

Design of Organic Electroluminescent Displays with Ultraviolet-Shielding Filters

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ABSTRACT: The electroluminescence properties of polymer light-emitting devices with and without an ultraviolet (UV)-shielding filter were studied. The polymer light-emitting devices were fabricated with poly(2-methoxy-5,2'-ethylhexyloxy-1,4-phenylene vinylene) as the light emitter and poly(ethylenedioxy thiophene) as the hole-transporting material. The UV-shielding filter was composed of alternating TiO₂ and SiO₂ dielectric multilayers made by a physical vacuum deposition process. The current density, brightness,

and photometric efficiency decreased significantly for the polymer light-emitting device without the UV-shielding filter after irradiation by UV light. The decay of PLEDs due to UV degradation was greatly reduced by the UV-shielding filter. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1432–1436, 2004

Key words: luminescence; light-emitting devices; ultraviolet; degradation

INTRODUCTION

Rapid advances (i.e., low turn-on voltage, luminescence intensity with sufficient operation lifetime, full-color displays, and reasonable power efficiency) have recently been made in organic light-emitting devices (OLEDs), and they appear ready to enter the commercial stage in the flat-panel-display market.¹ The research on OLEDs in recent years was first inspired by the high-efficiency small-molecule-based heterojunction OLEDs demonstrated by Kodak research teams in the late 1980s.² The surge in OLED research was then intensified further in the early 1990s when the Cambridge group reported polymer [poly(*p*-phenylene vinylene) (PPV)]-based light-emitting devices (PLEDs),³ which are attractive because of their simplicity and low fabrication cost in addition to their possible applications for flexible displays.⁴

PPV and its derivatives, with highly extended π -conjugated polymer main chains, show relatively high photon/electron conversion efficiency and have potential for applications in flat-panel display. However, the lifetime of these polymer-based devices is limited for practical commercial displays. The degradation processes of PLEDs have been extensively studied.^{5–13} The origins of PLED damage include the

degradation of the conjugated polymer chain, the oxidation of the low-work-function metal (cathode), and the presence of the particle on the indium tin oxide (ITO) glass surface, which result in, for example, defects or electrical shorts in the devices.^{5–7} Some researchers find that light-emitting polymers such as PPV are vulnerable to oxygen through a photochemical reaction in the excited state. The photochemical reaction results in the disruption of polymer chains, which act as defect sites leading to luminescence quenching.^{8–13} Therefore, reducing or avoiding the occurrence of photodegradation is an important issue for the improvement of the operation lifetime of PLEDs.

To avoid ultraviolet (UV) light damage to light-emitting polymer films, we deposited a UV-shielding filter on the reverse side of the ITO-coated glass substrates. The UV-protecting films were composed of alternating TiO₂ and SiO₂ multilayers. PLEDs were fabricated through the use of ITO glass coated by the UV-shielding filter as an anode, and poly(2-methoxy-5,2'-ethylhexyloxy-1,4-phenylene vinylene) (MEH-PPV) and poly(ethylenedioxy thiophene) (PEDOT) were used as the light-emitter and hole-transporting materials, respectively. A high-purity calcium cathode was thermally deposited on the MEH-PPV thin films, and this was followed by the deposition of silver metal as the top layer. The devices were then encapsulated by glass covers, which were sealed with a UV-cured epoxy glue, as shown in Figure 1. The electroluminescence properties of the PLEDs with and without the UV protecting film were studied. Our results indi-

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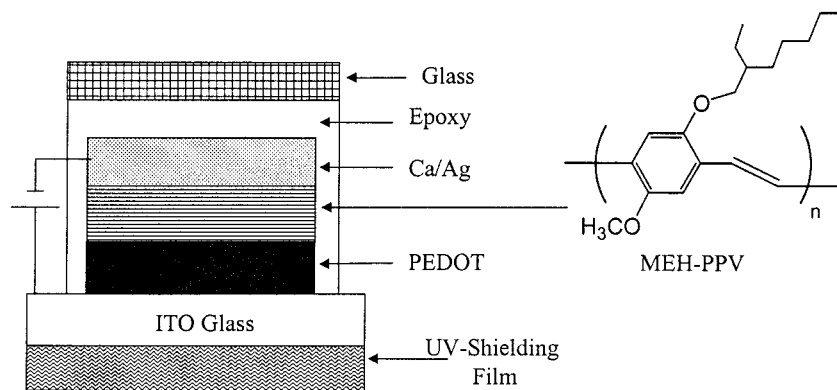


Figure 1 Structure of the PLED device with the UV-shielding filter.

cated that the decay of PLEDs due to UV degradation could be greatly reduced with the UV-shielding filter.

EXPERIMENTAL

A UV-shielding filter composed of TiO_2 and SiO_2 multilayers was deposited onto the reverse side of an ITO-coated substrate with a Leybold APS1104 E-beam gun system at an elevated substrate temperature of 300°C in a high-vacuum chamber. The deposition rate was controlled by the quartz-crystal monitor. The UV-vis transmittance spectra of the UV-shielding filter were measured with a Hitachi U4001 spectrophotometer. The optical refractive index and thickness of the TiO_2 and SiO_2 optical thin films on the glass substrate (BK7) were analyzed with a J. A. Woollam varied-angle-of-incidence spectroscopic ellipsometer.

The PLEDs, composed of PEDOT and MEH-PPV layers, were fabricated through the use of ITO glass coated by the UV-shielding filter as an anode. The ITO thin layer (1700 \AA) on the glass substrate had a sheet resistance of $15 \Omega/\text{sq}$ (applied film). Before ITO was used, its pretreatment included a routine chemical

cleaning with detergent and alcohol in sequence, followed by oxygen plasma cleaning. PEDOT was used as received (Baytron P, Bayer), and MEH-PPV was synthesized according to the literature.¹⁴ The PEDOT thin film ($\sim 600 \text{ \AA}$) was formed on the ITO layer of a glass substrate by the spin-casting method and was dried in an oven at 120°C for 30 min. The MEH-PPV layer was spin-coated from a 6 mg/mL cyclohexanone solution onto the PEDOT layer at a speed of 2000 rpm to give a thickness of 800 \AA and was dried at 70°C for 1 h in a glove box. A high-purity calcium cathode (150 \AA) was thermally deposited onto the MEH-PPV thin film, and this was followed by the deposition of silver metal (1500 \AA) as the top layer in a high-vacuum chamber ($<5 \times 10^{-6}$ Torr). The deposition rate was determined with a quartz thickness monitor (STM-100/MF, Sycon). The thickness of the thin film was determined with a surface texture analysis system (3030ST, Dektak). The device was then encapsulated by glass covers, which were sealed with UV-cured epoxy glue. The active emitting area was controlled to be 10 mm^2 . The photoluminescence and electroluminescence spectra of the PLED devices were measured

TABLE I
Composition and Thickness of the UV-Shielding Filter

Layer	Material	Thickness (nm)
Layer 1	TiO_2	18.43
Layer 2	SiO_2	56.34
Layer 3	TiO_2	39.89
Layer 4	SiO_2	47.80
Layer 5	TiO_2	36.63
Layer 6	SiO_2	66.55
Layer 7	TiO_2	31.45
Layer 8	SiO_2	54.00
Layer 9	TiO_2	43.80
Layer 10	SiO_2	49.32
Layer 11	TiO_2	23.22
Layer 12	SiO_2	151.5

TiO_2 $n = 2.34$ (550 nm). SiO_2 $n = 1.455$ (550 nm)

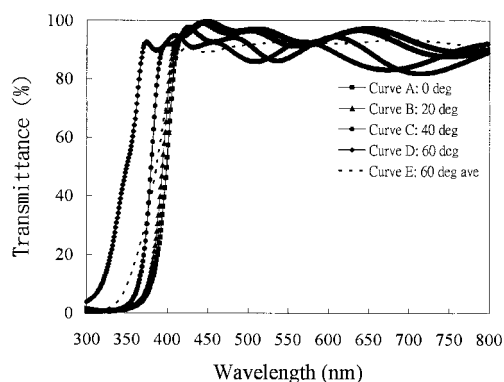
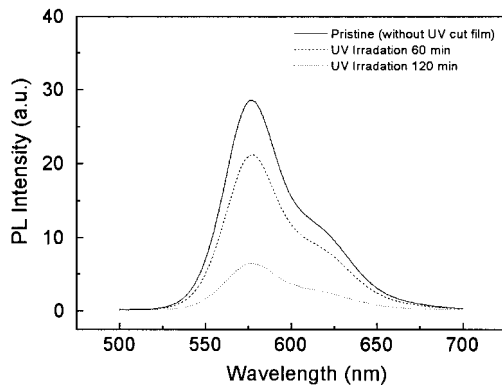
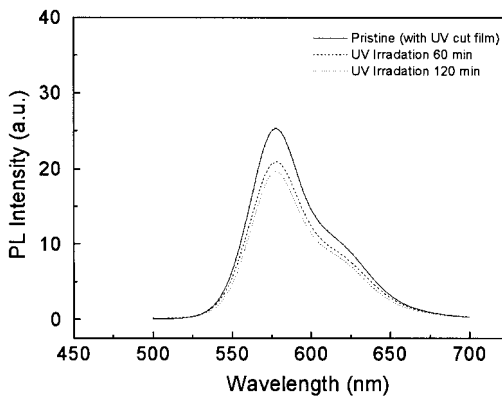


Figure 2 UV-vis transmittance spectrum of the UV-shielding filter.



(a)



(b)

Figure 3 Photoluminescence spectra of the PLEDs (a) without and (b) with the UV-shielding filter at various photoirradiation periods.

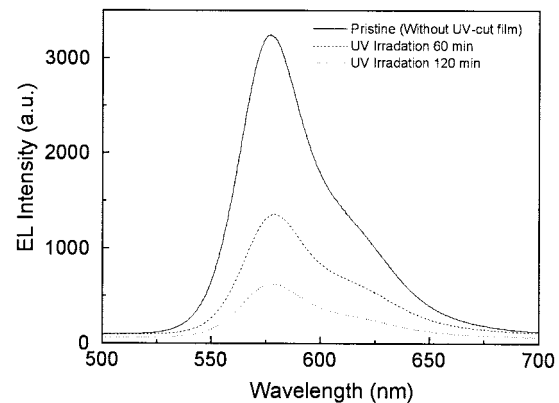
with a Hitachi F4500 fluorescence spectrophotometer. For the photooxidation experimental, the UV-light irradiation intensity and wavelength were $6 \text{ mJ}/\text{cm}^2$ and 365 nm , respectively. The current-voltage characteristics were measured on a programmable electrometer with current and voltage sources (Keithley). The luminance was measured with a BM-8 luminance meter (Topcon).

RESULTS AND DISCUSSION

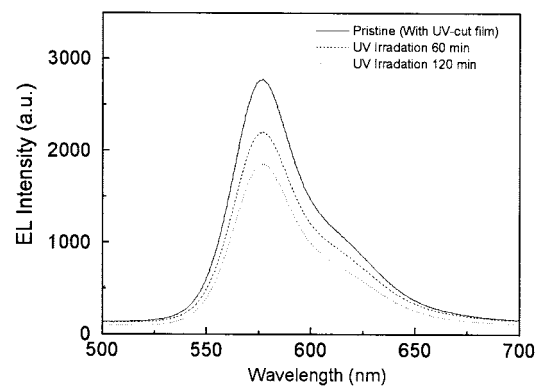
The thickness of each TiO_2 and SiO_2 dielectric layer is summarized in Table I. The multilayer coating design formula is substrate glass (BK7)/(0.5H L 0.5H) \hat{S} 2L/Air, where H is the high-index material TiO_2 (2.34 at 550 nm) and L is the low-index material SiO_2 (1.455 at 550 nm). The symmetrical period coating design inserts 2L just to match the thin-film multilayer structure from the air index; this can minimize the transmit-

tance ripple with almost no effect on the reflecting region. The UV-vis transmittance spectrum of the UV-shielding filter is shown in Figure 2. The protection effect of the UV-reflection mirror depends on the angle of incident light. The UV-shielding filter can completely cut off the light with a stop-band wavelength at 350 nm , and it shows a high optical transmittance ($>90.0\%$) at pass-band wavelengths above 410 nm when the incident cone half-angle is 0° (curve A). The UV-cut and half-transmittance wavelengths shift to shorter wavelengths as the incident angle increases (curves A–D). However, the average of the half-transmittance wavelength is greater than 375 nm when the incident cone half-angle varies from 0 to 60° (curve E).

The photoluminescence spectra of PLEDs with and without the UV-shielding filter at various photoirradiation periods are shown in Figure 3. In comparison with the photoluminescence intensity of the PLED with the UV-shielding filter, the photoluminescence

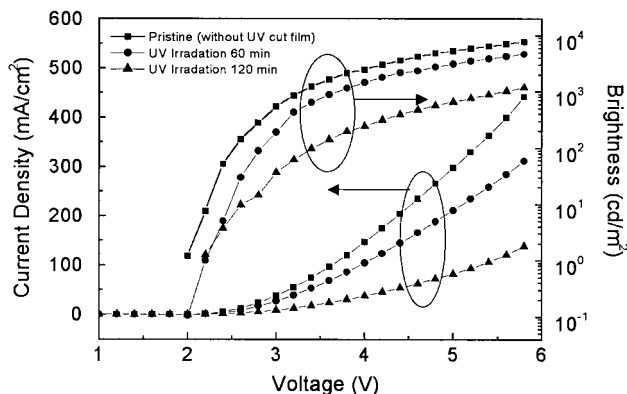


(a)

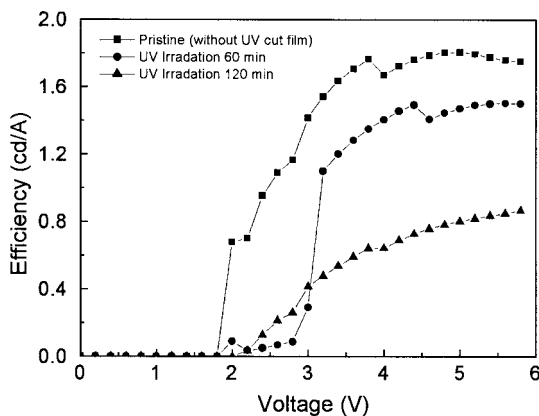


(b)

Figure 4 Electroluminescence spectra of the PLEDs (a) without and (b) with the UV-shielding filter.



(a)



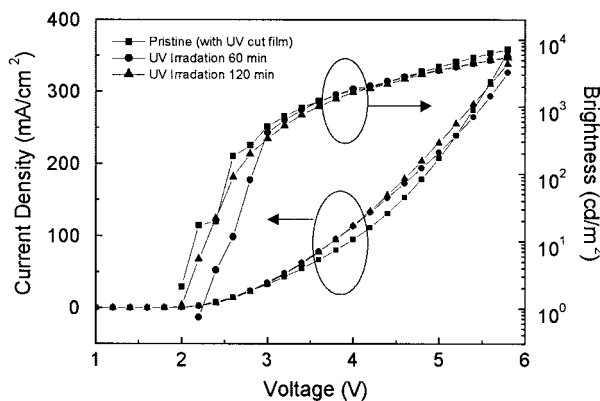
(b)

Figure 5 (a) Current–luminance–voltage and (b) efficiency–voltage characteristics of the PLED without the UV-shielding filter.

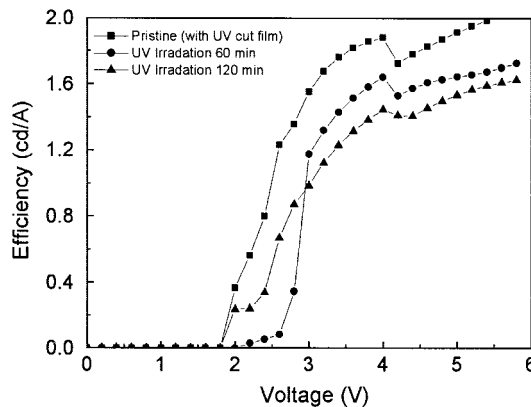
intensity decreases remarkably as the UV-light irradiation time increases for the PLED without the UV-shielding filter. The photoirradiation effect on the photoluminescence of the PPV derivative in air was studied by Tada and Onoda.^{12,13} The photooxidation leads to the scission of the polymer main chain and the formation of the carbonyl groups.^{12,13} The carbonyl groups make a luminescent species such as an exciton dissociate into an electron and a hole.^{12,13} As a result, the photoluminescence intensity decreases as the UV-light irradiation time increases for the PPV-derivative-based PLED. Figure 3(b) shows that the UV-shielding film prevents the photoirradiation of UV light onto the MEH-PPV film. Therefore, the decay of the photoluminescence intensity can be greatly reduced for the PLED.

The electroluminescence spectra of the PLEDs with and without the UV-shielding filter are shown in Figure 4. The emission maximum of the MEH-PPV-based

PLEDs appears at a wavelength of 570 nm. As with the photoluminescence spectra, the electroluminescence intensity decreases remarkably as the UV-light irradiation time increases because of the photooxidation of the PLED without the UV-shielding filter. Moreover, the MEH-PPV film can be protected by the UV-shielding filter, and this reduces the decay of the electroluminescence intensity. The photooxidation of the MEH-PPV main chain occurs because of the presence of oxygen in the polymer film and UV-light irradiation. The oxygen comes from the surface of ITO under an applied voltage or is present at the interface of PEDOT and MEH-PPV films during the spin-coating process.^{10,15,16} Some researchers have reported that oxygen fills the vacancies in the surface of ITO glass during the oxygen plasma treatment process and partially releases during device operation.^{10,15,16} The oxygen becomes the source of photooxidation in MEH-PPV films and subsequently results in the creation of



(a)



(b)

Figure 6 (a) Current–luminance–voltage and (b) efficiency–voltage characteristics of the PLED with the UV-shielding filter.

carbonyl groups, which act as quench centers for the electroluminescence.^{10,15,16}

The current density, luminescence intensity, and efficiency of the PLEDs without and with the UV-shielding filter at various photoirradiation periods are shown in Figures 5 and 6. For the PLED with the UV-shielding filter, the current density, luminescence intensity, and efficiency do not severely decrease as the UV-light irradiation time increases in comparison with the PLED without the UV-shielding filter. The PLED with the UV-shielding filter prevents UV-light irradiation onto the MEH-PPV film and also prevents photodegradation. However, the brightness and efficiency slightly decrease as the photoirradiation time increases for the PLED with the UV-shielding filter. This is due to the presence of other defects, such as the oxidation of the low-work-function metal (cathode) or particles on the ITO glass surface, that result in local electrical shorts or current leakage in the device.⁵⁻⁷

CONCLUSIONS

A PLED with a UV-shielding filter with alternating dielectric multilayers of TiO₂ and SiO₂ has been fabricated. The current density, brightness, and photometric efficiency decrease significantly in a PLED without a UV-shielding filter after UV-light irradiation.

The decay of PLEDs due to UV degradation can be greatly reduced with a UV-shielding filter.

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