



Composite film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and MoO₃ as an efficient hole injection layer for polymer light-emitting diodes



Yongwon Kwon^{a,1}, Yongnam Kim^{b,1}, Hyunkoo Lee^c, Changhee Lee^{a,*}, Jeonghun Kwak^{b,*}

^a School of Electrical and Computer Engineering, Inter-University Semiconductor Research Center, Seoul National University, Seoul 151-742, Republic of Korea

^b Department of Electronic Engineering, Dong-A University, Busan 604-714, Republic of Korea

^c OLED Research Center, Components & Materials Research Laboratory, Electronics and Telecommunications Research Institute (ETRI), Daejeon 305-700, Republic of Korea

ARTICLE INFO

Article history:

Received 26 November 2013

Received in revised form 13 January 2014

Accepted 11 March 2014

Available online 22 March 2014

Keywords:

Polymer light-emitting diodes

Molybdenum oxide

PEDOT:PSS

Hole injection layer

ABSTRACT

We demonstrate improved performances in polymer light-emitting diodes (PLEDs) using a composite film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and MoO₃ powder as a hole injection layer. The PLED with the composite film exhibits the current efficiency of 13.5 cd/A, driving voltage of 3.4 V, and half lifetime of 108.1 h, while those values of the PLED with a pristine PEDOT:PSS was 11.3 cd/A, 3.8 V, and 41.5 h, respectively. We also analyze the morphological, optical and electrical properties of the composite films by atomic force microscopy (AFM), UV–Vis–IR absorption, and ultraviolet photoemission spectroscopy (UPS). This work suggests that mixing MoO₃ into PEDOT:PSS is a simple and promising technique for use solution-based devices as an hole injection layer.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

There have been tremendous studies for polymer light-emitting diodes (PLEDs), as they provide for their potential applications to large-area full-color displays and solid-state lightings based on solution process [1–4]. Owing to the studies, not only material properties but also the characteristics of PLEDs have been developed significantly for a few decades [5,6]. Nevertheless, PLEDs still suffer from the lower performances in terms of their efficiency and life-

time. One main reason is considered as the poor charge carrier injection into polymers due to the difficulties in multilayer stacking of functional layers by solution process. The insertion of layers which facilitate the injection of electrons and holes into the adjacent layer should not be dissolved or damaged during the deposition of the light-emitting polymer. For instance, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), a water soluble conducting polymer, is commonly used as a hole injection layer (HIL) in PLEDs because its thin film is hardly dissolved in typical solvents for light-emitting polymers such as chlorobenzene or toluene. It also has high electrical conductivity (up to 1000 S/cm) and transparency in visible spectral range (up to 90%), thus it is highly suitable for organic optoelectronic applications. Despite these advantages, the efficiency and device stability of PLEDs using PEDOT:PSS are limited because its low work function (5.0–5.2 eV) and morphological inhomoge-

* Corresponding authors. Address: School of Electrical and Computer Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-742, Republic of Korea. Tel.: +82 2 880 9093 (C. Lee). Address: Department of Electronic Engineering, Dong-A University, Hadan-dong, Saha-gu, Busan 604-714, Republic of Korea. Tel.: +82 51 200 7707 (J. Kwak).

E-mail addresses: chlee7@snu.ac.kr (C. Lee), jkwak@dau.ac.kr (J. Kwak).

¹ These authors contributed equally to this work.

neity hinder the efficient hole injection into the highest occupied molecular orbital (HOMO) energy level of typical light-emitting polymers [7].

For a few years, transition metal oxides (TMOs) such as molybdenum trioxide (MoO_3), tungsten trioxide (WO_3) and vanadium pentoxide (V_2O_5) have been introduced as an efficient HIL for organic optoelectronic devices [8–12]. In-depth studies show that the efficient hole injection at the interface of TMO and organic layer is caused by electron extraction from the HOMO level of the neighboring organic layer to the deep conduction band (CB) of TMO [13,14]. But it is not practical for PLEDs to evaporate the TMOs since the process requires high temperature and high-vacuum condition, and sometimes the film can be washed out while spin-casting polymers. Recently, researchers have reported several deposition methods of TMOs based on solution process; sol–gel-derived TMO by using from precursor solution [8,9], dissolving TMO powder in a solvent [10], and TMO nanoparticles dispersed in solution [11,12]. From all of these methods, a thin film of TMO can be obtained. However, the sol–gel method requires high temperature in order to convert the precursor to the semiconducting film, and the TMO nanoparticles are hard to synthesize with controlling the dispersity. Dissolving the TMO powders in a solvent is one of the easiest methods for solution processing, but in general the solubility of TMOs is extremely low. Thus, the film has poor coverage as well as rough surface morphology.

Herein, we introduce a mixture of PEDOT:PSS and a small amount of MoO_3 powder as an effective HIL for PLEDs. The composite film had a superior morphological uniformity without any damage to the following polymer deposition process. We also investigated the electrical properties of the mixture layer with hole only devices (HODs) and PLEDs using phenyl-substituted poly(p-phenylene vinylene) copolymer (super yellow). The devices with the composite HIL exhibited longer lifetime by a factor of 2.5 as well as improved current density and current efficiency by 40% and 20% at 4 V, respectively, compared to the device with pristine PEDOT:PSS. The results indicate that the hole injection layer using MoO_3 mixed PEDOT:PSS makes hole injection more efficient.

2. Experimental

Powdered MoO_3 (CERAC, 99.9%) was mixed into PEDOT:PSS (Clevios™ P VP Al 4083) with different concentrations of 0.05, 0.1, 0.2 and 0.3 wt.%, and they were stirred for over 2 h. A thin film of PEDOT:PSS containing MoO_3 was fabricated by spin-coating the solution on UV–ozone-treated ITO glasses at 4000 rpm for 40 s, followed by drying at 120 °C for 30 min in vacuum.

In order to characterize the hole injection property of the composite film, HODs were fabricated in the structure of ITO/HIL (40 nm)/N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB, 100 nm)/ MoO_3 (10 nm)/Al (100 nm), where the HIL was PEDOT:PSS, the mixture of MoO_3 and PEDOT:PSS (0.05–0.3 wt.%), or the same concentration of MoO_3 dissolved in deionized water (0.05–0.3 wt.%). We incorporated the mixture HIL into

PLEDs composed of ITO/HIL (40 nm)/PDY-132 (super yellow, 80 nm)/LiF (0.5 nm)/Al (100 nm), as shown in Fig. 1. The light-emitting polymer (PDY-132, purchased from Merck) dissolved in toluene was spin-coated on the HIL at 2500 rpm for 60 s in a glove box. After annealing the films, LiF and Al were deposited at the base pressure of $<3 \times 10^{-6}$ Torr. The devices were encapsulated with a glass lid for the lifetime test. To measure the resistance of the films in the out-of-plane direction, the devices of ITO/HIL/Al (100 nm) were fabricated with the same concentration condition.

The surface morphologies were characterized using AFM (park systems XE-100). The optical absorption of the mixture films were measured with an UV–vis–IR spectrophotometer (Agilent Carry 5000) and their energy levels were measured by ultraviolet photoemission spectroscopy (UPS). The current–voltage characteristics of the HODs and resistance devices were measured using a source–measurement unit (Keithley 2400). The current–voltage–luminance characteristics of PLEDs were measured at room temperature using a source–measurement unit (Keithley 236) and a multimeter (Keithley 2000) equipped with a calibrated Si photodiode (Hamamatsu S5227-1010BQ) and a photomultiplier tube. Electroluminescence (EL) spectra were obtained with a spectroradiometer (Minolta CS-1000A). The lifetime of the devices was measured at room temperature using OLED lifetime test system (McScience MC620S).

3. Results and discussion

To investigate the effect of MoO_3 mixing in PEDOT:PSS as a hole injection layer, we fabricated the hole only devices consisting of a HIL using solution-processed MoO_3 , MoO_3 mixed PEDOT:PSS, or pristine PEDOT:PSS, and a typical hole transporting layer using 100 nm of NPB. The current density–voltage characteristics of the HODs are shown in Fig. 2. The devices with solution-processed MoO_3 exhibit much lower current densities compared to the devices using PEDOT:PSS and MoO_3 mixed PEDOT:PSS. Since the solubility of MoO_3 in water is limited to about 0.2 wt.% as reported previously [10], it is hard to form a homogeneous and smooth thin film for PLEDs (see Fig. 3c). As a result, the HODs showed low current densities for all concentrations of MoO_3 in water. On the contrary, the mixture of PEDOT:PSS and a small amount of MoO_3 powder forms a uniform film by spin-coating as reported previously [15], and which also can be seen in Fig. 3. The HODs with MoO_3 dissolved in PEDOT:PSS show slightly but distinctly increased current densities than the device using pristine PEDOT:PSS. If MoO_3 act as a p-type dopant such as the earlier reports of MoO_3 doped NPB [16], mixing MoO_3 will modify the energy level of PEDOT:PSS or form charge transfer state. However, because there was no noticeable change in their UPS and absorption spectra over UV–vis–IR before and after mixing small amount of MoO_3 powder as shown in Fig. S1 in Supporting Information, we consider that a p-doping effect of MoO_3 in PEDOT:PSS with a low concentration is not as remarkable as that of MoO_3 doped organic molecules. As shown in Fig. S2, the

Download English Version:

<https://daneshyari.com/en/article/10566583>

Download Persian Version:

<https://daneshyari.com/article/10566583>

[Daneshyari.com](https://daneshyari.com)