Ultra Thin Film Encapsulation of Organic Light Emitting Diode on a Plastic Substrate

Sang-Hee Ko Park, Jiyoung Oh, Chi-Sun Hwang, Jeong-Ik Lee,
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We have carried out the fabrications of a barrier layer on a polyethersulfon (PES) film and organic light emitting diode (OLED) based on a plastic substrate by means of atomic layer deposition (ALD). Simultaneous deposition of 30 nm AlO_x film on both sides of the PES film gave a water vapor transition rate (WVTR) of 0.062 g/m^2/day (@38°C, 100% R.H.). Further, the double layer of 200 nm SiN_x film deposited by plasma enhanced chemical vapor deposition (PECVD) and 20 nm AlO_x film by ALD resulted in a WVTR value lower than the detection limit of MOCON. We have investigated the OLED encapsulation performance of the double layer using the OLED structure of ITO / MTDATA (20 nm) / NPD (40 nm) / AlQ (60 nm) / LiF (1 nm) / Al (75 nm) on a plastic substrate. The preliminary life time to reach 91% of the initial luminance (1300 cd/m^2) was 260 hours for the OLED encapsulated with 100 nm of PECVD-deposited SiN_x and 30 nm of ALD-deposited AlO_x.

Keywords: OLED, thin film passivation, atomic layer deposition (ALD).

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I. Introduction

Flexible displays that can be embedded in our clothes or show information on our environment on demand, and can be rolled-up or folded for storage, have attracted much attention as the next-generation of displays. The micro-particle based display [1], liquid crystal display (LCD) [2], and organic light emitting diodes (OLEDs) [3] have intrigued researchers as candidates of a flexible display.

Among them, OLEDs that can be thin, robust, lightweight, and have high information contents have been the focus of much research activity [4], [5]. The development of thin film barrier (encapsulation) layers for OLEDs and flexible substrates has been recognized as a key technology for the realization of flexible OLEDs [6]. Although the requirement for the barrier layer of an OLED display has not been elucidated completely, it is generally understood that long-lived flexible OLEDs need a barrier layer that transmits less than 10^{-6} g/m^2/day of water and 10^{-5} cc/m^2/day of oxygen [7].

It has been reported that multi-layer combinations of polymer and inorganic dielectric layers can be more than three orders of magnitude less permeable to water and oxygen than an inorganic single layer [7]-[9]. Graff and others explained the mechanism of multi-layer effects with the increased lag time of permeation [10]. Permeation through the ultrabarrier layer is mostly controlled by the defects in inorganic film, therefore the deposition of a high barrier inorganic layer is the most important technology.

Several groups have reported on multi-layered barriers consisting of inorganic thin films fabricated by plasma enhanced chemical vapor deposition (PECVD) or sputtering [11], [12]. A good barrier layer should not only be free of

pinholes but also have good step coverage. In particular, it is also very important for the barrier deposition process to be compatible with the organic emitting layer beneath [13].

Our group reported on a new approach to the barrier layers of flexible OLED substrates using a traveling wave reactor type atomic layer deposition (ALD) [14] and plasma enhanced ALD (PEALD) [15]. ALD is a technique using a binary reaction, which is split into two self-limiting chemical reactions in a repeated alternate deposition sequence. Although ALD based on the surface chemical reactions can minimize the structural imperfection in films and substrate damage, a low growth rate is the main drawback for the application of a barrier layer. In addition, use of water vapor or ozone in the traveling type ALD method and oxygen plasma in the PEALD method as the precursor of oxygen are a concern in the application of ALD-deposited AlO_x barrier films directly on top of the OLED device.

However, we have observed that just the nanometer order of AlO_x single film deposited by ALD technology has excellent barrier properties and is suitable for the device encapsulation layer. In addition, we have optimized the structure of the encapsulation layer for OLED on a plastic substrate, consisting of parylene, PECVD deposited SiN_x, and ALD deposited AlO_x.

II. Experiments

Aluminum oxide thin films with a thickness in the range of 10 to 50 nm were grown on a polyethersulfon (PES) substrate in a 12" x 16" large traveling wave ALD reactor with nitrogen as a carrier gas in a temperature range of 80 to 100°C. Trimethylaluminum (TMA) and H_2O were used as precursors of Al and O, respectively. The sequence of pulses for one cycle deposition of AlO_x is TMA (0.5 s) / N_2 (0.8 s) / H_2O (0.5 s) / N_2 (2.5 s). Water vapor transmission rates (WVTRs) were measured for both the PES substrate and aluminum oxide coated samples on a 50 cm^2 active sample area at 38±2°C, 100% R.H. using MOCON permatran-W1A for 72 hours. Morphological properties were examined using a scanning electron microscope (SEM) and atomic force microscopy (AFM). UV-Vis spectra were taken using a Hitachi U-3501 spectrophotometer. The device structure of OLEDs grown by vacuum thermal deposition was ITO / 20 nm 4,4',4"-tris(3-methyl-phenylphenylamino) triphenylamine (MTDATA) / 40 nm N,N'-bis-[1-naphthyl-(N,N'-diphenyl- 1,1'-biphenyl-4,4'-diamine)] (NPB) / 60 nm tris-(8-hydroxyquinoline) aluminum(AlQ) / 1 nm LiF/ 75 nm Al. Polyethyleneterephthalate (PET) film was used for the substrate of an OLED device with an emitting area of 4 mm^2.

III. Results and Discussion

First, the dependences of barrier properties of AlO_x films on the deposition temperature and film thickness were investigated. With consideration of the low deposition rate of the ALD method and the application of the encapsulation layer for OLED, we have prepared ultra thin aluminum oxide films of 20 to 50 nm deposited at lower than 100°C. Table 1 shows barrier properties of an uncoated PES film and a AlO_x coated one. An uncoated PES substrate has a high WVTR, therefore it is good to compare the difference of WVTRs between the inorganic film of a high barrier and that of a low barrier. In addition, we could easily investigate just the properties of the inorganic layer because the surface of PES is smooth enough not to affect the intrinsic property of the inorganic layer. While most of the inorganic single layers deposited by other chemical or physical methods showed proper barrier properties with a thickness higher than 100 nm, single AlO_x films deposited by ALD exhibited good barrier properties with MOCON values lower than 1.3 g/m^2/day. The barrier property increased with increasing thickness and elevating deposition temperature, and the lowest MOCON value of 0.102 g/m^2/day was obtained from the 50 nm film deposited at 80°C in our experimental conditions.

One of the main advantages of a traveling wave type ALD is the ability to coat films on both sides of a substrate or device simultaneously. The PES film coated on both sides with 30 nm of AlO_x showed a MOCON value of 0.062 g/m^2/day, which to

Table 1. The barrier properties of PES substrates coated with AlO_x, SiN_x, parylene, and double layers.

Deposition temperature (°C)		Thickness (nm)	WVTR (g/m^2.day@ 38°C)	WVTR [1] (g/m^2.day@ 38°C)
Uncoated PES			92.8[2]	
AlO_x	80	20	1.25	
		30	0.409	0.062
		40	0.141	
		50	0.102	
	90	30	0.303	
	100	30	0.214	0.028
SiN_x	R.T.	200	High limit	
SiN_x/AlO_x	R.T./80	200/20	0.058	
Parylene	R.T.	3μm	24[2]	
Parylene/AlO_x	R.T./80	3μm/20μm	0.199	

1) WVTR of PES coated both sides with AlO_x
2) WVTR for 5cm^2 active area

our knowledge is the lowest value for a single inorganic layer with a thickness less than 100 nm. We believe that dual-sided coating can also reduce the film stress caused by the difference of coefficients of thermal expansions between the plastic substrate and the dielectric film.

The formation of conformal film by ALD resulted in coverage of pinholes in the inorganic or organic layers beneath. Deposition of 30 nm AlO_x on a 200 nm SiN_x thin film gave a MOCON value lower than the detection limit of MOCON measurement. In comparison, use of SiN_x only as a barrier resulted in a MOCON value at the upper measurement limit for the 50 cm^2 active area used. This indicates the defect decoupling effect of ALD-deposited AlO_x film. The superior step coverage property of ALD-deposited AlO_x film can even be applied to the coverage of the negative angle sloped separator used in the passive matrix OLED panel.

A surface SEM image of AlO_x film on a PES film is shown in Fig. 1. The amorphous aluminum oxide thin films show flat morphology and also good adhesion to the plastic substrate. When thin films are used for device packaging, it will be very important for films to have good adhesion to different materials such as metal, organic materials, and a substrate.

Figure 2 shows an AFM of an AlO_x-coated PES substrate. The RMS surface roughness of the 50 nm thick AlO_x film was 3.38 Å, while that of an uncoated PES film was 4.06 Å.

The transmittance of the AlO_x-coated film for visible light was more than 85% with air as a reference, which is a higher value than that of a bare PES film as a reference, as shown in Fig. 3. The high transparency of a barrier film is suitable for the top emitting OLED encapsulation.

For application to device encapsulation, we tested an ALD-deposited AlO_x film as an encapsulation layer of OLED on a PET plastic substrate having good chemical compatibility for an ITO patterning process. The OLED was prepared by vacuum evaporation, and 30 nm thick AlO_x films were deposited continuously in a separate reactor at 80°C. Since the oxygen precursor, water, is the source of severe device damage, we have tried to use a minimum amount. The damage of an OLED device caused by precursors could be minimized compared to other plasma enhanced deposition methods such as PECVD or sputtering because precursors including water vapor, oxygen plasma, or TMA are pulsed for only less than

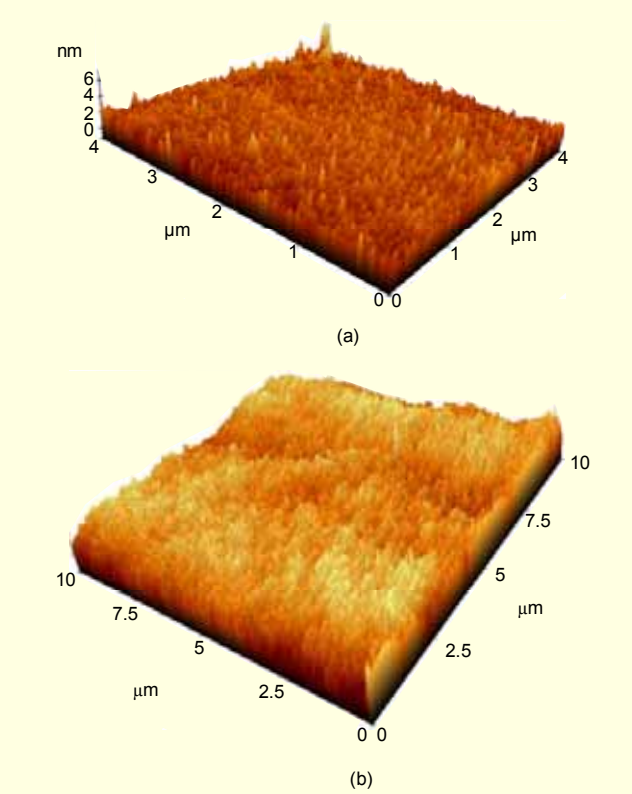

Fig. 2. AFM images of (a) bare PES and (b) 50 nm AlO_x-coated PES.

Fig. 1. SEM image of AlO_x thin film deposited at 80°C using 500 cycles.

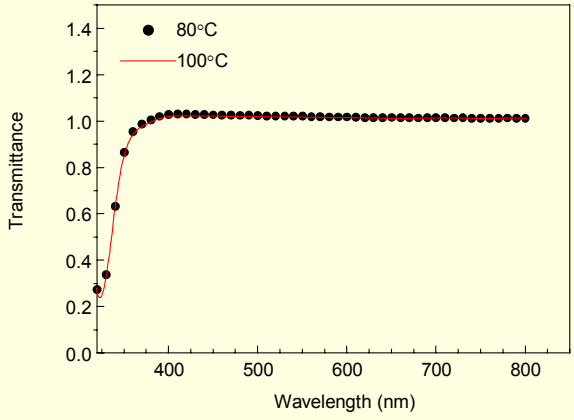

Fig. 3. Transmittance of 50 nm AlO_x-coated PES film for the visible light range with the PES substrate as a reference.

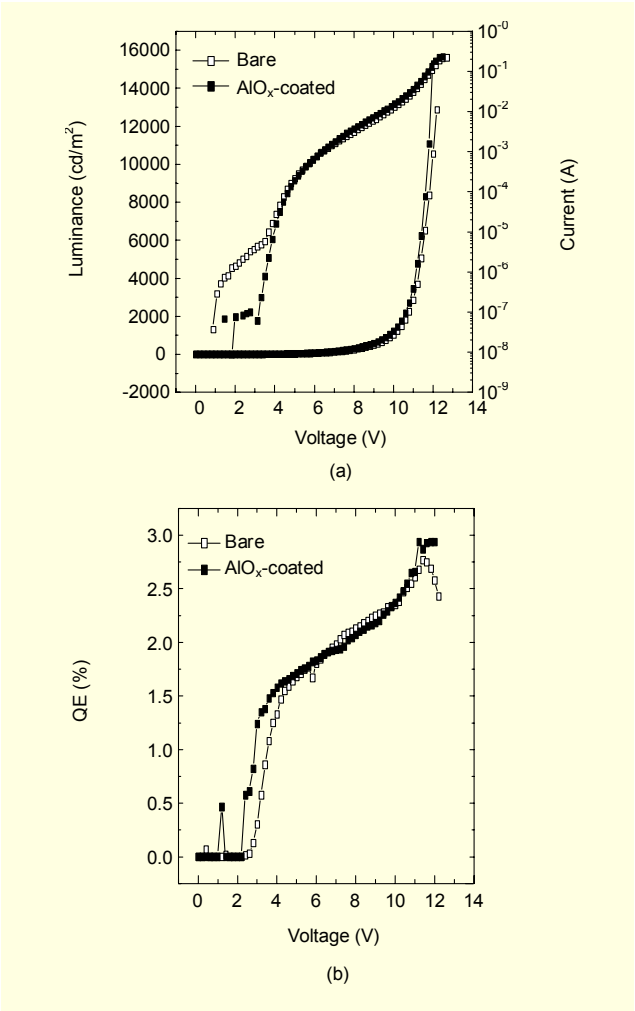

Fig. 4. I-V-L and efficiency characteristics of a bare OLED and 1μm parylene/30 nm AlO_x-coated OLED on a plastic substrate.

0.5 seconds for each cycle even in a reactor size larger than 12" × 14".

Although we have tried to minimize the device damage during the deposition, the direct deposition of the AlO_x film caused the formation of several dark spots with the device fabricated on the plastic substrate. We tried to prevent device damage by deposition of an organic polymeric buffer layer, parylene, between the device and the inorganic encapsulation layer. One-micrometer thick parylene and 30 nm thick AlO_x were deposited continuously in separate reactors at room temperature and 80°C, respectively, and we succeeded in obtaining an OLED with improved optical and electrical characteristics.

Figure 4 shows the I-V-L curves and efficiency of an OLED on a PET substrate encapsulated with parylene and AlO_x films. The parylene/AlO_x coated device showed no significant changes in I-V-L and efficiency compared to those of the uncoated device.

We have also put a PECVD-deposited SiN_x film between the parylene and the AlO_x film to minimize water vapor permeation during the AlO_x deposition. Furthermore, we expected that adapting an inorganic bi-layer system for the barrier of the OLED on the PET substrate would result in better encapsulation performance because the ultra thin ALD-deposited film showed a pinhole decoupling effect similar to much thicker organic films with a thickness of over a micron. The SiN_x film was deposited on a parylene-coated OLED on a PET at room temperature under the plasma power of 25 W with a gas ratio of N_2 (400 sccm) / SiH_4 (4 sccm) / NH_3 (26 sccm) / H_2 (100 sccm) / He (300 sccm). This is followed by a dual-sided aluminum oxide coating using 300 cycles at 80°C. When both sides of the device are coated simultaneously, permeation of water vapor and oxygen from the backside of the plastic substrate can be prevented effectively. Even though the SiN_x film deposited at room temperature showed a poor barrier property due to the pinholes, the additional deposition of AlO_x by the ALD method enhanced the film quality greatly.

For comparison of the lifetime, a 30 nm thick AlO_x film was simultaneously deposited at the front and backsides of the 1 μm thick parylene coated device. Figure 5 shows luminance decay curves of OLED devices packaged by parylene / SiN_x / AlO_x, parylene / AlO_x, and without encapsulation at a constant driving current of 1 mA and initial luminance of 1300 cd/m^2 in air at room temperature. While the lifetime of the uncoated device is less than 30 hours, the 1 μm-parylene/30nm-AlO_x coated OLED device maintains 80% of its initial luminance for 115 hours, and the parylene / SiN_x (100 nm) / AlO_x (30 nm) coated OLED maintains 90% of its initial luminance (1300 cd/m^2) for up to 260 hours.

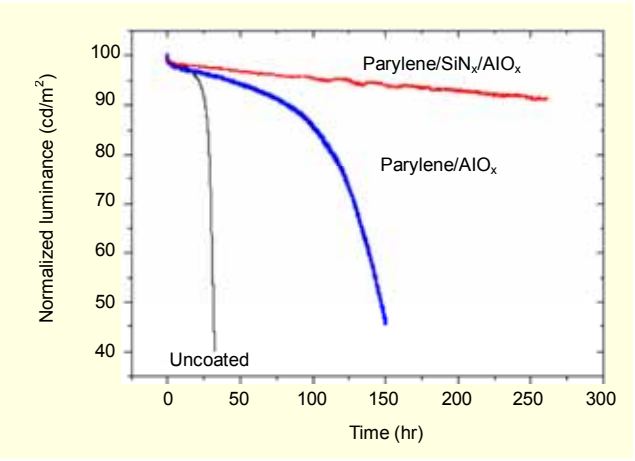

Fig. 5. Luminance decay curves of OLED devices on a PET packaged by parylene/SiN_x/AlO_x, parylene/AlO_x, and without encapsulation at a constant driving current of 1 mA and initial luminance of 1300 cd/m^2.

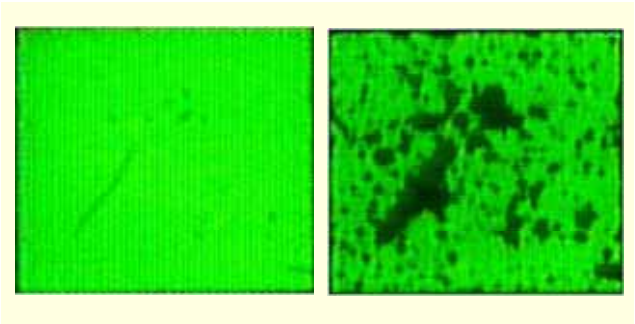

Fig. 6. CCD images of a light emitting area of the parylene/AlO_x-coated OLED on a PET before and after driving at 1 mA to give a 50% reduction of first luminance under 24°C, 45% R.H.

Degradation of the OLED was found to be mostly due to the formation of new dark spots and growth of the existing dark spot as shown in Fig. 6. The use of ultra thin ALD-deposited AlO_x thin films is effective as a barrier layer for significantly increasing the lifetime of an OLED device on a plastic substrate.

IV. Conclusion

The encapsulation of an OLED device on a plastic substrate with the films deposited using the ALD method has been carried out for the first time. ALD-deposited AlO_x films with a thickness of as low as 30 nm show excellent barrier properties. In addition, due to the defect decoupling effect, incorporation of an ultra thin ALD-deposited AlO_x film in a barrier layer stack of parylen and SiN_x can significantly enhance barrier properties for both a substrate and an OLED device on a plastic substrate.

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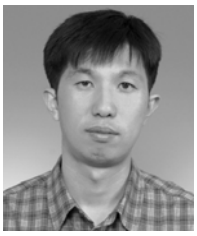

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