Journal of Luminescence 131 (2011) 199–205

Contents lists available at ScienceDirect

Journal of Luminescence

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

The enhanced electron injection by fluorinated tris-(8-hydroxy-quinolinato) aluminum derivatives in high efficient Si-anode OLEDs

N. Liu [a], M.M. Shi [a,*], Y.Z. Li [b], Y.W. Shi [a], G.Z. Ran [b], G.G. Qin [b], M. Wang [a], H.Z. Chen [a]

[a] *State Key Laboratory of Silicon Materials, MOE Key Laboratory of Macromolecule Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*

[b] *School of Physics, State Key Laboratory for Mesoscopic Physics, Peking University, Beijing 100871, China*

ARTICLE INFO

Article history:
Received 14 May 2010
Received in revised form
17 August 2010
Accepted 22 September 2010

Keywords:
Alq_3
Fluorination
Carrier injection balance
Si-anode based OLEDs

ABSTRACT

Fabrication of organic light-emitting diodes (OLEDs) and lasers on silicon substrates is a feasible route to integrate microelectronic chips with optical devices for telecommunications. However, the efficiency of Si-anode based OLEDs is restricted by the imbalance of hole–electron injection because a p-type Si anode owns better hole injection ability than ITO. We have used fluorinated tris-(8-hydroxy-quinolinato) aluminum ($FAlq_3$) derivatives to prepare Si-anode based OLEDs. We observed that, when tris-(5-fuloro-8-hydroxyquinolinato) aluminum ($5FAlq_3$) is used as the electron-transporting material instead of Alq_3, the cathode electron injection is enhanced due to its lower lowest unoccupied molecular orbital (LUMO) compared to the Alq_3. The device can keep the relative carrier balance even when a Si anode capable of stronger hole injection was used. Further optimization of the device structure by introducing 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole blocking layer showed significant increase in the device power efficiency from 0.029 to 0.462 lm/W. This indicates that use of fluorinated Alq_3 derivatives is an effective way to improve the performance of Si-anode based OLEDs.

1. Introduction

Silicon's wide availability along with its electrical and chemical properties has made it the key material for microelectronic industry. But its low luminescence efficiency, due to the indirect band gap, has resulted in its exclusion from optoelectronic application [1]. As a consequence, modern optoelectronics responsible for the bulk of long-distance telecommunications is dependent on III–V materials, which are incompatible with Si substrates [2]. Unlike III–V materials, organic light-emitting materials are amorphous and can be combined with Si easily [3]. Organic light-emitting diodes (OLEDs) have attracted unprecedented attention, and substantial progress had been made towards commercial applications during recent years [4]. Thus, fabrication of Si-anode based OLEDs can be a promising route to overcome the current problem in Si-based optoelectronic integration. Some pioneering work on Si-anode OLEDs had been reported [5]. In such devices, Si is always used as the anode due to its relatively high work function, which enhances the hole injection [6]. However, for usual OLEDs with indium tin oxide (ITO) anode, holes are major carriers and the hole–electron injection is unbalanced [7]. Using Si anode instead of ITO anode enhances further the pre-existing hole–electron injection imbalance in OLEDs, leading to a substantial decrease in device efficiency [8]. Qin et al. [9] passivated the Si anode by growing an ultra thin SiO_2 film between the Si anode and the hole-transporting layer in order to reduce the hole injection. They adjusted the hole injection current by changing the resistivity of the Si anode for a hole–electron injection balance in Si-anode OLEDs, which helped improving device efficiency remarkably. On the other hand, enhancing the device electron injection instead of suppressing the hole injection should be another efficient way to improve the hole–electron imbalance in Si-anode OLEDs and to achieve an even higher device efficiency. In our previous work [10], it was demonstrated that strong electron-withdrawing F substituent can lower the lowest unoccupied molecular orbital (LUMO) levels of organic semiconductors and enhances the electron injection, which is facilitated to improve the efficiency of OLEDs where holes are major carriers. In this work, fluorinated tris-(8-hydroxy-quinolinato) aluminum (Alq_3) derivatives are used to fabricate Si-anode OLEDs, where the electron injection is expected to be enhanced by lowering the electron injection barrier to get the hole–electron injection balance, aiming at a high electroluminescence efficiency.

2. Experimental section

2.1. Materials and characterization

Two fluorinated tris-(8-hydroxy-quinolinato) aluminum derivatives, tris-(5-fluoro-8-hydroxyquinoline) aluminum ($5FAlq_3$) and tris-(6-fluoro-8-hydroxyquinoline) aluminum ($6FAlq_3$) were

---

* Corresponding author.
E-mail address: minminshi@zju.edu.cn (M.M. Shi).

0022-2313/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2010.09.037

synthesized and purified according to the reported procedures in Ref. [10(b)]. All other chemicals and solvents were commercially available and used as received unless otherwise noted. Cyclic voltammetry (CV) measurements of Alq_3 derivatives were carried out on a CHI600A electrochemical workstation, with CH_2Cl_2 solution containing 0.1 M supporting electrolyte of tetrabutylammonium perchlorate, in a three electrode cell, where Pt plate was the working electrode, Pt wire was the counter electrode and the saturated calomel electrode (SCE) was used as the reference electrode. The scanning rate was 50 mV/s.

2.2. Device fabrication and testing

The p-type Si wafers with different resistivity (0.1–35 Ω cm) were used as the substrates for vacuum deposition. At first, Si substrates were cleaned by acetone, methanol and deionized water in succession, and etched by 5% HF solution to remove the oxides on the surface, followed by the formation of the Al contacts on the back sides to form ohmic contacts. Then, organic hole transport layer [1,4-bis (phenyl-*m*-tolylamino) biphenyl, TPD, or N,N′-bis (1-naphthl)-diphenyl-1,1′-biphenyl-4,4′diamine, NPB], the emissive layer (Alq_3, $5FAlq_3$, or $6FAlq_3$), the hole blocking layer (2,9-dimethyl-4, 7-diphenyl-1,10-phenanthroline, BCP) and the electron transport layer ($5FAlq_3$) were evaporated successively onto the substrates. Finally, an Ag (40 nm) or semitransparent Sm (15 nm)/Au (15 nm) cathode was vacuum deposited on the top of the organic layers through a shadow mask. Ag was selected as the cathode just to investigate the device carrier injection and all p-Si anodes were 1 Ω cm for devices with Ag cathodes. Sm is selected as the cathode material because it has low work function metal, low absorption coefficient and low reflectance, to enhance the light output in an electron-limited top-emission OLED [9(a),12]. The devices were capped with Au, which has a low reflectance in visible range and high chemical stability [9(a)]. The Si anodes were 0.1–35 Ω cm for devices with Sm/Au cathodes and the cathode area was 7 mm^2 delineated by a shadow mask. The complete fabrication of a device was finished in one chamber without a vacuum break. The typical deposition rate was ~1 Å/s, monitored by a quartz crystal oscillator. The base pressure of chamber was 4×10^{-6} Torr. The structures of all devices are shown in Fig. 1. Devices Al (100 nm)/Alq3 or $5FAlq_3$ (100 nm)/Al (100 nm) were prepared to measure the electron mobility of Alq_3 or $5FAlq_3$. The device preparation process is similar to that of light-emitting devices.

Electroluminescence (EL) spectra from the diodes were collected in air on a fluorescent spectrometer (SPEXFL-11), and the brightness was calibrated by a PR 650 spectrometer. Current density–voltage (*J*–*V*) measurements were made on a $6^1/_2$-digit multimeters (HP 34401).

3. Results and discussion

3.1. Effects of fluorinated Alq_3 derivatives' LUMOs levels on electron injection and emission peaks

Fig. 2 presents the cyclic voltammograms of Alq_3, $5FAlq_3$ and $6FAlq_3$ in CH_2Cl_2. The half-wave potentials ($E_{1/2}$) of the first reduction peaks for Alq_3, $5FAlq_3$ and $6FAlq_3$ are observed as −1.92, −1.68 and −1.49 V vs. SCE, respectively. Thus the energy values of LUMO levels (E_{LUMO}) for Alq_3, $5FAlq_3$ and $6FAlq_3$ can be calculated as −2.82, −3.06 and −3.25 eV, respectively, using the following equation [10b,13]

$$E_{LUMO}=-e\left|E_{1/2}+4.74\right| \tag{1}$$

The optical band gaps of Alq_3, $5FAlq_3$ and $6FAlq_3$ were, respectively, estimated from their absorption onsets as 2.81, 2.66 and 2.93 eV [10(b)], therefore, HOMO levels of Alq_3, $5FAlq_3$ and $6FAlq_3$ are located at −5.63, −5.72, and −6.18 eV, respectively, [10(b)].

EL spectra of Alq_3 derivatives are shown in Fig. 3. EL peaks of Alq_3, $5FAlq_3$ and $6FAlq_3$ are observed at 520, 560 and 504 nm, respectively. The results are similar with the photoluminescence results [10(b)], indicating that fluorination can tune the optical properties of Alq_3 derivatives.

Fig. 4 shows the *J*–*V* curves for Si-anode OLEDs employing Alq_3, $5FAlq_3$ and $6FAlq_3$ as both electron-transporting and emissive materials. It is found that, at the same voltage, the total current density increases in case of $5FAlq_3$ while decreases in $6FAlq_3$ when compared to the Alq_3. These results indicate that the electron injection or the electron transportation is increased for $5FAlq_3$ device and decreased for $6FAlq_3$ device. The first observation is reasonable due to the lower LUMO level of $5FAlq_3$ compared to Alq_3 (Fig. 5), giving a smaller electron injection barrier, that facilitates the electron injection. However for the second observation, it is unexpected that $6FAlq_3$'s much lower LUMO leads to a reduced current. It is assumed that $6FAlq_3$'s poorer electron transport ability may be responsible for the above phenomenon. Since this hypothesis still needs further confirmation, we investigated only the influence of $5FAlq_3$ on the Si-anode OLEDs performance.

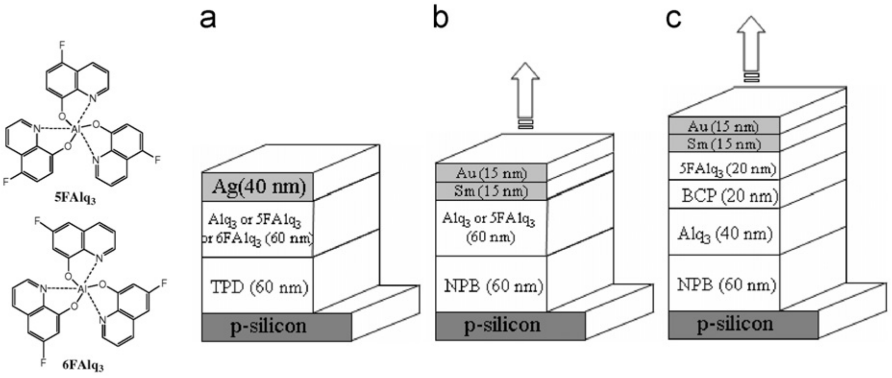

Fig. 1. Schematic configurations of the Si-anode OLEDs. Each device shown in (a) has a 60-nm-thick TPD hole-transporting layer. Alq_3, $5FAlq_3$, or $6FAlq_3$ was used as the electron-transporting material. Each device in (b) has a 60-nm-thick NPB hole-transporting layer. Alq_3 or $5FAlq_3$ was used as both electron-transporting and emissive material. For the device in (c), a 20-nm-thick $5FAlq_3$ layer was introduced to be the electron-transporting layer, and a 40-nm-thick Alq_3 layer was used as the emissive layer. A 20-nm-thick BCP layer was inserted between $5FAlq_3$ and Alq_3 layers as the hole-blocking layer. The insets are the molecular structures of $5FAlq_3$ and $6FAlq_3$.