Thin-film barriers using transparent conducting oxides for organic light-emitting diodes

Ho Nyeon Lee
Hyung Jung Kim
Young Min Yoon

Abstract — This study covers thin-film barriers using inorganic barriers of transparent conducting oxides (TCOs) such as zinc oxide (ZnO) and indium tin oxide (ITO). The TCOs were fabricated using a sputtering method with a process gas of pure argon at room temperature. ITO showed better properties as a barrier than the ZnO and exhibited the electronic performance necessary to perform additional functions. The ITO has superior barrier performance because it has a lower crack density due to its partial amorphous phase. For organic/inorganic multilayer barriers, the organic underlayer decreased the water-vapor transmission rate (WVTR) more than the organic upper layer, indicating that the planarization effect was important in reducing the WVTRs. The results of this organic/ITO multilayer barrier study are expected to be useful in finding a practical solution to OLED encapsulation.

Keywords — Thin-film barrier, TCO, ITO, WVTR, sputtering.

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1 Introduction

Advances in flat-panel-display (FPD) technology have brought about the use of organic light-emitting diodes (OLEDs).1–3 OLEDs have many advantages over prior FPDs, including liquid-crystal displays (LCDs) and plasma-display panels (PDPs). The image quality of OLEDs is superior to that of other FPDs. A wider color range than the National Television System Committee (NTSC) standard is easily achieved, and there is no limit to the viewing angle for OLEDs. The response time of OLEDs is so short that they are adequate for moving-image displays. Since OLEDs do not require backlight units and have very thin substrates, thin glass FPDs using OLEDs can be slimmer and lighter than other FPDs. Passive-matrix organic light-emitting diodes (PMOLEDs) have been used widely for small-sized displays; however, active-matrix organic light-emitting diodes (AMOLEDs) are more widely used in the OLED industry because of their superior performance. Samsung SDI started the first mass-production of AMOLEDs in 2007, and their products are focused on small-sized displays to be used for mobile devices such as cell phones, personal media players (PMPs), and Moving Picture Experts Group Audio Layer 3 (mp3) players. For large-sized OLEDs, Sony introduced personal televisions.

Although OLEDs exhibit great potential for applications, progress in the development of mass-produced products has been relatively slow. Several weaknesses of OLEDs have caused this slow progress, including the instability of organic light-emitting materials,4 the short lifetimes resulting from the device structures,5 an immature packaging process, and sealing material deficiencies.6 Hermetic sealing is crucial to OLEDs because organic light-emitting materials cannot tolerate the moisture or oxygen in the atmosphere.7 For conventional bottom-emititng OLEDs, a metal lid or a glass cap with a getter is attached to the glass substrate, which includes sequential layers of a cathode electrode, light-emitting materials, and an anode electrode. To attach a metal lid or a glass cap on a glass substrate, a low-moisture permeability adhesive resin is used as the sealant. These metal lids or glass caps are drawbacks in making larger and thinner OLEDs. The OLEDs’ thickness is over twice the thickness of the glass substrate if glass caps are used. It becomes harder to make lids or caps as the size of the displays grow larger. In addition, this conventional encapsulation method is inappropriate for flexible OLEDs because the metal lids and glass caps are rigid. As the competition in the FPD industry increases, the demand for thinner and lighter devices becomes greater. In addition, flexible displays are expected to be the ultimate solution for mobile displays. To make thinner and lighter OLEDs and flexible OLEDs, an encapsulation technology that does not use rigid metal lids or glass caps is essential. Therefore, thin-film encapsulation has become one of the major research topics regarding OLEDs.

Thin-film encapsulation technology uses multilayer barrier films instead of glass caps or metal lids to prevent the permeation of air from the outside of the device. The thickness of thin-film encapsulation is on the order of microns, which is very thin compared with conventional encapsulation. These thin barrier films are bendable so that they can be applied to flexible displays. Flexible displays can be constructed using flexible substrates, such as thin plastic films or thin metal foils, and a thin-film encapsulation for the OLEDs. Thin films over 2 µm on each side can be deposited using conventional production equipment, so that the thin-film encapsulation technology is adaptable for large-dis-
plays. Therefore, thin-film encapsulation is an essential technology for display industries in the near future.

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/m²/day of water and less than $10^{-5}$ cc/m²/day of oxygen. Multilayer 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. Organic and inorganic multilayer barriers were used for prototypes and evaluated for effectiveness. Films with gradually varied compositions between organic and inorganic were also studied as water permeation barriers. The mechanism of the multilayer effects could be explained by the increased lag-time of permeation. The inorganic layer mostly controls the permeation rate through the multilayer barrier. However, the organic layers between the inorganic layers fulfill important roles of increasing the lag-time through defect isolation and of planarization of the morphology and the particle underneath. In using this multilayer encapsulation, the organic and inorganic layers must be carefully paired in order to meet a suitable water-vapor transmission rate (WVTR) and oxygen transmission rate (OTR). Simplifying the structure of the thin-film barriers is an important step in adapting thin-film barrier technology for mass production. In addition, the deposition of the high-performance inorganic barrier layers is the most important technology in reducing the number of layer pairs.

In this work, we studied thin-film barriers with a focus on inorganic barrier technologies; transparent conducting oxides (TCOs) such as indium tin oxide (ITO) and zinc oxide (ZnO) were evaluated. In general, insulator films such as aluminum oxide, silicon oxide, and silicon nitride are being used as the inorganic barriers of multilayer thin-film barriers. However, it is expected that an inorganic barrier of conducting oxide can perform additional functions such as acting as a part of a touch sensor or as an electromagnetic interference shield. In this paper, results of studies on inorganic barriers using TCOs and multilayer structures are reported.

2 Experiments and results

In this work, ITO and ZnO were deposited using the sputtering method. Both a conventional RF sputtering method and a face-target-sputtering (FTS) method were used for the deposition. The conventional RF sputtering was performed using a target with a 3-in. diameter. The base pressure was on the order of $10^{-6}$ Torr, and the working pressure was 8 mTorr. The process gas was pure argon. Normally for the deposition of ITO, a mixed gas of argon and oxygen is used to obtain better electrical properties; however, in this work, oxygen was not used in order to prevent damage to the under layer from the oxygen plasma. As shown in Fig. 1, the FTS system is composed of a pair of facing targets and a substrate apart from the plasma region between the targets. In this system, DC power was applied between two targets. The target size was about 200 mm on the long side and about 100 mm on the short side. A turbo-molecular pump was used to achieve a base pressure on the order of $10^{-7}$ Torr. The working pressure was 8 mTorr. The process gas was pure argon. FTS is a remote plasma sputtering system.

![Diagram of FTS system.](image)

**FIGURE 1** — Diagram of FTS system.

![Visible-light transmittance of TCO films: (a) ZnO deposited on a glass substrate, (b) ITO deposited on a PES substrate. RF sputtering at room temperature was used for the depositions. These spectral transmittances were measured using references of the same substrates used for the depositions.](image)

**FIGURE 2** — Visible-light transmittance of TCO films: (a) ZnO deposited on a glass substrate, (b) ITO deposited on a PES substrate. RF sputtering at room temperature was used for the depositions. These spectral transmittances were measured using references of the same substrates used for the depositions.
This system prevents high energetic ion bombardments on the growing surface so that surface damage due to the plasma is reduced. This decreased damage makes FTS more suitable for an OLED process. In the FTS process, the major source of film growth is low-energy neutrals, so that there is a tendency to obtain more amorphous phase films than with other conventional sputtering systems. In this study, the FTS method was used to produce high-density films with less damage to the under layers. To restrict the temperature of substrates below the deformation temperature of plastic, the substrate was not heated during deposition.

Basic film properties were measured using samples deposited on the 0.5-mm-thick glass substrate. Film thickness and visible range transmittance data were obtained using a Schmadzu UV-1650PC UV-VIS transmission measurement system, and the optical gap was measured using the Tauc method. Electrical properties such as sheet resistance, Hall mobility, and carrier density were also measured using the samples on the glass substrates. For the measurement of sheet resistance, a four-point probe system with a Keithley 2400 source meter was used. For the Hall-effect measurement, an Ecopia HMS-3000 system was used. Measurements for the UV-VIS transmission, the sheet resistance, and the Hall effect were performed at room temperature in an air environment. After the initial characterization using the samples on the glass substrates, samples on 0.2-mm-thick polyether sulfon (PES) substrates were also fabricated to evaluate WVTR. All of the process conditions for the PES substrates were the same as those used for the samples on the glass substrates.

Figure 2(a) shows the visible-light transmission ratios for the ITO and ZnO on glass. As shown in the figure, the transmission ratio was over 80% for all of the visible range; this meant these films could be used for encapsulation of top-emission organic light-emitting diodes (TEOLEDs). ZnO and ITO showed almost the same transmittance values. Figure 2(b) shows the transmittance of ITO on the PES substrate; transmittance was over 85% for all of the visible range and was not less than that of the ITO on the glass substrate. Figure 3(a) shows the electron concentration of...
ITO as a function of the applied RF power with conventional RF sputtering. The electron concentration was dependent on the applied RF power and was on the order of $10^{20}$–$10^{21}$ cm$^{-3}$. The Hall mobility of the electron carrier was over 30 cm$^2$V$^{-1}$sec$^{-1}$, and there was relatively little dependence of the Hall mobility on the applied RF power, as shown in Fig. 3(b). The carrier concentration and the Hall mobility in this study were good enough that the ITO films could perform additional electrical functions in addition to acting as encapsulation barriers.

Images from optical microscopes of the surfaces of the ITO and ZnO are shown in Fig. 4. These figures show surface cracks of the ITO and ZnO deposited on the 200-µm PES films using RF sputtering with an Ar process gas at room temperature. As shown in the figure, the crack density of the ZnO was higher than that of the ITO. In general, in this study, the ITO exhibited fewer cracks than the ZnO given similar process conditions. These denser cracks of the ZnO are likely related to its lower barrier properties. The crack density seemed to be related to the film phase because grain boundaries are often the starting points of cracks. Partially amorphous ITO films are easily obtained using the sputtering method at room temperature, but it is very difficult to get amorphous ZnO films using sputtering. Given this information, we have determined that ZnO films may be less suitable as a barrier layer for OLED than ITO films.

Figure 5 shows the surface cracks of the ZnO on the PES with different RF power levels used in the sputtering process. The ZnO films were deposited on the 200-µm PES using RF sputtering with an Ar process gas at room temperature. As shown in the figure, high RF power caused more cracks. Samples with more cracks showed higher WVTRs. The crack density of the ITO showed almost no dependence on the RF power, and the cracks of the ITO were hardly seen using the optical microscope.

Figure 6 shows the WVTRs of the ZnO barrier and the ITO barriers. The films were deposited on the PES substrates using conventional RF sputtering method at room temperature and PES substrates were used for the sample fabrications. The WVTR of bare PES film was about 28 g/(m$^2$-day).
substrates using the conventional RF sputtering method, and their thickness was 500 nm. As shown in the figure, ITO had superior WVTR performance to ZnO. The lower surface crack density shown in Fig. 4 could be related to these results. For the ITO barrier layers, there was an optimum density of RF power as shown in the figure. The carrier density and mobility of these ITO layers were about $10^{21}$ cm$^{-3}$ and greater than 30 cm$^2$V$^{-1}$sec$^{-1}$, respectively. These values were obtained using the Hall-effect measurement. An ITO layer with these properties can be used as an inorganic barrier with additional electronic functions.

Figure 7(a) shows the WVTR results of the organic and inorganic bi-layers. On the PES substrates, 1 µm of organic barrier was deposited and then 500 nm of inorganic barrier was deposited on the organic layer. The organic barriers were coated using novolac resin. The ZnO and ITO of Figs. 7(a) and 7(b) were deposited using the FTS system at room temperature. As shown in the figure, ZnO exhibited inferior barrier properties compared to ITO, even with this double-layered structure. Figure 7(b) shows the WVTR results of barriers with different layered structures. As shown in the figure, an additional organic layer added to ITO decreased the WVTR from that of the ITO monolayer. The effect of the decreased WVTR from the additional organic layer was better when the organic layer was the first.

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**FIGURE 7** — WVTRs of inorganic/organic multilayer barriers: (a) multilayered structures composed of inorganic underlayers and organic upper layers and (b) multilayer structures using an organic upper layer or an organic mid layer. Inorganic layers were 500 nm thick and organic layers were 1 µm thick. FTS was used to fabricate inorganic layers at room temperature. PES substrates were used.

**FIGURE 8** — XRD results of (a) a 200-nm-thick ZnO film deposited using FTS, (b) ITO films with different thicknesses deposited using a conventional RF sputtering, and (c) a 300-nm-thick ITO film deposited using FTS. Samples were deposited on glass substrates at room temperature.
layer than when the organic layer was deposited after an ITO film. It seems that the surface planarization of the organic layer is essential to improving the barrier properties for thin-film encapsulation. The roles of the organic barriers are classified as follows. The isolation of defects of the inorganic barriers makes the permeation paths longer. Planarization and stress passivation of the underlayer decrease the crack density. For these effects, multilayer barriers perform better than an inorganic single layer.

Figure 8 shows the results of x-ray diffraction (XRD) analysis of the ZnO and ITO samples. As shown in Fig. 8(a), the ZnO had clear crystalline peaks. The ZnO film was fabricated using the FTS system at room temperature with argon process gas. Figure 8(b) shows the XRD results of the ITO films deposited using the conventional sputtering system; thinner films were almost in the amorphous phase, but crystalline peaks increased as the thickness increased. However, the amorphous phase persisted even for thicker ITO samples. The ITO deposited using the FTS system had a definite amorphous phase partially mixed with crystalline peaks as shown in Fig. 8(c).

The PES/TCO/organic-barrier/TCO structure showed little improvement in WVTR performance as compared to the PES/ITO/organic-layer structure and the PES/organic layer/ITO structure. This means that defect isolation and stress relaxation are less effective than surface planarization in lowering WVTR.

3 Conclusions

Inorganic barriers for thin-film encapsulation were studied. TCO films were used as inorganic barriers to make inorganic barriers that perform additional functions using the electrical properties of the TCOs. ITO exhibited better barrier properties than ZnO. This was related to the lower crack density of ITO as compared to ZnO. ITO deposited at room temperature has a partially amorphous phase compared with the fully polycrystalline phase ZnO, so that there may be less of a permeation path related to the grain boundaries. In addition, organic/inorganic multilayer structures were tested; an organic underlayer for the planarization of the substrate’s surface showed a larger effect than upper and mid layers of organic films that perform the defect isolation and the stress relaxation.

The TCO films with barrier properties and electric conducting nature could be used as multi-functional layers. Additional functions, such as touch sensing and electromagnetic-interference blocking, can be integrated into the encapsulation barrier using these TCO barriers.

In this study, we showed the usefulness of TCO films as inorganic barriers for thin-film encapsulation, and we showed the dependence of barrier properties on the multilayer structure. This study and its results may be important in developing better OLEDs, including flexible displays and high-performance TEOLEDs.

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References