Thin Solid Films 531 (2013) 419–423

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Degradation mechanism of green phosphorescent dye doped polymer light-emitting diodes

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ARTICLE INFO

Article history:
Received 5 October 2011
Received in revised form 13 January 2013
Accepted 14 January 2013
Available online 20 January 2013

Keywords:
Phosphorescent organic light emitting diodes
Stability
Iridium
Poly (N-vinylcarbazole)

ABSTRACT

Poly (N-vinylcarbazole) (PVK) based polymer light-emitting diode doped with green phosphorescent dye *fac*-tris (2-phenylpyridinato)iridium(III) [Ir(ppy)$_3$] showed two orders of magnitude shorter lifetime than 4,4′-bis (N-carbazolyl)-2,2′-biphenyl : Ir(ppy)$_3$ based device with the same device structure. Rapid degradation of the polymer based device was primarily originated from the instability of the doubly reduced Ir(ppy)$_3^{2-}$ in PVK, which was found from the reduction of photoluminescence intensity under electrical stress in hole only and electron–hole flowing devices, and the cyclic voltammetry experiments. Large difference of the lowest unoccupied molecular orbital energy level between PVK and Ir(ppy)$_3$ (~0.5 eV) and low electron mobility of PVK allow electrons transport only through Ir(ppy)$_3$, so that there is large probability for Ir(ppy)$_3$ to be doubly reduced upon electron injection.

1. Introduction

Recently, highly efficient and stable phosphorescent dye doped organic light-emitting diodes (PHOLEDs) have been achieved using small molecule based devices with proper design of device structure and encapsulation [1–3]. In the mean time, highly efficient polymer based phosphorescent light-emitting diodes (PHPLEDs) have also been fabricated by several groups [4–7]. The large band gap polymer such as poly (N-vinylcarbazole) (PVK) is commonly used as the host in green and red PHPLEDs because of the high triplet energy of PVK compared with that of the phosphorescent dyes.

The lifetime of devices is an important issue in PHPLEDs. There are many possible degradation mechanisms, such as the growth of dark spots, morphological instability, electrochemical instability, electrode migration, immobile positive charge accumulation and instability of poly(3,4-ethylenedioxy thiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) under electron injection. Many groups have reported the degradation mechanisms of the fluorescent organic light emitting diodes and well reviewed by Popovic et al. [8], but very few for the phosphorescent polymer light emitting diodes [9].

Here, it is reported that PVK based PHPLEDs doped with *fac*-tris (2-phenylpyridinato) iridium (III) [Ir(ppy)$_3$] as the emitter shows much shorter lifetime than that of small molecule (4,4′-bis(N-carbazolyl)-2,2′-biphenyl) (CBP) based devices. The rapid degradation of PVK based PHPLEDs is mainly due to the instability of Ir(ppy)$_3^{2-}$ anion which is demonstrated by the reduction of photoluminescence (PL) intensity of Ir(ppy)$_3$ under electrical aging and by the electrochemical stability of Ir(ppy)$_3$ examined by cyclic voltammetry (CV) experiments.

2. Experimental details

2.1. Device fabrication

All solvents were purchased from Across and used without further purification.

Patterned indium tin oxide (ITO) glass substrates were cleaned using acetone and isopropylalcohol, dried in an oven and then exposed to ultraviolet (UV)–ozone for 10 min before use. Polymer solution was prepared by dissolving PVK and Ir(ppy)$_3$ in chlorobenzene with a predetermined weight ratio. The polymeric thin film with a thickness of 30 nm was formed by spin coating the solution on the ITO substrates, pre-coated with 40 nm thick PEDOT:PSS layer (device I). The polymeric thin films were annealed at 80 °C for 30 min. The resulting thin film coated specimen was transferred immediately to a vacuum chamber for the further film deposition. On top of the emitting layer, 10 nm of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 30 nm of tris(8-hydroxyquinolinato) aluminum (Alq$_3$), 1 nm of LiF and 100 nm of Al layers were successively deposited for all the devices. Schematic device structures and energy level are shown in Fig. 1. The polymer films were fabricated in a nitrogen gas filled glove box ($H_2O<0.1$ ppm, $O_2<0.1$ ppm), and the organic layers and the cathodes were deposited by thermal evaporation at a pressure of around 10^{-5} Pa. For comparative study, three different devices with the structure of ITO(150 nm)/PEDOT(40 nm)/CBP:6 wt.% Ir(ppy)$_3$(30 nm)/BCP(10 nm)/Alq$_3$(30 nm)/

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http://dx.doi.org/10.1016/j.tsf.2013.01.017

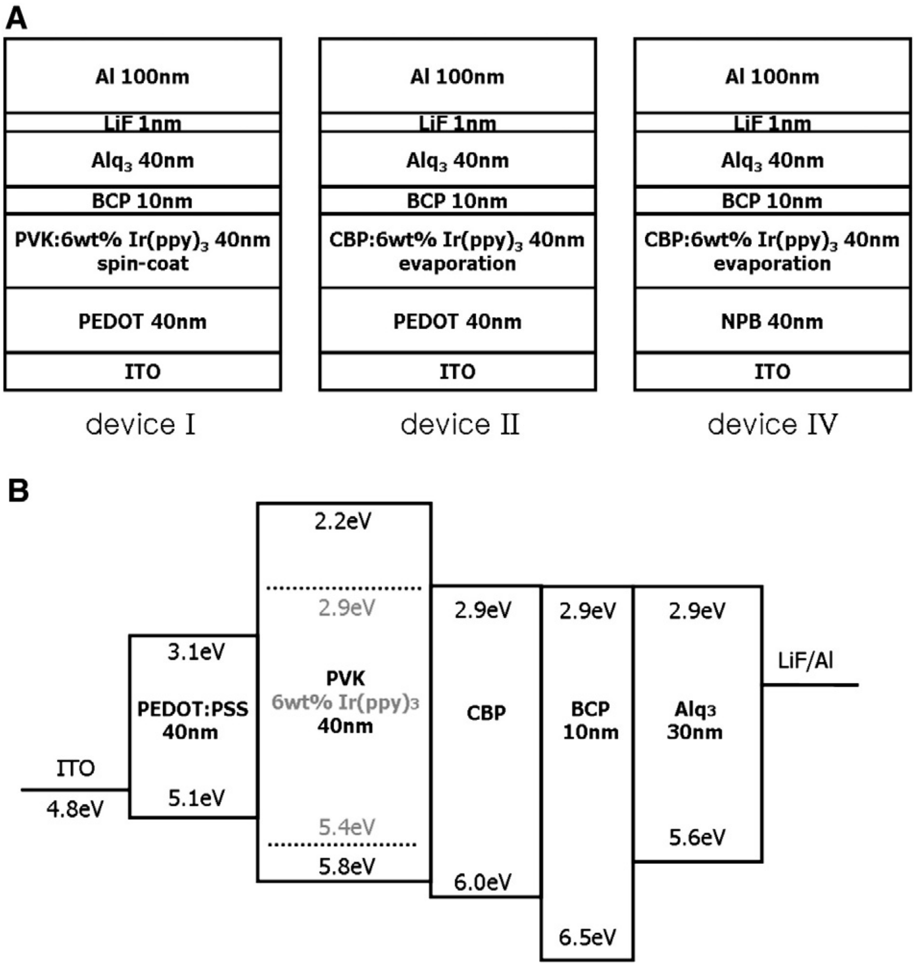

Fig. 1. Device structures (A) and materials' energy level diagram (B). Gray lines represent the energy levels of Ir(ppy)$_3$. PVK is used as a host matrix for the device I and CBP is for the other devices.

LiF(1 nm)/Al(100 nm) (device II), ITO(150 nm)/PEDOT(40 nm)/CBP:6 wt.% Ir(ppy)$_3$(30 nm)/BCP(10 nm)/Alq$_3$(30 nm)/LiF(1 nm)/Al(100 nm) (device III, where CBP layer is fabricated by spin-casting), and ITO(150 nm)/NPB(40 nm)/CBP:6 wt.% Ir(ppy)$_3$(30 nm)/BCP(10 nm)/Alq$_3$(30 nm)/LiF(1 nm)/Al(100 nm) (device IV) were fabricated. CBP: Ir(ppy)$_3$ layer was formed by co-evaporation except for the device III and *N*,*N*′-diphenyl-*N*,*N*-bis(1-naphthyl)-(1,1-biphenyl)-4,4-diamine (NPB) layer by thermal evaporation, respectively. CBP:6 wt.% Ir(ppy)$_3$ chlorobenzene solution is spun-cast for the device III on PEDOT:PSS surface at 1500 rpm and annealed at 80 °C for 30 min to obtain a 30 nm thick (confirmed by alpha step) homogeneous surface confirmed by atomic force microscope (root mean square roughness ~0.3 nm). Finally, all the devices were encapsulated with glass caps in an inert environment. The pixels have a dimension of 2 × 2 mm^2.

2.2. Characterization

The current density–voltage–luminescence (J–V–L) characteristics of the devices were measured by a Kiethley 2400 semiconductor parameter analyzer and a Photo Research (PR-650) spectrophotometer. The cyclic voltammograms were recorded with a computer controlled potentiostat (CH instrument, Model 660) at a constant scan rate of 0.1 V/s. Measurements were performed at a platinum working electrode in a degassed electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate dissolved in acetonitrile-1,4-dioxane (1:1(v/v)). Internal standard ferrocene/ferrocenium was used as a reference material.

3. Results and discussion

The luminous efficiency-current density characteristics and the device lifetimes of the three kinds of devices are shown in Fig. 2. The devices II, III, and IV with the CBP host showed almost the same maximum efficiency of about 45 cd/A. In contrast, the device I (ITO/PEDOT:PSS/PVK:6 wt.% Ir(ppy)$_3$/BCP/Alq$_3$/LiF/Al) with the PVK host shows lower efficiency of 26 cd/A. The inset shows the current density versus voltage for the three devices.

The half decay lifetime of the devices are displayed in Fig. 2(B). The device IV with CBP as the host and NPB as the hole transporting layer (HTL) shows much longer lifetime than that of the device II with PEDOT:PSS as the HTL, which can be understood by the formation of irreversible oxidation moieties of PEDOT:PSS [10] and reduction of the hole injection [11]. The lowest unoccupied molecular orbital (LUMO) energy level of NPB is sufficiently high (LUMO(NPB) = −2.3 eV) to confine electrons on CBP site (LUMO(CBP) = −2.9 eV) and it shows reversible oxidation process which means NPB is electrochemically stable under hole injection and transport [12]. Interestingly enough, the PVK based device I shows even much shorter lifetime of only a few minute at an initial luminance of 1500 cd/m^2 than the CBP based devices II and III. The emitting layer of device III is fabricated in solution process, while device II is made with vacuum evaporation. However, their device performances such as efficiency and lifetime have same order of magnitude meaning the effect of the fabrication method is minimal. Since all the devices I, II, and III employed PEDOT:PSS as the hole injection layer (HIL), two orders of magnitude shorter lifetime of the PVK based device I requires another reason for the degradation. From now on,