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Poly(pyridine-2,5-diyl) as electron-transport/hole blocking layer in poly(phenylene vinylene) light-emitting diode

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Abstract

The high electron affinity conjugated polymer, poly(2,5-pyridinediyl) (PPy), can be used as the electron-transport/hole blocking layer in a light-emitting diode with poly(phenylene vinylene) (PPV) as the emitting layer, ITO as the anode and aluminum as the cathode. The incorporation of PPy layer provides an improvement in the conversion efficiency of current density to brightness by a factor of 17. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(pyridine-2,5-diyl); Poly(phenylene vinylene); Light-emitting diode

1. Introduction

Poly(phenylene vinylene) (PPV) and its derivatives are p-type semiconductors and exhibit higher hole transport rates than electron transport rates. In recent years, both low molecular weight oxadiazole derivatives and oxadiazole-containing polymers [1–5] have been shown to provide improved quantum efficiency, and are often regarded as electron transport layer (ETL). For a light-emitting diode (LED) with PPV as the emitting layer, when a 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) layer is introduced between the PPV and cathode, the efficiency (photon/electron) increases from 0.1 to 0.8% [1]. However, a comparison of the electron affinity (EA) and ionization potential (IP) of PBD (EA = 2.6 eV, IP = 5.9 eV [6]) with those of PPV (EA = 2.7 eV, IP = 5.1 eV [7]) indicates that PBD should behave only as a hole-blocking material owing to its IP being higher and its EA being lower than those of PPV. Due to the π-deficient nature of pyridine units, poly(2,5-pyridinediyl) (PPy) has electron-accepting and *n*-type electrically conducting properties [8].

In this work we report the use of PPy as an electron transport/hole blocking layer in LEDs with PPV as the emitting layer, allowing an increase in the conversion efficiency of current transfer to brightness by a factor of 17.

2. Experimental

2.1. Polymerization

PPV was prepared by the precursor route according to the method proposed by Gagnon and Karasz [9]. PPy was synthesized by the method proposed by Yamamoto and Maruyama [10]. The chemical structure of PPy was examined by infra-red (IR) and ultra-violet–visible (UV-Vis) spectroscopies and found to be identical to that reported by Yamamoto and coworkers [8,10].

2.2. Device fabrication and characterization

The single-layer LED with PPV as emitting layer was prepared by coating a thin layer (about 75 nm) of PPV precursor on an ITO glass plate from its methanol/water solution (2.85 mg/mL) via spin coating at 1000 rpm, drying in a dust-free environment, converting into PPV by thermal elimination at 250°C for 6 h under dynamic vacuum at a pressure below 1×10^{-1} torr, and finally depositing a layer of aluminum on the surface of the PPV film by thermal evaporation at a pressure of 2×10^{-6} torr. For the bilayer device, a PPy film (45 nm thick) was coated on the PPV film by spin-coating then heated at 100°C under dynamic vacuum for 24 h prior to the aluminum deposition. Since the wettability of PPy in formic acid on the PPV surface is poor, the coating of PPy film was carried out using a PPy solution in formic acid (5 mg/mL) containing the fluorinated alkyl ester surfactant from 3M company, FC-430 (0.8 mg/

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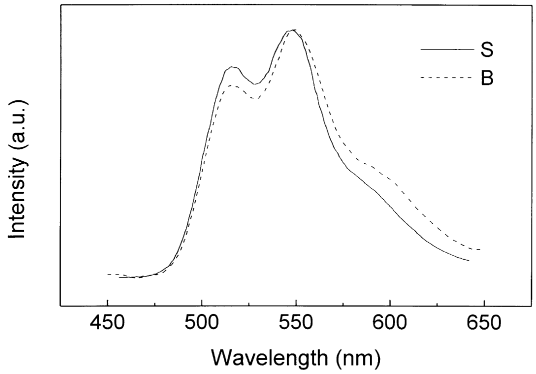

Fig. 1. EL spectra of ITO/PPV/Al (device S) and ITO/PPV/PPy/Al (device B).

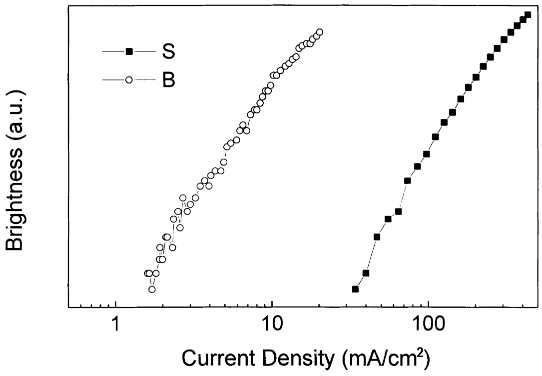

Fig. 2. Brightness–current density characteristics for ITO/PPV/Al (device S) and ITO/PPV/PPy/Al (device B).

mL), under a spin speed of 3000 rpm. The PPy film so obtained is smooth.

Electroluminescence (EL) spectra were measured by a fluorescence spectrometer (SLM and AMICO, Model AB2). Luminance of the device was measured using a luminance meter (TOPCON, Model BM-8) with measuring angle 2° and attachment lens AL-8. The thickness of the polymer film was measured by a Tencor P-10 Surface Profiler.

3. Results and discussion

The EL spectra of the LEDs with and without PPy layer are shown in Fig. 1. The EL spectrum of the bilayer LED, ITO/PPV(75 nm)/PPy(45 nm)/Al (device B), is very close to that of the single-layer PPV device, ITO/PPV(75 nm)/Al (device S), indicating that PPV acts as the emitting layer in the bilayer device.

For the bilayer device, its turn-on electric field is about 2×10^6 V/cm, and the operating voltage is higher than that of the single-layer device (7.6×10^5 V/cm) due to significant resistive voltage drop across the PPy layer.

The brightness versus current density of these devices are shown in Fig. 2 (both axes are plotted in logarithmic scale). It shows that device B has a conversion efficiency of current to brightness (0.12 cd/A) higher than device S by a factor of about 17. The low conversion efficiency of device S results from the fact that it is essentially a ''hole-only'' device, since the barrier height of the ITO/PPV interface is only 0.4 eV, while the barrier height at the PPV/Al interface is 1.7 eV. Therefore the hole injection rate will be faster.

A cyclic voltammogram of PPy coated on a Pt electrode was obtained by scanning at a rate of 100 mV/s between 2 and − 2.5 V versus the reference electrode, Ag/AgCl (the concentration of electrolyte, LiCl in ethanol, is saturated) in the 0.1 M $[N(n\text{-}C_4H_9)_4][BF_4]$/acetonitrile solution. PPy has a reduction potential at − 1.4 V versus Ag/AgCl ($E_{\mathrm{red,onset}}$) (or − 1.5 V versus SCE (saturated calomel electrode)), and is electrochemically inactive in the positive potential region. The measurement of electrochemical redox potentials helps us to establish the electronic structure of PPy. The estimated EA and IP of PPy are 2.9 eV ($\mathrm{EA} = E_{\mathrm{red,onset}} + 4.4 = -1.5 + 4.4 = 2.9$) [11] and 5.7 eV ($\mathrm{IP} = E_g + \mathrm{EA} = 2.8$ [from [12]] $+ 2.9 = 5.7$), respectively. This high IP value indicates that PPy is difficult to be oxidized (or p-doped). Both values are larger than those of PPV (EA = 2.7 eV, IP = 5.1 eV) [7] and lower than the values (EA = 3.5 eV, IP = 6.3 eV) reported by Miyamae et al. [12] measured using ultraviolet photoelectron spectroscopy (UPS) and UV-Vis. The band diagrams of these devices constructed therefrom are shown in Fig. 3. As can be seen, the energy barrier for electron injection decreases from 1.6 eV (in the single-layer

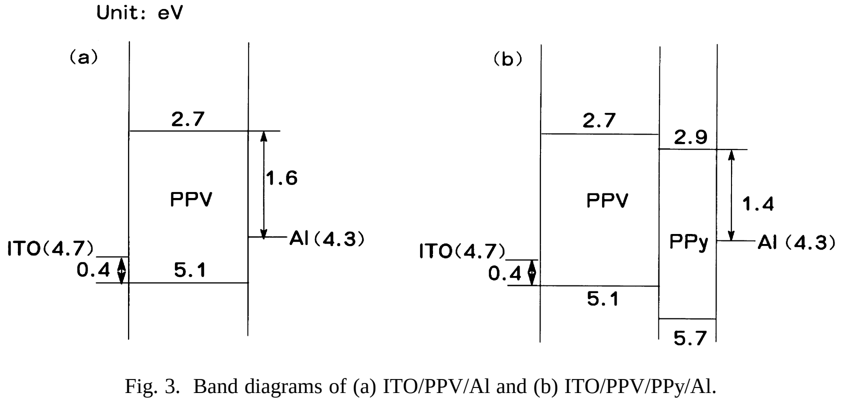

Fig. 3. Band diagrams of (a) ITO/PPV/Al and (b) ITO/PPV/PPy/Al.

device) to 1.4 eV (in the bilayer devices). Moreover, the IP of PPy (5.7 eV) is larger than that of PPV (5.1 eV); thus the PPy layer also provides a hole blocking effect. Since PPy has a high EA and IP, electron injection from the cathode is enhanced and holes injected from the anode are blocked. This will greatly enhance the probability of radiative recombination. In addition, the PPy layer separates the recombination zone from the metal electrode so that the recombination at the metal/polymer interface is avoided.

In conclusion, PPy can be used as an electron transport/hole blocking layer in the LED with PPV as the emitting layer and provides an increase in the conversion efficiency of current density to brightness by a factor of 17.

Acknowledgements

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