Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 7930–7934
www.elsevier.com/locate/tsf

Dual-color polymer light-emitting diodes based on hybrid films of soluble poly(*p*-phenylenevinylene) derivatives

C. Liu, M. Wang *, M. Wu, T.X. Liu *, G.Y. Zhong, H.B. Yao

Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai 200433, PR China

Received 20 December 2005; received in revised form 8 January 2007; accepted 19 March 2007
Available online 27 March 2007

Abstract

Polymer light-emitting diodes with red and green emissions were fabricated on the same indium-tin oxide (ITO) substrate. The basic device structure is ITO/electroluminescent polymer/Al. The polymer light-emitting layer of the dual-color device fabricated in this work has two parts, one part is the single (poly[2,5-dimethyldodecylsilyl-1,4-phenylenevinylene]) (Si-PPV) film, and the other part consists of the hybrid films of Si-PPV and cyano-substituted poly[2,5-didecyloxy-1,4-phenylenevinylene] prepared by a simple two-step spin-coating method. The device characteristics have been investigated, and the possible electroluminescent mechanisms were discussed.

Keywords: Polymer light-emitting diodes; Electroluminescent polymer; Poly(*p*-phenylenevinylene); Spin-coating

1. Introduction

Since the first report of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by Burroughes et al. [1], soluble PPV derivatives have been widely used as the emissive layer in light-emitting diodes due to their solution processability, various color generation and excellent properties in luminous efficiency, color purity and stability [2–5]. The soluble electroluminescent (EL) polymer is typically deposited by spin-coating and the substrate is covered by single material, thus only single-color devices can be fabricated [6,7]. However, integration of red, green or blue (RGB) PLEDs onto the same substrate to realize different color emissions has been a goal long sought in the display field.

One way to achieve full-color display is to arrange red, green, and blue emitters "side by side" on the substrate, and polymer layers need to be patterned into RBG subpixels. It is difficult to pattern polymer layers by conventional photoresist and wet processing techniques because of their solubility in aqueous and organic solvents. Ink-jet printing has been proved to be one feasible technique to directly pattern different color materials for making RGB pixels. However, there are some problems that still need to be overcome in this technique, for example, the uniformity of the polymer films [8]. Other efforts have also been made to integrate organic light emitting diodes from different color materials on the same substrate. Multi-color light emitting diodes fabricated by three repeated processes of the spin coating of polymer thin films and the vacuum deposition of top metal, as well as the patterning of polymer thin film by plasma etching were reported by Wu et al. [9]. RGB dot-emission on one substrate with multi-layer polymer structures through three times of spin-coating and vacuum deposition process was reported by Zhang et al. [10].

In this paper, (poly[2,5-dimethyldodecylsilyl-1,4-phenylenevinylene]) (Si-PPV) and cyano-substituted poly[2,5-didecyloxy-1,4-phenylenevinylene] (CN-PPV) are chosen as the EL polymers because of their excellent electroluminescent properties compared to other PPV derivatives. And, dual-color PLEDs were prepared by a simple way of two-step spin-coating followed by vacuum deposition of top metal to realize red and green emission on the indium-tin oxide (ITO) substrate.

* Corresponding authors. Tel.: +86 21 55664180; fax: +86 21 55664192.
E-mail addresses: minwang@fudan.edu.cn (M. Wang), txliu@fudan.edu.cn (T.X. Liu).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.03.041

2. Experimental details

The PLEDs discussed here were fabricated with the following structures:

(a) ITO/CN-PPV/Al;
(b) ITO/Si-PPV/Al;
(c) ITO/CN-PPV: Si-PPV and Si-PPV/Al.

All devices were fabricated on glass substrates, half coated with ITO strips which served as the anode. The general structure of PLEDs consists of ITO (a transparent conductor), the EL polymer layers, and a patterned top metal aluminum (Al) as the cathode. The bottom ITO contact and the top metal contact have been patterned to define the active area of the devices. 4×4 PLEDs were fabricated on one substrate, and the active area for all devices is 12 mm^2. The devices emit light out of the bottom of the ITO-coated glass substrate.

CN-PPV (M_w about 80,000) and Si-PPV (M_w about 130,000) were chosen as the active materials which were synthesized in our lab according to the procedures described in the literature [11,12]. The CN-PPV and the Si-PPV used in this work are easily processable and have good solubility in chloroform, toluene and THF. Their chemical structures were shown in Fig. 1.

ITO-coated glass substrates with a sheet resistance less than 30 ohm/square (Ω/□) were patterned and carefully cleaned by a routine procedure prior to use, which includes sonication in detergent followed by rinsing sequentially in deionized water, ethanol, acetone and chloroform for ten minutes, and finally treated with ultraviolet/ozone.

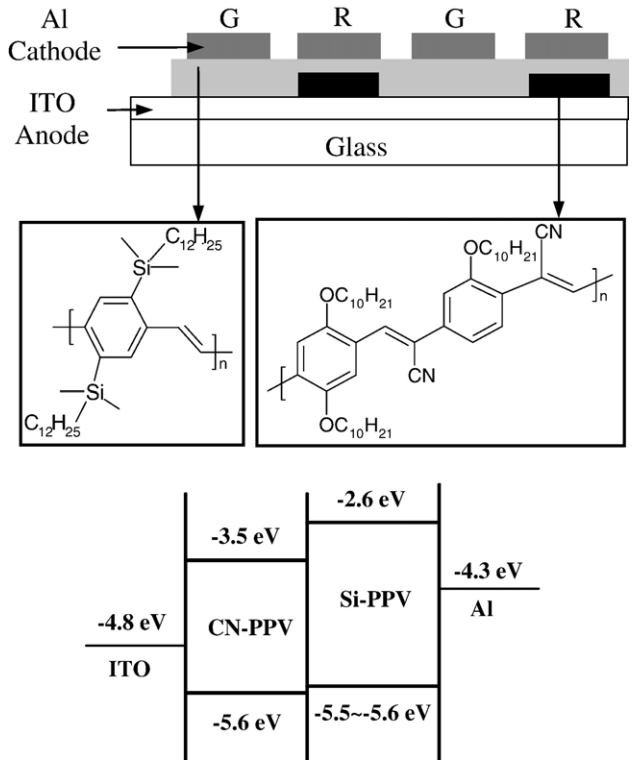

Fig. 1. The device structure and the energy band structure of dual-color PLEDs, together with the chemical structures of CN-PPV and Si-PPV.

Table 1
The UV–Vis absorption and photoluminescent properties for CN-PPV and Si-PPV films

Polymer	CN-PPV	Si-PPV
UV $\lambda_{abs,max}$	504 nm	439 nm
λ_{edge}/E_g	610 nm/2.03 eV	520 nm/2.39 eV
PL $\lambda_{em,max}$	685 nm	512 nm
PLQE	35%	60%

All EL polymer/chloroform solutions were prepared and spin-coated at a speed of 3000 rpm for 60 s using a spin processor (Model WS-400A-6NPP/Lite, from Laurell Co.), and then baked at 80 °C for 2 h to eliminate residual solvent.

For the preparation of device (a) and (b), the chloroform solutions (5 mg/ml) of CN-PPV and Si-PPV were spin-coated onto the ITO substrates respectively. For device (c), firstly CN-PPV layer was made by spin-coating to cover the whole substrate. In order to define different color emitting area, some of the CN-PPV film was wiped off carefully using linen-free sponge stick dipped with chloroform according to a strip mask superposed on the substrate. After removing the mask, Si-PPV solution was then spin-coated to cover the whole substrate. Therefore, there are two parts of EL polymer layer on ITO substrate for device (c): one part is covered by single material (Si-PPV), and the other part is covered by the hybrid films of CN-PPV and Si-PPV. At last, the polymer film on one side of the substrate was wiped away to reveal the anode contact. The structure of device (c) was shown in Fig. 1. The thicknesses for the CN-PPV, Si-PPV and CN-PPV: Si-PPV hybrid films were measured using a profilometer (KLA-Tencor P-15, Tritek Technologies Co.).

The cathode of the PLEDs was formed by thermal evaporation of Al from tungsten threads at a pressure lower than 5×10^{-4} Pa and patterned by a strip mask. The thickness of the Al layer was approximately 200 nm.

The UV–Vis absorption and photoluminescence (PL) spectra of polymer solutions and films were obtained by SHIMADZU UV-3150 spectrophotometer and SHIMADZU RF-5301 spectrofluorophotometer. The electroluminescence spectrum was measured using a Spectra-scan PR 705. The absolute PL quantum efficiency was measured using a calibrated integrating sphere (IS-080) and a calibrated Optical Power Meter (Model 1830-C).

The luminance–current–voltage curves were determined by Keithley 238 SMU (source measure unit) and Keithley 2001 multimeter which were connected with a calibrated photometer (produced by Photoelectric Instrument Factory of Beijing Normal University) and controlled by a computer program.

3. Results and discussion

The absolute PL quantum efficiencies (PLQE) for several PPV derivatives were measured by integrating sphere method in order to select materials with relatively good luminescent properties. The PLQE of CN-PPV and Si-PPV were measured to be 35% and 60%, respectively. Compared with other PPV derivatives (poly[2-(2′-phenyl-4′,5′-bis(2″-ethylhexyloxy))