Permeation Properties of Composite Thin Film for Organic Based Electronic Devices

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Abstract

We fabricated composite materials as a pellet structure with the various kinds of inorganic material powder. The composite materials were deposited onto the plastic film by the electron beam evaporation and water vapor transmission rates (WVTRs) were measured by the MOCON facility. As a result of WVTRs, the composite materials had lower WVTR value than any other inorganic materials. So, these films were proposed to protect the organic light emitting device (OLED) from moisture and oxygen. We can consider that the composite thin-film is one of the more suitable candidates for the thin-film passivation layer in the OLED. And, we are processing the XRD, XPS and EPMA to analyze the property of the composite material. We will also analyze properties of the current-voltage and luminescence for lifetime both the composite thin-film passivated OLED and non-passivated OLED.

1. Introduction

Organic light emitting device (OLED) became very attractive for their applications in the flat-panel display. Because the OLED has an excellent performance such as full color display, low manufacturing, small thickness, lightweight, good daylight visibility through high brightness and contrast, high resolution, fast response time, wide viewing angle. However, the environmental stability and reliability of the device was still a major problem. Degradation of the OLED due to the growth of dark spots could be attributed to the lifetime[1]. Especially, OLED was polluted by moisture and oxygen. To protect the device, the canister-type encapsulation was generalized. In the case of canister-type process, process steps and manufacturing costs were increased and the canister-type encapsulation is impossible to apply the flexible display[2-3]. Therefore, thin-films passivaiton should be seriously considered to substitute for the canister-type encapsulation. In case of the existing inorganic materials such as Al_2O_3 and SiO_2, material structures of the base material itself are not able to do an important role as the barrier property owing to the high permeability by moisture and oxygen[4-6]. So, we adapted that composite materials consisted of the original materials were added another materials to change the material structure should be improved the permeability. Of course, the deposition temperature should be as low as possible, preferably less than 100℃. Low film stress is needed, if thin-film stress is high, the organic layer may peel off.

In this study, we fabricated the composite thin-films and characterized its barrier properties through measuring the WVTR values. The applicability of passivation layer using the composite thin-films will be played an important role for improving the lifetime of the OLED.

2. Experimental

Composite thin-films were fabricated according to the following procedure. Several kinds of inorganic materials were closely rubbed into the powder to composite at a constant rates. These materials were made of MgO, CaO, SiO_2, Al_2O_3, Na_yO_x and all the rest of it. After weighing the powders as the balance, mixing the portion of rates up.

The mixed powders made a pellet structure by the lever-press. The substrate consisted of the bare PC film and PES film had WVTR values of 33 g/m^2.day and 72 g/m^2.day, respectively. The composite materials of the pellet structure were deposited on the 200㎛-thick plastic film using the electron beam evaporation. When the electron beam is focused on the source material, composite material is melted and deposited.

To measure the permeability of the composite thin-films from the water vapor, the WVTR values were measured using the Permatran-W 3/31 made by MOCON Corporation. The WVTR data was obtained at atmospheric pressure under 100% relative humidity and temperature from 37.8℃. During the test, water vapor that permeated through the composite thin-films was executed by dry nitrogen gas to an infrared detector. All WVTR values were reported in units of g/m^2 per day.

3. Results and discussion

In order to discriminate the WVTR value between inorganic materials and composite materials, we preliminary performed permeation test to have a reference data of inorganic materials. Table 1 shows that deposition conditions and WVTR results about the various kinds of inorganic materials. In this table, we can see that the WVTR of the MgO showed the lowest value compare to other inorganic materials. Also, deposition temperature was the low and thin-film was the thick. Thus, we can consider that the MgO was applied to the base material.

Table 1. Deposition conditions and WVTR values about the various kinds of inorganic materials.

Inorganic materials	Working temperature (°C)	Working pressure (Torr)	Thickness (nm)	WVTR (g/m^2.day)
CeO_2	80	1.2×10^{-4}	340	39.08 (PC)
Al_2O_3	80	1.5×10^{-4}	10	36.77 (PC)
ZrO_2	80	1.7×10^{-4}	10	36.70 (PC)
TiO_2	80	2.0×10^{-4}	25	35.47 (PC)
SiO_2	52	2.3×10^{-5}	500	34.08 (PC)
	63	2.4×10^{-5}	650	74.94 (PES)
MgF_2	27	2.2×10^{-5}	150	29.18 (PC)
MgO	50	4.0×10^{-5}	1000	3.361 (PC)
	62	5.0×10^{-5}	1000	8.330 (PES)

And, we fabricated composite material powder by adding other inorganic material powder such as CaO, SiO_2, Al_2O_3 and Na_yO_x to the MgO powder of base material. Figure 1 shows that composite material as the pellet structure was mixed the MgO and SiO_2 at a constant rates. It was not difficult to the process of the fabrication.

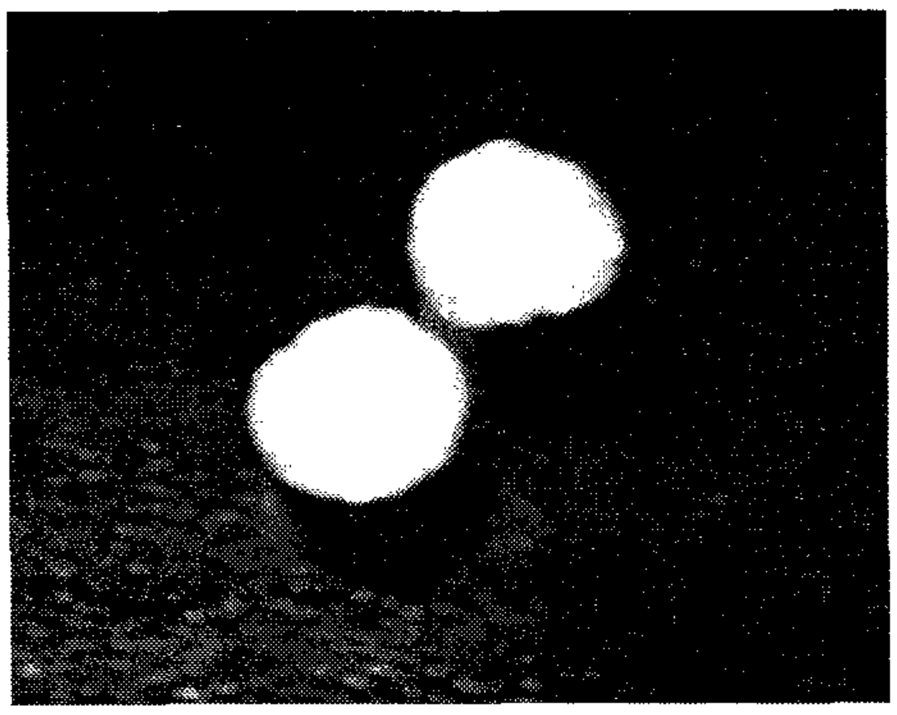

Figure 1. Composite material as the pellet structure was mixed with the MgO and SiO_2 at a constant rates.

And composite material powder was deposited onto the plastic film and measured WVTR values. As observed by the optical microscopy, composite thin-films were very clean surface on the PES film. We confirmed that the thickness of composite material could be increased under the low deposition temperature. The surface of composite material was not seen an abnormality such as crack and pinhole. But, the powder of Al_2O_3 was considered less than 100℃ owing to the high deposition temperature. The deposition conditions and WVTR values for composite materials were showed in Table 2. As a result of WVTRs, the composite materials had lower WVTR value than any other inorganic materials. The permeation rate is decreased, owing to increasing the impurity rate. We can define that the impurity is able to help the composite material as a cooperated material. As above the experiment, we confirmed the characteristics of composite thin-films to protect the OLED. Therefore, we can consider that the WVTR value can be decreased if impurity can be adopted in the general inorganic thin-films.

Table 2. Deposition conditions and WVTR values about the various kinds of composite materials

Composite materials	Substrate	Working temperature (°C)	Working pressure (Torr)	Thickness (nm)	WVTR (g/m^2.day)
$MgO : Na_yO_x$	PES	60	3.0×10^{-5}	600	8.407
$SiO_2 : Na_yO_x$	PES	42	4.0×10^{-4}	300	6.211
$MgO : SiO_2$	PES	80	5.0×10^{-4}	300	1.623
	PC	80	$5.0 \times 10^{-}$	300	1.252
	PES	80	4.0×10^{-6}	250	1.752
	PC	75	4.0×10^{-6}	300	0.4369
	PES	70	3.0×10^{-5}	250	1.868
	PC	66	3.0×10^{-6}	250	0.2936
$SiO_2 : CaO$	PES	63	3.0×10^{-4}	1300	0.8206
	PES	63	3.0×10^{-5}	1000	1.823
$MgO : Al_2O_3$	PES	92	7.0×10^{-5}	300	1.972
	PES	94	5.0×10^{-5}	380	1.099
$MgO : SiO_2 : Al_2O_3$	PES	90	1.0×10^{-4}	500	0.5912

And, we adopted that the thin-film as a multi-layer was deposited on the PES film using the composite materials, metal materials and inorganic materials. Figure 2 shows WVTR values for the triple-layer including metal layer such as Al, Mg, Cr and Au. In this figure, we can see that WVTR value of the MgO/Au/MgO film was 0.0961 g/m^2.day. Figure 3 shows WVTR values for the multi-layer including the various kinds of the materials as a change of the thickness. As you can see that Figure 3, thin-film was deposited on the backside of PES film to reduce the film stress. In this figure, we can see that WVTR value of SM13/MgO/Al/SM13/MgO/Back-MgO/SM 13 was 0.0036 g/m^2.day. So, the WVTR value dramatically decreased using the composite material and metal material. This result can be considered that thin-film passivaiton for OLED was used not only composite materials but also metal materials.

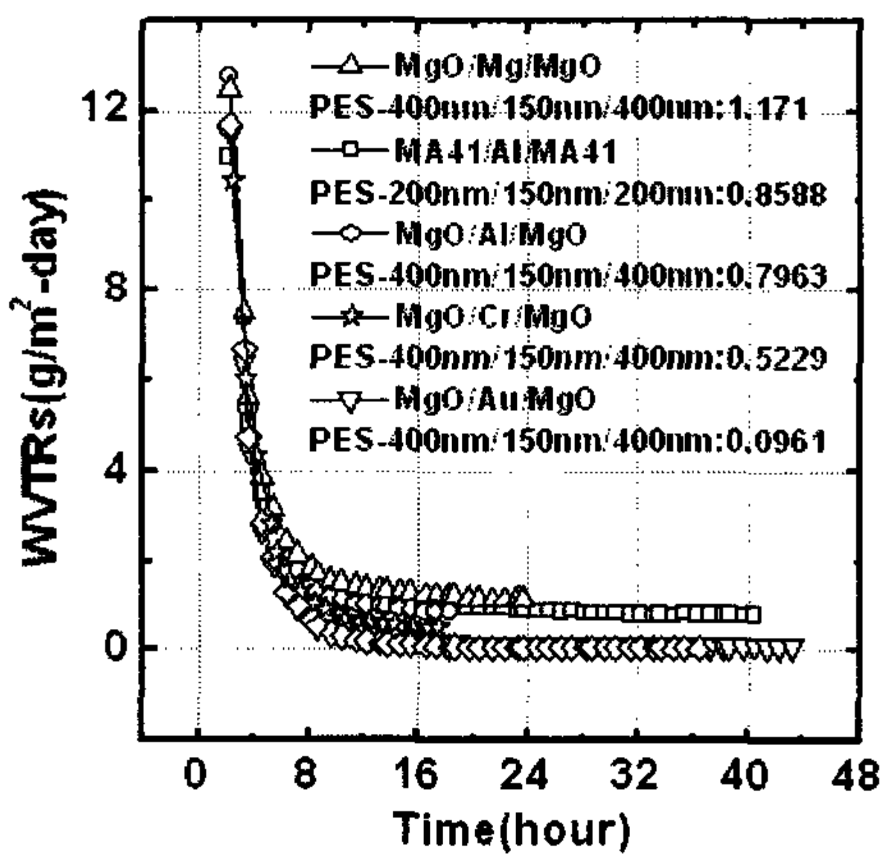

Figure 2. The WVTR values of the triple-layer including the metal layer.

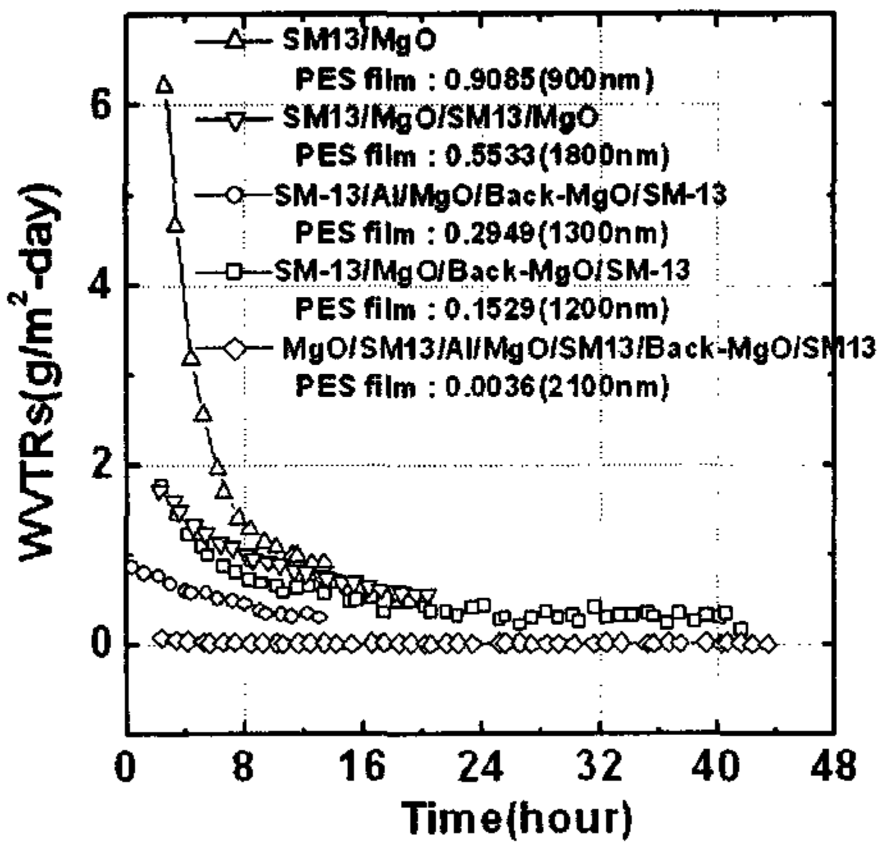

Figure 3. The WVTR values of the multi-layer including the various kinds of the materials as change of the thickness.

We analyzed properties of the current-voltage and the luminescence for composite-passivated OLED and non-passivated OLED. Measuring instruments were used Keithley 237 measure units and TPCON luminance meter BM-9M as the current-voltage and the luminescence, respectively. After packaging the MgO and the SM13 of the thin film, normalized lifetime data was investigated under dc drive and constant current condition. To compare the lifetime properties of the OLED, the normalized luminescence was measured to 60% of initial value over operating time. In the Fig. 4, we can see that non-passivated OLED had a short lifetime about 12 hours in ambient condition, MgO-passivated OLED and composite-passivated OLED had a relatively long lifetime about 46 hours and 150 hours, respectively. Because the cathode and organic layer was sensitive to the moisture and oxygen, non-passivated OLED can not operate for long. Through the optical microscope, we confirmed that the dark spot from degradated pixel was decreased owing to passivation layers. So, composite-passivated OLED had a remarkably improved the lifetime compared to non-passivated OLED. Therefore, we can consider that the composite material is the most suitable material as passivation layer for OLED.

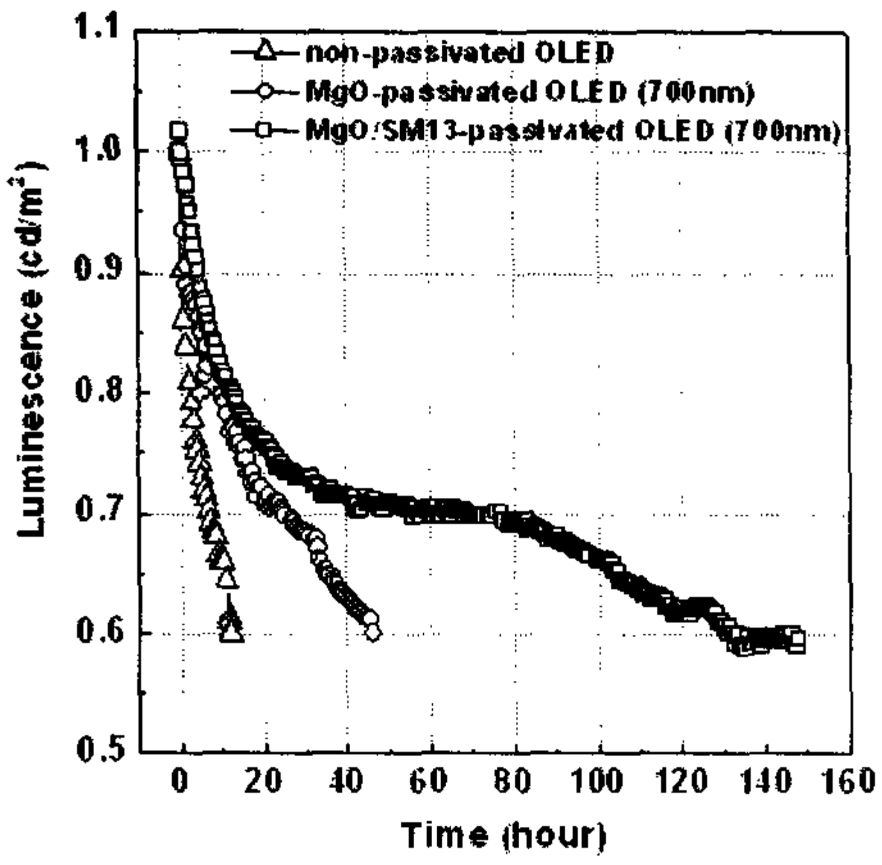

Figure 4. The lifetime of the passivated OLED and non-passivated OLED

4. Conclusion

In this paper, composite thin-films for passivation layer of OLED were investigated and the WVTR values were estimated by comparing inorganic thin-films to composite thin-films. We confirmed that WVTR value of the thin film passivation was 10^{-2} order and 10^{-3} order, respectively. So, we thought that the composite thin-film was the more suitable material as a passivation layer to protect the OLED. Continuously, we are processing the property of the thin-film through the XRD, XPS and EPMA, and so on. The lifetime of composite-passivated OLED was more enhanced than non-passivated OLED. To more estimate the lifetime of OLED, we are fabricating the OLED

5. References

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