devices were controlled to be comparable, the threshold voltage is probably dependent on the degree of band bending. The operation of the Al-cathode device requires an additional bias potential to that under the "flat-band" condition in order for the electrons to overcome the high barrier height [turn-on threshold voltage, $V_{\text{on}} = 2.4$ V]. For the devices with PS and PMMA insulating nanolayers, V_{on} decreased to 1.75 and 2.1 V, respectively, indicating that lower electric fields

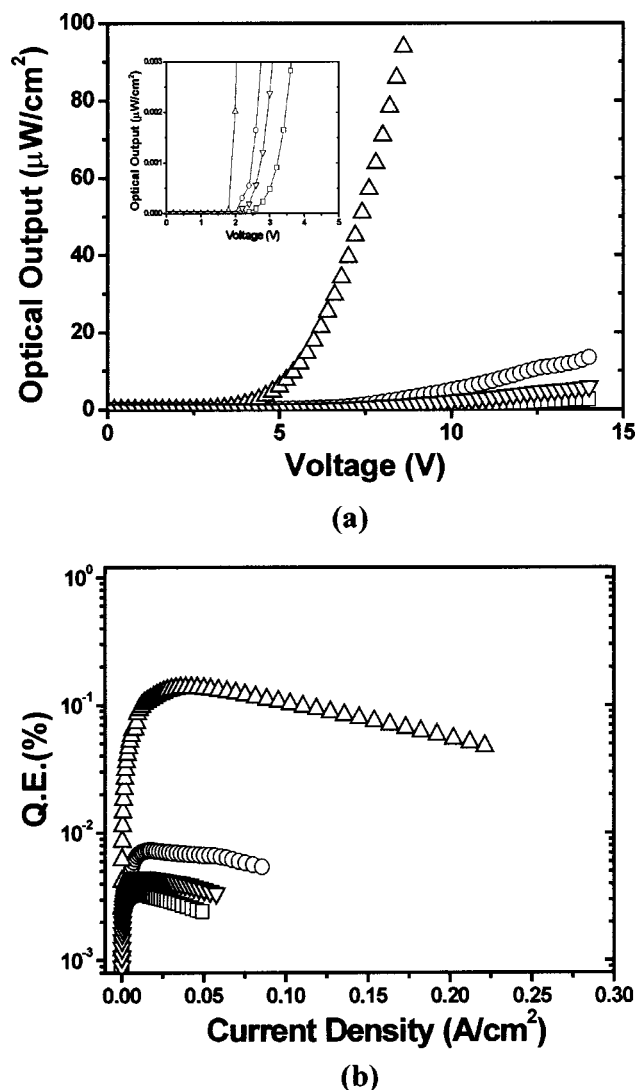


FIG. 3. (a) Radiance vs voltage characteristics and (b) EL quantum efficiency vs current density for the EL devices of the ITO/MEH-PPV/Al (\square), ITO/MEH-PPV/PEO/Al (∇), and ITO/MEH-PPV/PMMA/Al (\circ), ITO/MEH-PPV/PS/Al (\triangle) structures. The inset of (a) shows a closer look of the turn-on voltage region.

are required for electron injection as depicted in the inset of Fig. 3(a).

From Eq. (1), it is expected that the thickness of emitting layer (d_1) affects the potential barrier between the emitting layer and the Al cathode. Figure 4 shows the current–voltage–luminance characteristics of the ITO/MEH-PPV(120 nm)/PS(10 nm)/Al and ITO/MEH-PPV(80 nm)/PS(10 nm)/Al devices. The electron injection and optical output of the device with an 80-nm-thick MEH-PPV layer was hugely improved compared with the device with a 120-nm-thick MEH-PPV layer, which implies that the emitting layer thickness plays a crucial role in controlling the band bending and the electron injection from the cathode. There are several factors that influence the electron injection to the device with an insulating nanolayer, however, control of the dielectric constant of the insulating layer as well as the emitting layer thickness provides the most effective way because the insulating layer thickness can be varied only within the tunneling range.

In conclusion, the major advantage of the dielectric polymer nanolayer in the device is the effective reduction of

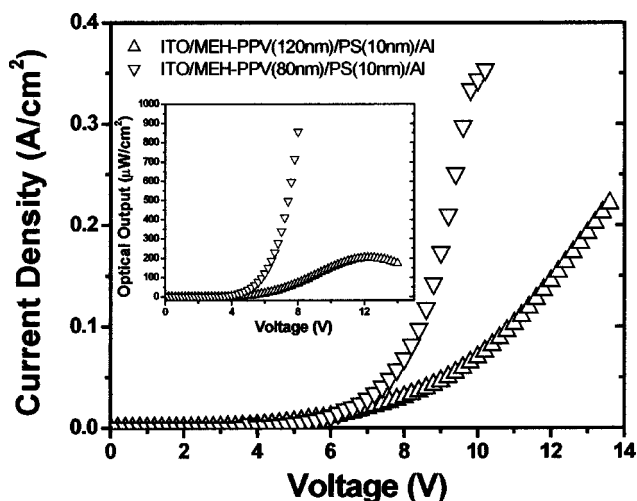


FIG. 4. Current density vs voltage characteristics of the ITO/MEH-PPV(80 nm)/PS/Al and ITO/MEH-PPV(120 nm)/PS/Al devices. The inset shows radiance vs voltage characteristics of the same devices.

the electron injection barrier height at the cathode/emitting layer interface. Especially, the employment of the PS nanolayer not only brings about a highly improved Q.E. but also lowers the turn-on threshold voltage compared with the single layer device. The presence of the low dielectric constant nanolayer of PS at the Al-MEHPPV interface causes a considerable lowering of the electron injection barrier height, which can be attributed to the improved balancing of charge injection.

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