Japanese Journal of Applied Physics
Vol. 45, No. 7, 2006, pp. 5970–5973

Enhancement of Barrier Properties Using Ultrathin Hybrid Passivation Layer for Organic Light Emitting Diodes

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(Received February 26, 2006; revised April 10, 2006; accepted April 12, 2006; published online July 7, 2006)

The hybrid thin-film (HTF) passivation layer composed of the UV curable acrylate layer and MS-31 ($MgO : SiO_2 = 3 : 1$ wt %) layer was adopted in organic light emitting diode (OLED) to protect organic light emitting materials from penetrations of oxygen and water vapors. The moisture resistance of the deposited HTF layer was measured by the water vapor transmission rate (WVTR). The results showed that the HTF layer possessed a very low WVTR value of lower than 0.007 g/(m^2·day) at 37.8 °C and 100% RH. Therefore, the HTF on the OLED was found to be very effective in protect what from the penetrations of oxygen and moisture. [DOI: 10.1143/JJAP.45.5970]

KEYWORDS: organic light emitting diode (OLED), thin film passivation, permeation, barrier film, water vapor transmittance rates (WVTRs)

1. Introduction

As a next generation display, the organic light emitting diode (OLED) has to great performances such as potentially low manufacturing cost, high brightness, thin thickness, low power consumption and fast response time and so on.[1)] Furthermore, the OLED can be fabricated onto flexible polymeric substrates instead of the rigid glass substrates for flexible display applications. However, the moisture sensitivity of OLEDs has prevented the realization of their full potential to become the basis for next-generation emissive displays on lightweight or flexible plastic substrates, resulting from the extremely rapid permeation of both water and oxygen through all known plastic substrates.[2)] The main reason for the degradation of OLEDs is the formation of non-emissive dark spots due to moisture or oxygen ingress.[3–6)] Up to now, many groups have tried to increase the lifetime of OLEDs by various techniques that involve encapsulation of OLEDs. Recently, a hermetic encapsulation technique using a glass or metal lid has been proposed as a method to protect devices from oxygen and water vapors. However, these encapsulation seals are heavy, thick and rigid properties that severely limit their applications to flexible OLEDs. It has been reported that multilayer combinations of polymer and inorganic dielectric layer can be more than three orders of magnitude less permeable to water and oxygen than an inorganic single layer.[7–11)]

In this study, we chose the UV curable acrylate films as a soft polymer film, and from this, developed double-layered passivation films (thin composite inorganic film/UV curable acrylate film) for OLED displays. The films showed good moisture barrier performance below the limit of the measurable detection range of the water vapor transmittance rate (WVTR) measurements. Thus, the double-layered passivation films were considered to have specific high barrier features against moisture and oxygen. Also, we found that these passivation films can be applied to the flexible and top emissive OLEDs for various applications because most barrier polymers are flexible and transparent.

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2. Experimental Procedure

The hybird thin film (HTF) passivation layer was formed onto a PES substrate ($5 \times 5\,cm^2$ and 500 μm thick) to evaluate permeation properties. The HTF passivation film consisted of the MS-31 (300 nm thick) and UV curable acrylate resin (1000 nm thick). Prior to the deposition of the passivation layers, Poly(ether sulfone) (PES) substrate is washed with isopropyl alcohol (IPA) and methanol in an ultrasonic bath and then dried in a stream of nitrogen. Antistatic instrument (Aldrich ZEROSTAT® 3) was used to eliminate residual particles on the surface of the PES substrate by static force. The $MgO : SiO_2 = 3 : 1$ wt % (MS-31) thin composite film was deposited onto PES substrate by using the electron beam evaporator (Edwards AUTO 306, FL-400) at a working pressure below 2×10^{-5} Torr and deposition rate of 0.15 nm/s.[12)] After the deposition processes, the UV curable acrylate resin (Dongjin Semichem DCS-SP210) was coated onto the MS-31 thin film by spin coating technique and was carefully cured to form a cross-linked passivation layer without pores by the hotplate, UV exposure instrument and oven. The coated acrylate resin was thermally pre-cured by using the hotplate at a temperature of 80 °C and curing time of 3 min. Then the resin was post-cured by using UV exposure. The UV light source produced 30 mW/cm^2 and 365 nm and the exposed UV energy was 2700 mJ/cm^2. The UV cured resin was processed with a complementary thermal cure at 120 °C for 2 h in an oven.

To explore the effect of our HTF passivation layer, a glass-based device structure including a small molecular light-emitting device was fabricated, as shown in Fig. 1. The device structure included a 3 nm thick copper phthalocyanine (CuPc), which was used as a hole injection layer (HIL); a 30 nm thick [*N*,*N*′-di(naphthalene-l-yl)-*N*,*N*′-diphenyl-benzidine] (α-NPD), which was used as a hole transporting layer (HTL); a 60 nm thick tris(8-hydroxyquinoline) aluminum (Alq_3), which was used as a green emitting material and a cathode. The cathode included a 1 nm thick LiF and a 150 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 $10 \times 10\,mm^2$.

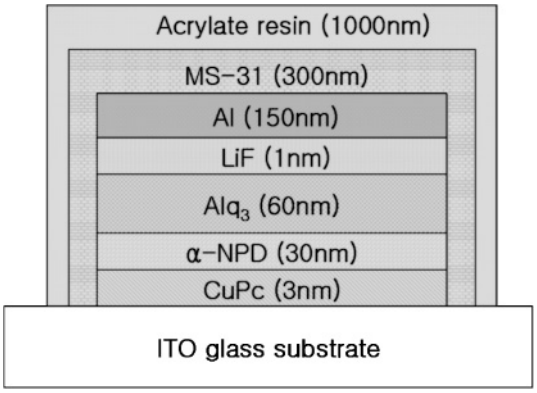

Fig. 1. Schematic diagram of organic light-emitting device with HTF passivation layer.

The WVTR was measured to evaluate permeation properties. During the WVTR measurements (Mocon, Permatran W 3/31 MA), the temperature and relative humidity in the test system were set to 37.8 °C and 100% RH, respectively. The surface image and cross sectional image were obtained by using the field emission scanning electron microscope (FE-SEM; Hitachi S-4700). The transmittance of the passivation layers was measured by using the transmittance and absorption measurement instrument (Hewlett Packard HP-4852A). The electrical properties, the lifetime and the luminance of the OLED with the HTF passivation layer and without the layer were investigated at room temperature in air. The electrical characteristics of the device were measured by a high voltage source-measurement unit (Keithley, Model 237, U.S.A.). The luminance characteristics were determined by measuring the photocurrent induced by the light emission from the device using a luminance meter (Topcon, BM-9).

3. Results and Discussion

The WVTR was measured to evaluate permeation properties according to various structures of the passivation layers by the Permatran W 3/31 MA test instrument. The results are presented in Fig. 2. In this figure, the WVTR of MS-31 film is 1.847 g/(m^2·day). However, in case of the MS-31/acrylate resin double layered passivation film (HTF), the WVTR was decreased dramatically below 0.007 g/(m^2·day) at 37.8 °C and 100% RH. This result showed that the permeation rate of the HTF passivation layers depend on the packing density of the solid-state structure and the interaction between the MS-31 film and acrylate resin film. In case of the inorganic passivation layer, when the inorganic thin-film was deposited, pinholes and grain boundaries were generated on the thin-film surface. These defects can affect the barrier property severely.[13] However, we obtained the HTF passivation layer by using an inorganic composite material of high packing density and using an organic material to fill the defects of the inorganic film. Thus, the main function of the interaction between the inorganic film and the organic film can be considered that the acrylate passivation film (second barrier layer) can compensate the barrier properties of the MS-31 film (first barrier layer), by intercepting the penetration path and extending the penetration path of water vapor and oxygen.[14]

The surface image of the MS-31 thin film indicated very dense deposit as shown in Fig. 3(a). As mentioned above, these characteristics of the adopted HTF passivation film can improve the barrier performance through the extension of the penetration length for water vapor and oxygen. We confirmed through the cross-sectional image in which bubble-like shapes did not exist at the organic barrier thin film as shown in Fig. 3(b). Since gas is evolved at the organic barrier thin film during the pre-curing process, the micro-nano sized pinholes can be created and they provide the penetration path for water vapor and oxygen. This fact decreases the barrier properties of the organic film, significantly. However we obtained excellent barrier property from the interception of the penetrated water vapor through the defect-free HTF passivation layer using UV curing method.

Adhesion of coating is an important criterion in protective ability of the HTF passivation layer.[13] In order to provide an

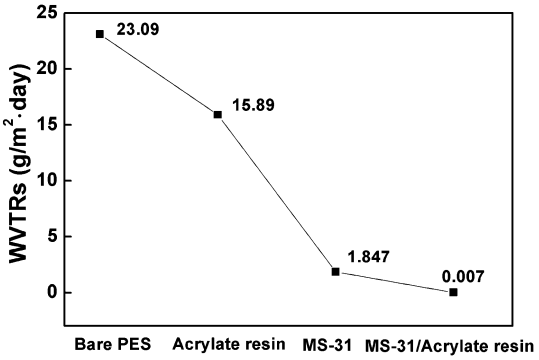

Fig. 2. The WVTRs of the bare PES, Acrylate resin film, MS-31 film and the MS-31/Acrylate resin films.

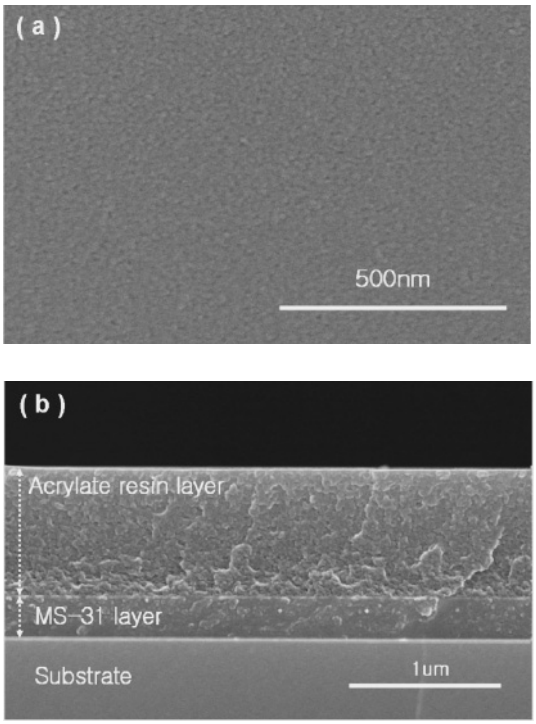

Fig. 3. FE-SEM images of (a) the MS-31 surface (b) the HTF cross-section.

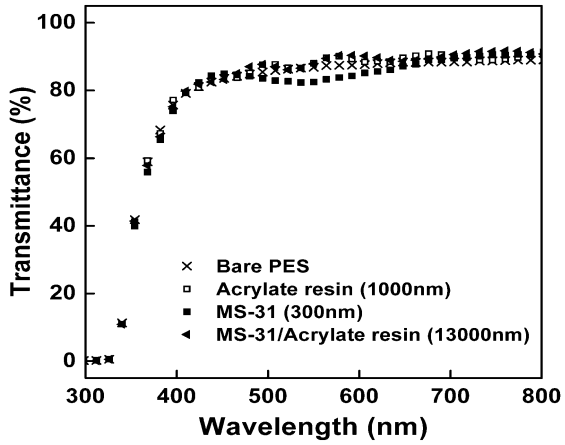

Fig. 4. Transmittances of the bare PES, Acrylate resin film on PES, MS-31 film on PES and MS-31/acrylate resin films on PES.

excellent protection from water vapor and oxygen, the coating must be uniform and well adhered on the substrate. The adhesion test of the inorganic–organic HTF passivation layer was tested in accordance with ASTM 3359-93B standard. The interfacial adhesion test of the PES substrate/MS-31 film and the MS-31/acrylate film shows good adhesion of 98 and 93%, respectively. These good adhesion properties of the two films can effectively protect OLED from water vapor and oxygen to penetration in the lateral direction as well as the vertical direction.

Figure 4 shows the transmittances of the bare PES and the adopted passivation layers. In this figure, the MS-31/acrylate resin double layered passivation films shows almost same value as ~80% in the visible range, even though there are some fluctuations as a function of wavelength. Consequently, the HTF shows great potential as a passivation layer for the top-emitting OLED as well as conventional OLED.

The luminance–voltage (*L–V*) and the current density–voltage (*J–V*) characteristics were examined to compare the electrical behavior of the device before and after forming the HTF passivation layer, as shown Fig. 5. When the photopolymerizable acrylate resin is cured to form the passivation layer, both the light-emitting material (Alq_3) and the cathode metal (LiF:Al) were minutely influenced by photopolymerization. And this photo curing process can damage the organic materials by outgas from polymer when exposed to UV to harden the layer. However, the passivated device showed similar *L–V* and *J–V* characteristics to those of the bare device. Although the *L–V* and *J–V* profiles of the passivated device were slightly shifted to high dc voltage, its electrical properties did not vary substantially. These results indicate that the deposition of the MS-31 passivation layer (the e-beam evaporation process) and the polymerization of the acrylate resin passivation layer (UV-thermal curing processes) did not induce the change in the electrical and the emission properties of the device, noticeably.

Figure 6 shows the pictures of OLEDs before and after HTF passivation and during driven lifetest at room temperature (dc, constant current density). Dark spots induced by water vapor and oxygen were formed inevitably since the devices were tested in air. However, the growth of dark spots of the passivated device was slower than the bare device, as

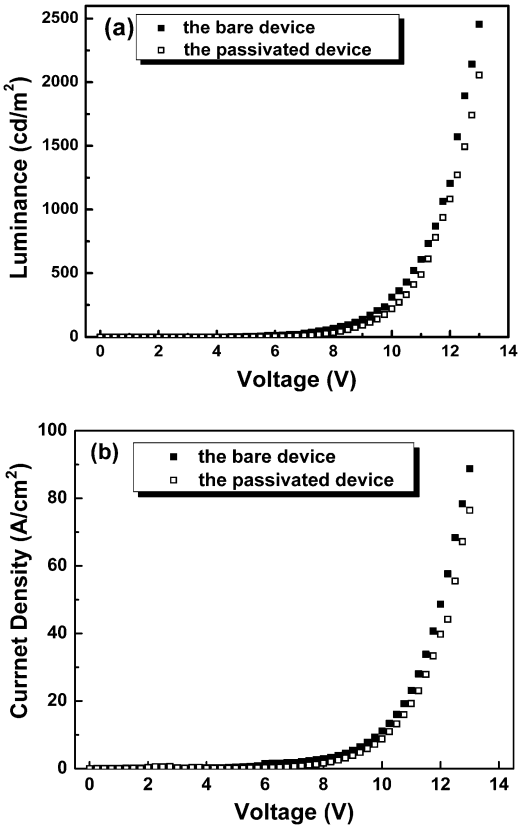

Fig. 5. (a) *L–V* and (b) *J–V* characteristics of organic light-emitting device with and without the passivation layer at room temperature.

shown figures. This fact presents that the HTF passivation layer can delay the growth of the dark spot by the interception of the penetration path of water vapor and oxygen.

Figure 7 shows the degradation characteristics of the bare device and the passivated device. The lifetimes of the bare device and the passivated device were measured from an initial luminance of 500 cd/m^2 and a dc constant current density of 15 mA/cm^2 in air. The time duration required for the luminance of the OLED device to become half the initial value is referred to as the lifetime of the OLED device. The initial luminance of the passivated device decayed to 50% of its initial luminance in 288 h whereas, the bare device did in 79 h. Though the HTF protection layer was very thin, the lifetime of the passivated device was almost three times longer than that of the bare device, which might be due to exclusion of external contamination such as water, oxygen, particles and so on. The extended lifetime of the ultrathin HTF passivated device represents a significant step towards realization of advanced flat panel display devices like OLED.

4. Conclusions

In this study, the HTF passivation layer fabricated by UV curing method showed very low WVTR values, below 0.007 g/(m^2·day), at 37.8 °C and 100% RH. This value was within the limited range of the sensitivity of WVTR measurements. And the initial luminance of the HTF passivated device decayed to 50% of its initial luminance in 288 h whereas the bare device did in 79 h. This result showed that a very thin HTF passivation layer of less than 1.3 μm has an excellent barrier property against oxygen and

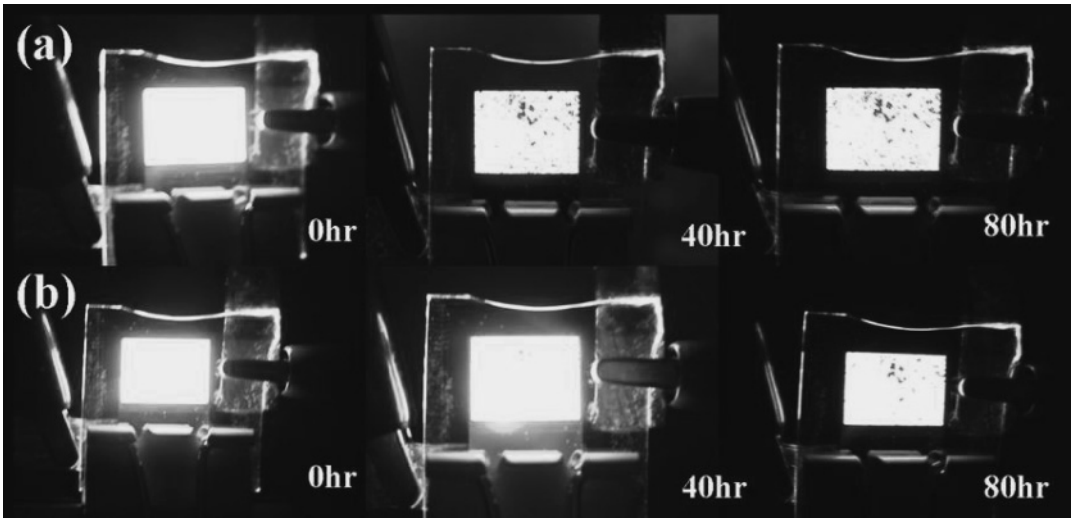

Fig. 6. Pictures of OLEDs (a) before and (b) after HTF passivation and during driven lifetest at room temperature (dc, constant current density).

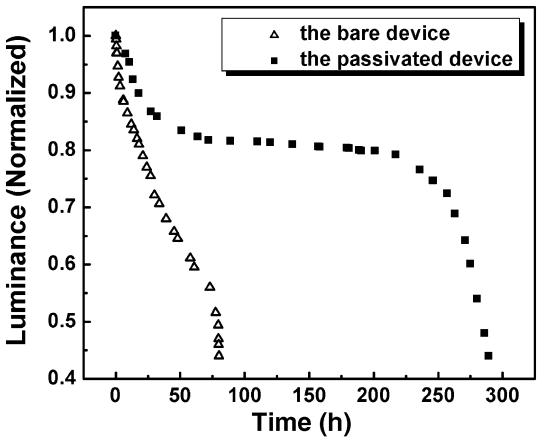

Fig. 7. Lifetime of OLED with and without the passivation layer (current density was 15 mA/cm^2 at room temperature).

moisture. Also, we found that the MS-31/acrylate resin double layered passivation films showed almost the same value of ~80% in the visible range, even though there were some fluctuations as a function of wavelength. Consequently, the proposed HTF was found to have great potential as the passivation layer for the top-emitting OLEDs as well as the conventional OLEDs.

Acknowledgements

This work was supported by the New Growth Engine Display Center, Ministry of Commerce, Industry and Energy.

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