CHIN. PHYS. LETT. Vol. 27, No. 9 (2010) 097801

Polymer Light-Emitting Diode Using Conductive Polymer as the Anode Layer *

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(Received 2 June 2010)

The analysis based on series equivalent circuit indicates that the resistance of electrode layers is the major factor limiting the current density of polymer light-emitting diodes (PLEDs) at higher voltages. The conductivity of 790 S/cm for the PEDOT:PSS film is achieved by secondary doping. At a thickness of 240 nm, the sheet resistance of the polymer layer is 51 Ω/sq, which is comparable to that of ITO films. The current density and luminance of the PLEDs with the polymer anode layer is higher than the ITO anode device, suggesting that it is feasible to replace ITO anode with a highly conductive polymer in PLEDs.

PACS: 78. 60. Fi, 72. 80. Le DOI: 10.1088/0256-307X/27/9/097801

Polymer light-emitting diodes (PLEDs) have attracted much interest worldwide since their discovery by Friend and co-workers in 1990.[1] It opens the door to a new field of using conjugated polymers as optoelectronic materials. Since then, conjugated polymers have been explored extensively in the application of organic optoelectronics, especially in light-emitting diodes and organic photovoltaic (OPV). A typical PLEDs device usually consists of three parts: the transparent conductive oxide (TCO) layer working as a transparent anode; the active charge-transfer and emitting polymer layers; and the low-work-function metal cathode. Indium tin oxide (ITO) is a commonly used TCO layer, which requires the sputtering method for deposition. The attempts to replace the TCO layers with soluble conductive polymer are worthwhile for the following reasons: (1) The simple pattern techniques[2,3] and simple film forming techniques involved. (2) The potential cost reduction resulting from this process as well as the cancellation of the expensive indium needed in ITO. (3) The enhanced mechanical flexibility of flexible devices.

Of conducting polymers poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) has emerged as a promising material for electrodes in optoelectronic devices. It has many exciting features such as high transparency in the visible range, excellent thermal stability,[4] and processable in aqueous solution. The applicability of PEDOT:PSS in optoelectronic device is closely related to its electrical conductivity. The conductivity of PEDOT:PSS is affected by the PEDOT-to-PSS molar ratio of dispersion.[5] Another important method of controlling conductivity is called the secondary doping, i.e. some inert solvents, such as sorbitol,[6] N-methylpyrrolidone,[7] (poly)-ethylene glycol and other alcohols,[8–10] dimethyl sulfoxide (DMSO), N,N-dimethylformamide, and tetrahydrofuran,[11] are mixed into the PEDOT:PSS dispersion, resulting in a conductivity increase of 2–3 orders of magnitudes. Low conductive PEDOT:PSS is not possible to act as an independent electrode layer but was found to be an excellent hole-injection buffer layer on ITO anode in organic light-emitting diodes. In order to act as an independent electrode layer, its high conductivity is crucial because low resistance is required to avoid excessive voltage drop on the electrode layer. In organic photovoltaic device the replacement of ITO layer by polymer film is successful.[12–14] However in PLEDs, highly successful cases of using conducting polymer as the electrode layer are rarely seen. The reason is that much lower resistance is required for the electrode layer in PLEDs because the working current density in organic light-emitting device is 1–2 orders higher than that in photovoltaic device. The PEDOT:PSS films with the sheet resistance of 1850 Ω/sq[15] and the conductivities of 160 S/cm[10] and 360 S/cm[3] were used as anode layers in organic light-emitting diodes, but the results showed that the current density and luminance of the polymer-anode devices are significantly lower than that in the ITO-anode devices, especially at high driving voltages. The attempt to achieve high current density and luminance in the polymer-anode PLEDs is the interest of this study.

In this study, the commercially available conductive polymer PEDOT:PSS, formulation PH750 from H.C. Starck, is used as the starting material. The conductivity of 790 S/cm for PEDOT:PSS films is

*Supported by the National Natural Science Foundation of China under Grant No 60776039, and Beijing Key Laboratory of Printing & Packaging Materials and Technology, Beijing Institute of Graphic Communication.

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achieved by secondary doping of DMSO and Isopropanol. The performances of PLEDs with the PEDOT:PSS as the anode layers are investigated and compared with the ITO-anode PLEDs.

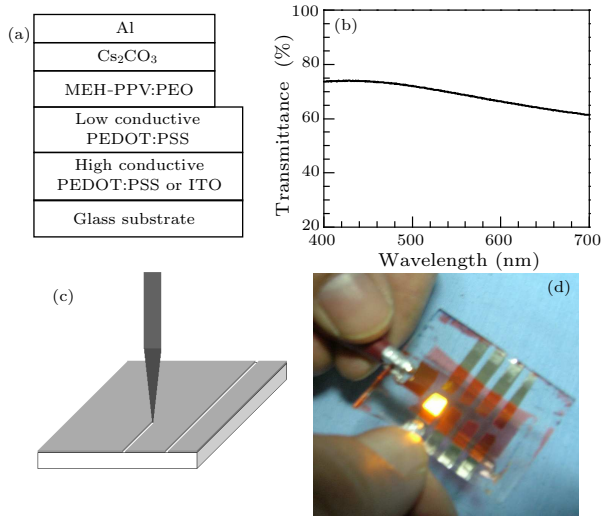


Fig. 1. (a) Device configuration of the PLEDs. (b) Optical transmittance of the 240-nm doped PEDOT:PSS film. (c) Schematic diagram of the PEDOT:PSS anode layer by scribing the film with a hard tip. (d) Photograph showing the operation of the PLEDs with the highly conductive polymer anode under a forward bias.

The recipe for the secondary doping of the PEDOT:PSS dispersions PH750 is for 10 g of PEDOT:PSS; 0.6 g of DMSO, 1.6 g of isopropanol. In order to produce a smoother film, the resulting dispersions were filtered with a 0.45 μm fiber filter. After spin coated on cleaned glass substrate, the films were transferred to a vacuum oven and heated to 150°C for 5 min, intending to remove the DMSO and isopropanol from the films. The thickness of the films was measured with an Ambios XP-2 profilometer. The thickness of spin-coated PEDOT:PSS layer is about 60 nm at the rotation rate of 2000 rpm. In this study, various thicknesses of the doped PEDOT:PSS films are investigated and they are realized by repeating the same spin-coating procedure multiple times. The sheet resistance of the films was measured by four-point-probe measurement. The optical transparency of the films was measured with a UV-3101PC spectrophotometer. The PLEDs devices with the PEDOT:PSS anode layer were fabricated. The device structure is shown in Fig. 1(a), in which the high conductive PEDOT:PSS (or ITO) is the anode layer, the low conductive PEDOT:PSS (Baytron P VP Al 4083) is the hole-injection layer, the Cs_2CO_3 layer functions as electron-injection layer,[16] and the light-emitting layer MEH-PPV:PEO is a mixing layer of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly(ethyleneoxide) (PEO) at the weight ratio of 12 : 1. The mixing MEH-PPV layer after heat treatment was found to be more robust than pristine MEH-PPV film, and thus is more favorable for the following Cs_2CO_3 spin coating. The PEDOT:PSS layer was spin-coated and patterned by mechanical scribing technique, then the MEH-PPV:PEO layer and the Cs_2CO_3 layer were spin-coated and heat-treated respectively, and finally the aluminum cathode layer was deposited on top by vacuum evaporation at a pressure of about 10^{-3} Pa. The emitting area is 9 mm^2. The heat treatment condition to MEH-PPV:PEO is 70°C for 30 min, to Cs_2CO_3 is 140°C for 5 min, all in vacuum. The current-voltage characteristics were measured with a Keithley 2400 source meter. The luminance of the devices was measured with a PR650 spectra scanner.

Table 1. Conductivity and sheet resistance of the anode layers by four-point-probe measurement.

Materials	Conductivity (S/cm)	Thickness (nm)	Sheet resistance (Ω/sq)
PEDOT:PSS	1.1	60	1.4×10^5
PEDOT:PSS doped with DMSO and Isopropanol	790	60	210
		120	110
		180	72
		240	51
ITO	5500	60	30

As shown in Table 1 the conductivity of the film prepared from the original PEDOT:PSS (refered as "undoped PEDOT:PSS" in the following text) dispersion is 1.1 S/cm measured by four-point-probe method. After doping with DMSO and Isopropanol, the conductivity increases dramatically to 790 S/cm, resulting in significant reduction of the sheet resistance. The change of conductivity is due to the screening effect of the DMSO (polar) solvent.[11] The purpose of adding Isopropanol is to improve the wetting quality of the film. The sheet resistance of the secondary doped film is 210 Ω/sq for the 60-nm layer and it is reduced further by thickening the layer. In the 240-nm layer the sheet resistance is 51 Ω/sq, which is comparable to the commonly used ITO film. The sheet resistance could be reduced further in the layer thicker than 240 nm; however it becomes difficult to control the thickness and uniformity of the thicker film as more repeated spin-coating are involved.

The optical transmittance of the 240-nm PEDOT:PSS film is shown in Fig. 1(b). The transmittance is over 62% over the visible range. This is lower than that of the ITO film, which is over 92%. The PEDOT:PSS electrode layer is patterned for the fabrication of the device. Figure 1(c) is a schematic diagram showing the scribing process with a proper hard tip. The simple scribing method is effective in separating and confining the emitting area of the PLEDs device, as shown in Fig. 1(d), which is a photograph showing the operation of the PEDOT:PSS anode PLEDs under a forward bias.

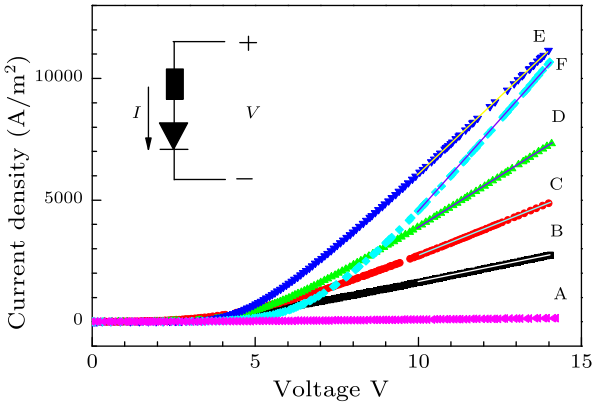


Fig. 2. The $I-V$ curves of the PLEDs with different anode layers. The anode layers are (a) 60-nm undoped PEDOT:PSS, (b) 60-nm doped PEDOT:PSS, (c) 120-nm doped PEDOT:PSS, (d) 180-nm doped PEDOT:PSS, (e) 240-nm doped PEDOT:PSS, (f) ITO. The straight lines on the curves in the range of 10–14 V are guide for the eyes. The inset is the equivalent circuit of the PLEDs in which the resistance of the anode layer cannot be ignored.

Figure 2 shows the current-voltage ($I-V$) characteristics of the PLEDs devices with different anode layer. It is clear that the $I-V$ curves are sensitive to the resistance of the anode layers. In the PLEDs with the undoped PEDOT:PSS anode layer the current density is low, below 140 A/m^2. The current densities are significantly increased in the PLEDs with the doped polymer anode, especially in the thicker layer. The role of the electrode resistance is shown in the equivalent circuit in the inset of Fig. 2. The electrode layer functions as a resistance in the series circuit composed of the resistance and an ideal diode. Therefore the $I-V$ curve obeys the equation

$$V = \frac{nKT}{q} \ln\left(\frac{I+I_0}{I_0}\right) + IR_{\rm SA}. \qquad (1)$$

The first term is the voltage drop on the diode, in which I_0 is the reverse-bias saturation current of the diode, n the ideality factor, q the electron charge, k Boltzmann's constant, T the temperature; the second term is the voltage drop on the electrode resistance where $R_{\rm SA} = AR_{\rm sh}$ is the specific series resistance, in which $R_{\rm sh}$ is the sheet resistance of the PEDOT:PSS film and A is a factor related to the shape of the electrode. Because the first term is logarithm of current, which means that the voltage drop on the diode becomes almost constant at high current density, the current-voltage characteristics is mainly determined by the second term at higher voltage. Therefore in higher voltage range the $I-V$ curves become straight line and the slopes of the curve reflect the value of the series resistance in the first approximation. The analysis on the slope of the $I-V$ curves at the voltage range of 10–14 V shows that $R_{\rm sh}$ of the 60-nm, 120-nm 180-nm 240-nm PEDOT:PSS anode and ITO anode layer are 210, 110, 70, 48 and 36 Ω/sq, respectively, under the condition of $A = 1.8$. These results are consistent with the values from four-point-probe measurement, indicating that the series resistance is really the major factor determining the current-voltage characteristic of PLEDs in higher voltage range. It is notable that although ITO sheet resistance is lower than the 240-nm doped PEDOT:PSS film, the current density in the polyer anode device is higher than that in the ITO-anode PLEDs, implying that other current-limiting element exists in the ITO-anode PLEDs. A possible reason may be that the hole injection from the ITO film is not as efficient as from the PEDOT:PSS layer and thus cause limitation on the current density.

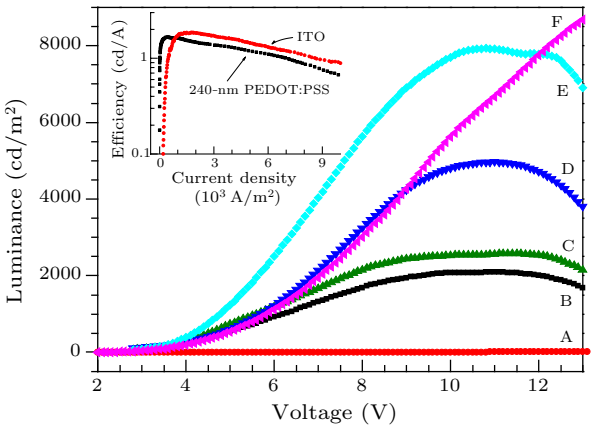


Fig. 3. The luminance of the PLEDs with different anode layers. The anode layers are (a) 60-nm undoped PEDOT:PSS, (b) 60-nm doped PEDOT:PSS, (c) 120-nm doped PEDOT:PSS, (d) 180-nm doped PEDOT:PSS, (e) 240-nm doped PEDOT:PSS, (f) ITO. The inset shows the efficiencies of the PLEDs with the 240-nm doped PEDOT:PSS anode and the ITO anode.

Figure 3 shows the luminance of the PLEDs as a function of the driving voltage. The luminance is roughly proportional to the current density of the device. As a result the luminance of the device with undoped PEDOT:PSS anode is low, below 10 cd/m^2, because of its low current density. As expected, the luminance is greatly increased in the PLEDs with the doped PEDOT:PSS anode. It is notable the luminance of the 240-nm polymer-anode device is higher than that of the ITO device at most measuring voltages, and a maximum of 7900 cd/m^2 in luminance is observed in the PLEDs at 11 V. The inset in Fig. 3 compares the current efficiency of the polymer anode PLEDs and the ITO anode device. The efficiencies of the PLEDs rise rapidly with increasing current density at low current density. The maximum efficiency is 1.7 cd/A at the current density of 300 A/m^2 in the polymer-anode PLEDs, while in the ITO-anode PLEDs it is 1.9 cd/A at the current density of 1400 A/m^2. After the maximum points the efficiencies decline gradually, while the efficiency of the polymer-anode PLEDs kept about 25% lower than the

ITO-anode device. This difference is reasonable taking into account that the transparency of the 240-nm polymer film is 32% lower than that of the ITO film.

In conclusion, the analysis base on the series equivalent circuit indicates that the resistance of the polymer electrode layer is the major factor limiting the current of the PLEDs device in the higher voltage range. After the secondary doping of DMSO and Isopropanol, the PEDOT:PSS film shows the conductivity of 790 S/cm, and in a 240-nm layer the sheet resistance is as low as 51 Ω/sq, which is comparable to that of the ITO film. The results show that the current density and the luminance of the polymer anode PLEDs can exceed that of the ITO anode PLEDs, suggesting it is feasible to replace the TCO anode with a highly conductive polymer in PLEDs.

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