Characterization of a passivation layer comprising MgO-SiO₂ and ZrO₂

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Thin films with magnesium oxide (MgO) and silicon oxide (SiO₂) compounds mixed at various mixture ratios were deposited on flexible polyether sulfone (PES) substrates by an e-beam evaporator to investigate their potential for transparent barrier applications. In this study, as the MgO fraction increased, thin films comprising MgO and SiO₂ compounds became more amorphous, and their surface morphologies became smoother and denser. In addition, zirconium oxide (ZrO₂) was added to the above-mentioned compound mixtures, and the properties of the compound mixture comprising Mg-Si-Zr-O were then measured. ZrO₂ made the thin mixture films more amorphous, and made the surface morphology denser and more uniform. Whole thin films of 250 ± 30 nm in thickness were formed, and their water vapor transmission rates (WVTRs) decreased rapidly. The best WVTR was obtained by depositing thin films of Mg-Si-Zr-O compound among the whole thin films. The WVTRs of the PES substrate in the bare state decreased from 47 to 0.8 g m⁻² day⁻¹. This Mg-Si-Zr-O compound was deposited on polyethylene terephtalate (PET) substrates again to confirm the availability of the compound mixture. Thin films on the PET substrates decreased the WVTRs remarkably from 2.96 to 0.01 g m⁻² day⁻¹. These results were similar to those of thin films on PES substrates. As the thin mixture films became more amorphous and surface morphology denser and more uniform, the WVTRs decreased. Therefore, the thin mixture films became more suitable for flexible organic light emitting displays (OLEDs) as transparent passivation layers against moisture in air. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: passivation; water vapor transmission rates (WVTRs); organic light-emitting devices (OLEDs); inorganic layer

INTRODUCTION

Since Tang and VanSlyke¹ in 1987 demonstrated the operation of high-luminance, green organic light-emitting diodes (OLED) at a reasonably low voltage, extensive studies have been carried out to achieve the characteristics suitable for their use in commercial displays. In recent years, the OLED technology has advanced considerably, and several types of OLED displays have been commercialized.^{2–4} In addition, many companies have developed active matrix-type OLED displays using thin film transistors (TFTs).^{5–7} OLEDs have many attractive features for display applications, i.e. high brightness, high efficiency, wide viewing angle, and quick response time. In addition, they can be fabricated by depositing or printing organic materials on a single substrate, so the substrate features can be used. However, one of the dangerous conditions for an OLED is attacks by the moisture and oxygen in air. Too much exposure to moisture and oxygen can lead to remarkable dark spots in an OLED, and its lifetime can be reduced. Therefore, it is necessary to protect the organic and cathode layers in an OLED against air damage.^{8,9}

Recently, OLEDs have been fabricated on glass substrates and then encapsulated with metal or glass lids using a UVcurable epoxy resin.¹⁰ However, a glass substrate cannot be used in flexible display panels.^{11,12} By replacing the glass substrate with a plastic substrate, we can increase the number of OLED applications. An OLED display on a plastic substrate is thinner and lighter than that on a glass substrate. Moreover, by utilizing the flexibility of the plastic substrate, various forms of displays can be fabricated, including the socalled flexible display.¹³ However, the key issue in fabricating OLEDs on a plastic substrate is the protection of OLEDs from the moisture and oxygen in air.14 Plastic substrates also do not have sufficiently high impermeability against moisture and oxygen. Therefore, OLEDs must be covered with a thin passivation layer instead of glass or metal lids. The passivation layer must be formed as thin films to provide



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flexibility and transparency for top-emitting devices. Many interested companies and laboratories have explored various barrier layers against oxygen and moisture through various methods and materials. Methods using organic materials, inorganic materials, and both have been considered.^{9,15,16}

In this work, inorganic materials such as oxides have been considered as materials of passivation layers for OLEDs against exposure to atmospheric oxygen and moisture: specifically, MgO and SiO₂ were selected. To form the passivation layer for an OLED, MgO and SiO₂ in the powder state, which are generally used as absorbents, were mixed and deposited by an electron-beam evaporator. In addition, ZrO₂ was mixed with the above-mentioned mixtures and formed into thin films by an e-beam evaporator. Then, this three-component mixture was applied as a passivation layer against moisture in air.

The structure and formation of the deposited thin films were analyzed by X-ray diffraction, atomic force microscopy (AFM), energy dispersive X-ray spectrometry, field-emission scanning electron microscopy (FESEM),> etc. In addition, the deposited thin films were further characterized in terms of the water vapor transmission rates (WVTRs).

EXPERIMENTAL

MgO (3 ~ 6 mm in diameter, Dasom, Korea) and SiO₂ (1 ~ 2 mm in diameter, Photox Optical Systems, UK) of 99.9% purity were ground into powders using a mortar and mixed at various ratios by 24-h ball milling. The ratios of MgO and SiO₂ in the mixtures were 1:1, 2:1, and 3:1, which are represented by η , which is the weight percentage of MgO at the source of an e-beam evaporator [$\eta = MgO/(MgO + SiO_2)$] (Table 1). The mixed powders were formed into rod-shaped pellets of 13 mm diameter using a level press at a pressure of 603 MPa.

The polyether sulfone (PES: i-components, Korea) substrates used in this study were 0.5 mm in thickness. The substrate surface was cleaned by ultrasonication in isopropyl alcohol (IPA) for 1 h and rinsed with methanol. Then, it was preheated at 120 °C for 1 h.

An electron-beam evaporator was used to deposit the Mg–Si–O films on the PES substrate. The electron-beam gun was in the chamber, and a shield plate was placed between the gun and the substrate to control the evaporation time. The accelerating voltage was fixed, and the current was varied to control the deposition rate. The base line vacuum level was 10^{-3} Pa. The substrate was rotated at 4 rpm and was not heated during deposition. The deposition rate and thickness were controlled by monitoring the film thickness, and thin films were deposited at regular deposition rates between 0.8 and 1.2 Å s⁻¹.

Table 1. Wt% fraction and mol% fraction in the mixture films

MgO:SiO ₂ (:ZrO ₂)				MC7024
	$\eta = 0.5$	$\eta = 0.67$	$\eta = 0.75$	M5Z934
Mol% fraction	50:50 60:40	67:33 75:25	75:25 82:18	56:19:25 64.5:14.5:21

Subsequently, the powder of $\eta = 0.75$ and ZrO_2 powder were mixed at a ratio of 3:1 (MgO:SiO₂: $ZrO_2 = 9:3:4$; MSZ934) and the mixture was deposited on PES substrates by an e-beam evaporator.

This thin film was formed on PES and polyethylene terephtalate (PET: SKC, Korea) substrates, both of 0.25 mm thickness. The PET substrate was cleaned the same way as the PES substrate and then preheated at 110 °C for 1 h. The preheating process was done at a lower temperature because the PET substrate has a lower melting point than the PES substrate. This thin film was deposited at a fixed voltage of 4.5 kV at a controlled current of 55 ± 15 mA and at a sustaining deposition rate equal to that of the above-mentioned Mg–Si–O thin films. A higher deposition power was needed because the vaporization point of ZrO₂ is higher than that of SiO₂.

The film thicknesses obtained are 240 ($\eta = 0.5$), 280 ($\eta = 0.67$), 240 ($\eta = 0.75$), 260 (MSZ934 on PES), and 230 nm (MSZ934 on PET), respectively. The film thicknesses were measured by using a Tencor Alpha-Step 500 surface profiler (KLA-Tencor, San Jose, CA). According to Ref. 17, the thickness changes of the oxide films on the PES substrate between 100 and 400 nm do not influence moisture transmittance.

Cross-sectional structures were observed by using a FESEM (FESEM: Hitachi S4700), after the samples were coated with gold. Their composition was analyzed with a sample of size $1 \times 1 \mu m$ using an energy dispersive X-ray spectrometer (EDX: Horiba EX-200). An X-ray diffractometer (XRD: Rigaku ATX-G) was used to analyze the microstructure of the films with a Cu anode (40 kV, 126 mA). The surface morphology and roughness of thin films evaporated on the PES substrate were characterized by AFM.

WVTRs were investigated to compare the applicability of thin films as passivation layers for OLEDs against moisture in air. The Permatran W3/31 (Mocon Inc., Minneapolis, MN)^{18–20} instrument was employed to measure the WVTR characteristics of a wide variety of inorganic thin films. The most common method for measuring WVTRs is based on a technique that grasps the aggregate amount of the infiltrating moisture into the OLED with the passivation layer in an extreme humid atmosphere. During the WVTR measurements, the temperature and relative humidity in the test system was set to 50 °C and 100% RH, respectively.

RESULTS AND DISCUSSION

XRD was used to determine the microstructural changes of thin films composed of MgO and SiO₂ compounds. Figure 1 shows the X-ray diffraction patterns of the four types of films above. When $\eta = 0.5$, $\eta = 0.67$ and $\eta = 0.75$, the Mg–Si–O protective layers had (200) orientation of SiO₂ diffraction peaks at a 2 θ of 44.32°, 43.1° and 44.72°, respectively, under all deposition conditions. In addition, it was observed that (121) or (042) orientations of SiO₂ can be obtained from all Mg–Si–O thin films at a 2 θ of 18.14°, 18.46° and 18.28°, respectively.

Generally, the peak of MgO indicates the transformation of MgO into an amorphous state after being melted



Figure 1. XRD patterns of various films as a function of the mixture ratio at the source of the e-beam evaporator: (a) $\eta = 0.5$; (b) $\eta = 0.67$; (c) $\eta = 0.75$; (d) MgO-SiO₂-ZrO₂ (MSZ934).

and formed into the Mg–Si–O thin films by an e-beam evaporator. Here, this peak was not obtained. According to Ref. 21, mixed ZrO_2 –SiO₂ films start to show an amorphous structure when the SiO₂ content is more than 17 mol%. Silica is a glass former, and pure silica films are deposited in the amorphous state, which influence the degree of crystallinity of ZrO_2 mixed with silica. The mixed ZrO_2 –MgO thin films showed a similar behavior as well. The films became more amorphous as the MgO composition increased, and they had amorphous structures when MgO fraction was over 41%. In the mixed MgO–SiO₂ films used in this study, the mol% of MgO and SiO₂ were more than 42% and 17%, respectively, and XRD patterns of the Mg–Si–O films became gentle and low.

The MSZ934 thin film indicated only one SiO₂ diffraction peak at a 2 θ of 17.53°. This means that all elements in this film became amorphous except SiO₂ during deposition. In addition, the (200) phase shown in Mg–Si–O films did not appear. This means that they became more amorphous than the Mg–Si–O films. The molar ratio of SiO₂ to ZrO₂ was 14.5:21 so that the fraction of SiO₂ was about 41%. According to Ref. 21, ZrO₂–SiO₂ thin films become completely amorphous when SiO₂ is over 21%. In the MSZ934 film, SiO₂ became more amorphous as ZrO₂ was added to the Mg–Si–O films.

The substrate temperature during deposition also affected the crystallinity of the films. According to Ref. 21, the more the temperature of the substrate is from normal temperature when depositing ZrO₂, the more is the indicated crystalline structure, and the most amorphous diffraction pattern is obtained when the film is formed at normal temperature. For all deposited Mg–Si–O and Mg–Si–Zr–O films, the deposition was carried out on the substrates at normal temperature.

The SEM (FESEM: Hitachi S4700) images show the crosssectional grain of the $\eta = 0.75$ film and the MSZ934 film on the PES substrate (Fig. 2). The grains became bigger and more amorphous when ZrO₂ was added.





Figure 2. SEM images of (a) MgO-SiO₂ ($\eta = 0.75$) and (b) MSZ934 films.

AFM was applied to measure the surface roughness of thin films composed of a mixture of MgO and SiO₂. Thin films of $\eta = 0.5$ had root-mean-square (RMS) roughness of 0.554 nm, that of $\eta = 0.67$ had 0.362 nm, and that of $\eta = 0.75$ had 0.143 nm. The surface roughness became gentle and smooth as the MgO fraction in these films increased. Figure 3 shows the morphology of the films by AFM. The $\eta = 0.5$ film was the most rugged, followed by $\eta = 0.67$ and $\eta = 0.75$ films, and the particle sizes also decreased. MSZ934 showed a smoother morphology than the others (Fig. 3(d)).

In addition, the RMS roughness values for the thin films of Mg–Si–O materials on the PET substrate were 2.8 ($\eta = 0.5$), 2.1 ($\eta = 0.67$), 1.6 ($\eta = 0.75$) and 1.0 nm (MSZ934), respectively. They were tending downwards as the MgO content increased, so we can confirm the effect of surface morphology on the moisture permeation.

The mixture ratios as real wt% of the elements Mg, Si, and O in thin films comprising MgO and SiO₂ were measured by an EDX (Horiba EX-200) (Table 2). These results show the difference between the real mixture ratios on the thin films formed and those in the source in the chamber of the e-beam evaporator before being evaporated. In the thin film of $\eta = 0.5$, the real wt% of Mg to Si is 8.98:22.59, which occupied about 29% in the thin film except oxygen (58% of MgO in an e-beam source). There is a large difference in the vaporization points of MgO and SiO2, so that a low electron-beam energy is enough to deposit the thin film of $\eta = 0.5$, which has more SiO₂ relatively at an equivalent deposition rate. Because the low electron-beam energy makes SiO₂ evaporate before MgO, the thin film is deposited with a higher ratio of SiO_2 than that in the source. Magnesium occupied 56% in the thin film of $\eta = 0.67$ (83.6% of MgO in the source) and 79% in the thin film of $\eta = 0.75$ (105.3% of MgO in the source) except oxygen. As η increased, the ratio of magnesium occupied in the thin film that was evaporated and formed actually increased more than that in the source during evaporation. A larger current is essential to increase the evaporation rate of MgO at the same deposition rate. In addition, once MgO obtains enough energy to evaporate vigorously, the ratio of Mg in the thin film increases as the MgO ratio becomes larger at the source because the melting densities of MgO and SiO₂ are 3.58 and 2.20 g cm⁻³, respectively.

This result applies to MgO and SiO_2 deposited by the evaporator. In this deposition method, the vaporization points and melting densities influence the real ratio of each element forming the thin film.



Figure 3. AFM images of surface morphologies: (a) $\eta = 0.5$; (b) $\eta = 0.67$; (c) $\eta = 0.75$; (d) MSZ934.

Table 2. EDX analysis of various thin films of Mg–Si–O. The ratio of magnesium in the thin film increased more than that in the source during evaporation as η became larger

	Wt%				
	0	Mg	Si		
$\eta = 0.5$	68.43	8.98	22.59		
$\eta = 0.67$	62.47	21.29	16.24		
$\eta = 0.75$	58.09	33.86	8.05		



Figure 4. WVTR results as a function of a mixture ratio for inorganic thin films: Mg–Si–O films and MSZ films on PES substrates.

Figure 4 shows the WVTRs of single thin films comprised of Mg–Si–O compound and Mg–Si–Zr–O compound, respectively. For the thin films of Mg–Si–O compound on PES substrates, WVTRs are 2.8 g m⁻² day⁻¹ at $\eta = 0.5$, 1.8 g m⁻² day⁻¹ at $\eta = 0.67$, and 1.5 g m⁻² day⁻¹ at $\eta = 0.75$, respectively, which show that the WVTR values decrease as η increases. This result means that the moisture infiltration decreases with increasing η . In other words, as the ratio of MgO in the compound increases, the amount of permeating moisture decreases further. Therefore, the thin film becomes more suitable for OLEDs as a passivation layer. However, a single thin film of MgO has a very much higher WVTR than the mixture at a similar thickness; therefore, a proper mixture ratio with SiO₂ is necessary. The thin film of $\eta = 0.75$ reduced the WVTR value of the PES substrate in bare state $(47 \text{ g m}^{-2} \text{ day}^{-1})$ to $1.5 \text{ g m}^{-2} \text{ day}^{-1}$ by more than 96%, and decreased from 10 to 1 order. The WVTR value of the PES substrate in the bare state is shown in Fig. 5(b) in the log scale. The thin film of $\eta = 0.75$ that had the best WVTR among three Mg-Si-O films gave better WVTR value when it was mixed with ZrO₂ for OLEDs. As Fig. 5(b) shows, this film formed on the PES substrate has a WVTR value of 0.8 g $m^{-2} day^{-1}$, which increased 98% from that of the film on the PES substrate in bare state and about 47% from that of the thin film of $\eta = 0.75$. In other words, it has a better WVTR value than the thin film of $\eta = 0.75$ not containing ZrO₂.

This film was applied to another substrate to ascertain the effect that prevents it from percolation of moisture. A 250- μ m



Figure 5. WVTR results for inorganic thin films in the log scale: (a) Bare PES substrate (47 g m⁻² day⁻¹); (b) PES substrate covered with a mixed MSZ934 film (0.8 g m⁻² day⁻¹); (c) Bare PET substrate (2.96 g m⁻² day⁻¹); (d) PET substrate covered with a mixed MSZ934 film (0.01 g m⁻² day⁻¹).

thick PET film was employed, which was half as thick as the PES substrate used. Figure 5 shows the WVTR patterns of the PET substrate in the bare state and that covered with the film of MSZ934 in the log scale. The WVTR of the PET substrate in the bare state was 2.96 g m⁻² day⁻¹, which is much lower than that of the PES substrate in the bare state. On coating the Mg–Si–Zr–O film of the PET substrate, the WVTR of this film decreased to 0.01 g m⁻² day⁻¹. The WVTR decrease from 1 to 0.01 is a reduction of 2 orders in magnitude like the WVTR in the films on the PES substrate. That is, MSZ934 on PET substrates as a passivation layer improved the WVTR as much as the film on the PES substrate.

CONCLUSIONS

Normally, glass or metal can be used to encapsulate OLEDs to protect them against moisture and oxygen in air. Although this encapsulation is simple and quite efficient, it cannot be applied for the flexible OLEDs, which are built on a flexible plastic substrate. In this study, inorganic passivation methods for OLEDs using an electron-beam evaporator were investigated. Among the inorganic materials, MgO, SiO₂, and ZrO₂ were employed as passivation layers to be applied against moisture infiltration.

The effects of the surface morphology and crystallization on the characteristics of the deposited samples were investigated. The more amorphous, denser and smoother the thin mixed films, the better the WVTR values for the OLEDs.

The Mg–Si–Zr–O film deposited on the PES substrate had the best WVTR value among the various films, and the ratio MgO:SiO₂:ZrO₂ was 9:3:4 in the source for e-beam evaporation. The film had a quality similar to that on the PET substrate and reduced the WVTR values down by 2 orders of magnitude compared to those of both bare substrates (from 47 to 0.8 g m⁻² day⁻¹ on the PES substrate and from 2.96 to 0.01 g m⁻² day⁻¹ on the PET substrate). The WVTR of the Mg–Si–Zr–O film was found to decrease rapidly even when the thickness of the film was very small (~280 nm). Generally, commercial OLED devices require WVTRs of $\leq 5 \times 10^{-6}$ g m⁻² day⁻¹. The WVTRs of the films



are insufficient to prevent rapid degradation of the OLED pixels due to moisture. However, the films have a high potential as an ultrathin and transparent barrier layer for topemitting OLEDs and for future flexible display applications.

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