



Ultrathin Film Encapsulation of an OLED by ALD

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Fabrication of barrier layers on a PES film and an organic light emitting diode (OLED) based on a glass substrate by atomic layer deposition (ALD) have been carried out. Deposition of 30 nm of AlO_x film on both sides of PES film at 90°C gave film MOCON value of 0.0615 $\text{g/m}^2/\text{day}$. The passivation performance of the double layer consisting of SiN_x deposited by plasma-enhanced chemical vapor deposition and AlO_x by ALD on the OLED has been investigated using the OLED based on a glass substrate. Preliminary life time of two pairs of double layer coated OLED to 65% of initial luminance was 600 h at the initial luminance of 1200 cd/m^2 .

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Organic light emitting diodes (OLEDs) that could be thin, robust, conformal, and rolling have attracted much attention as the next-generation display.¹ However, the technology of thin film barrier layers, substituting for a glass or metal can for OLED encapsulation, must be established for the realization of ultrathin and light OLEDs.² Although the requirement for the barrier layer of an OLED display is not yet understood, it has been found that long-lived OLEDs need a moisture barrier layer which transmits less than 10^{-6} $\text{g/m}^2/\text{day}$ of water and 10^{-5} $\text{cm}^3/\text{m}^2/\text{day}$ of oxygen.³

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.⁴ Several groups have reported multilayered barriers consisting of inorganic thin films fabricated by plasma-enhanced chemical vapor deposition (PECVD) or sputtering.^{5,6} To be a good barrier layer, it should not only be free of pinholes but also have good step coverage. It is also very important for the barrier deposition process to be compatible with the organic emitting layer beneath.⁷

Our group reported a new approach to the barrier layers for a plastic substrate using traveling wave reactor typed atomic layer deposition (ALD)⁸ and plasma-enhanced ALD (PEALD).⁹ 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 the substrate damage, the low growth rate of 1.05 Å/cycle is the main drawback for the application of barrier layer. In addition, use of water vapor or ozone in traveling type ALD method and oxygen plasma in PEALD method as the precursor of oxygen, made us hesitate to apply ALD-deposited AlO_x films as the barrier layer for an OLED device directly.

However, we have observed that just nanometer order of AlO_x single film deposited by ALD technology has excellent barrier properties and is suitable even for the device encapsulation layer. Through the further optimization using the ALD deposited AlO_x film and another inorganic film of PECVD deposited SiN_x , we have successfully obtained encapsulation layers for an OLED on a glass substrate.

Aluminum oxide thin films 10-50 nm thick were grown on a PES substrate in a 12 × 16 in. large traveling wave ALD reactor with nitrogen as a carrier gas in the temperature range of 80-100°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 (1.43 s)/ N_2 (2.5 s). Water vapor transmission rates (WVTRs) were measured for both a PES substrate and AlO_x coated samples on a 50 cm^2 active sample area

at $38 \pm 2^\circ\text{C}$, 100% R.H. using MOCON permatran-W1A for 72 h. Morphological properties were examined by scanning electron microscope (SEM) and atomic force microscope (AFM). UV-vis spectra were taken using Hitachi U-3501 spectrophotometer. The device structure of an OLED grown by vacuum thermal deposition was ITO/20 nm MTDATA/40 nm NPd/60 nm Alq/1 nm LiF/75 nm Al. Glass was used for the substrate of an OLED device with emitting area of 2×2 mm.

First, the dependences of the barrier properties of AlO_x films on the deposition temperature and film thickness were investigated. With the considerations of low deposition rate of the ALD method and the application of encapsulation layer to an OLED, we have prepared ultrathin (20-50 nm thick) AlO_x films deposited at lower than 100°C. Table I shows permeation properties of uncoated PES film and AlO_x coated one. While most inorganic single layers deposited by other chemical or physical methods showed proper barrier properties with the thickness higher than 100 nm, 20 nm thick single aluminum oxide film deposited by ALD at 80°C exhibited barrier properties of the MOCON values lower than 1.3 $\text{g/m}^2/\text{day}$. The barrier property has increased with increasing film thickness and elevating deposition temperature. The lowest MOCON value of 0.102 $\text{g/m}^2/\text{day}$ was obtained from the 50 nm thickness of the film deposited at 80°C in our experiment conditions.

One of the main advantages of traveling wave type ALD is the capacity for film coating on both sides of substrate or device simultaneously. The PES film coated both sides with 30 nm of AlO_x showed 0.0615 $\text{g/m}^2/\text{day}$ of MOCON value that is, to our knowledge, the lowest value for single inorganic layer with the thickness less than 100 nm. Simultaneous coating of both sides is good technology for the encapsulation of plastic substrates or an OLED based on the plastic, because it could not only reduce the film stress caused by the difference of coefficients of thermal expansions between the plastic substrate and the dielectric film but also prevent permeation of moisture from the back side of the device substrate.

Moreover, the combination of ALD deposited AlO_x with another inorganic film, PECVD deposited SiN_x , or polymeric organic film, parylene, resulted in better barrier properties as shown in Table I. We believe that the formation of conformal film by ALD resulted in coverage of pinholes in inorganic or organic layer beneath. Deposition of 30 nm of AlO_x on 200 nm of SiN_x thin film, having MOCON value as high as upper limitation with 50 cm^2 measuring area, gave the MOCON value lower than the detection limit of MOCON measurement in our experimental condition. Excellent step coverage property of ALD deposited AlO_x film can even be applied to the coverage of negative angle sloped separator used in the passive matrix OLED panel.

The surface SEM image of AlO_x film on a PES film is shown in Fig. 1. The amorphous AlO_x thin film showed flat morphology and also good adhesion to the plastic substrate. When thin films are used

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Table I. The barrier properties of PES substrates coated with AlO_x , SiN_x , parylene or double layer

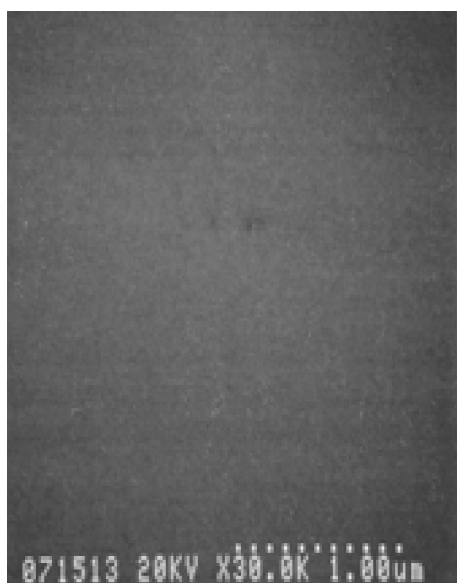
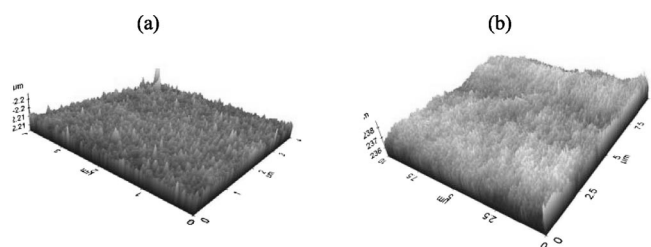
Deposition temperature ($^{\circ}\text{C}$)	Thickness (nm)	WVTR ($\text{g/m}^2/\text{day}$ at 38°C)	WVTR ^a ($\text{g/m}^2/\text{day}$ at 38°C)
Uncoated PES		92.8 ^b	
AlO_x	20	1.25	0.0615
	30	0.409	
	40	0.141	
	50	0.102	
	30	0.303	
	90	0.214	0.0276
	100	0.214	
SiN_x	R.T.	200	
$\text{SiN}_x/\text{AlO}_x$	R.T./80	200/20	
parylene	R.T.	3 μm	
parylene/ AlO_x	R.T./80	3 $\mu\text{m}/20$	
		0.199	

^a WVTR of PES coated both sides with AlO_x .^b WVTR for 5 cm^2 active area.

for the device packaging, it would be important for films to have good adhesion to different materials such as metal, organic materials, and substrate.

The barrier layer should also have smooth surface. Figure 2 showed AFM images of the uncoated PES film and the AlO_x coated PES film. The RMS surface roughness of the 50 nm thick AlO_x film was 3.38 Å while that of uncoated PES film was 4.06 Å. The transmittance of the AlO_x coated film for the whole visible light range is more than 85% with the air reference and higher value than that of bare PES film with the reference of a PES film as shown in Fig. 3. The high transparency of barrier film is suitable for the top emitting OLED encapsulation.

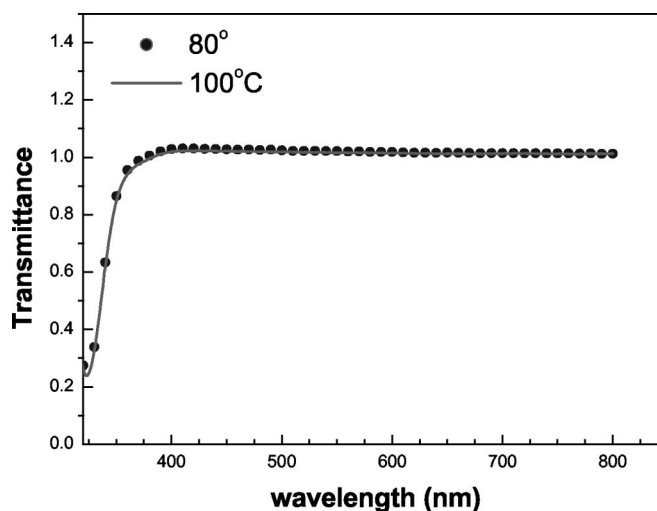
For the application of device encapsulation, we tested ALD deposited AlO_x film as an encapsulation layer of an OLED on a glass substrate. Because the oxygen precursor, water, is the severe source of device damage, we thought the buffer layer between the OLED and the AlO_x film might be needed. The organic polymer, parylene, was used for this purpose. The OLED was prepared by the vacuum evaporation and 3 μm thick parylene and 30 nm thick AlO_x were deposited continuously in a separated reactor at room temperature and at 90°C , respectively. With usual pulsing time of 1.43 s for

**Figure 1.** SEM image of AlO_x thin film deposited at 80°C by 500 cycles.**Figure 2.** AFM images and histograms of (a) bare PES and (b) 50 nm AlO_x coated PES.

water, we observed several dark spots formed in the emitting image. However, with the reduced pulsing time of water to 0.5 s, we have succeeded in obtaining an OLED without damages during the deposition even without buffer layer of parylene. The damage of the OLED device caused by precursors in ALD technology could be minimized compared to other plasma enhanced deposition methods such as PECVD or sputtering because the precursor including water vapor, oxygen plasma, or TMA is pulsed for just less than 0.5 s for each cycle even in a reactor size larger than 12 in.

It has been reported that organic layers, especially hole transport layer, are crystallized at the temperature higher than 55°C to induce degradation of device.¹⁰ Therefore, most researchers have tried to deposit barrier layer at lower than 50°C . However, AlO_x deposition carried out at 90°C did not cause any degradation of EL characteristics of an OLED on the glass substrate optically and electrically. Figure 4 shows I-V and L-V curves of an OLED on glass substrate encapsulated with AlO_x films. The AlO_x coated device showed no big changes in L-V, I-V, and efficiency compared to that of the uncoated device.

Because ultrathin ALD deposited film showed good coverage for the defects below it as the micro-order thick organic film does, we adapted inorganic double layer system for the barrier of an OLED to obtain better encapsulation performance. The 200 nm SiN_x film was deposited on the OLED device at room temperature under the plasma power of 25 W with the gas ratio of N_2 (400 sccm)/ SiH_4 (4 sccm)/ NH_3 (26 sccm)/ H_2 (100 sccm)/He(300 sccm). Aluminum oxide coating was followed by 300 cycles at 90°C . Even though the SiN_x film deposited at room temperature showed poor barrier property due to the pin-holes, additional deposition of AlO_x by ALD method enhance the film quality greatly. Figure 5 presents

**Figure 3.** Transmittance of 50 nm AlO_x coated PES film for the visible light range with the PES substrate reference.

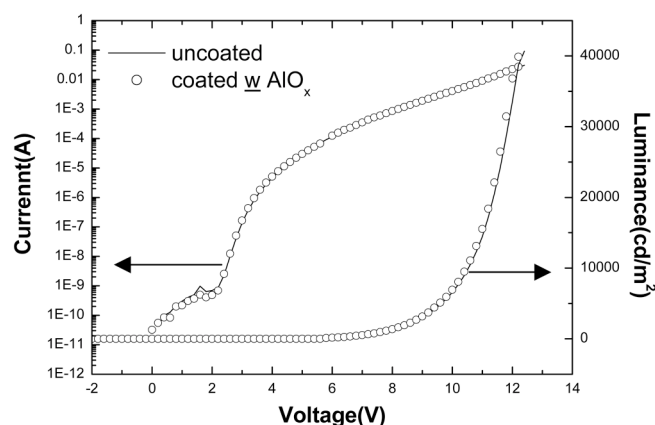


Figure 4. I-V-L characteristics of an uncoated OLED and a 30 nm AlO_x coated OLED on a glass substrate.

changes of the emitting areas of the device uncoated, coated with $\text{SiN}_x/\text{AlO}_x$, and encapsulated with glass, that were stored during the indicated time under 25°C, 80% R.H.

The uncoated device degraded to 20% of emitting area with the severe pixel edge shrinkage and new dark spot formation within 72 h. For the thin film encapsulated device, however, the emitting area has been kept almost same over 320 h. The device finally showed edge degradation without any formation of new dark spots after 384 h while the glass encapsulated device showed no change. This suggests that the barrier property of one pair of double layer is not enough to achieve the level of the glass encapsulation as shown in Fig. 5c. Therefore, we adapted two pairs of double layer of $\text{SiN}_x/\text{AlO}_x$ to the OLED fabricated on a glass substrate. Life time was measured for the uncoated and thin film coated devices at initial luminance of 1200 cd/m^2 under dc drive and constant current of 1mA at room temperature and ambient pressure.

Figure 6 shows lifetimes of an OLED devices packaged by one pair of $\text{SiN}_x/\text{AlO}_x$, two pairs of $\text{SiN}_x/\text{AlO}_x$ thin film layers, and without encapsulation. While the lifetime of an $\text{SiN}_x/\text{AlO}_x$ coated OLED to 76% of initial luminance (1200 cd/m^2) was 193 h, that of two pairs of coated OLEDs maintained 65.4% of initial luminance

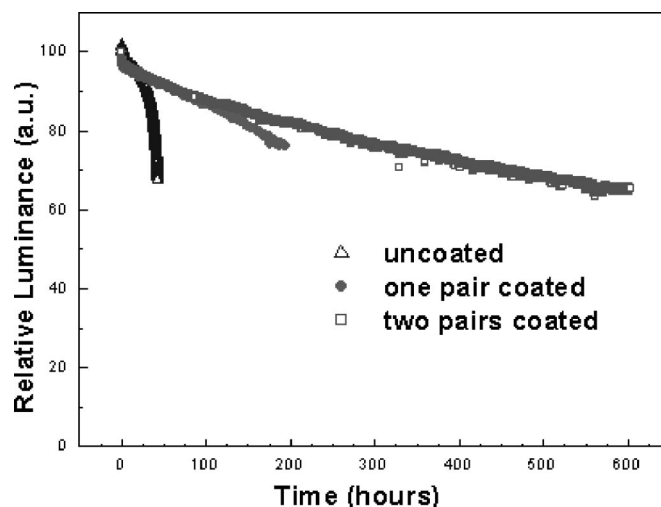


Figure 6. Luminance decay curves of OLED devices packaged by one pair of $\text{SiN}_x/\text{AlO}_x$, two pairs of $\text{SiN}_x/\text{AlO}_x$ thin film layers, and without encapsulation at constant driving current of 1 mA and initial luminance of 1200 cd/m^2 .

for 600 h. The two pairs of inorganic double layer thin films consisting of ALD deposited AlO_x showed similar degradation properties to that of glass encapsulated device. The use of ALD deposited AlO_x thin film for the barrier layer can not only reduce the total thickness of barrier layer also increase the lifetime of an OLED device based on a glass substrate significantly.

In summary, the encapsulation of an OLED device on a glass substrate with the films deposited by the ALD method has been carried out. Because even 30 nm thick AlO_x films show superior barrier properties, it is considered that ALD technology is suitable for the barrier layer fabrication. Due to the effect for decoupling of defect, introduction of ALD deposited AlO_x film in double layered thin films can significantly enhance barrier properties for an ultra-thin OLED device. Further studies are under investigation for the effects of oxygen precursor of AlO_x process on the characteristics of encapsulation layer.

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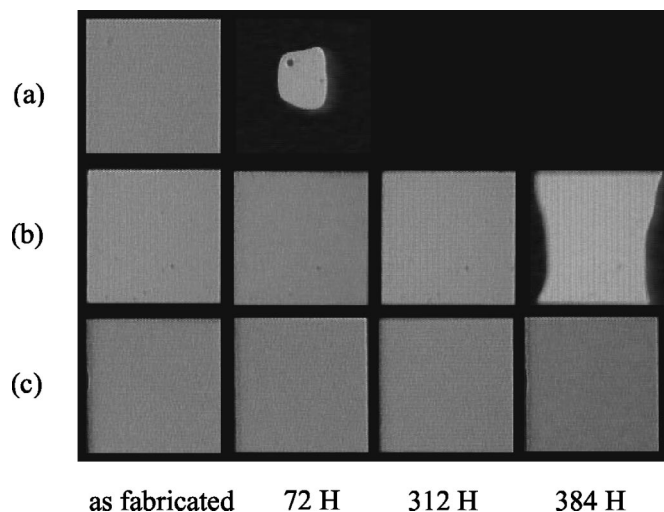


Figure 5. Photographs of the emitting areas of the devices (a) uncoated, (b) coated with $\text{SiN}_x/\text{AlO}_x$, and (c) encapsulated with glass lid, that were stored during the indicated time under 25°C, 80% R.H.