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Encapsulation of organic light-emitting devices by means of photopolymerized polyacrylate films

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Abstract

For encapsulation of organic light-emitting devices (OLEDs) built on glass substrate, photopolymerizable blend consists of pentaerythritol triacrylate (PETIA) and HSP188 (photoinitiator) was spin-coated onto an OLED and then cured to form a cross-linked passivation layer. The electroluminescence (EL) and the rate of degradation were examined to compare the electrical and the emissive properties of the device before and after forming the passivation layer. In this case, wet process encapsulation, which did not influence the EL characteristic of the device, enhanced the lifetime of the device in air.

Keywords: Photopolymerization; Passivation; Organic light-emitting devices

1. Introduction

Organic light-emitting devices (OLEDs) have been extensively studied due to their possible use in a wide range of display applications [1–4]. However, stability of OLED is still a major problem, which should be overcome in order to realize the practical use of OLED. It has been demonstrated that some of organic materials used to form light-emitting layers of OLEDs are very sensitive to contamination, oxidation and humidity [5–7]. Furthermore, most of the metals used as contact electrodes for OLEDs are susceptible to corrosion in air or other oxygen containing environments [4,5]. It is also likely that such highly reactive metals undergo a chemical reaction with the nearby organic materials, which also could have negative effects on device performance. As a result, conventional OLEDs exhibit a short lifetime (generally defined as the time necessary to reduce luminance to 50% of initial luminance value at constant current) as a usual device in atmospheric conditions. If operation in a normal atmosphere is desired, high quality encapsulation of OLED is required.

To increase the lifetime of OLEDs, various methods and techniques have been devised for encapsulating OLEDs [8–13]. At present, a hermetic encapsulation technique using a glass or metal lid has been extensively performed to protect the devices from oxygen and water vapors. However, these types of seals are very expensive to fabricate and require extensive labor to assemble. In addition, these seals are large and heavy so that they severely limit the applications of OLEDs. For thin and lightweight encapsulation of OLEDs, encapsulation method based on dry process has been studied [8–13]. Yamashita et al. [11] and Kho et al. [12] reported a thin film encapsulation technique for OLEDs by plasma-polymerized parylene film. Kwon et al. [13] used multilayer of high-density polyethylene (HDPE) and aluminum(Al)–lithium(Li) alloy. However, encapsulation method by mean of wet process, which is obviously advantageous for various display applications because of its simplicity and reliability in handling, has hardly been studied. In this study, we report a new passivation layer formed by using spin coating method.

2. Experimental

2.1. Materials

Pentaerythritol triacrylate (PETIA) and HSP-188 (photoinitiator) were provided by SK ucb Co., Ltd. and used without further purification. PETIA (Fig. 1) is a

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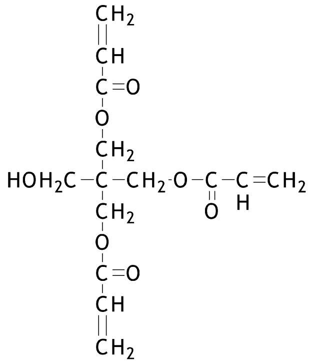

Fig. 1. Chemical structure of pentaerythritol triacrylate.

multifunctional monomer containing a mixture of tri- and tetra-acrylates.

2.2. Preparation of a small molecular light-emitting devices

Glass substrate coated with indium tin oxide (ITO) (sheet resistance, 14 Ω/sq) was washed with acetone and methanol in an ultrasonic bath and then dried in a stream of nitrogen. To explore the effect of our passivation layer, a glass-based small molecular light-emitting device was fabricated. The device structure included a 20 nm-thick 4,4′,4″-tris(*N*-3-(3-methylphenyl)-*N*-phenylamino)triphenyl amine (MTDATA) as a hole injection layer (HIL); a 40 nm-thick *N*,*N*′-biphenyl-*N*,*N*′-bis(1-naphenyl)-[1,1′-biphenyl]-4,4′-diamine (NPB) as a hole transport layer (HTL); a 60 nm-thick tris-(8-hydroxyquinoline) aluminum (Alq3) as a light-emitting layer and an electron transport layer (ETL), and a cathode. The cathode included a 2 nm-thick LiF and a 100 nm-thick Al layer. The device was successively deposited by employing the conventional thermal evaporation at 10^{-7} Torr without breaking the vacuum. The active area of the device was $2 \times 2\ \mathrm{mm}^2$.

2.3. Formation of a passivation layer

Photopolymerizable blends were prepared by a mixture of PETIA (10 g) and HSP188 (1 g). Polymerizations were initiated using a high-pressure mercury (Hg) lamp with light intensity of $7\ \mathrm{mW/cm}^2$ (at 366 nm). In order to form a passivation layer, the photopolymerizable blends were spin-coated onto the device at 2500 rpm for 50 s and then irradiated to form a 14.5 μm-thick cured passivation layer (exposed light energy, $1260\ \mathrm{mJ/cm}^2$). Conversion of the obtained polyacrylate was about 91%. Fig. 2 shows a schematic structure of the device with the passivation layer.

2.4. Characterization

Double bond conversion of PETIA was evaluated with a Nicolet 560 infrared spectrometer at a resolution of $4\ \mathrm{cm}^{-1}$. The polyacrylate films were prepared on KBr disks for IR measurements. UV–visible absorption spectrum of the polyacrylate was measured at ambient temperature in air using a spectrophotometer (Hitachi U-3501). The surface roughness of the polyacrylate, which is basis for subsequent encapsulation process, was studied by atomic force microscopy (AFM). Change in the polyacrylate surface components was measured by electro spectroscopy for chemical analysis (ESCA, VG Microtech MT 500/L). The polyacrylate thickness was measured using a Tencor Instrument Alpha-Step 500. Water vapor transmission rate of the polyacrylate films were evaluated at 37.8 °C and 100% relative humidity (RH) with MOCON detection instrument (PERMATRANW® 3/31 MA).

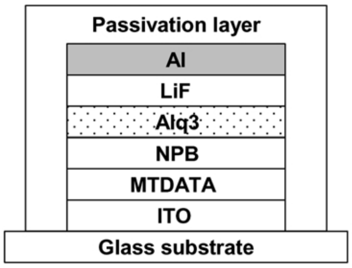

Fig. 2. Schematic diagram of an organic light-emitting device with a polyacrylate passivation layer used in this study.

For electrical measurements of the fabricated devices, a Keithley 238 electrometer was used as a voltage source and current measurement unit. The luminance characteristics of the devices were determined by measuring the photocurrent induced by the light emission from the device using a luminance meter (Minolta LS-100/CS-1000).

3. Results and discussion

The polyacrylate films exhibit good adhesion to the glass-based device. By AFM, the surface of the polyacrylate appears almost completely unstructured. The layer possesses an rms roughness of 1 nm, and the maximum difference in height (peak-to-valley) is about 7 nm. In addition, the spin-coating and photocuring of PETIA (liquid monomer) results in a flexible and transparent polymer film. The cross-linked polyacrylate films are insoluble to common organic solvents and alkaline solution. Typical physical properties of the polyacrylate are given in Table 1.

We investigated the effect of wet process encapsulation on the electroluminescence (EL) characteristic of the

Table 1
Physical properties of the polyacrylate

Items	Results
Light transmittance (%) (at 550 nm)	>99
Water vapor transmission rate (g/m^2[day])	39.0
Conversion (%)	91.0
Surface roughness (nm)	1 (rms)
Thickness (μm)	14.5

device. The luminance–voltage ($L-V$) and the current–voltage ($I-V$) characteristics were examined to compare the electrical behavior of the device before and after forming the passivation layer, as shown in Fig. 3. It was observed that with increasing applied dc voltage across the device, the luminance remained unchanged until ~3 V and then increased steeply. We also measured the $L-V$ characteristic of the passivated device and a luminance of ~100 and 21,600 cd/m^2 was achieved at 8.0 and 15.6 V, respectively. The passivated device showed a similar $L-V$ behavior to that of the device without the passivation layer (bare device). Although the $L-V$ profile of the passivated device shifted to low dc voltage, substantial variations in electrical properties were not observed. As shown in Fig. 3(b), no notable difference in the $I-V$ behavior between the bare device and the passivated device was observed. When the photopolymerizable blend is cured to form the passivation layer, both the light-emitting material (Alq3) and the cathode metal (LiF:Al) were minutely influenced by photopolymerization. This result indicates that the photopolymerizable blend and the fabrication process of the passivation layer did not induce the change in the electrical and the emission properties of the device.

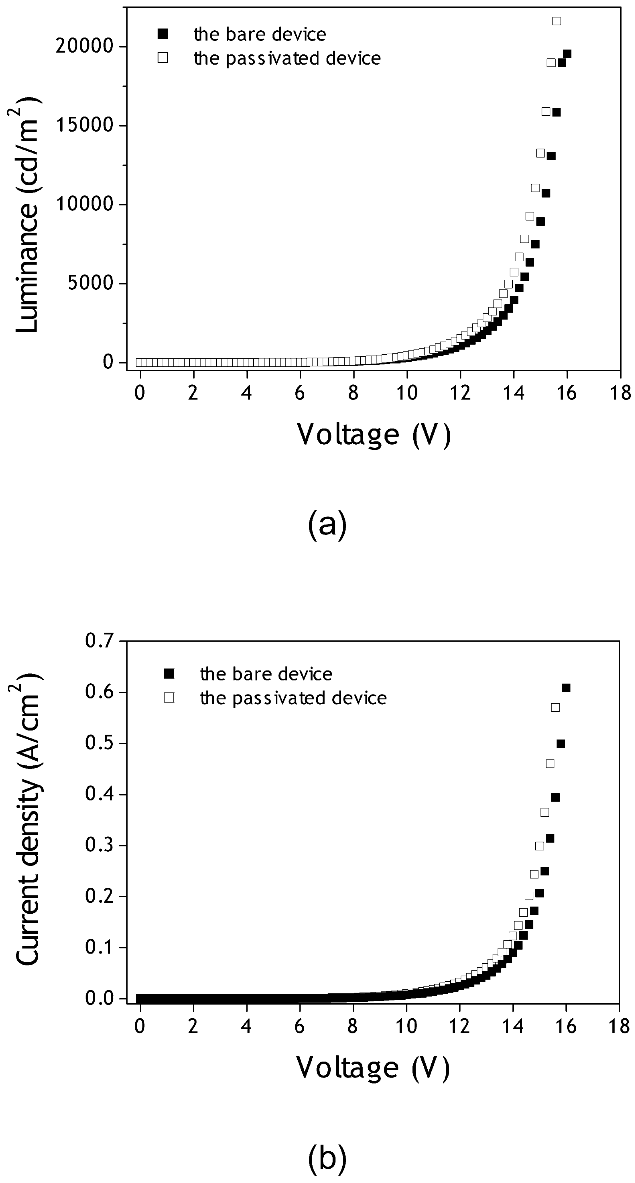

Fig. 3. (a) Luminance–voltage and (b) current–voltage characteristics for both the bare deice and the passivated device.

We next studied the rate of degradation of the fabricated devices. The lifetime of the bare device and the passivated device were measured from an initial luminance of 170 cd/m^2 and a dc constant current of 0.039 mA/mm^2 at 40 °C and 60% RH in air. Our measurement is that one of an acceleration test because driving current, temperature and humidity are higher than that of a practical measurement. Fig. 4 shows a typical plot of normalized luminance versus driving time for these devices. The bare device decays to 50% of its initial luminance in 2.3 h compared to 7.4 h for the passivated device. The lifetime of the passivated device is almost three times longer than that of the bare device, which might be due to exclusion of external contamination such as water, oxygen, dust and the like. Assuming the operational lifetime is inversely proportional to the initial luminance [14], this result of the passivated device corresponds to lifetime of 12.6 h at 100 cd/m^2. The shorter lifetime of the passivated device than that of commercial OLEDs (>5000 h) may be interpreted in terms of a relatively low barrier property (39 g/m^2[day]) of the passivation layer and diffusion of moisture and/or oxygen through the interface between the glass substrate and the passivation layer.

3.1. Effect of the polyacrylate thickness

In order to explore the effect of the polyacrylate thickness on the stability of the device, we prepared three devices of differing polyacrylate thickness. Fig. 5 shows the effects of the polyacrylate film thickness on the permeation

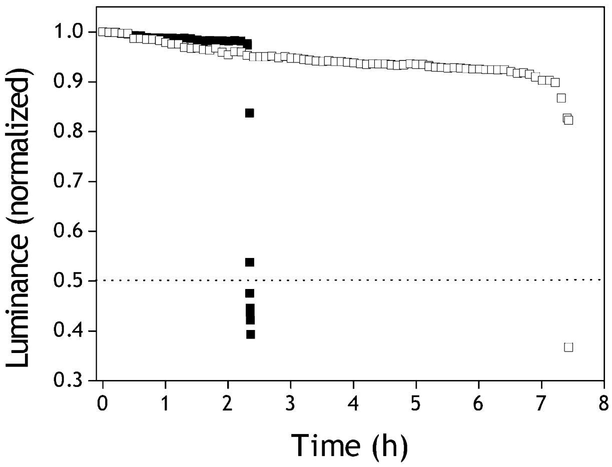

Fig. 4. (■) Lifetime of the bare device and (□) the passivated device with a dc electric field of 0.039 mA/mm^2. These measurements were carried at 40 °C and 60% RH.

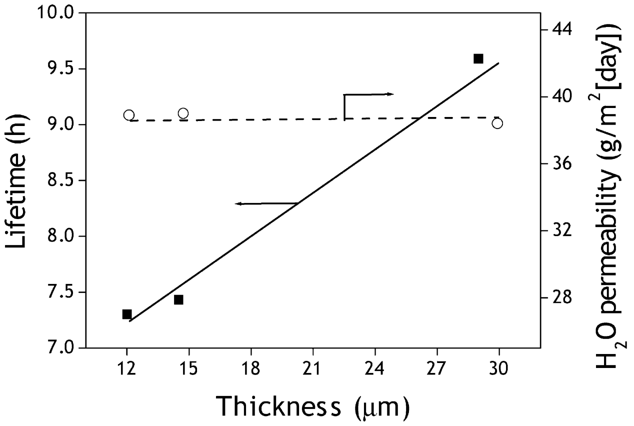

Fig. 5. Dependence of the polyacrylate film thickness on the lifetime of the passivated devices and the water vapor transmission rate. The lifetime were examined at 40 °C and 60% RH with a dc electric field of 0.039 mA/mm^2. The water vapor transmission rate was measured at 37.8 °C and 100% RH.

rate of water vapor and the lifetime of the devices. The lifetime of three devices, which show dependence on the passivation film thickness, are 7.3 h (thickness, 12 μm), 7.4 h (thickness, 14.5 μm) and 9.6 h (thickness, 29 μm), respectively. It is unlikely that the passivation film thickness causes the change of the interface between the substrate and the passivation layer. Therefore, such changes in the lifetime might not be by diffusion of moisture and oxygen through the interface, but mainly by permeation through the passivation layer. Even though the barrier property hardly changed, the slope of the moisture permeation rate can be affected by the thickness of the polyacrylate. Yamashita et al. reported that the lifetime of an OLED increased with increasing thickness of parylene film as a passivation layer [11].

3.2. Effect of the initiator concentration

We next investigated the lifetime of the passivated devices as a function of material composition. We prepared three devices with the passivation layer of differing initiator concentration: device 1, PETIA (10 g)/HSP188 (2 g) (thickness, 6.9 μm); device 2, PETIA (10 g)/HSP188 (1 g) (thickness, 14.5 μm); device 3, PETIA (10 g)/HSP188 (0.5 g) (thickness, 21.7 μm). In this experiment, the same light energy (1260 mJ/cm^2) used to form the cross-linked polyacrylate. As shown in Fig. 6, the lifetime of the passivated devices are 7.3 h (device 1), 7.4 h (device 2), and 8.7 h (device 3), respectively. The lifetime is affected by composition of the photopolymerizable blend for forming the passivation layer. To confirm the effect of the initiator concentration, we compared the lifetime of the passivated devices of differing polyacrylate thickness (Fig. 5) and the polyacrylate composition (Fig. 6). As shown in Fig. 7, although device 1, device 2 and device 3 have different polyacrylate composition, it was observed that the lifetime increased with increasing the polyacrylate thickness. This result indicates that the changes in the lifetime might not be by the initiator concentration, but mainly by the thickness change of the passivation layer.

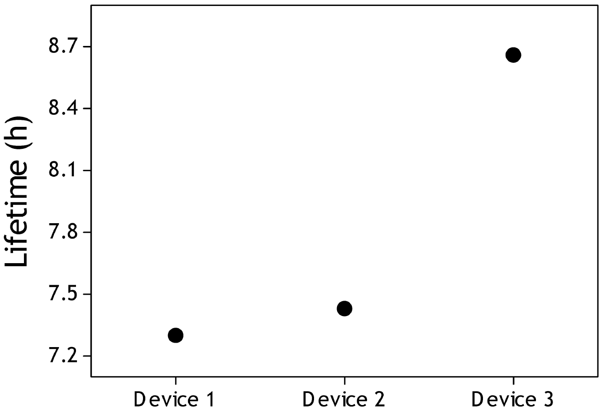

Fig. 6. Lifetime of the passivated devices with a dc electric field of 0.039 mA/mm^2 as a function of material composition. These measurements were carried at 40 °C and 60% RH.

3.3. Effect of the exposed light energy

Change of the polyacrylate surface components after irradiation was measured with ESCA. As shown in Table 2, the polyacrylate surface exposed to light remained unchanged until ~6200 mJ/cm^2. This result indicates that the photochemical reaction did not occur on the polyacrylate surface by high-energy irradiation. In order to explore a correlation between the stability of the device and the light energy exposed to induce the photopolymerization, the lifetime of two devices exposed by differing light energy were examined: device 4 (exposed light energy, 1260 mJ/cm^2; conversion of the polyacrylate, 91%); device 5 (exposed light energy, 6200 mJ/cm^2; conversion of the polyacrylate, 92%). The lifetime of the passivated devices are 7.4 h (device 4) and 6.8 h (device 5). The passivated device exposed by high-energy irradiation (exposed light

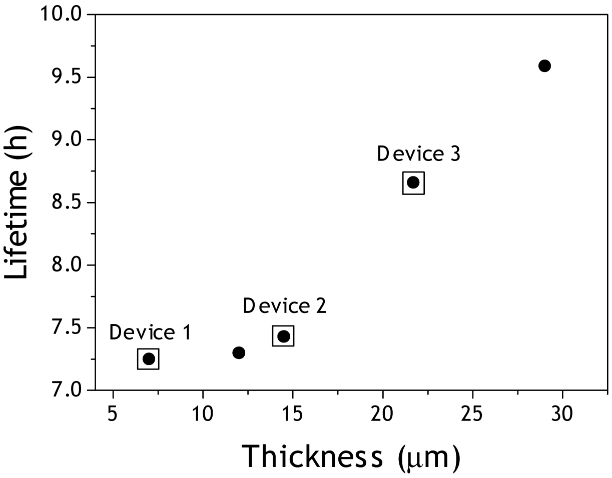

Fig. 7. Dependence of the polyacrylate film thickness on the lifetime of the passivated devices.

Table 2
ESCA atomic compositions of the polyacrylate films after photoirradiation

Film	Atomic concentration (%)	
	C	O
Polyacrylate		
Exposed to light		
1260 mJ/cm^2	67.74	32.26
6200 mJ/cm^2	67.85	32.15

energy, 6200 mJ/cm^2) exhibited the shorter lifetime than that of device 4. Such change in the lifetime induced by irradiation may be interpreted in terms of photophysical and/or photochemical changes of the device.

4. Conclusions

We found that the polyacrylate passivation layer were formed by using a spin-coating method, which could effectively protect the glass-based device. The passivated device showed similar $L-V$ and $I-V$ characteristics to those of the bare device, indicating that its fabrication process for forming the passivation layer did not influence the performance of the device notably. The lifetime of the passivated device was three times longer that that of the bare device, which is affected by the polyacrylate film thickness. Wet process encapsulation, which is simple and convenient to perform, is a novel encapsulation of OLED displays. Although this method is not a perfect encapsulation for OLED displays, the polyacrylate passivation layer might be applied to plastic-based OLED displays and to pre-encapsulation for thin film encapsulation of glass-based OLED displays.

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