Journal of Luminescence 131 (2011) 801–807

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Enhancement of efficiency of multilayer polymer light-emitting diodes by inserting blocking layers

Su-Hua Yang *, Dao-Wu Zhuang

Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan, ROC

ARTICLE INFO

Article history:
Received 13 May 2010
Received in revised form
19 November 2010
Accepted 6 December 2010
Available online 15 December 2010

Keywords:
Electroluminescence
Blocking layer
Spin-coating
Thermal evaporation

ABSTRACT

In this study, the electroluminescence efficiency of the blue–green polymer light-emitting diodes (PLEDs) is enhanced by the insertion of blocking layers. PLEDs are multilayered structures prepared with spin-coating and thermal evaporation. Blue host is doped with green guest to form a single emission layer. Poly(9-vinylcarbazole) (PVK) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) are used as materials for the blocking layers. The optimal thicknesses of the PVK and BCP layers are 10 and 0.2 nm, respectively. PVK plays an important role of blocking holes and electrons, and BCP not only confines holes in the emission layer but also enhances the injection of electrons from Alq_3 to the emission layer. The efficiency of a PLED with a dual-blocking layer is 2.37 times higher than that of a PLED without a blocking layer prepared because of the improved carrier balance and the enhanced carrier recombination.

1. Introduction

Recently, polymer light-emitting diodes (PLEDs) have attracted considerable attention because of their potential applications in large-scale flat-panel displays and light sources [1,2]. However, there are still many challenges in the realization of a high-efficiency PLED. As is well-known, the luminance of PLEDs is dependent on the carrier injection and carrier recombination efficiencies [3,4]. In order to achieve high carrier recombination efficiency, a balance of electrons and holes in the emission layer is required. Therefore, a number of investigations focusing on the enhancement of carrier transport, the improvement of emitter characteristics, and the modification of the device structure have been carried out [5–8]. In recent years, multilayered structures have been developed for improving the efficiency of small-molecule organic light emitting diodes (SM-OLEDs) [9,10], which have a hole transporting layer (HTL), an emission layer (EML), a hole/electron blocking layer (HBL/EBL), an electron transport layer (ETL), and an electron injection layer (EIL). Further, it has been found that the insertion of blocking layers is one of the effective methods for enhancing the efficiency of SM-OLEDs [11,12]. The materials of the blocking layers conventionally have a large energy gap and a high ionization potential. However, the fabrication of a multilayer PLED is difficult because it is hard to find a solvent which dissolves the material of the layer under preparation but is immiscible with the material of the prepared bottom layer.

In this study, multilayer PLEDs were fabricated by spin-coating and thermal evaporation, and blocking layers were inserted at different locations in order to improve the luminance of the devices. Then, the characteristics of the PLEDs were investigated.

2. Experimental

The multilayer PLEDs consisted of an HTL, an EML, an HBL/EBL, an ETL, and an EIL. Poly(3,4-ethylenedioxy-thiophene)/poly(styrene sulfonate) (PEDOT:PSS) was used as the material for fabricating the HTL. PEDOT:PSS is a p-type conductive polymer, which improves the hopping ability and reduces the tunneling effect of holes. The materials used for fabricating the EML were blue poly (9,9-dioctyl-fluorene-2,7-diyl) (PFO) and green poly[(9,9-dioctyl-2,7-bis(2-cyano) vinylenefluorenylene)-alt-co-(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene)] (OPA3008) [4,13]. The blue–green light from PFO: OPA3008 was emitted with an internal energy transfer, in which the energy was transferred from the wider-bandgap PFO to the narrower-bandgap OPA3008. An effective energy transfer was achieved even though a low concentration of OPA3008 was doped. In this study, the doping concentration of OPA3008 was varied from 0 to 0.9 wt%. For increasing the electron transport and injection, tris-(8-hydroxyquinoline)aluminum (Alq_3) and LiF were selected as the materials for fabricating the ETL and the EIL, respectively.

Three multilayer PLEDs with different structures were fabricated, and their characteristics were compared and discussed. For obtaining the optimal composition of the EML and the optimal thicknesses of the organic layers, Device-1 with the structure of indium tin oxide (ITO)/PEDOT:PSS/PFO:OPA3008/Alq_3/LiF/Al was

* Corresponding author. Tel.: +886 7 3814526; fax: +886 7 3814526.
E-mail address: shya@cc.kuas.edu.tw (S.-H. Yang).

0022-2313/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2010.12.007

fabricated; in this case, no blocking layer was deposited. First, an ITO glass substrate was spin-coated with a PEDOT:PSS solution and then baked at 100 °C in vacuum for 60 min; the thickness of the PEDOT:PSS layer was 80 nm. In addition, for the preparation of the PFO:OPA3008 emission layer, PFO:OPA3008 was dissolved in THF and then spin-coated on the PEDOT:PSS layer; then, it was annealed at 100–110 °C in vacuum for 100 min. Subsequently, the ETL of Alq_3, the EIL of LiF, and the cathode of Al were deposited in sequence by thermal evaporation at a pressure of 5×10^{-6} Torr. Furthermore, for improving the luminance of the PLEDs, devices with blocking layers were prepared; poly(9-vinylcarbazole) (PVK) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were used as the blocking layer materials [13,14]. The structure of Device-2 was ITO/PEDOT:PSS/PVK/PFO:OPA3008/Alq_3/LiF/Al; this device had a single PVK blocking layer. Further, the structure of Device-3 was ITO/PEDOT:PSS/PVK/PFO:OPA3008/BCP/Alq_3/LiF/Al; this was a dual-blocking layer device. Fig. 1 presents the energy diagram of Device-3. In order to prepare the PVK layer, 0.28 wt% PVK was dissolved in toluene; the solution was spin-coated on PETDOT:PSS and then annealed at 160 °C for 60 min. The immiscible property between the layers is crucial to the process of spin-coating. The preparation method of the BCP layer was different from that of the PVK layer; the BCP layer was deposited by thermal evaporation.

A surface profiler (Dektak M6) was used for measuring the thickness of the films. The absorption spectra of the films were measured with a UV–visible spectrophotometer (Hitachi U-2800); and the photoluminescence (PL) and PL excitation (PLE) spectra were recorded by using a fluorescence spectrophotometer (Hitachi F-7000). The current–voltage characteristics of the PLEDs were measured by a Keithley 2410 power source. The luminance and Commission Internationale de l'Eclairage (CIE) coordinates were measured using the Minolta chromameter CS-100A. The electroluminescence (EL) spectra were measured using the Newport OSM-400 spectrophotometer. All the measurements were carried out at room temperature in air without encapsulating the devices.

3. Results and discussion

In this study, PFO and OPA3008 were used as host and guest materials, respectively. The absorption and PL spectra of the PFO and OPA3008 are shown in Fig. 2(a), where the excitation wavelength for PL measurement was set at 325 nm. The absorption peaks of the interband transition were at 393 nm for PFO and at 426 nm for OPA3008. In the meantime, the PL emission peaks of PFO were at approximately 435, 460, 490, and 530 nm, attributing to the electron transitions from the excited state S_10 to the ground states of S_00, S_01, S_02, and S_03, respectively [15–19]; and the PL peaks for OPA3008 were at approximately 465, 498, and 547 nm. The spectral overlap between the emission of PFO and the absorption of OPA3008 shows that an efficient Forster energy transfer takes place between PFO and OPA3008. The PLE spectrum of the PFO:OPA3008 is shown in Fig. 2(b); this spectrum was monitored at wavelength of 465 nm (the emission peak of OPA3008, λ_{em}). It shows an absorption peak at 392 nm; this is referred to the absorption of PFO. Obviously, the excitation energy was absorbed by PFO, and then partially transferred to OPA3008 for light emission.

As regarding to the electroluminescence (EL), the empirical results show that the relative emission intensity of the EL peaks might be different from that of the PL peaks because EL and PL have different excitation mechanisms, i.e., charge recombination and direct excitation, respectively [20]. In addition, the relative emission intensity of the peaks and emission spectrum of EL change when the emitter material, the interfacial states of layers, the thickness of films, cathode material, device structure, and applied bias are varied. Moreover, the preparation procedure of films is also important because the emission intensity and wavelength are sensitive to the physical state of the films [21].

Thus, in order to evaluate the influence of the blocking layer on the EL properties of the device, three devices with different structures were prepared (Table 1). The structure of Device-1 was ITO/PEDOT:PSS (80 nm)/PFO:OPA3008 (x wt%, 150 nm)/Alq_3 (10 nm)/LiF (2.5 nm)/Al (150 nm); there were no blocking layers in

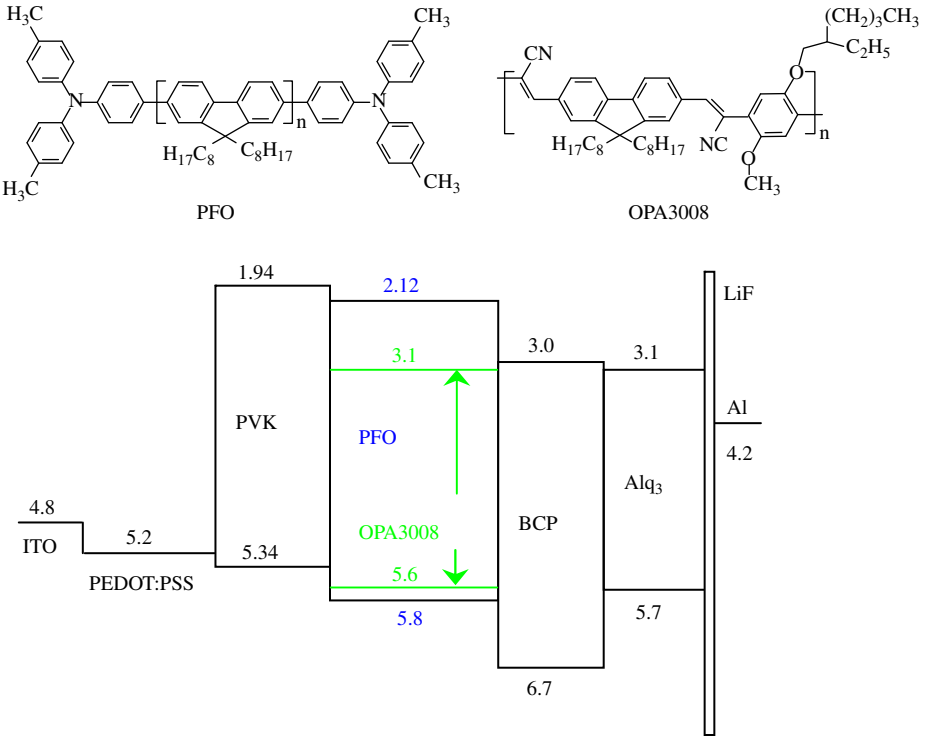

Fig. 1. Chemical structures of polymers and energy band diagram of a PLED.