Effects of plasma polymerized para-xylene intermediate layers on characteristics of flexible organic light emitting diodes fabricated on polyethylene terephthalate substrates

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Received 10 November 2005; received in revised form 23 December 2005; accepted 24 January 2006
Available online 26 January 2007

Abstract

Characteristics of flexible organic light emitting diodes (FOLEDs) with the plasma polymerized para-xylene (PPpX) intermediate layer were investigated. For the purpose of reducing moisture permeation through plastic substrates, a PPpX intermediate layer was inserted between FOLEDs and the plastic substrates. As the concentration of C–H bonding in the PPpX film deposited at 25 °C was increased, PPpX films showed increased transmittance. Surface morphologies of polyethylene terephthalate (PET) covered with the PPpX intermediate layer were improved compared to PET without PPpX on it. Due to the highly cross-linked network structure in the plasma polymer film, water vapor permeability of PET substrates with the PPpX intermediate layer of 75 nm was decreased compared to PET substrates without PPpX on it. FOLEDs with the PPpX intermediate layer showed improved optical and electrical characteristics as well as lifetimes than FOLEDs without the PPpX intermediate layer. © 2006 Elsevier B.V. All rights reserved.

Keywords: Luminescence; Plastics; Thin films; Optical properties

1. Introduction

Since successful fabrication of high efficiency organic light emitting devices (OLEDs) with multilayer structures in 1987, there has been rapid improvement in the device performance of OLEDs [1]. OLEDs were considered as a promising flat panel display, because of their advantages such as wide view angle, low operating voltage, low cost, and possibility of flexible display. Flexible OLEDs (FOLEDs) fabricated on flexible substrates provide ability to conform, bend or roll a display into any shape, and also will give possibility of fabricating displays by continuous roll processing. FOLEDs were made on plastic substrates by many research groups [2–5]. Generally, plastic substrates have good properties such as high transmittance and flexibility, however, it suffered from low glass transition temperature (Tg) below 200 °C and decreased the lifetime of FOLEDs because of crystallization of organic materials at around 200 °C by diffused moisture and/or oxygen through the plastic substrate [6,7]. For the purpose of reducing moisture permeability through the plastic substrate, it was attempted to insert a barrier layer between the FOLEDs and the plastic substrates. Burrows et al. utilized the Barix™ process using mitigated layers of polyacrylate between multiple layers of the inorganic material such as SiO2, Si3N4, and Al2O3 [5]. However, there is a limit to various deposition process and flexibility. The low flexibility of inorganic films can diffuse moisture and/or oxygen in atmosphere through the micro cracks or pinholes [8,9]. On the other hand, plasma polymerized thin films deposited by plasma enhanced chemical vapor deposition (PECVD) at 25 °C have the characteristics such as high transmittance as a function of deposition condition, pinhole-free, and high flexibility [10]. Since any previous investigation about the FOLEDs using intermediate barrier layer with plasma polymerized thin film is not reported yet in detail, a primary work is very necessary for development of the next generation of flexible flat panel displays.
In this work, we report that, in the fabrication of the FOLEDs, insertion of a plasma polymer barrier layer improved the interface properties and lifetimes of FOLEDs. The plasma polymer barrier layer was deposited by PECVD using para-xylene as the precursor, and was referred to as plasma polymerized para-xylene (PpX). The PpX film with carbon and hydrogen at para-xylene precursor has the flexibility and high density properties.

2. Experimental

In our experiments, polyethylene terephthalate (PET) was used as the plastic substrate and PET used in our experiment was a SiO2 coated PET. PpX film was fabricated on and under PET substrate, respectively, for reducing an influence by contamination generated in PET substrate and a degradation effect by moisture and/or oxygen penetrated through the atmosphere [11]. Also, PpX films were used as the passivation layer for measuring the lifetime characteristic as the previous report [10]. PpX film was deposited by radio frequency (rf) plasma enhanced CVD system at 0.2 Torr and 25 °C, which is described in detail elsewhere [12]. The bubbler of para-xylene monomer was kept at 40 °C. Ar carrier gas of 8 sccm was utilized for delivering the monomer into the deposition chamber. The deposition power was varied in the range of 30–90 W. In our experiment, the thickness of PpX barrier film fixed at 75 nm because the transmittance of films deposited over 80 nm was decreased at blue light range. Transmittance of PpX film deposited at various plasma powers was measured by UV–vis spectrometer. Surface roughness values of PET surface with and without PpX film, root mean square (RMS) and peak-to-valley height (Rz), were measured by atomic force microscope (AFM). Fourier transform infrared (FTIR) spectra for PpX films to investigate the chemical structures of the films. Water vapor permeability (WVP) of PpX film was determined using Modern Controls Inc. (MOCON). In order to investigate the characteristics of FOLEDs, the structures of FOLEDs were formed with the indium thin oxide (ITO, 150 nm), N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD, 40 nm), tris-(8-hydroxyquinoline) aluminum (Alq3, 60 nm), and Al (100 nm), which were used as the anode, hole transport layer (HTL), the emitting layer (EML), and the cathode, respectively. For the FOLEDs, we measured the lifetime characteristics in atmosphere, and observed the bubble by optical image. A Keithley 2400 electrometer was used for current density–voltage (J–V) characteristics as a voltage source and current measurement equipment. Brightness of the FOLEDs was investigated by measuring the photocurrent induced by light emission from the FOLEDs using a Keithley 485 picameter.

3. Results and discussion

The intermediate film in FOLEDs using PET substrate requires the high transmittance, impermeability, and smooth surface morphology [5]. Amorphous hydrogenated carbon (a-C:H) film, such as PpX, changed the density of film and permeability in atmosphere as a function of deposition power and deposition pressure [12,13]. The transmission spectra and the optical band gap (see also inset) of PP films deposited plasma power of 30–90 W and 25 °C are shown in the Fig. 1(a). Optical band gap was calculated by Tauc’s relation [14]. Since the electroluminescence light is extracted through the barrier layer, high transmittance of the barrier layer deposited on substrate is required. The PpX film deposited at plasma power of 30 W showed the highest transmittance of average 85% in visible light range due to the high concentration of sp2 bonding in the PpX film. Transmittance in blue light range and the optical band gap of PpX films were decreased as the plasma power increased, which was due to decrease of C=C or C=O bonding in the plasma polymer films [15]. Moreover, it was also previously reported that, the optical band gap of plasma polymer films were increased as the increased sp3(C–H) and C–C bondings in the film [16]. Fig. 1(b) shows FTIR spectra of PpX films deposited at various plasma powers. The absorption peaks near 1710, 1600, and 3400 cm−1 shows, respectively, C=O stretching, C=C bending, and O–H stretching, some of which are formed from reaction of radicals remaining in the deposited plasma polymer films with oxygen in air [17]. The absorption peaks near 2800–3000 and 1300–1500 cm−1 shows C–H, stretching and C–H2 bending, respectively, in a structure of C8H10, para-xylene precursor [18]. As the deposition power was increased, the peak intensity of C–H2, stretching was decreased. In the inset of Fig. 1(b), the PpX films as a function of plasma power showed a sp3(C=H)-related peak with asymmetry (2953 cm−1) and symmetry (2888 cm−1) of stretching mode and a sp2(C=H)-related peak with asymmetry (2927 cm−1) and symmetry (2868 cm−1) of stretching mode. As a result of permeability test, WVP (2.8 g/(m² day)) of PpX barrier film deposited on PET substrate at 30 W and 25 °C is similar to that of the PET substrate. WVP (3.4 g/(m² day)) of PET used in our experiment is lower than WVP (10.7 g/(m² day)) of con-
Fig. 2. AFM images of (a) PET and (b) 75 nm PPpX coated PET.

Fig. 3. Change of (a) $J-V$, (b) $B-V$ characteristics, and (c) external quantum efficiency of the FOLEDs with the variation of the PPpX barrier layer.

Fig. 4. Lifetime of FOLEDs with the variation of the PPpX barrier layer.
and 25 °C, and then tested three types (see Fig. 3) of FOLEDs as followings: FOLED without PpX barrier layer (FOLED-A), FOLED with PpX barrier layer under PET substrate (FOLED-B), and FOLED with PpX barrier layer above PET substrate (FOLED-C). Fig. 3(a)–(c) shows the optical and electrical characteristics of current density–voltage (J–V), brightness–voltage (B–V), and quantum efficiency–voltage (QE), respectively. Turn-on voltages of FOLED-B and FOLED-C were 9 V, and their J–V and B–V characteristics at low voltage range were similar to those of FOLED-A. Maximum brightness of FOLED-C in high voltage range was improved as 2200 cd/m² compared with 1900 cd/m² of FOLED-A and FOLED-B. We think that the maximum brightness at high voltage range was increased because of the planarize effect at surface and relatively low permeability, as the RMS value of ITO electrode with PpX film was improved from 2.1 to 1.7 nm, and this work was mentioned elsewhere [4].

The existences of PpX intermediate layer not only improve the interface properties in FOLEDs, and can also reduce the contact resistance between the organic layer and the ITO substrate by the good adhesion.

Fig. 4 shows degradation characteristics of FOLEDs. The lifetimes of FOLEDs were measured at dc constant current of 9 mA/cm² in air at room temperature. Measured initial brightness of FOLED-A–FOLED-C in the lifetime testing experiment was, respectively, about 135 cd/m² (12.2 V), 138 cd/m² (12.3 V), and 177 cd/m² (11.9 V) at 9 mA/cm². The time duration required for the brightness of the FOLEDs to become half of the initial value was referred to as the lifetime of the FOLEDs. The lifetime of FOLED-A was 1.86 h while the FOLED-B was 3.5 h, twice larger than that of the FOLED-A. The lifetime of FOLED-C was 4.38 h, indicating 2.3 times longer than that of FOLED-A. It is thought that the PpX intermediate layer reduced the penetration of moisture through the PET substrates in FOLED-C.

It is known that plasma polymers have very low density of pinholes due to the highly cross-linked network structure and adhere well to underlying layers due to the activation of the growing surface by plasma at the beginning of and/or during the PECVD deposition process [17]. The above results show that the PpX layer reduces moisture penetration through PET substrates into FOLEDs, playing a role of an intermediate layer.

In order to check why the lifetime of FOLED-C was so long compared with others, we checked the optical microscopy images of the used FOLEDs. Fig. 5 shows optical microscopy images of the used FOLEDs. We measured the bubbles through organic layer by lifting the cathode layer after driving of device. The bubble size of FOLED-A increase after 2 h and show the state like current shot by fast degradation of device after 4 h, while the bubble of FOLED-C show a little increase. This is considered due to prevention of moisture and/or oxygen diffusion by PpX intermediate layer. We think that the PpX intermediate layer used in FOLED-C is certain barrier material because FOLED-C showed the longest lifetime and the little bubbles after driving of the devices by reducing the factors of degradation like contamination or metal diffusion from PET substrate to organic layer.

4. Conclusions

In summary, the PpX film was used as an intermediate barrier layer of FOLED. The PpX film deposited at the plasma power of 30 W showed the higher transmittance than PpX films deposited at higher deposition plasma power, and the $R_\theta$ of PET substrate with PpX film were reduced. Insertion of the PpX intermediate layer between the FOLEDs and the PET substrates increased the lifetime of the FOLED-C due to a highly cross-linked network structure in the plasma polymerized thin film.
The lifetime of FOLED-C was \( \sim 2.3 \) times longer than that of the FOLED-A without barrier layer. The FOLEDs with the PpX intermediate layer were improved in both electrical and optical characteristics and lifetimes, as well as in prevention of moisture and/or oxygen diffusion in atmosphere.

Acknowledgements

This work was supported by the SRC program (Center for Nanotubes and Nanostructured Composites) of MOST/KOSEF, and Korea Research Foundation Grant (KRF-2005-005-J11902).

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