Thin film encapsulation for organic light emitting diodes using a multi-barrier composed of MgO prepared by atomic layer deposition and hybrid materials

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We demonstrated an organic/inorganic multi-barrier and encapsulation for flexible OLED devices. The multi-barrier consisted of a silica nanoparticle-embedded hybrid nanocomposite, in short, S-H nanocomposite, and MgO, which were used as organic and inorganic materials, respectively. The S-H nanocomposite was spin-coated followed by UV curing. The thickness of the S-H nanocomposite was 200 nm, and 40 nm of MgO was deposited by atomic layer deposition (ALD) using Mg(CpEt)2 and H2O at 70 °C. The results of a Ca test showed that the 4.5 dyads of the MgO/S-H nanocomposite had a low water vapor transmission rate (WVTR) of 4.33 × 10^-6 g/m2/day and an optical transmittance of 84%. The normalized luminance degradation of the thin film encapsulated OLED was also identical to that of glass-lid encapsulation after 1000 h of the real operation time. We proposed low temperature ALD as a deposition method to create relatively thin film for OLED passivation without degradation, such as creation of dark spots. The results confirmed that it may be feasible for our multi-barrier to passivate flexible OLEDs devices.

1. Introduction

The display industry has developed from cathode ray tubes (CRTs) to flat panel displays including AC plasma display panels (ACPDPs), liquid crystal displays (LCDs), and organic light emitting diodes (OLEDs). Furthermore, it is axiomatic that the display paradigm is shifting to flexible and transparent displays. Over the past few years, several studies have been made on flexible displays on substrates such as plastic or ultra-thin glass. Among such displays, OLEDs are the most promising candidate for next generation flexible displays. OLEDs have several advantages, such as ultra-thinness, light weight and excellent flexibility. Nevertheless, there are problems to be solved to realize flexible displays. The reliability problem of OLEDs has recently emerged as the most important issue. The dark spot, which is a non-emitting area of OLEDs, arises from various causes, including the following. First, hole traps or metal ion that have diffused from the electrode act as a non-radiative recombination center [1]. Second, ITO surface roughness is a major factor contributing to device failure through dark spot formation during device operation [2]. Third, it is caused by delamination at the ETL/cathode interface due to the formation of a crystalline organic material from the influence of humidity [3].

It especially is well known that OLEDs are extremely vulnerable to water and oxygen [4,5]. In the case of flexible OLEDs, a plastic substrate has a very high WVTR value, which causes degradation of organic-based electronics. To address the reliability issue, there have been several studies aimed at increasing the lifetime of flexible displays [6]. In particular, thin film encapsulation using an
inorganic/organic multi-barrier (Barix™ encapsulation) structure was studied as a one of solutions [7,8].

Our initial work addressed characteristics of a multi-barrier consisting of MgO deposited by an e-beam evaporator and polymerized cycloaliphatic epoxy hybrid materials (hybrimer) [9]. We suggested a simple passivation method with a solution process and low temperature deposition of MgO, which was a new material for thin film encapsulation using an electron evaporator. However, the remaining problem was that the total thickness of the multi-barrier was too thick and number of dyads was too many to be used in flexible OLED devices.

We have taken a two-pronged approach here to solve the above insufficiency. The first was to use a deposition method for the inorganic layer. According to common consensus, permeation through multi-barriers is controlled by defects in the inorganic layer [10]. This suggestion reflects that using the deposition method is a critical factor for creating the characteristics of the multi-barrier. There are many kinds of deposition methods for depositing the inorganic layer of a multi-barrier: e-beam evaporator, CVD, sputter and ALD. More and more these days, among the various deposition methods, the ALD system has been attractive as a deposition method of inorganic layers because ALD has many advantages, such as excellent conformality, uniformity, simple and accurate film thickness control [11]. Numerous studies have attempted to apply an inorganic layer deposited by ALD for OLED passivation. Notably, a barrier with a WVTR below $6.5 \times 10^{-5}$ g/m²/day at 60 °C produced by an ALD method was reported [12]. As in another study, the WVTR of thin films grown by Al₂O₃ atomic layer deposition (ALD) and SiN plasma-enhanced chemical vapor deposition (PECVD) have been measured by the Ca test, and the result was a less than $5 \times 10^{-5}$ g/m²/day at 38 °C/85% RH [13]. The second was to use an organic layer that exhibits improved barrier performance by extending the diffusion path of vapor permeation.

In this paper, we investigated a multi-barrier for encapsulation of OLEDs using MgO deposited by ALD and an S-H nanocomposite. We assumed MgO films deposited by ALD have lower defect density than other deposition methods. Furthermore, in the case of thin film encapsulation, it is considered to be virtually impossible to use getter materials for OLEDs. Thus, we have studied the barrier performance of ALD MgO, which is an efficient moisture absorbent, as a preliminary study. We will evaluate the effect of MgO as a desiccant as further work. We adopted a silica nanoparticle-embedded hybrid (S-H) nanocomposite as an organic layer to extend the diffusion path of vapor permeation [14]. In our previous work, we used an organic material, which was a hybrimer, as the first layer of a multi-barrier because the OLED was attacked when MgO was deposited by the e-beam method. Here, we deposited the MgO layer first to reduce the number of dyads without any degradation of the OLEDs. Finally, we demonstrated multi-barriers that have a considerably low WVTR and lifetime of OLEDs thin film encapsulated which is identical to that of the glass lid encapsulated OLEDs.

2. Experimental set-up

2.1. Preparation of the multi-barrier

We prepared a multi barrier-coating on a 100 μm-thick polyethylene terephthalate (PET) substrate. MgO was deposited by NCD ALD (Lucida D100, Korea) using bis(ethylcyclopentadienyl)magnesium (Mg(CpEt)₂) and H₂O during 350 cycles to create a 40 nm-thick inorganic layer at a chamber temperature of 70 °C [15]. The purge time and exposure time were 10 s and 0.2 s, respectively, for both the Mg(CpEt)₂ and H₂O. The Mg(CpEt)₂ was kept in the canister at 85 °C, and we used assist pulses that consisted of N₂ to drag the Mg(CpEt)₂ out of the canister well. Nitrogen (N₂) was also used as a carrier gas. The thickness of the MgO was measured by a Woollam Spectrometer ellipsometer (M2000D, USA). The MgO layer has been also investigated by Thermo VG Scientific X-ray photoelectron spectroscopy (Sigma Probe, USA) to verify the quality of the MgO film. According to Fig. 1a, which presents the survey spectra (0–1100 eV) from the XPS analysis, the MgO film surface consisted of oxygen, magnesium, and carbon [16]. For the chemical state of surface species, high resolution spectra of the O 1s and Mg 2p were obtained using 20 eV analyzer pass energy of the and 0.1 eV steps. Fig. 1b shows that the Mg 2p signal was composed of 49.35 eV and 50.72 eV. The main peak at 50.72 eV represents Mg oxide and that at 49.35 eV indicates metallic Mg [16]. Two peaks were present in Fig. 1c for the O 1s signal. The lower binding energy (BE) at 531.23 eV indicates MgO oxygen atoms [16]. The higher BE at 533.46 eV indicates chemisorbed OH⁻ of MgO. The ratio of MgO/MgO was 0.999, which coincided with the theoretical value of 1 [16]. In addition, the ratio of OH⁻/(O²⁻ + OH⁻) was 0.225. We attributed this result to the MgO film’s moisture absorption characteristic [17].

In a previous study, we made a UV-curable silica nanoparticle-embedded hybrid nanocomposite using Nanopox® E600 (Nanoresins, Germany) dispersed in cyclo-aliphatic epoxy ologosiloxane resin [14]. The S-H nanocomposite with 100 wt% silica content was diluted with a pre-set amount of polyethylene glycol methyl ether acetate (PGMEA, Aldrich, USA) and spin-coated at 4000 rpm for 10 s to create a 200-nm thick organic layer. UV curing was then conducted by I-line UV light for 100 s ($\lambda = 365$ nm, optical power density = 11 mW/cm²). These processes were repeated to deposit a 4.5 dyads inorganic/organic multi-barrier. Fig. 2 shows scanning electron microscopy image was taken by FEI Dual Beam Focused Ion Beam (Helios NanoLab™, Netherlands).

2.2. Ca test for moisture permeation rates

We prepared a calcium (Ca) pad for the Ca test. First, aluminum (Al) was deposited by means of thermal evaporator to produce a 100-nm Al film on the glass (2.5 cm × 4 cm). As the following step, 250 nm of Ca was also deposited by thermal evaporation. A 1.5 cm × 1.5 cm area of the 250-nm Ca film was subsequently encapsulated with a multi-barrier coated on the PET substrate using
Nagase UV sealant (XNR5570, Japan). Finally, we conducted resistance measurements using a Keithley source-meter (DMM 2750, USA) in a climate chamber (temperature: 30 °C, relative humidity (R.H.): 90%). We used a 4-wire resistance measurement system for precise measurement. In the case of the 4-wire resistance measurement system, resistance can be measured in a range from 1 μΩ to 120 MΩ. Furthermore, we limited the voltage to 20 mV in order to prevent electrical corrosion of Ca.

Fig. 1. XPS (a) survey, (b) Mg 2p and (c) O 1s spectra of ALD MgO film deposited at 70 °C.

Fig. 2. SEM cross section image of MgO/S-H nanocomposite 4.5 dyads on a Si wafer.
2.3. Fabrication of thin film encapsulated OLEDs devices

We fabricated the OLED on the indium thin oxide (ITO) coated glass after plasma treatment for 10 min. The structure of the OLED was ITO [150 nm]/4,4',4'-Tris-(N-(naphthyl-2-yl)-N-phenylamine)triphenylamine (2-TNATA) [60 nm]/N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1',1''-triphenylamine (NPB) [30 nm]/Tris(8-hydroxyquinolino-aluminum (Alq3) doped with 2, 3, 6, 7-tetrahydro-1, 1, 7, 7-tetramethyl-1H, 11H-10-(2-benzothiazolyl) quinolizino-[9, 9a, 1gh] coumarin (C545t) [35 nm]/Alq 3 [30 nm]/LiF [8 nm]/Al [150 nm]. 2-TNATA and NPB were used as a hole injection layer and a hole transfer layer, respectively. Alq3 was co-host and C545t was a green dopant. The Alq3 was used as an electron transfer layer. The following step was thin film encapsulation. We deposited the MgO layer first using the ALD method, and the S-H nanocomposite was spin-coated. The above processes were repeated to deposit 4.5 dyads MgO/S-H nanocomposite films. The inset in Fig. 6 shows the schematic diagram of the final structure of the device. I–V–L characteristics were measured using a Konica Minolta spectro-radiometer (CS-2000, Japan) and Keithley source-meter (2400, USA). The lifetimes of the OLEDs were measured by the Mcscience OLED Lifetime Test System (Polaronix® M6000PMX, Korea) for continuous operation at a constant current and room temperature.

3. Results and discussion

3.1. The water vapor transmission rate of the multi-barrier

It is well known that OLEDs have to be protected by encapsulation that has a WVTR less than 10⁻² g/m²/day [18]. As a consequence, we need a sensitive measurement method to measure the WVTR for application to OLEDs. Therefore, we conducted a Ca test. The Ca test uses a resistance measurement to determine the degree of Ca corrosion with high accuracy [19]. We determined the WVTR using the following equation.

\[ P = -n \frac{M(H_2O)}{M(Ca)} \frac{d(1/R)}{l} \]

where \( n \) is the molar equivalent of the degradation reaction, \( M(H_2O) \) and \( M(Ca) \) are the molar masses of the permeating H₂O and Ca, respectively, are the density and resistivity of Ca, respectively, and \( l \) is the length and \( b \) is the width of the Ca. We can then calculate the WVTR(\( P \)) using the slope of the conductance as a function of \( t \).

Fig. 3a shows that the minimum point of the WVTR, which was 5.83 × 10⁻² g/m²/day, was at 60 nm of MgO. The dependence of the thickness of the MgO film on the WVTR was quite low. In addition, the WVTR was 7.89 × 10⁻² g/m²/day at 100 nm, which exhibited a greater barrier characteristic than the MgO deposited by e-beam evaporator; the WVTR was 0.46 g/m²/day at the same thickness of MgO in our previous work [9]. Therefore, we concluded that the ALD system produced good quality films, which means ALD MgO was deposited with a low defect concentration, such as pin-hole, compared to the e-beam method. The WVTR of the 40-nm single layer of MgO was 7.13 × 10⁻² g/m²/day, which does not satisfy the required WVTR conditions for OLED passivation. However, Fig. 3b shows that the WVTR decreased dramatically when the number of dyads was 4.5. In Fig. 3, the average WVTR of 4.5 dyads of the MgO/S-H nanocomposite was 1.49 × 10⁻⁵ g/m²/day. This result resulted from an increasing diffusion path of water and oxygen with the growing number of dyads [10].

Fig. 4 shows the normalized conductance curves versus time. Using the slope of the graph, we calculated the WVTR. In case of the 4.5 dyads MgO/S-H nanocomposite, the WVTR was 4.33 × 10⁻⁶ g/m²/day. The WVTR of the glass-lid encapsulation was 3.96 × 10⁻⁶ g/m²/day. From the above result, we confirmed that thin film encapsulation using the 4.5 dyads of MgO/S-H nanocomposite is comparable to glass-lid encapsulation. Furthermore, the WVTR of the multi-barrier using ALD was lower than the multi-barrier deposited by the e-beam method even when
the total thickness is 1 μm; in previous work, the total thickness was 6.6 μm.

3.2. Transmittance of the multi-barrier

We also measured the transmittance of the multi-barrier. In order to employ the multi-barrier to display devices, the multi-barrier must be transparent. Fig. 5 shows that the average transmittance measured 84% in range of 400 nm to 700 nm for the 4.5 dyads using a Shimadzu spectro-photometer (UV-2550, Japan); the base line was air and the inset is a photograph of the multi-barrier. In case of the bare PET, the transmittance was 85%. Therefore the multi-barrier had a high transmittance.

3.3. Performances of thin film encapsulated OLED devices

Finally, we applied the MgO/S-H nanocomposite multi-barrier to OLED passivation. Fig. 6 shows that the I–V–L characteristics of the thin film encapsulated OLED were identical to those of the glass-lid encapsulated OLED. The maximum luminance was 57,071 cd/m² when current density was 399 mA/cm² for the glass-lid encapsulation and that of the thin film encapsulated OLED was 56,741 cd/m² at 399 mA/cm². The efficacies were also identical for both devices, 14 cd/A. The above results and Fig. 7 allow us to make the following conclusion: the thin film encapsulation process can be applied to OLED devices without degradation or dark spots. Apparently, the precursors of MgO did not attack the OLED devices during the MgO deposition process as a first layer.

Fig. 7 shows results of lifetime measurement. The initial luminance was 600 cd/m² at 0.165 mA. The real operation time was 1000 h and the normalized luminance was 60% after 1000 h in thin film encapsulation. For the glass-lid encapsulation, the normalized luminance was 57%. As a result, the normalized luminance degradation of the thin film encapsulated OLED was almost identical to that of the glass-lid encapsulation. This result accords with the consequence of the Ca test.

4. Conclusion

In conclusion, we developed a thin film encapsulation method using MgO deposited by an ALD system and a silica nanoparticle-embedded hybrid (S-H) nanocomposite. The 4.5 dyads of the multi-barrier had a high performance for the OLED encapsulation. The WVTR was $4.33 \times 10^{-6}$
g/m²/day, which is sufficient to protect OLEDs from oxygen and water. The multi-barrier was highly transparent. Finally, we applied the multi-barrier to OLED devices and confirmed that the OLED was encapsulated without degradation, which means that the OLED performance after thin film encapsulation was the same as glass-lid encapsulation. The normalized luminance degradation of the thin film encapsulated OLED was also identical to that of glass-lid encapsulation after 1000 hours of operation. The inset figures show photographs of the 2 mm × 2 mm emitting area of the OLED (i) before driving and (ii) after driving. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 6.** (a) A comparison of I–V characteristics between a glass-lid encapsulated OLED and thin film encapsulated OLED: The black solid-square is glass-lid encapsulation and the red open-circle is thin film encapsulation, (b) current efficacy and luminance versus current density: the black solid-square is the luminance versus the current density of glass-lid encapsulation and the red solid-circle indicates thin film encapsulation. The black open-square and red open-circle denote the efficacy of glass-lid encapsulation and thin film encapsulation, respectively. In figure (a), the inset figure shows the schematic of a fully fabricated OLED structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 7.** A comparison of lifetime between a glass-lid encapsulated OLED (black solid-square) and a thin film encapsulated OLED (red open-circle): The initial luminance \( L_0 \) was 600 cd/m². The inset figures show photographs of the 2 mm × 2 mm emitting area of the OLED (i) before driving and (ii) after driving. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

This study reveals that the multi-barrier composed of ALD MgO and an S-H nanocomposite exhibit excellent barrier performance and that ALD produced conformal film and the S-H nanocomposite extended the diffusion path. This result confirms that an additional solution to flexible display encapsulation could be provided for new material deposited by ALD, for example, MgO can be applied for OLED passivation.

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**Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/10.1016/j.orgel.2013.04.011](http://dx.doi.org/10.1016/j.orgel.2013.04.011).

**References**


