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.

Polyaniline-type material has been employed in PLEDs.3–5 For this purpose, many an electron-injecting or transporting material has been employed in PLEDs.4 It greatly enhanced the luminance and the electron injection, resulting in unbalanced charge injection. It is necessary to use a low work function metal such as calcium (Ca) or aluminum (Al) cathode has proved more difficult to occur than hole 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 \[ \left[ \sigma_{\text{poly}(2.5)} < \sigma_{\text{poly}(methylmethacrylate)} (3.0) < \sigma_{\text{polyethylene oxide}} (4.0) \right] \] 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’-ethoxyhexyloxy)-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 \( \sim 10 \) 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 cathode.
where layers 1 and 2 represent the emitting layer consisting of two polymer layers between anode and cathode, respectively. Figure 2 illustrates the band gap structures of the devices controlling electron injection in the devices with insulating nanolayers. A schematic representation of the charge injection barrier lowering is shown in Fig. 3.

If the potential \( V \) is applied between the two electrodes, the potential drop in each layer at the steady state can be expressed as follows:

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V_1 = \frac{(e_2/d_2)V - \sigma}{e_1/d_1 + e_2/d_2}, \quad V_2 = \frac{(e_1/d_1)V + \sigma}{e_1/d_1 + e_2/d_2}, \quad V_1 + V_2 = V,
\]

where \( e_i \) is the dielectric constant, \( d_i \) the thickness of the \( i \)th layer, and \( \sigma \) 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. It has been also reported that the inorganic insulating materials, such as \( Al_2O_3 \) (Refs. 15 and 16) and LiF (Ref. 17), 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 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 \( \sim 50 \) 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, \( V_{on} = 2.4 \) 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...
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/Al (\(\bigtriangledown\)), ITO/MEH-PPV/PEO/Al (\(\bigtriangleup\)), and ITO/MEH-PPV/PMMA/Al (\(\bigcirc\), ITO/MEH-PPV/PS/Al (\(\bigtriangleup\)) structures. The inset of (a) shows a closer look of the turn-on voltage region.

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