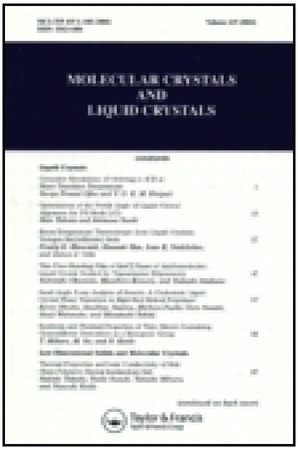

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Reduction in the Threshold Voltage of a Polymer Light-Emitting Diode by High Molecular Density on a Photo-Crosslinking Layer

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The operation voltage of a polymer light-emitting diode (PLED) is significantly reduced using a photo-crosslinking layer whose thickness is of the order of 10 nm. A thin photo-crosslinking layer of a poly(methyl methacrylate)-based photo-polymer, coated on the hole injection electrode (anode), was treated with a linearly polarized ultraviolet (LPUV) light. Compared to the unpolarized UV exposure case, for a poly(2-methoxy,5-(2′-ethyl-hexoxy)-1,4-phenylenevinylene) (MEH-PPV) film spin-coated on the LPUV exposed photo-crosslinking layer, the threshold voltage of the PLED was found to be reduced by about 35% and the current density was greatly enhanced. The underlying physical mechanism comes from the increase of the packing density in addition to a partial order of the MEH-PPV on the photo-crosslinking polymer upon the LPUV exposure.

Keywords: packing density; photo-crosslinking layer; polymer light-emitting diode

INTRODUCTION

Electroluminescence (EL) using conjugated polymers have been extensively investigated since the first development of a device based on poly(p-phenylene vinylene) (PPV) [1]. Organic light-emitting displays

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have many advantages such as wide viewing angles, fast response, high luminance, and high contrast ratio. The polymer light-emitting diode (PLED), especially, can be fabricated through a simple process of a printing or an ink-jet method which is potentially cost-effective. In recent years, the PLEDs have been employed for mobile displays and other portable devices. However, the operating voltage and the power efficiency need to be improved for such applications. Several attempts to reduce the operation voltage by the use of a tunneling layer or a doping process with a rare-earth complex have been made so far [2,3]. The use of a thin tunneling layer was found to enhance the current efficiency by balancing the carrier injection. A thin insulating layer in the tunneling range can be formed by the Langmuir-Blodgett technique which involves a complicated process. Moreover, an additional layer is often required not to deteriorate the performances of the PLED.

In this work, we demonstrate that a thin photo-crosslinking layer, poly(methyl methacrylate)-based photopolymer (PMMA), can be used to obtain a more densely packed state of the electroluminescent (EL) layer through the exposure of a linearly polarized ultraviolet (LPUV) light. The LPUV exposed PMMA layer was found to increase the packing density and the effective conjugation length in the EL layer of a poly(2-methoxy,5-(2′-ethyl-hexoxy)-1,4-phenylenevinylene) (MEH-PPV). This results in the reduction of the operating voltage and the enhancement of the power efficiency.

MATERIALS AND METHODS

The device structure of our PLED is shown in Figure 1(a). An anode was made with indium-tin-oxide (ITO) having high conductivity and

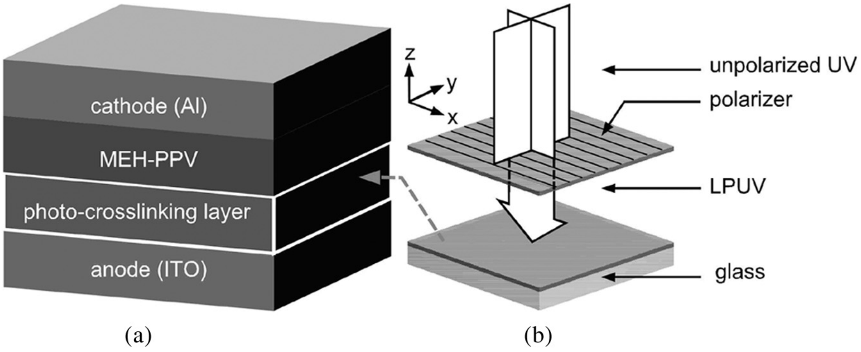


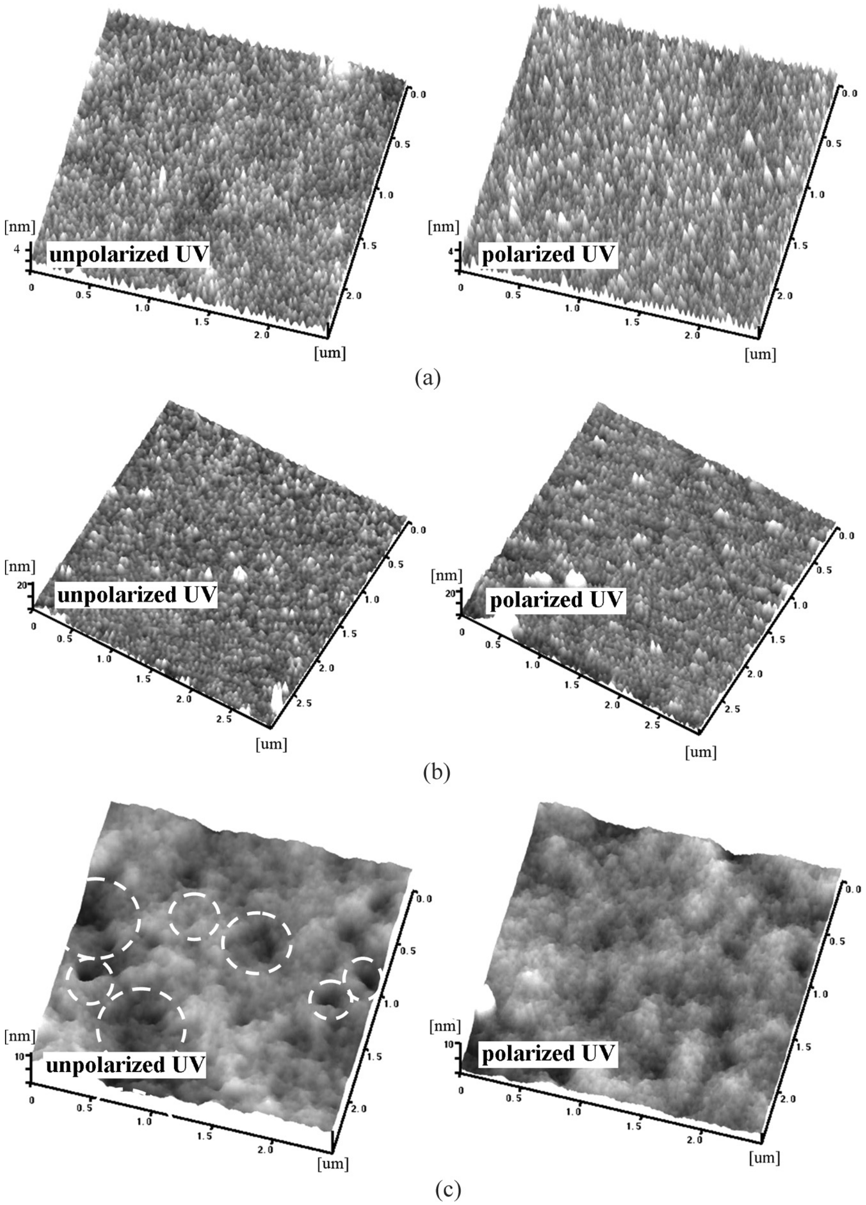
FIGURE 1 (a) The device structure of our PLED and (b) the schematic diagram of the UV exposure.

transparency over the visible range. Note that ITO has a high work function for hole injection. Aluminum (Al) was used as an electron injection electrode (cathode). The photo-crosslinking layer was prepared using the PMMA with alkyl end group $-OC_5H_{11}$ attached to a photo-sensitive group containing cinnamoyl moiety. The photo-crosslinking layer was exposed to the LPUV light for the surface treatment. The MEH-PPV was used as the EL material.

In fabricating a PLED, the PMMA dissolved in cyclopentanone (0.2 wt.%) was spin-coated onto the ITO deposited glass substrate. The PMMA layer was then baked at 150°C for 1 hour. The thickness of the PMMA layer was measured as about 20 nm. The PMMA layer was exposed to the LPUV light of an Hg lamp (Oriel) as shown in Figure 1(b). The UV intensity after passing through a linear polarizer was about $10\,\mathrm{mW/cm^2}$. The exposure time was 200 seconds. The MEH-PPV dissolved in chlorobenzene (0.5 wt.%) was coated onto the PMMA layer. The MEH-PPV layer was then baked at 60°C for 2 hours. The Al was subsequently deposited to form a cathode. The active, light-emitting area of the device was about $8.75\,\mathrm{mm^2}$. For the dichroic UV/visible absorption and photoluminescence (PL) measurements, fused silica substrates were also used for the PLED devices. The absorption spectra were measured using a UV/Vis. spectrophotometer (Jasco V-530). The PL was measured using a spectrofluorometer (Jasco FP-6500) after the UV exposure on each sample. Light output was monitored using a spectrometer (Photo Research Inc. PR-650 SpectraColorimeter). Surface morphologies were determined with an atomic force microscope (AFM) (Seiko Instruments SPA400).

RESULTS AND DISCUSSION

The surface roughness of the unpolarized UV exposed PMMA layer and that of the LPUV exposed PMMA layer were nearly same as $5.3 \pm 0.3\,\text{Å}$. The contact angles in both cases were about 77.0°. Interestingly, no difference in the surface roughness as well as the contact angle between the two PMMA layers was observed as shown in Figure 2(a). This is consistent with the previous results on poly(vinyl cinnamate) (PVCi) layers upon the UV exposure [4]. The effect of the solvent dissolving the MEH-PPV on the morphological change in the PMMA layer was shown in Figure 2(b). The surface roughness of the PMMA layer due to the solvent effect was found to be $13.0 \pm 2.0\,\text{Å}$. Note that the surface roughness of the MEH-PPV on the LPUV exposed PMMA layer was decreased to $8.0 \pm 0.5\,\text{Å}$ while that on the unpolarized UV exposed PMMA layer was essentially unchanged ($14.0 \pm 1.0\,\text{Å}$) as shown in Figure 2(c). Moreover, fewer void sites of



(a)

(b)

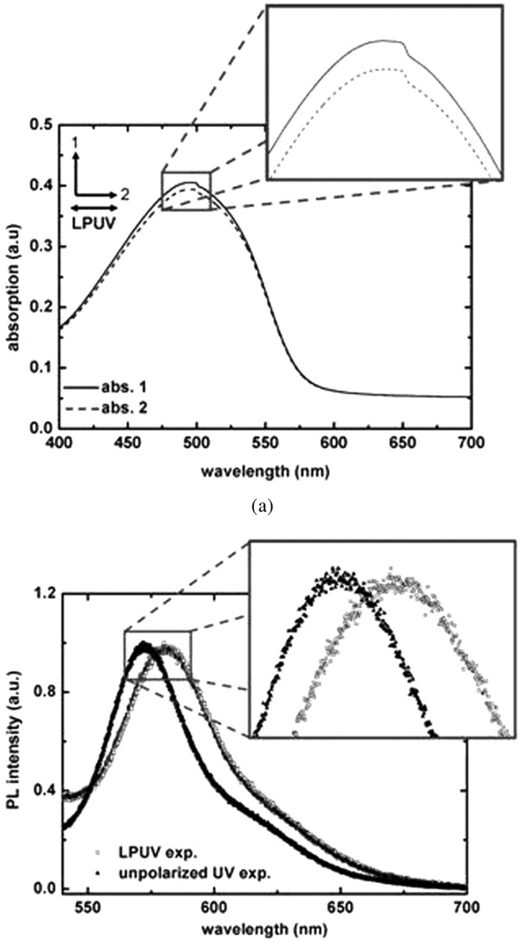
(c)

FIGURE 2 The AFM images: (a) the PMMA layers, (b) the PMMA layers after coated with the solvent of the MEH-PPV, and (c) the MEH-PPV layers on the unpolarized UV exposed PMMA layer and the LPUV exposed PMMA layer. The void sites were denoted by white dashes.

the MEH-PPV, represented by white dashes in Figure 2(c), were seen on the LPUV exposed PMMA layer than on the unpolarized UV exposed PMMA layer. This indicates that in addition to the partial order of the MEH-PPV molecules, both the structural packing density and the void sites are expected to influence the performances of the PLED device.

In order to examine the partial order and the conjugation length, associated with the structural arrangement of the MEH-PPV molecules, upon the LPUV exposure, we measured the UV/visible absorption spectra and the PL spectra. Figure 3(a) shows the absorption spectra of the MEH-PPV layer measured through a polarizer parallel and perpendicular to the polarization of the LPUV. As shown in Figure 3(a), the absorption along the parallel direction is slightly higher than that along the perpendicular direction. This means that the MEH-PPV molecules were partially aligned perpendicular to the polarization direction of the LPUV. This is similar to the alignment of liquid crystal molecules on a LPUV exposed polymer layer like a PVCi layer [5]. In contrast, the absorption spectra of the MEH-PPV on the unpolarized UV exposed PMMA layer along the two directions were found to be equal. For the PL spectra, in the LPUV exposed case, a PL peak was shifted to a longer wavelength as shown in Figure 3(b) in relative to the unpolarized UV exposed case. From the fact that the polymer having a longer conjugation length shows a PL peak at a longer wavelength and exhibits broadening properties [6], it is reasonable to conclude that a high packing density of the MEH-PPV molecules plays a significant role on the increase of the effective conjugation length. This supports that the MEH-PPV molecules are more densely packed on the LPUV exposed PMMA layer as observed by our AFM measurements in Figure 2(c). It is noted that the partial order of the MEH-PPV molecules on the LPUV exposed PMMA layer would increase the molecular packing density due to the directional alignment.

Figure 4 shows the EL characteristics of three PLEDs with different UV exposure conditions for the MEH-PPV layer. No UV, unpolarized UV, and LPUV exposed cases are represented by S1, S2, and S3, respectively. The current density is shown as a function of the applied voltage in Figure 4(a). The threshold voltage, defined at the onset of transition, for S3 was found to be about 3.5 V and that for S2 was 5.5 V. This difference in the threshold voltage results from the difference in the packing density in addition to the change of the effective conjugation length of the MEH-PPV in a partially aligned structure. It is interesting to note that the dense molecular packing of semiconducting polymers tends to promote the charge transport [7]. In Figure 4(b), the power efficiency is shown as a function of the applied voltage.

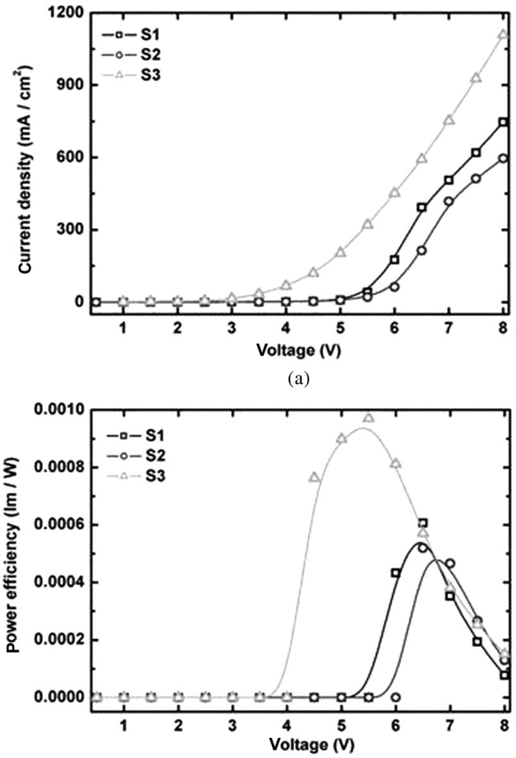


(a)

(b)

FIGURE 3 (a) The dichroic UV/visible absorption spectra of the MEH-PPV on the LPUV exposed PMMA layer and (b) the PL spectra of the MEH-PPV on the PMMA layers exposed to the unpolarized UV and the LPUV light.

As expected from Figure 4(a), the S3 case exhibits the highest power efficiency and the maximum efficiency at the smallest applied voltage. The improvement of the power efficiency comes from both the enhanced charge transport and the reduction in the threshold voltage. Although the alignment of the EL polymers is known to produce polarized light emission [8], our S3 PLED sample shows negligible polarization-dependence. More specifically, $L_{\parallel}/L_{\perp} \approx 0.98$ where



(a)

(b)

FIGURE 4 The EL characteristics of three PLED's with different exposure conditions for the MEH-PPV as a function of the applied voltage: (a) the current density (mA/cm^2) and (b) the power efficiency (lm/W). The symbols of S1, S2, and S3 represent no UV, the unpolarized UV, and the LPUV exposed case, respectively.

$L_\parallel$ and $L_\perp$ represent the luminance parallel and that perpendicular to the polarization direction of the LPUV light, respectively. In our case, the degree of molecular ordering of MEH-PPV is quite low since the difference in the absorption spectra between the two directions is very small as shown in Figure 3(a). It should be emphasized that the directional alignment of the MEH-PPV on the LPUV exposed PMMA layer plays a secondary role on the performance enhancement of the PLED in our case.

Figure 5 shows the brightness of our PLEDs as a function of the applied voltage with varying the thickness of the LPUV exposed PMMA layer. The symbols of sx, sp1, sp2, and sp3 represent the

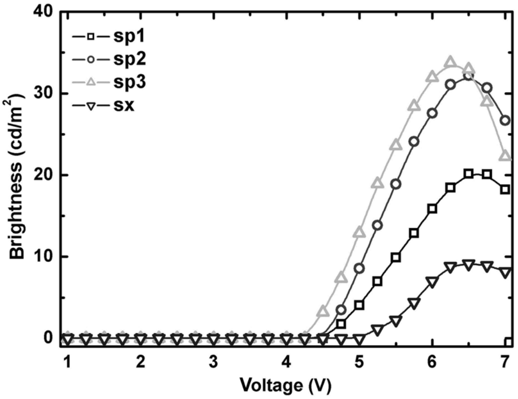


FIGURE 5 The brightness (cd/m^2) of our PLED's as a function of the applied voltage with varying the thickness of the LPUV exposed PMMA layer. The symbols of sx, sp1, sp2, and sp3 represent the thickness of 0, 27, 25, and 22 nm, respectively.

thickness of 0, 27, 25, and 22 nm, respectively. The thinner PMMA layer gives higher brightness and higher efficiency. This is probably due to the enhanced charge transport by the tunneling effect [2].

CONCLUSION

We have demonstrated that the reduction in the threshold voltage of the PLED can be achieved by increasing the packing density of the EL polymers on the LPUV exposed photo-crosslinking layer. The use of the photo-crosslinking sites as interaction sites is one of the powerful methods of producing densely packed organic films. The reduction in the threshold voltage, the increase in the current density, and the improvement in the power efficiency of the MEH-PPV EL device were obtained using the photo-crosslinking PMMA layer.

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